

Review

# Electropositive Promotion by Alkalies or Alkaline Earths of Pt-Group Metals in Emissions Control Catalysis: A Status Report

Ioannis V. Yentekakis <sup>1,\*</sup>, Philippe Vernoux <sup>2</sup>, Grammatiki Goula <sup>1</sup> and Angel Caravaca <sup>2</sup>

<sup>1</sup> Laboratory of Physical Chemistry & Chemical Processes, School of Environmental Engineering, Technical University of Crete (TUC), 73100 Chania, Crete, Greece; mgoula@science.tuc.gr

<sup>2</sup> Univ. Lyon, Université Claude Bernard Lyon 1, CNRS—IRCÉLYON—UMR 5256, 2 Avenue A. Einstein, 69626 Villeurbanne, France; philippe.vernoux@ircelyon.univ-lyon1.fr (P.V.); angel.caravaca@ircelyon.univ-lyon1.fr (A.C.)

\* Correspondence: yyentek@isc.tuc.gr

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**Abstract:** Recent studies have shown that the catalytic performance (activity and/or selectivity) of Pt-group metal (PGM) catalysts for the CO and hydrocarbons oxidation as well as for the (CO, HCs or H<sub>2</sub>)-SCR of NO<sub>x</sub> or N<sub>2</sub>O can be remarkably affected through surface-induced promotion by successful application of electropositive promoters, such as alkalies or alkaline earths. Two promotion methodologies were implemented for these studies: the Electrochemical Promotion of Catalysis (EPOC) and the Conventional Catalysts Promotion (CCP). Both methodologies were in general found to achieve similar results. Turnover rate enhancements by up to two orders of magnitude were typically achievable for the reduction of NO<sub>x</sub> by hydrocarbons or CO, in the presence or absence of oxygen. Subsequent improvements (ca. 30–60 additional percentage units) in selectivity towards N<sub>2</sub> were also observed. Electropositively promoted PGMs were also found to be significantly more active for CO and hydrocarbons oxidations, either when these reactions occur simultaneously with deNO<sub>x</sub> reactions or not. The aforementioned direct (via surface) promotion was also found to act synergistically with support-mediated promotion (structural promotion); the latter is typically implemented in TWCs through the complex (Ce–La–Zr)-modified γ-Al<sub>2</sub>O<sub>3</sub> washcoats used. These attractive findings prompt to the development of novel catalyst formulations for a more efficient and cost-effective control of the emissions of automotives and stationary combustion processes. In this report the literature findings in the relevant area are summarized, classified and discussed. The mechanism and the mode of action of the electropositive promoters are consistently interpreted with all the observed promoting phenomena, by means of indirect (kinetics) and direct (spectroscopic) evidences.

**Keywords:** platinum; palladium; Rhodium; iridium; NO; N<sub>2</sub>O; propene; CO; methane; alkali; alkaline earth; platinum group metals; deNO<sub>x</sub> chemistry; lean burn conditions; TWC; catalyst promotion; EPOC

## List of Contents

<b>1</b>	<b>Introduction</b>	<b>2</b>
<b>2</b>	<b>Promotion Methodologies and Catalysts Formulations/Designs</b>	<b>3</b>
2.1	Electrochemical Catalysts Formulations. The Electrochemical Promotion of Catalysis (EPOC) Concept	3

2.1.1	Operation Modes of the Electrochemical Promotion of Catalysis (EPOC) . . . . .	5
2.1.2	Certain Characteristics of EPOC Concept: . . . . .	7
2.2	Conventional Catalyst Formulations. The Conventional Catalysts Promotion (CCP) Method . . . . .	8
2.2.1	Estimation of the Promoter Coverage . . . . .	8
2.2.2	EPOC and CCP Comparison Issues . . . . .	9
<b>3</b>	<b>Results and Discussion</b>	<b>9</b>
3.1	Promotion of Simple, “Model” Reactions . . . . .	9
3.1.1	CO Oxidation . . . . .	9
3.1.2	Light Hydrocarbons Oxidation . . . . .	17
3.1.3	NO Reduction by CO . . . . .	23
3.1.4	NO Reduction by Hydrocarbons or H <sub>2</sub> . . . . .	29
3.1.5	N <sub>2</sub> O Decomposition and/or Reduction . . . . .	40
3.2	Electropositive Promotion of PGMs Operated Under Simulated Practical Conditions . . . . .	45
3.2.1	Simulated TWC Conditions . . . . .	45
3.2.2	Oxygen Excess Conditions (Simulated Lean-Burn and Diesel Exhausts Gases) . . . . .	52
3.3	Mechanistic Implications: The mode of Action of Electropositive Promoters . . . . .	57
3.3.1	Main Promotion Characteristics and Mechanistic Implications . . . . .	57
3.3.2	Direct Spectroscopic and Other Analytical Technique Evidences . . . . .	63
<b>4</b>	<b>Conclusions and Perspectives</b>	<b>68</b>
	<b>References</b>	<b>69</b>

## 1. Introduction

The development of new catalyst formulations for a more efficient and cost-effective control of unburned hydrocarbons, CO and NO<sub>x</sub> pollutants emitted by mobile and stationary combustion processes is currently an urgent need [1–3]. Commercial three-way catalytic converters (TWCs) have been highly successful in controlling NO<sub>x</sub>, CO and hydrocarbon emissions from conventional stoichiometric gasoline engines. However, some problems, that emerged during their four decades of implementation, concerning the economy of their production process, their composition, their operational/life time behaviour and their recycling still need to be resolved. The most significant issues of TWC technology are the following:

1. Commercial TWCs use formulations based variously on two or three noble metals (Pt, Pd and Rh) where Rh is essential for an efficient control of NO<sub>x</sub> emissions (Rh is highly effective and therefore the key component in TWCs for the NO dissociation/reduction; Pt and Pd, although very active for CO and hydrocarbons oxidations, are almost ineffective for NO<sub>x</sub> reduction). However, Rh is rare, therefore its successful reduction or even replacement by another De-NO<sub>x</sub> efficient catalyst in TWC formulations is highly desirable.
2. A small but significant portion of NO is still converted to the undesirable by-product N<sub>2</sub>O in commercial TWCs; Nitrous oxide emission control, due to N<sub>2</sub>O harmful impact on stratospheric ozone depletion and its outstanding global warming potential (the latter is about 310 and 21 times greater than that of CO<sub>2</sub> and CH<sub>4</sub>, respectively [4,5]), is a current challenge in environmental catalysis technology.
3. TWCs recycling for the noble metals recovery is nowadays marginally profitable, mainly due to the costly final separation of the recovered noble metals; simpler TWCs formulations (i.e., consisting of only one noble metal) are expected to substantially reduce both TWCs' production and recycling costs.

4. Commercial TWCs are no longer efficient in controlling NO<sub>x</sub> emissions from the advanced lean-burn and diesel engines that operate at net-oxidising conditions.

In general, catalytic systems with suitable efficiency under oxygen rich conditions are a great challenge in emissions control technology. Besides lean-burn and diesel engines' effluent gases, such conditions are also typical in several stationary processes of significant environmental footprint, such as in soil fuels combustion processes for heat production in industry, in solid wastes combustion processes and certain chemical processes such as ammonia oxidation processes (e.g., nitric acid plants), adipic acid and other specific industries.

Prompted by these issues, numerous efforts are currently reported in open literature, by several research groups, on discovering means for enhancing the catalytic performance of Pt and Pd or even Rh, for reactions related to CO, NO<sub>x</sub> and hydrocarbons abatement under stoichiometric and/or oxygen rich conditions. A notable part of these studies is focussed on the reduction or replacement of the Rh usage due to its scarcity and consequently higher cost compared to Pt and Pd.

It has been recently shown that the catalytic performance of precious metals can be strongly promoted by alkalis and alkaline earths for reactions related to emissions control catalysis. Two promotion methods were implemented towards this aim: (i) the Electrochemical Promotion of Catalysis (EPOC) concept or NEMCA effect (Non-Faradaic Electrochemical Modification of Catalytic Activity), proposed three decades ago by Vayenas and co-workers (e.g., [6–13]) and (ii) the Conventional Catalysts' Promotion (CCP), applicable by means of highly dispersed (supported) catalysts, as typically used in industrial applications (e.g., [14,15]). On these bases, rational/more efficient catalyst formulations and catalytic systems have been designed with significantly widened operational and/or implementation windows.

The present review summarises and comparatively analyses these literature results, paying attention on both fundamental and practical issues emerged. Mechanistic considerations (involving the mode of action of electropositive promoters in emissions control catalytic chemistry) are described in confrontation with recent spectroscopic and surface analysis studies evidencing their rightness.

## 2. Promotion Methodologies and Catalysts Formulations/Designs

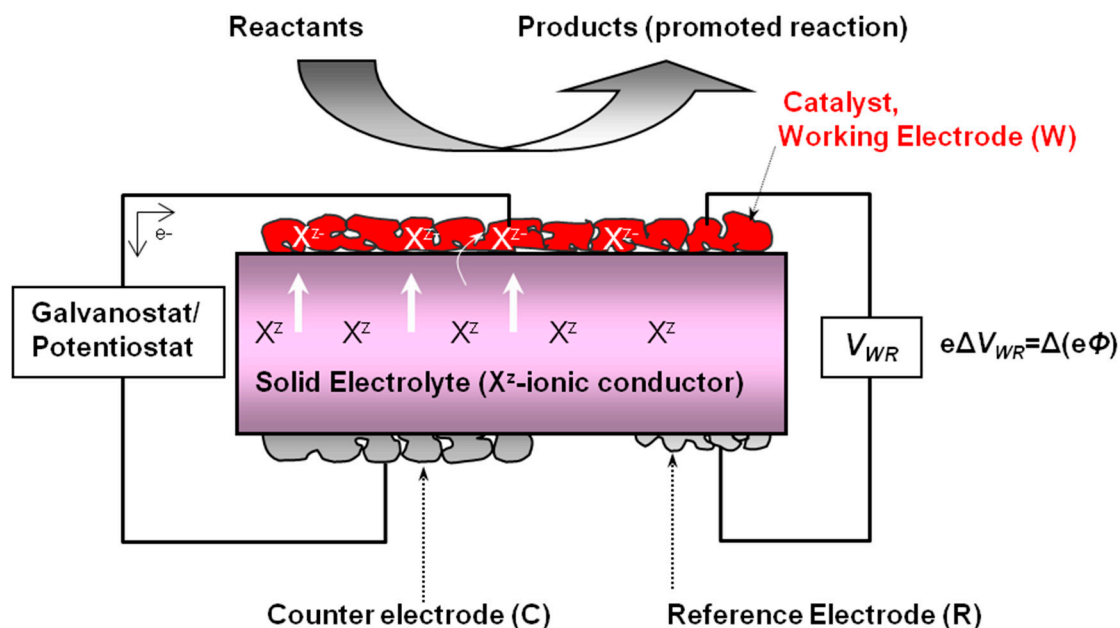
Materials formulations and designs, experimental setup and other specific characteristics and/or rules regarding the two promotion methods, EPOC and CCP, are briefly described below.

### 2.1. Electrochemical Catalysts Formulations. The Electrochemical Promotion of Catalysis (EPOC) Concept

It has been shown by Vayenas and co-workers (e.g., [6,7]) that the chemisorptive and catalytic properties of metal catalysts, in the form of thin polycrystalline porous metal films, interfaced with solid electrolytes (X<sup>z</sup>-ionic conductors: X is the type of ion transferred, z is its positive or negative charge) are subjected to in situ controlled electrochemical promotion via external bias applications, that is, currents or voltages imposed between the catalyst metal film and a separate counter electrode deposited on the same solid electrolyte specimen, which constitute a solid state electrochemical galvanic cell schematically shown in Figure 1.

In this way, applying small electric currents (typically some tens of μA units) or potentials (typically −2 to +2 V) between the working (catalyst film) and the counter electrodes via a Galvanostat/Potentiostat (Figure 1), ions are supplied from (or to) the solid electrolyte to (or from) the catalyst-electrode surface. Ions flux direction is determined by the direction of the applied current in combination with their charge, while their flux rate by the Faraday's law,  $r_z = I/zF$  (I is the applied current in A; z is the ion's charge; F is the Faraday's constant = 96,485 Cb/mol). As we shall see in detail in Section 3.3, there is compelling evidence that these ions (together with their compensating charge in the metal thus forming surface dipoles) spill over (migrate) onto the gas-exposed catalyst surface, establishing an effective electrochemical double layer on the catalytically active surface altering its electron availability (work function). This strongly affects the binding strength of chemisorbed reactants and intermediates resulting to a significant modification on catalytic reaction rate (and

or selectivity), typically greatly larger than the rate of ions flux that created these modifications (i.e., non-Faradaic behaviour), the so-called NEMCA (Non-Faradaic Electrochemical Modification of Catalytic Activity) phenomenon or EPOC (Electrochemical promotion of Catalysis).



**Figure 1.** Schematic representation of a solid state electrochemical cell, through which the EPOC concept can be applied. X: type of ion transferred from the solid electrolyte to the catalyst surface and z: ion charge (e.g.,  $O^{2-}$ ,  $Na^+$ ,  $K^+$ ,  $H^+$ ).

The EPOC was then applied to a large number of catalytic reactions [6,7,13], including reactions related to emissions control catalysis (e.g., [16–22]). Numerous EPOC studies regarding electrochemically imposed electropositive promotion by alkalis of Pt-group metals' catalysed emissions control reactions have also been reported, which are subject of the present review.

Alkali-conducting solid electrolytes such as  $Na^+$  or  $K^+$  substituted  $\beta$ - and  $\beta''$ -aluminas,  $(Na \text{ or } K)_{1+x}Al_{11}O_{17+x/2}$  and  $(Na \text{ or } K)_{1+x}M_xAl_{11-x}O_{17}$ , respectively [6], are used for the construction of electrochemical galvanic cells with the following configuration (Figure 1):



These cells are exposed to the reacting gas mixture by means of a continuous flow well-mixed reactor, as that shown in Figure 2, described as “single-pellet” (reactor) configuration and behaved similarly to a classical Continuous-Stirred-Tank-Reactor (CSTR) [12]. Controlled amounts of promoting species (alkali cations) can therefore be in situ supplied through the solid electrolyte onto the catalyst surface, causing significant alterations on the catalytic properties of the latter.

For the sake of simplicity, inert (in respect to the studied reaction) counter and reference electrodes (e.g., Au) are typically applied in EPOC studies conducted in reactor configurations similar to this shown in Figure 2; avoiding their participation in the catalytic reaction vectors (activity, selectivity) simplifies the data analysis, interpretation and understanding. It is also worth noting that besides their role as an in situ and reversible promoting species sources, solid electrolytes involved in the configuration of EPOC galvanic cells do not actually play any additional role on the promotional phenomena obtained.



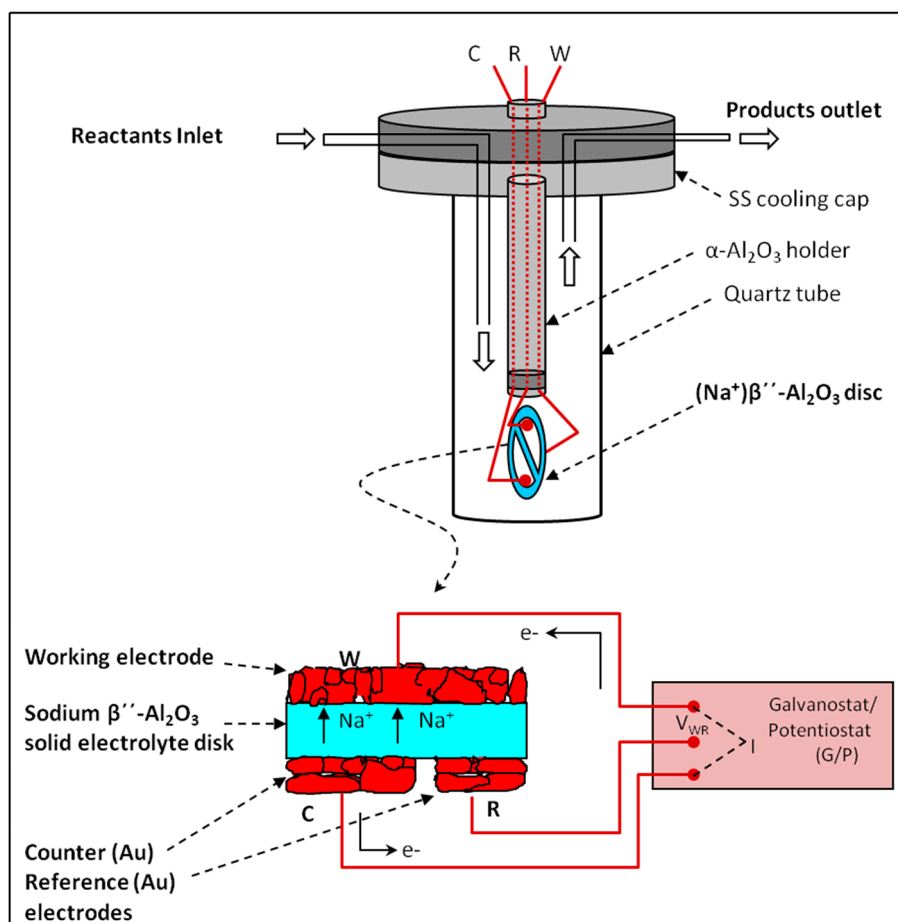


Figure 2. The single pellet reactor configuration for electrochemical promotion studies [12].

### 2.1.1. Operation Modes of the Electrochemical Promotion of Catalysis (EPOC)

#### (i) Galvanostatic transient operation:

One can use the galvanostatic transient mode of EPOC operation, described in detail in ref. [16], in order to be able to calculate the coverage,  $\theta$ , of the promoting species (electrochemically supplied) on the catalyst surface as a function of time. Briefly, transient galvanostatic operation concerns the application of a constant current,  $I$ , between the catalyst and counter electrodes via the galvanostat. In cells of the type described by the formula (1), imposition of a constant negative current corresponds to a constant flux of alkali cations to the catalyst surface at a rate equal  $I/F$  (in moles of alkali/s).

The obtained alkali coverage,  $\theta_{\text{Alk}}$ , can therefore be calculated from Faraday's law [6,16],

$$\theta_{\text{Alk}} (\%) = 100 \cdot (-It / FN_o) \quad (2)$$

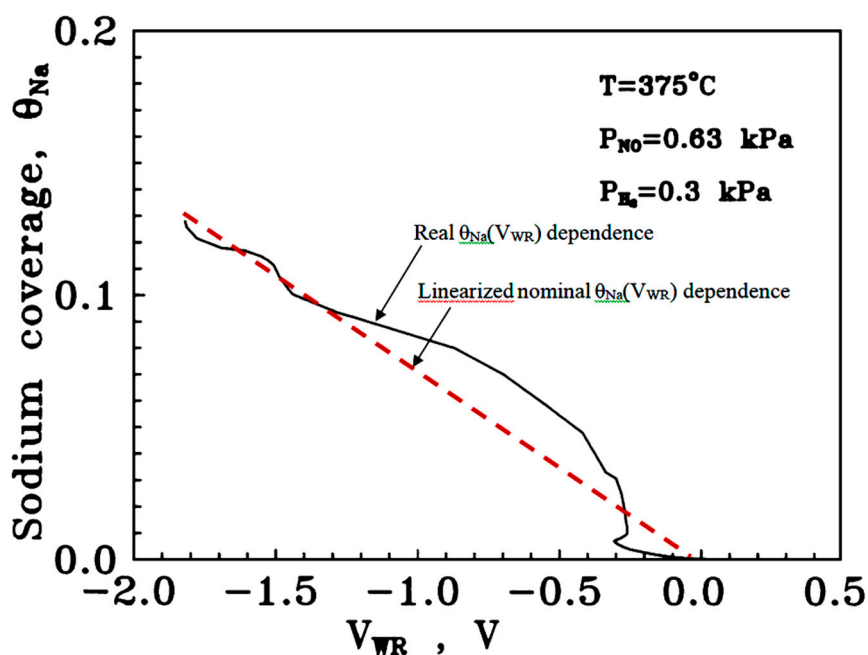
where,  $t$  is the time of current ( $I$ ) application,  $F$  is the Faraday's constant and  $N_o$  is the number of catalyst active sites independently measured via surface titration. Recording the metal-solid electrolyte polarization transient during the galvanostatic experiment that is, the time variation of catalyst potential by means of a reference electrode,  $V_{\text{WR}}$  (Figure 1), this permits establishment of the relationship  $\theta_{\text{Alk}}(V_{\text{WR}})$  between alkali coverage and catalyst potential  $V_{\text{WR}}$  (Figure 3).

This relationship is in general dependent on gaseous composition but this dependence is relatively weak because the catalyst work function  $e\Phi$  varies according to [6,7,11]:

$$e\Delta V_{\text{WR}} = \Delta(e\Phi) \quad (3)$$

and is determined primarily by the coverage of alkali, due to the large dipole moment of alkalis on the Pt-group metal surfaces.

Galvanostatic operation concerns a continuous supply and accumulation of alkali on the catalyst surface (Equation (2)). Current interruption at a desired alkali coverage can then provide an optimally alkali-promoted catalyst surface. Alkali species are not typically consumed during the catalytic reaction, which allows working under stable reaction conditions. Hence, the promotional effect induced by the alkali coverage remains practically constant, even after the interruption of the applied current.



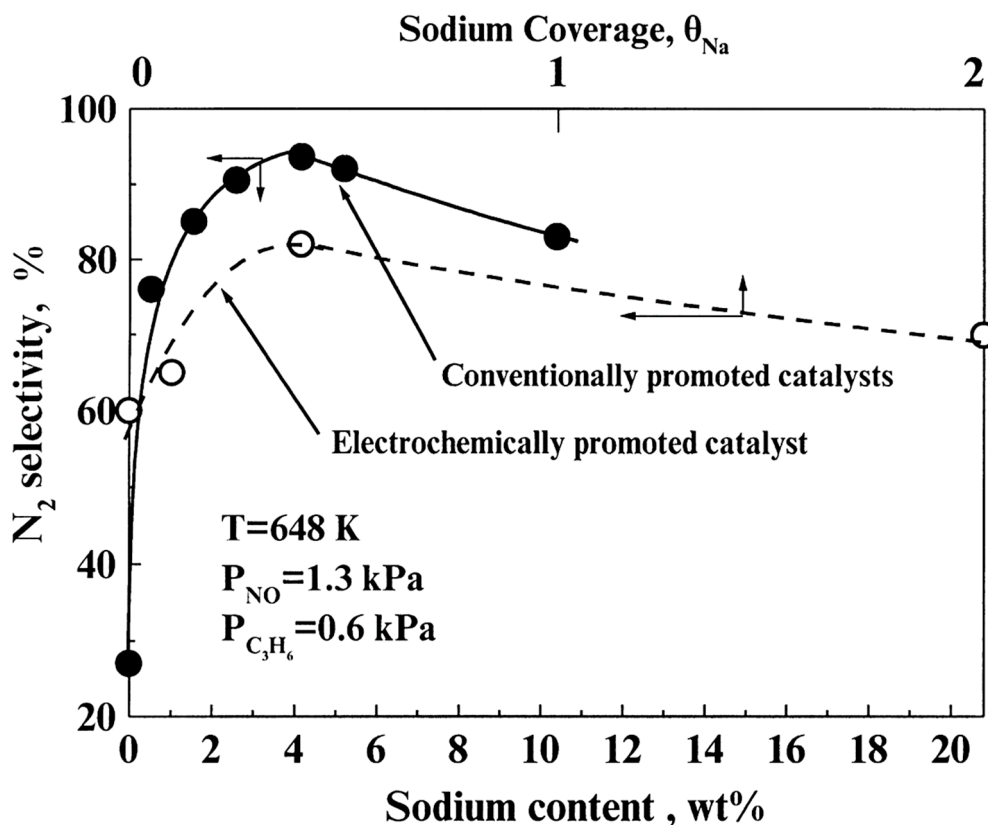
**Figure 3.** Dependence of alkali coverage on catalyst potential  $V_{WR}$  under certain reaction conditions (Reproduced with permission from Ref. [19]. Copyright 1997, Elsevier).

It is worth noting that galvanostatic EPOC operation provides a rapid method for assessing the response of the reaction rate to promoter coverage (Figure 4); it consequently offers a very quick and easy way to find, at any set of conditions, the optimal promoter loading. This information could then be used for the direct design of optimally promoted conventional catalysts formulations for practical applications (Figure 4) [21].

(ii) Potentiostatic operation (a steady-state mode of operation):

The potentiostatic mode of EPOC operation corresponds to catalyst operation under the imposition of a constant catalyst polarization ( $V_{WR}$ ) via the potentiostat. This is a steady-state mode of operation: since the desired catalyst potential  $V_{WR}$  is imposed via the potentiostat, a very rapid transfer of the appropriate amount of alkali cations to the catalyst surface takes place, which supplies the required amount of alkali in order to develop and stabilize the externally imposed polarization value  $V_{WR}$ ; then the current is sharply vanished, asymptotically approaching the zero value.

Since the  $\theta_{Alk}(V_{WR})$  relationship between alkali coverage and catalyst potential can be obtained through a galvanostatic transient conducted at the desired reaction conditions (as described in (i); e.g., Figure 3), the potentiostatic mode of operation is more suitable and commonly used in EPOC studies. It allows to work under steady-state conditions at several constant catalyst potentials, that is, at several constant coverages of the promoter. The steady-state reaction rate response on promoted catalyst surfaces, upon varying of the other reaction parameters (e.g., temperature, reactants' composition, etc.) can then be studied (e.g., [6,7]).



**Figure 4.** Comparison of electrochemically promoted (EPOC) and conventionally promoted (CCP) Pt with respect to N<sub>2</sub>-selectivity under the NO + C<sub>3</sub>H<sub>6</sub> reaction at T = 375 °C and [NO] = 1.3%, [C<sub>3</sub>H<sub>6</sub>] = 0.6% feed. Similar well-correlated dependences of the variation of N<sub>2</sub>-selectivity on nominal sodium coverage ( $\theta_{Na}$ , upper abscissa) were obtained by the two methods of promotion (EPOC and CCP) applied. EPOC was performed in a Pt/(Na) $\beta''$ Al<sub>2</sub>O<sub>3</sub>/Au galvanic cell (Reprinted with permission from Ref. [22]. Copyright 2000, Elsevier).

#### 2.1.2. Certain Characteristics of EPOC Concept:

##### (i) Reversibility of the electrochemically imposed promotional phenomena:

By reversing the direction of the applied current in the galvanic cell represented in Figure 1 or even by setting the potential value that corresponds to an alkali-free catalyst surface (Figure 3), the catalyst restores its initial un-promoted intrinsic properties. In other words, the electrochemically imposed promotional phenomena are totally reversible; EPOC provides an in situ, controlled and reversible way of catalyst promotion [6,7].

##### (ii) EPOC can be used as a fast probe for the optimal promoter loading determination:

Inter alia, EPOC can be successfully used as an effective research tool for evaluating the influence of a candidate promoter to a catalytic system and at the same time for determining the optimal promoter loading (coverage) at any reaction conditions of our interest. After the understanding that electrochemical and conventional promotions in catalysis, EPOC and CCP, are subjected to the same physicochemical rules (this has been proved both experimentally [21,22] and theoretically [23,24]), the findings and knowledge obtained by the application of the electrochemical promotion can be successfully applied for the design of effective conventional catalyst formulations for practical applications [21,22,25]. This strategy enabled us to design novel catalyst formulations extremely active and selective in emission control catalysis, for example, optimally alkali-promoted noble metal catalysts [21].

## 2.2. Conventional Catalyst Formulations. The Conventional Catalysts Promotion (CCP) Method

The wet impregnation method was used in most cases for the production of conventional type (i.e., highly dispersed on large surface area carriers), alkali-promoted noble metal catalysts. Typical carriers used were  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, yttria stabilized zirconia (YSZ) and rare earth oxides (REOs: La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>) modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The preparation of the conventional promoted catalysts was performed either by two subsequent impregnation steps (where the noble metal was first deposited, followed by that of the promoter) or by simultaneous, one-step impregnation, in a solution containing both the noble metal and the promoter precursors, typically nitrate but also chloride salts). When using only nitrate precursors, pre-treatment procedures typically involve a high temperature (ca. 500–600 °C) treatment step in air for the decomposition of the nitrates (active phase and promoter) and a subsequent treatment of the resulted catalysts under reaction conditions (i.e., under the studied reaction) for several hours or days in order to ensure stable operation. On the other hand, when a chloride precursor is used, pre-treatment in H<sub>2</sub> flow at temperatures typically 400–450 °C for several hours (>2 h) is applied as a first step for the precursor decomposition and the removal of the residual chlorine (e.g., [14,15]); the inhibitory behaviour of the latter on the reactions related to emissions control catalysis is well known. Then, for performance stabilization purposes, operation at certain reaction conditions is applied, as well [14,15].

### 2.2.1. Estimation of the Promoter Coverage

The coverage of the promoter species on the active catalyst surface is a significant factor not only for ranking but also for better understanding its promoting effects. Its knowledge is also useful for comparison purposes between electrochemically and conventionally promoted catalysts. For the former case (EPOC) we have already shown (Equation (2)) that the coverage of the alkali promoter can be directly estimated via the Faraday law applied to the data of a galvanostatic transient. In the latter case (CCP), a “nominal” percentage surface coverage of the alkali promoter ( $\theta_{\text{Alk}}$ ) could be calculated from the alkali wt% content of the catalyst (e.g., [14,21]) by the assumption that all the promoter is present at the surface and distributed uniformly over the entire available area (noble metal + support), without any incorporation into the bulk and that an one-to-one correlation between alkali adatoms and active metal sites exists. Hence, the following equation can be used:

$$\theta_{\text{Alk}} (\%) = (\text{wt\% of Alkali on the catalyst}) \cdot (N_{\text{AV}} / M_{\text{Alk}} \cdot A \cdot d) \quad (4)$$

where  $N_{\text{AV}}$  is the Avogadro number,  $M_{\text{Alk}}$  is the molecular weight of alkali used,  $A$  is the BET catalyst surface area (m<sup>2</sup>/g) and  $d$  is the surface density (atoms/m<sup>2</sup>) of the active metal (PGM) (e.g.,  $d_{\text{Pt}} = 1.53 \times 10^{19}$ ,  $d_{\text{Pd}} = 1.27 \times 10^{19}$ ,  $d_{\text{Rh}} = 1.33 \times 10^{19}$  for {111} crystallites). Considering  $d$  in Equation (4) as the surface density of the alkali adatom used (i.e.,  $8.84 \times 10^{19}$ ,  $3.314 \times 10^{19}$ ,  $1.8 \times 10^{19}$ ,  $1.115 \times 10^{19}$  or  $1.45 \times 10^{19}$  for Li, Na, K, Cs or Rb, respectively; values calculated on the basis of the alkali ionic radius), one can probably be led to a better estimation of the nominal alkali coverage [22,25]. In any case and since the issues about the alkali distribution (preference between active metal or support surface, formation of 2D and/or 3D aggregates) are not clear yet, it is apparent that Equation (4) leads to a quite rough estimation of alkali coverage, which however, in the absence of more rigorous estimations or experimental measurements, can be of some interest and applicable as a first approximation upon comparing the EPOC and CCP methods of promotion on a catalytic system (e.g., [22,25]).

The fixed bed, single pass, quartz (or stainless steel) tube reactor configuration is typically used for testing the conventional type catalysts (in the form of powder, small particle clusters or even structured honeycomb monolithic configurations) at the desired reactions. On-line gas chromatography, on-line mass spectroscopy and continuous NO<sub>x</sub> chemiluminescence's analysis were used for the analysis of the influent and effluent reactor streams in most studies.

### 2.2.2. EPOC and CCP Comparison Issues

In order to have a solid basis for comparison between electrochemically promoted or conventional promoted catalysts, the rate enhancement ratio ( $\rho$ ), is introduced in both cases, defined as:

$$\rho = r_x/r_o \quad (x = \text{EPOC or CCP}) \quad (5)$$

$r_o$  is the unpromoted rate and  $r_x$  is the promoted by alkali rate, where the alkali species are either supplied electrochemically ( $x = \text{EPOC}$ ) or conventionally ( $x = \text{CCP}$ ).  $\rho$  values as high as 420 (42,000% rate increase) have been reported for some important emissions control catalytic systems (e.g.,  $\text{NO} + \text{C}_3\text{H}_6/\text{Pt}$ ) by means of alkali promotion. It must be emphasized here that in literature studies (either EPOC or CCP) involving  $\rho$  values estimation, particular attention was devoted in order the catalytic activity data to be acquired in the intrinsic kinetic regime, not influenced by mass transfer limitations (i.e., under low conversions, no limiting reactant, differential reactor operation, small catalyst particles, etc.)

In the case of EPOC an additional parameter, the Faradaic efficiency ( $\Lambda$ ) is also introduced [6], which can describe the magnitude of promotion; however, this has no meaning in CCP studies:

$$\Lambda = (r_{\text{EPOC}} - r_o)/(I/zF) = \Delta r/(I/zF) \quad (6)$$

where  $F$  is the Faradaic constant and  $I$  is the current. The term  $I/zF$  ( $z$  is the promoting ion charge;  $z = +1$  in the case of alkali promotion) corresponds to the rate of promoting ions supplied electrochemically to the catalyst surface according to the Faraday's law.

Another useful parameter to quantify of the magnitude of the EPOC is the promotion index  $Pi$  [16,26]:

$$Pi = (r_{\text{EPOC}} - r_o)/\Delta\theta_i \quad (7)$$

where  $\Delta\theta_i$  is the coverage of the promoting species such as  $\text{Na}^+$ .

## 3. Results and Discussion

### 3.1. Promotion of Simple, "Model" Reactions

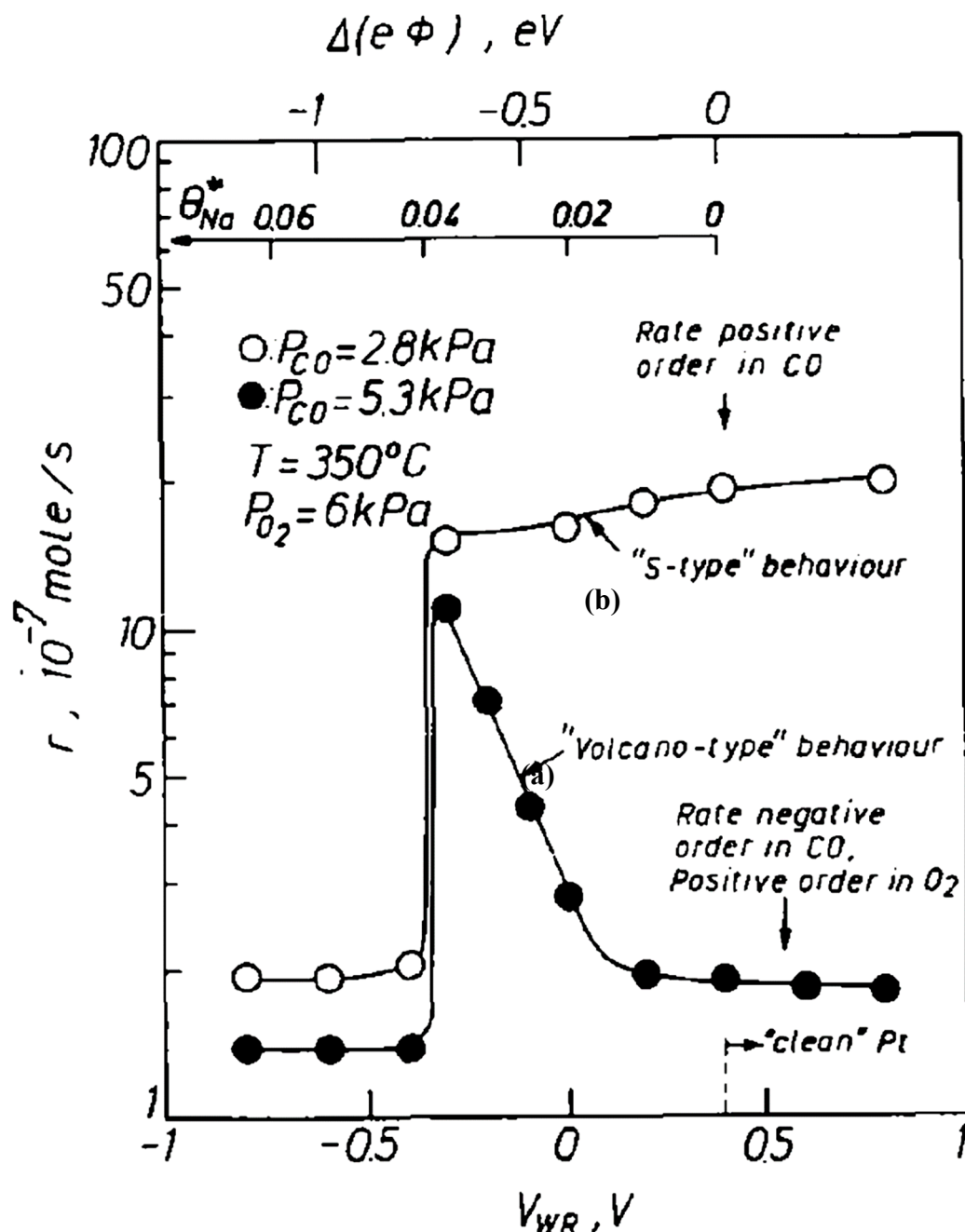
Literature studies concerning "model" (i.e., simple) reactions, catalysed by Pt-group metals under electropositive promotion by alkalis or alkaline earths, conducted either by EPOC or CCP, are listed in Table 1 and discussed below.

#### 3.1.1. CO Oxidation

Several publications concern the promotion of the PGMs-catalysed CO oxidation by alkalis. Significant promotional effects have been achieved either on thin metal film electrocatalysts interfaced with an alkali-contacting solid electrolyte (EPOC), playing the role of in situ source of alkali cations or on conventional type highly dispersed catalysts dosed with several amounts of alkali promoter (CCP). However, the promoting phenomena were found to be strongly depended on the  $\text{CO}/\text{O}_2$  gas phase composition and on the alkali loading of the catalyst.

In particular, Yentekakis et al. [16] using the continuous flow, well-mixed, single-pellet reactor described in Figure 2 have shown that the rate of CO oxidation can be markedly enhanced via EPOC by up to 600% (at  $T = 350^\circ\text{C}$ ) under CO-rich conditions (i.e., at conditions where CO oxidation kinetics obey negative order in CO, positive order in  $\text{O}_2$ ) over a Pt film electrocatalyst interfaced with a  $\text{Na}^+$ -conducting  $\beta''\text{Al}_2\text{O}_3$  solid electrolyte (Table 1). Those rate enhancements were achieved at sodium coverages on Pt surface of about 2–4%, while higher sodium coverages were found to depress the catalyst activity, thus leading to a "volcano" type behaviour upon increasing the coverage of the promoting species (Figure 5, curve a). However, at  $\text{O}_2$ -rich conditions (i.e., when the rate is of positive order in CO) only poisoning phenomena occurred upon increasing Na coverage on the

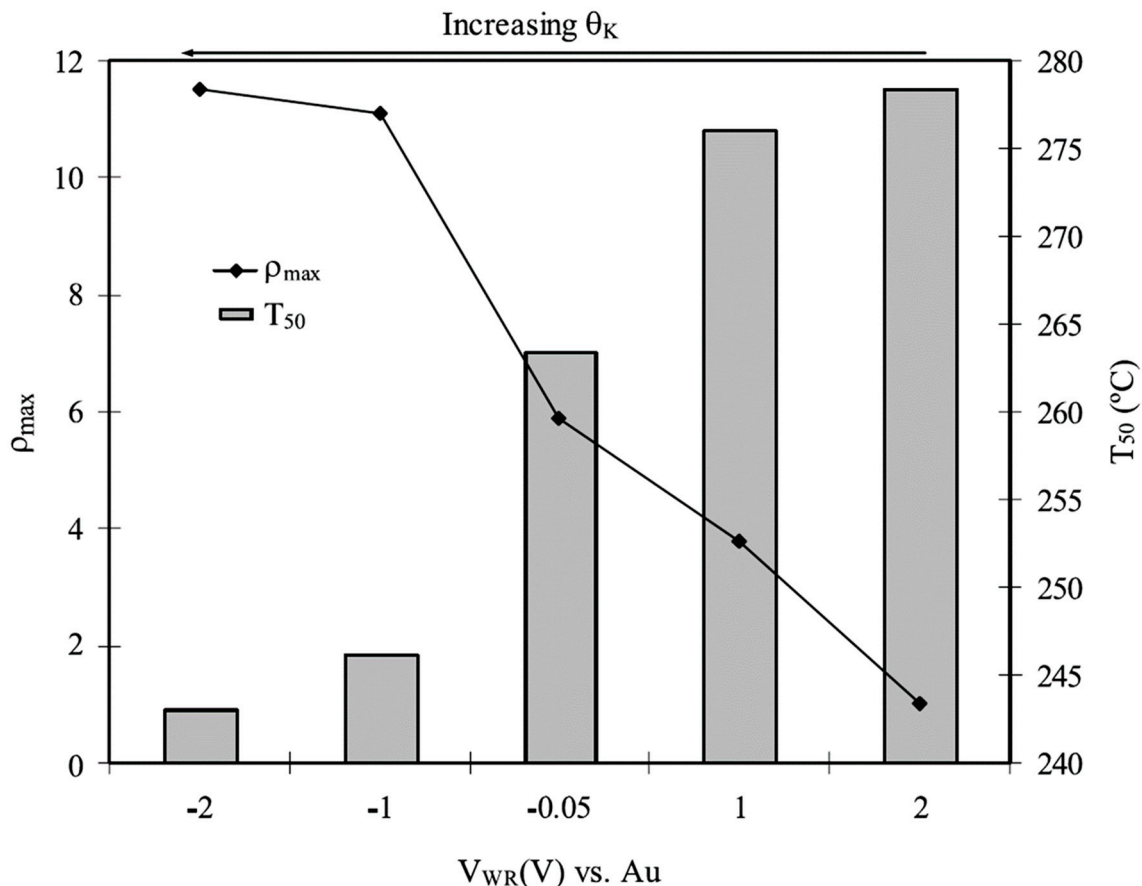
catalyst surface (Figure 5 curve b). According to the rules of catalyst promotion, Na promoters modify the chemisorptive properties of CO and O<sub>2</sub> reactants on Pt active sites. At CO-rich conditions and for Na coverages up to ~4%, the promotional effect was attributed to a Na-induced enhancement in oxygen chemisorption as a result of a strengthening of the Pt–O bond. The rate poisoning behaviour at higher Na coverages was attributed to active sites blocking phenomena due to the formation of a CO–Na–Pt surface complex.



**Figure 5.** Effect of Na coverage  $\theta_{Na}$  on the rate of CO oxidation at oxygen lean (a:  $T = 350^\circ\text{C}$ ,  $[\text{O}_2] = 6\%$ ,  $[\text{CO}] = 5.3\%$ ; filled symbols) and at oxygen rich ((b):  $T = 350^\circ\text{C}$ ,  $[\text{O}_2] = 6\%$ ,  $[\text{CO}] = 2.8\%$ ; open symbols) conditions. The volcano type behaviour upon increased Na coverage is obvious in case (a). Data was acquired in a Pt/(Na) $\beta''$ Al<sub>2</sub>O<sub>3</sub>/Au galvanic cell (Reprinted with permission from Ref. [16]; Copyright 1994, Elsevier).



Another EPOC study was reported by De Lucas-Consuegra et al. [27] on the effect of electrochemically imposed potassium (K) on the Pt-catalysed CO oxidation at 200–350 °C. Rate enhancement ratios of about  $\rho = 11$  (1100%) at  $T = 278$  °C and light-off temperature decreases by  $\sim 40$  °C were achieved at equimolar reactant composition,  $[CO] = [O_2] = 5000$  ppm (Figure 6 and Table 1).



**Figure 6.** Effect of catalyst overpotential (VWR) on the maximum rate enhancement ratio ( $\rho_{max}$ ) and on  $T_{50}$  of CO oxidation on Pt. Conditions:  $[CO] = [O_2] = 0.5\%$  He balance,  $F_t = 108$  cm<sup>3</sup>/min. Data was acquired in a Pt/(K) $\beta''$ -Al<sub>2</sub>O<sub>3</sub>/Au galvanic cell. (Reprinted with permission from Ref. [27]; Copyright 2008, Elsevier).

The maximum promotional effect was found under the application of  $-2$  V; the appropriate parameters necessary for the estimation of the K coverage corresponding to this catalyst polarization are not available. The reversible promotional phenomena were attributed to the formation and decomposition of potassium compounds on the Pt surface (probably potassium carbonates and/or oxides) that enhanced the adsorption of oxygen at the expense of CO on a surface predominately covered by CO under unpromoted conditions in the reaction temperature range studied.

Regarding CCP studies, CO oxidation activity enhancements were also reported by Mirkelamoglu and Karakas [28,29] over conventional type 0.1wt% Na-promoted 1wt% Pd/SnO<sub>2</sub> catalyst tested at two different  $[CO]/[O]$  ratios, 1.25 and 0.5. The authors found that in the case of CO-rich gas composition ( $[CO]/[O] = 1.25$ ), Pd can be up to 2.6-fold times (260%) more active on CO oxidation at 150 °C (Table 1), while non or moderate promotional effects were observed at O<sub>2</sub>-rich conditions ( $[CO]/[O] = 0.5$ ). A surface segregation of Pd atoms increasing the reactive sites for CO oxidation, together with the formation of super-oxide species observed over Na-PdO/SnO<sub>2</sub> were considered to be the origin of the observed promotional effects on the Na-dosed catalyst [29].

The effect of alkali oxide additives (Na<sub>2</sub>O, K<sub>2</sub>O) on the alumina support of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts on CO oxidation was investigated by Lee and Chen [30]. They concluded that the addition of alkalis

on  $\text{Al}_2\text{O}_3$  influences the basicity of the catalyst, which in turn results to higher oxidation activities. Higher promotional effect was achieved by potassium, which resulted in a decrease of CO light-off temperature by 90 °C under CO/ $\text{O}_2$  stoichiometric conditions. The study, however, was performed under simulated two-stroke motorcycle emissions (involving  $\text{C}_3\text{H}_6$ ,  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the feed, besides CO and  $\text{O}_2$ ) at the stoichiometric point and oxygen-deficient environments. Therefore, this work will be further analysed in the proper Section 3.2.1.

The influence of alkaline earths on CO oxidation activity was also investigated over Pd catalysts supported on Ba-modified  $\gamma\text{-Al}_2\text{O}_3$  or  $\text{CeO}_2\text{-ZrO}_2$  carriers by Tanikawa and Egawa [31]. They found that the activity of Pd/ $\gamma\text{-Al}_2\text{O}_3$  catalyst can be significantly improved by increasing the Ba promoter loading; an amount of 10–15wt% Ba decreases the light-off temperature by ~45 °C compared to the un-modified catalyst (Table 1). However, an adverse effect upon Ba addition was observed for Pd/ $\text{CeO}_2\text{-ZrO}_2$  catalysts; an amount of 10 wt% Ba leads to an increase of light-off temperature by ~100 °C. The pronounced effect of Ba over Pd/ $\gamma\text{-Al}_2\text{O}_3$  catalysts was ascribed to the weakening of CO adsorption strength, whereas its inhibiting role over Pd/CZ catalysts was attributed to the suppression of Pd interaction with ceria-zirconia support.

In addition, the pronounced effect of electropositive promoters on CO preferential oxidation (PROX) under  $\text{H}_2$ -rich conditions has been recently demonstrated [32–41]. Minemura et al. [32,33] showed that the addition of alkalis (Li, Na, K, Rb and Cs) in a 2wt% Pt/ $\gamma\text{-Al}_2\text{O}_3$  catalyst results in very significant promotional effects on the selective oxidation of CO under  $\text{H}_2$ -rich environments (Table 1). The promotional effects followed “volcano” type behaviour upon increasing alkali loading, thus providing an optimal loading for each alkali; a 10–15 alkali/Pt loading ratio was found to optimize the promotional effects of Na and K, while the optimal alkali/Pt ratios were 3 and 5 for Cs and Rb, respectively. For a constant alkali/Pt loading equal to 3, the order on the promoting effect on CO conversion (and TOFs) was found to be  $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li} \sim \text{alkali-free Pt}$ , while the order of the selectivity to  $\text{CO}_2$  was  $\text{K} > \text{Rb}$ ,  $\text{Na} > \text{Cs} > \text{Li}$ . At higher alkali loadings (alkali/Pt = 10), the order of the turnover frequency rates of CO oxidation were  $\text{K} > \text{Na} > \text{Rb} > \text{Cs} \sim \text{Li} > \text{alkali-free Pt}$ , with a similar order for the selectivity towards  $\text{CO}_2$ . The changes in the order of the activity of the catalysts were due to over-promotion, that is, for some alkalis (e.g., Rb and Cs) their optimal loading was exceeded under the conditions used. In these studies, turnover rate enhancement ratio values up to  $\rho = 10$  for the optimal K promotion at  $T = 100\text{ °C}$  [32] and even better (up to  $\rho = 20$ ) at  $80\text{ °C}$  [33] were achieved. Further studies by the research group, focused on the optimal promoter (K) when applying different supports ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$ ) for the dispersion of Pt, have shown that the most remarkable promoting effects are obtained on Pt/ $\gamma\text{-Al}_2\text{O}_3$  [34] (Table 1). Corroborative characterization studies by means of a variety of techniques, e.g., Transmission Electron Microscopy (TEM), Extended X-ray Absorption Fine Structure (EXAFS), X-ray Absorption Near Edge Structure (XANES), Fourier-Transform Infrared Spectroscopy (FTIR), enable the authors to consistently interpret the promotion features [35,36]. FTIR spectroscopic evidences for a K-induced weakening in the strength of CO adsorption on Pt and drastic changes on the adsorption site of CO (bridge and three-fold hollow CO species) found on the Pt (10wt% K)/ $\gamma\text{-Al}_2\text{O}_3$  catalyst were considered responsible for the observed promotional effects attributed to the change in the electronic state of K-modified platinum [35,36]. OH co-adsorbed species (originating from  $\text{H}_2$  and  $\text{O}_2$  interaction under PROX conditions) that promote the CO oxidation were found by in situ FTIR on the highly active K-modified Pt/ $\gamma\text{-Al}_2\text{O}_3$  catalyst [36]. The inhibiting effects on PROX reaction under over-promotion conditions (beyond the optimal promoter loading) were attributed to aggregation of Pt metal particles caused by the larger amount of alkali metal used [36].

CO preferential oxidation was also found to be very pronounced over Pt clusters dispersed on alkali (Na, Rb or Cs)-modified  $\text{SiO}_2$  by Pedrero et al. [37]. Optimum promotional effects were obtained with Cs at a surface concentration of 1.6 atoms/ $\text{nm}^2$ ; CO oxidation turnover rates (TOFs) more than one order of magnitude higher than those obtained on the un-promoted Pt/ $\text{SiO}_2$  catalysts were recorded, which were accompanied by CO oxidation selectivity >90% (Table 1). In accordance to the authors, the beneficial effect of alkalis can be interpreted based both on the electronic interactions between

alkali atoms and metals and on the inhibition of spill over-mediated  $H_2$  oxidation pathways induced by alkalis.

The effect of Na promoter on CO PROX reaction was also investigated over bimetallic PtCo/ $Al_2O_3$  catalysts by Kwak et al. [38]. They found moderate promotion of PROX activity on monometallic Pt catalyst while substantial rate promotion on the bimetallic PtCo counterpart catalyst up to a sodium loading of 2.0wt%; the CO-PROX selectivity was not influenced in both cases (Table 1). They concluded that the formation of Na-O-Al bonds by incorporation of Na ions into the alumina lattice, that happens at low sodium content, suppresses the formation of the surface spinel cobalt species and promotes the formation of bimetallic Pt-Co species; at higher Na content (ca. 3wt%) bulk sodium particles on the catalyst surface interact with the active species inhibiting PROX activity.

On the other hand, a notable increase on both CO conversion and  $CO_2$  selectivity under PROX conditions was attained with Mg-promoter over Pt/ $Al_2O_3$  catalysts by Cho et al. [39] (Table 1). The maximum values of CO conversion and  $CO_2$  selectivity for Pt-Mg/ $Al_2O_3$  catalysts were 93.1 and 62%, respectively, at 170 °C, compared to 70.2 and 46.8% at 200 °C over the un-promoted Pt/ $Al_2O_3$  catalysts. The effect of  $CO_2$  and  $H_2O$  in the feed was also studied in this work under PROX conditions, as well as the CO oxidation reaction in the absence of excess  $H_2$  under Mg-promotion. The superior performance of Mg-modified catalysts was attributed to an increase in Pt electron density, as well as to an increase of hydroxyl groups on catalyst surface.

Finally, de Lucas-Consuegra and co-workers [40] demonstrated the pronounced effect of electropositive modifiers ( $K^+$  ions) on the preferential oxidation of CO via EPOC by the use of a Pt/ $K^+$ -conducting- $\beta-Al_2O_3$ /Au galvanic cell. At a 195 °C and a feed composition of  $CO/O_2/H_2 = 0.4\%/0.2\%/16\%$ , the authors found up to  $\rho = 1.3$  rate enhancements, achievable at a potassium coverage of  $\theta_K \sim 2\text{--}4\%$ . A concomitant increase in  $CO_2$  selectivity of  $\sim 10\%$  was recorded as well (Table 1). The effect of the alkali on the chemisorptive bonds of CO, H and O on Pt surface was considered to be the origin of the observed promotional phenomena.

For more information, a short review has been recently published regarding the promotional effect of alkali promoters (CCP) on PGMs (Pt, Ru and Ir)-catalysed CO PROX reaction [41].

A comparative overview of the literature findings included in Section 3.1.1 and in Table 1 leads to the following general remarks: Among PGMs only Pt and Pd were investigated so far for CO oxidation under electropositive promotion (by alkalis or alkaline earths). No studies exist that were performed at similar conditions using both EPOC and CCP methods, preventing us from making a direct one-to-one comparison of the outputs of the two methods. The general view is that alkalines efficiently promote the Pt and Pd catalysed CO oxidation only at conditions where the reaction rate is negative order in CO, positive order in  $O_2$  (the so-called CO-rich conditions at which CO coverage predominates on the catalyst surface; not necessary at  $CO/O_2 > 1$ ), while non, moderate or only poisoning was found under  $O_2$ -rich conditions. Even in the former case, the promotion follows volcano type behaviour upon increasing promoter loading, reversed to poisoning for high promoter loadings; optimal promoter loadings were typically low. The maximum rate enhancement ratios were reported for Pt/ $CO+O_2$  catalytic system under EPOC:  $\rho = 6$  with Na at 350 °C [16] and  $\rho = 11$  with K at 278 °C [27].

Volcano-type promotion was the main feature of the electropositive promotion of PGMs under the preferential CO oxidation (PROX), as well. Moreover, for similar reaction and promoter loading conditions larger alkalis (Cs, Rb, K) offered superior promotion. For this reaction two studies exist that concern usage of the same promoter (K) and active metal (Pt), one performed using CCP the other EPOC. Although  $\rho$  values obtained by CCP were significantly larger ( $\rho = 10$  [32–36]) than that obtained by EPOC ( $\rho = 1.3$  [40]), the applied conditions were quite different, preventing us from making a creative comparison.

The alkaline-induced pronounced enhancement on oxygen adsorption compared to that of CO was a key argument in most of the aforementioned studies upon explaining their findings, whereas the formation of large surface alkali complexes was considered responsible for the rate poisoning at high alkali loadings.

**Table 1.** Electropositive promotion of PGMS-catalysed CO oxidation (CO+O<sub>2</sub>) and Preferential CO oxidation (PROX: CO+O<sub>2</sub>+excess H<sub>2</sub>).

Reactants	Catalyst, (promotion method applied)	Promoter	Reaction conditions	Promotion highlights and optimal achievements	Ref.
CO, O <sub>2</sub>	Pt-film over (Na)β''Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	Na	T = 300–450 °C [CO] = 0–4% [O <sub>2</sub> ] = 0–6%	<ul style="list-style-type: none"> <li>✓ Volcano behaviour of promotion upon increasing <math>\theta_{Na}</math>, under CO-rich conditions.</li> <li>✓ Promotion occurs at <math>\theta_{Na} = 2</math>–4%, under CO-rich conditions; moderate inhibition at low <math>\theta_{Na} = 2</math>–4%, under O<sub>2</sub>-rich conditions; strong inhibition for <math>\theta_{Na} &gt; 4\%</math> in both cases.</li> <li>➤ <math>\rho = 6</math> at <math>\theta_{Na} = 4\%</math>, T = 350 °C, CO-rich conditions ([CO] = 5.3%, [O<sub>2</sub>] = 6%)</li> </ul>	[16]
CO, O <sub>2</sub>	Pt-film over (K)β''Al <sub>2</sub> O <sub>3</sub> (EPOC)	K	T = 200–350 °C [CO] = [O <sub>2</sub> ] = 500 ppm	<ul style="list-style-type: none"> <li>✓ Significant K-induced promotion, providing a system proper for LT CO oxidation.</li> <li>➤ <math>\rho = 11</math> at T = 278 °C and <math>\Delta T_{50} = -40</math> °C; [CO] = [O<sub>2</sub>] = 500 ppm</li> </ul>	[27]
CO, O <sub>2</sub>	1 wt% PdO/SnO <sub>2</sub> (CCP)	Na	T = 150 °C [CO]/[O] = 1.25 [CO]/[O] = 0.5 ([CO] = 2400 ppm) Na-loading: 0.1 wt%	<ul style="list-style-type: none"> <li>✓ Significant promotion at CO-rich conditions; more effective on pre-reduced catalysts</li> <li>➤ Achievements on pre-oxidized catalysts: <math>\rho = 1.5</math>, <math>\Delta T_{50} = -12</math> °C (at [CO]/[O] = 1.25); <math>\rho = 0.66</math>, <math>\Delta T_{50} = +4</math> °C (at [CO]/[O] = 0.5)</li> <li>➤ Achievements on pre-reduced catalysts: <math>\rho = 2.6</math>, <math>\Delta T_{50} = -25</math> °C (at [CO]/[O] = 1.25); <math>\rho = 1.3</math>, <math>\Delta T_{50} = -8</math> °C (at [CO]/[O] = 0.5)</li> </ul>	[28] [29]
CO, O <sub>2</sub>	1 wt% Pd/γ-Al <sub>2</sub> O <sub>3</sub> and 1 wt% Pd/CZ (CCP)	Ba	T = 50–250 °C [CO] = 2.2%, [O <sub>2</sub> ] = 1.1% Ba-loadings: 0, 1, 5.5, 10, 15 wt%	<ul style="list-style-type: none"> <li>✓ Promotion on Pd(Ba)/γ-Al<sub>2</sub>O<sub>3</sub>; poisoning on Pd(Ba)/CZ</li> <li>➤ Promotion: <math>\Delta T_{50} = -45</math> °C, with 10–15wt% Ba loading on Pd(Ba)/γ-Al<sub>2</sub>O<sub>3</sub></li> <li>➤ Poisoning: <math>\Delta T_{50} = +100</math> °C, with 10wt% Ba loading on Pd(Ba)/CZ</li> </ul>	[31]

Table 1. Cont.

Reactants	Catalyst, (promotion method applied)	Promoter	Reaction conditions	Promotion highlights and optimal achievements	Ref.
CO, O <sub>2</sub> , H <sub>2</sub> excess	2 wt% Pt/( $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , ZrO <sub>2</sub> , Nb <sub>2</sub> O <sub>5</sub> or TiO <sub>2</sub> ) (CCP)	Li, Na, K, Rb, Cs	T = 100–160 °C [CO] = [O <sub>2</sub> ] = 0.2% Alkali loadings: A/Pt molar ratio = 0–20	<ul style="list-style-type: none"> <li>✓ Volcano-type promotion upon increasing alkali loading. K was the superior promoter.</li> <li>✓ For A/Pt &lt; 3 the promoting effect of alkalis followed the order: Cs &gt; Rb &gt; K &gt; Na &gt; Li</li> <li>✓ For A/Pt &gt; 5 the promoting effect of alkalis followed the order: K &gt; Na &gt; Rb &gt; Cs &gt; Li</li> <li>✓ An A/Pt=10–15, 3 and 5 optimizes Na or K, Cs and Rb promotion, respectively.</li> <li>➤ <math>\rho = 10</math> with K, with a loading of K/Pt = 10 molar ratio</li> </ul>	[32] [33] [34] [35] [36]
CO, O <sub>2</sub> , H <sub>2</sub> excess	1.6 wt% Pt/SiO <sub>2</sub> (CCP)	Na, Rb, Cs	T = 110 °C [CO] = [O <sub>2</sub> ] = 1%, [H <sub>2</sub> ] = 70% Cs surface density = 0–6 atoms/nm <sup>2</sup>	<ul style="list-style-type: none"> <li>✓ Volcano-type promotion upon increasing alkali loading. Cs was the superior promoter.</li> <li>✓ Promotion is maximized at a Cs loading = 1.6 Cs/nm<sup>2</sup> of catalyst surface.</li> <li>➤ <math>\rho = 10</math> and <math>\Delta S_{CO} = +30\%</math> (from 60%→90%) with an 1.6 Cs/nm<sup>2</sup> alkali surface density.</li> </ul>	[37]
CO, O <sub>2</sub> , H <sub>2</sub> excess	1 wt% Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> 1 wt% Pt-1.8wt%Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Na	T = 25–300 °C [CO] = 0.1%, [O <sub>2</sub> ] = 0.1%, [H <sub>2</sub> ] = 1% Na loading: 0.5–3 wt% Na	<ul style="list-style-type: none"> <li>✓ Moderate promotion of Na on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.</li> <li>✓ Significant volcano-type promotion (maximized at 2 wt% Na) on PtCo/Al<sub>2</sub>O<sub>3</sub> catalyst.</li> <li>➤ <math>\Delta X_{CO} = 75\%</math> (from 25%→100%) on 2 wt% Na promoted PtCo/Al<sub>2</sub>O<sub>3</sub>.</li> </ul>	[38]

Table 1. Cont.

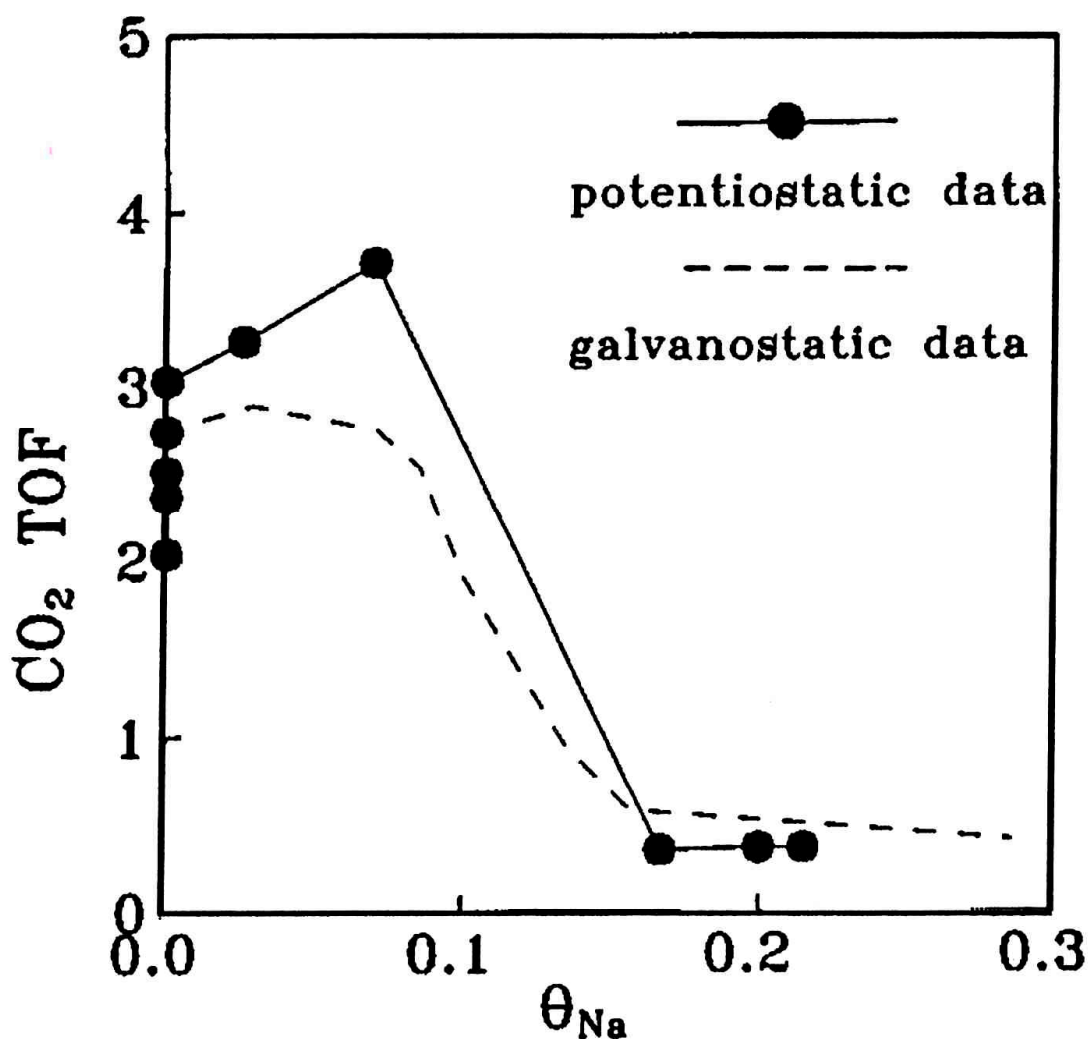
Reactants	Catalyst, (promotion method applied)	Promoter	Reaction conditions	Promotion highlights and optimal achievements	Ref.
CO, O <sub>2</sub> , H <sub>2</sub> excess	2wt%Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Mg	T = 100–250 °C [CO] = 1%, [O <sub>2</sub> ] = 0.75%, [H <sub>2</sub> ] = 65% [CO <sub>2</sub> ] = 20%, [H <sub>2</sub> O] = 2% Mg loading = 3 wt% Mg	<ul style="list-style-type: none"> <li>✓ Both CO oxidation and PROX reactions were significantly promoted by 3wt% Mg.</li> <li>✓ For PROX reaction both CO conversion and selectivity were enhanced in 150–230 °C.</li> <li>➤ <math>\Delta T_{50} = -20</math> °C for CO + O<sub>2</sub> reaction at moist conditions (2% H<sub>2</sub>O on stream).</li> <li>➤ <math>\Delta X_{CO} &gt; 35\%</math> and <math>\Delta S_{CO} &gt; 15\%</math> for PROX reaction (max <math>X_{CO} = 93\%</math> and max <math>S_{CO} = 62\%</math> at 170 °C) on 3wt% Mg-promoted catalyst.</li> </ul>	[39]
CO, O <sub>2</sub> , H <sub>2</sub> excess	Pt film on (K) $\beta$ Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	K	T = 195 °C [CO] = 0.4%, [O <sub>2</sub> ] = 0.2%, [H <sub>2</sub> ] = 16% $\theta_K = 0$ –4%	<ul style="list-style-type: none"> <li>✓ Both PROX activity and selectivity were significantly enhanced by K addition.</li> <li>✓ K effect allows activating the Pt at lower temperatures for PROX.</li> <li>✓ The inhibiting effect of H<sub>2</sub> on PROX was attenuated. The inhibiting effect of temperature on CO oxidation selectivity was attenuated.</li> <li>➤ <math>\rho = 1.3</math> and ~10% increase in CO oxidation selectivity, within <math>\theta_K = 2</math>–4%.</li> </ul>	[40]



### 3.1.2. Light Hydrocarbons Oxidation

#### (i) Alkenes oxidation

The oxidation of ethylene over polycrystalline Pt films has been extensively studied under electropositive promotion (EPOC) by Na via a  $\text{Na}^+$ -conducting  $\beta''\text{Al}_2\text{O}_3$  solid electrolyte, by Vayenas and co-workers [18,42] (Table 2). Both promoting and poisoning effects induced by alkali have been observed: low Na coverages (typically <8%) were found to cause increases in the reaction rate (up to  $\rho = 2$ ), while larger Na coverages led to a significant decrease of rate, which eventually falls well below the initial value corresponding to Na-free Pt surface (Figure 7). The data was interpreted in terms of (i) Na-enhanced oxygen chemisorption and (ii) poisoning of the surface by accumulation of Na compounds.



**Figure 7.** Rate as a function of Na coverage for both potentiostatic and galvanostatic experiments for  $[\text{O}_2] = 8.0\%$   $[\text{C}_2\text{H}_4] = 4.2\%$  (balance He) mixture at  $352^\circ\text{C}$ . Data was acquired in a  $\text{Pt}/(\text{Na})\beta''\text{Al}_2\text{O}_3/\text{Au}$  galvanic cell (Reprinted with permission from Ref. [18]; Copyright 1996, Elsevier).

According to the authors, low Na coverage gives rise to an enhanced chemisorption of  $\text{O}_2$  at the expense of ethylene, resulting in an increased rate. At high sodium coverages both (i) and (ii) factors operate synergistically to poison the system: the increased strength of the Pt–O bond and the coverage of the catalytic surface by compounds of Na strongly suppress the rate. Kinetic results obtained over a  $\text{Pt}(111)$ –Na model catalyst, dosed with several amounts of Na by vapour deposition (CCP), were found to mirror the behaviour of the  $\text{Pt}/\beta''\text{Al}_2\text{O}_3$  catalyst promoted by the EPOC concept [18]. This

strongly suggested that Na pumped from the solid electrolyte via electrical polarization is indeed the key species for the promoting or poisoning phenomena. In addition, these results demonstrated that electrochemical promotion of catalysis (EPOC) and surface promotion by conventional means (CCP) obey the same physiochemical rules in the case of alkaline promoting cations. This is well documented nowadays but it was unclear at those early steps of electrochemical promotion studies.

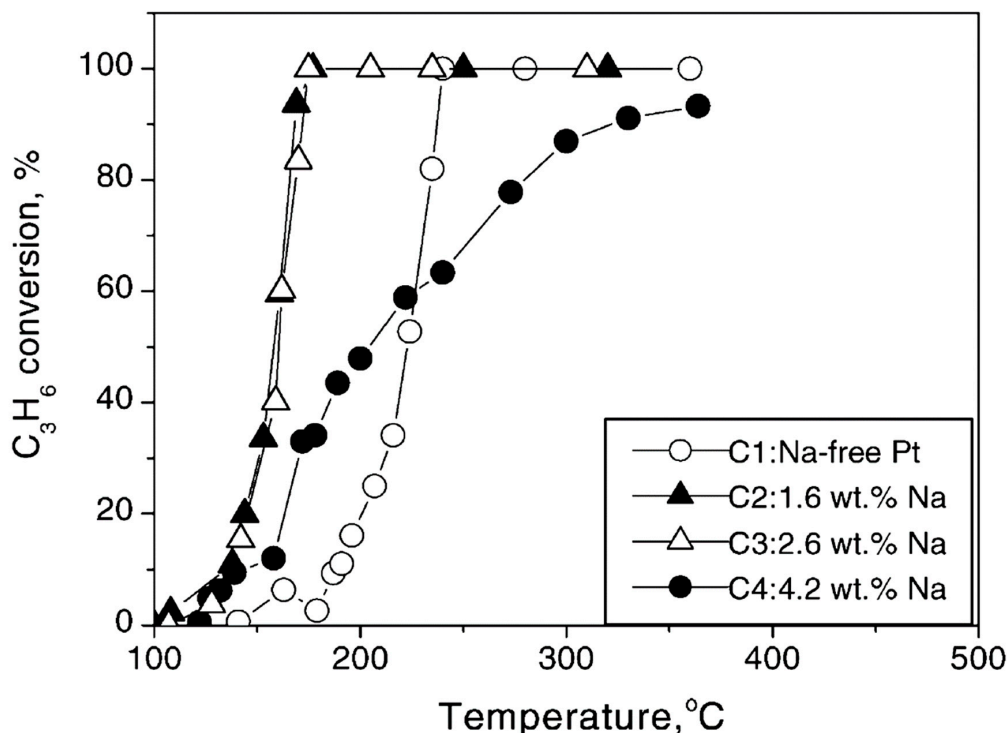
The Pt-catalysed propene oxidation has been also extensively studied by Filkin et al. [20] under in situ electrochemical promotion (EPOC) by sodium, using polycrystalline Pt films deposited on  $\text{Na}^+$ -conducting  $\beta''\text{Al}_2\text{O}_3$ . Depending on propene and oxygen reactants partial pressures, fully reversible promotion and poisoning effects were observed as a function of sodium coverage as follows. As  $[\text{O}_2]/[\text{C}_3\text{H}_6]$  decreases, the effects of Na promotion rapidly increase: for  $[\text{O}_2]/[\text{C}_3\text{H}_6] = 5.7$ , where the activity of Na-free Pt is highest, the maximum enhancement ratio  $\rho_{\text{max}} = r_{\text{max}}(\text{on Na-promoted Pt})/r_0(\text{on Na-free Pt})$  is equal to 1.1, which then increases to  $\rho_{\text{max}} = 2.3$  at  $[\text{O}_2]/[\text{C}_3\text{H}_6] = 2.0$ , where Na-free Pt activity is lower. These maxima enhancement ratios were obtained at moderate Na coverages (not specified) while higher Na coverages cause poisoning of the propene oxidation rate. The larger poisoning was obtained in the case of  $[\text{O}_2]/[\text{C}_3\text{H}_6] = 5.7$  (Table 2). A Na-modified chemisorption of the reactants considered (Na enhances oxygen chemisorption and inhibits propene chemisorption) on a Langmuir-Hinselwood type reaction accounted all the experimental findings. Using X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) and postreaction Na K edge XANES (X-ray Absorption Near Edge Structure) the authors have demonstrated that under reaction conditions the promoter phase consists of small amounts of 3D sodium carbonate crystallites, while thick layers of this sodium surface compound were responsible for rate inhibition in the poisoning regime. Notably, these promoter and poisoning phases, although stable at reaction temperatures investigated, were readily destroyed via electrochemical Na pumping away from the catalyst by the application of electrical polarizations of opposite sign [20].

Other studies involving the propene oxidation over Pt films using the EPOC concept as well, were reported by Vernoux and co-workers [43,44]. In these studies Pt was interfaced with NASICON ( $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ), an alternative  $\text{Na}^+$ -conductor, acting therefore as a Na source for its electrochemical pumping to the Pt catalyst surface. The authors used two distinguished propene/oxygen gas phase compositions, near stoichiometric ( $\text{C}_3\text{H}_6/\text{O}_2 = 0.04\%/0.2\%$ ) and excess oxygen ( $\text{C}_3\text{H}_6/\text{O}_2 = 0.04\%/8.3\%$ ) conditions, to investigate the effect of Na on the catalytic system under consideration at  $T \sim 300^\circ\text{C}$  (Table 2). They found that under oxygen excess Na coverages larger than 3% cause a slight poisoning of the propene oxidation rate ( $\rho \sim 0.8$ ). However, under near-stoichiometric conditions, sodium had strong beneficial effect ( $\rho = 3.5$ ) on the Pt-catalysed propene oxidation rate, which is maximized at a  $\theta_{\text{Na}} \sim 3.6\%$ ; the rate was then slightly decreased when higher (up to 6%) sodium coverages were supplied. Cyclic voltammetry studies indicated that sodium promoter exists in the form of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  surface phases during reaction [43], in agreement with earlier studies by Filkin et al. [20].

In this line, de Lucas-Consuegra et al. [45,46] have more recently studied the propene oxidation under EPOC of a Pt film interfaced with a  $\text{K}^+$ -conducting  $\beta\text{Al}_2\text{O}_3$  solid electrolyte, that is, using potassium as promoter species. They found that the reaction can be strongly promoted at the temperature interval of  $\sim 200\text{--}300^\circ\text{C}$ , under both near-stoichiometric and oxygen-rich conditions. Rate enhancement ratios of the order of  $\rho = 7$  were achieved for a catalyst polarization of about  $-2\text{ V}$  (Table 2); parameters' values necessary for the estimation of the corresponding alkali coverage are not available in the paper. Cyclic voltammetry, FTIR and SEM-EDX studies enable the authors to identify the formation of stable potassium oxide and superoxide phases upon electrical polarization. These species were responsible for the promotional phenomena. In addition, due to the stability of the potassium surface compounds formed, a permanent promotional effect was observed.

The effect of electropositive modifiers on hydrocarbons oxidation over conventional highly dispersed catalysts (CCP) was also investigated by Yentekakis and co-workers [47]. In particular, they studied the propene oxidation over Na-promoted  $\text{Pt}(\text{Na})/\gamma\text{-Al}_2\text{O}_3$  catalysts under oxygen excess

(1000 ppm propene + 5% O<sub>2</sub>). Significant activity enhancements were observed for a Na-loading of ~1.5–2.6 wt % (or  $0.68\text{--}1.13 \times 10^{-3}$  mmol effective Na/g<sub>cat</sub>) [47]. Optimal promotion was achieved for 2.6 wt% Na loading, corresponding to a nominal sodium coverage of  $\theta_{\text{Na}} \sim 23\%$  (Equation (4) by using  $d_{\text{Na}} = 3.314 \times 10^{19}$  atoms/m<sup>2</sup>), causing a significant shift of the propene light-off temperature to about 60 °C lower values (Figure 8, Table 1). Rate enhancement ratios as high as  $\rho \sim 10$  can be calculated from these results. It is worth noting that the aforementioned promotional effects were recorded under oxygen excess conditions, typical of lean-burn combustion engines. The Na-induced enhancement of oxygen adsorption on the Pt surface, which is predominately covered by propene even at these excess oxygen gas phase conditions, was considered to be responsible for the observed promotional effect.



**Figure 8.** The effect of temperature on the conversion of C<sub>3</sub>H<sub>6</sub> Na-dosed Pt(Na)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts under C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> reaction at oxygen rich conditions: 1000 ppm C<sub>3</sub>H<sub>6</sub> + 5% O<sub>2</sub>; catalyst weight 70 mg; total flow rate was varying as  $F_t = 210, 126, 62.5$  and  $52 \text{ cm}^3/\text{min}$  for C1, C2, C3 and C4 catalysts, respectively, in order to keep the effective contact time of C<sub>3</sub>H<sub>6</sub> constant at 4 s. (The effective contact time is defined as: surface Pt atoms/reactant molecules/s) (Reprinted with permission from Ref. [47]; Copyright 2005, Elsevier).

## (ii) Alkanes oxidation

An EPOC study regarding the propane oxidation on Pt-based catalysts under Na-promotion supplied via a (Na) $\beta''$ -Al<sub>2</sub>O<sub>3</sub> solid electrolyte has been reported by Kotsionopoulos and Bebelis [48]. The activity was dramatically inhibited by Na-addition even at low Na coverages, over a wide range of propane/oxygen ratios (Table 2). Under stoichiometric conditions ( $[\text{O}_2]/[\text{C}_3\text{H}_8] = 1\%/0.2\%$ ) and  $T = 320 \text{ }^\circ\text{C}$ , a Na coverage as small as  $\theta_{\text{Na}} \sim 2.5\%$  leads to a significant decrease of the reaction rate of 625 times. The poisoning effect was more pronounced at higher temperatures (e.g., 360, 400 and 440 °C). This poisoning effect of electropositive promoters on Pt for alkanes oxidation can be attributed to the weak adsorption of alkanes compared to oxygen. A latter study published by the same authors dealt with the electrochemical characterization of the aforementioned catalytic system [49]. In this work they observed, in good agreement with some of the studies mentioned above, that the sodium promoter is on the metal surface mainly forming carbonate, bicarbonate and oxide phases.

**Table 2.** Electropositive promotion of PGMs-catalysed alkenes and alkanes oxidation.

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and optimal achievements	Ref.
<b>Alkenes oxidation (Alkene + O<sub>2</sub>)</b>					
C <sub>2</sub> H <sub>4</sub> , O <sub>2</sub>	Pt-film over (Na)β''Al <sub>2</sub> O <sub>3</sub> (EPOC)	Na	T = 291 °C; [C <sub>2</sub> H <sub>4</sub> ] = 0.021%, [O <sub>2</sub> ] = 5%; θ <sub>Na</sub> = 0–3%	<ul style="list-style-type: none"> <li>✓ Only rate inhibition was found at such extreme fuel lean conditions.</li> <li>➤ A Na coverage of θ<sub>Na</sub> &gt; ~1.5% suffices to cause a 70% rate inhibition (poisoning).</li> </ul>	[42]
C <sub>2</sub> H <sub>4</sub> , O <sub>2</sub>	Pt film over (Na)β''Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	Na	T = 300–470 °C; [C <sub>2</sub> H <sub>4</sub> ] = 4.2%, [O <sub>2</sub> ] = 8 and 16.2%; θ <sub>Na</sub> = 0–35%	<ul style="list-style-type: none"> <li>✓ Na induces both promotion and poisoning. Moderate θ<sub>Na</sub>, typically &lt;8%, causes promotion, larger θ<sub>Na</sub> causes rate inhibition. Results obtained on a Pt(111)-Na model catalyst mirror the behaviour of the EPOC system.</li> <li>✓ No promotional and/or poisoning effects occur at high temperatures (T &gt; ~460 °C).</li> <li>➤ ρ~2 with θ<sub>Na</sub> = 8% at 280 °C and [C<sub>2</sub>H<sub>4</sub>] = 4.2%, [O<sub>2</sub>] = 1 6.9%; ρ~2 with θ<sub>Na</sub> = 8% at 352 °C, [C<sub>2</sub>H<sub>4</sub>] = 4.2%, [O<sub>2</sub>] = 8%</li> </ul>	[18]
C <sub>3</sub> H <sub>6</sub> , O <sub>2</sub>	Pt film over (Na)β''Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	Na	T = 340 °C [C <sub>3</sub> H <sub>6</sub> ] = 0.62%, [O <sub>2</sub> ] = 0–7%	<ul style="list-style-type: none"> <li>✓ Volcano type promotion optimized at moderate Na coverages. Promotion effects increase with decreasing [O<sub>2</sub>]/[C<sub>2</sub>H<sub>4</sub>] (promotion is superior under fuel-rich conditions). High Na coverages deactivate catalyst due to excessive accumulation of 3D Na<sub>2</sub>CO<sub>3</sub> species; these species can be readily removed electrochemically, accomplishing catalyst re-activation.</li> <li>➤ P = 1.1 at [O<sub>2</sub>]/[C<sub>2</sub>H<sub>4</sub>] = 5.7, T = 340 °C; ρ = 2.2 at [O<sub>2</sub>]/[C<sub>2</sub>H<sub>4</sub>] = 4.0, T = 340 °C; ρ = 2.3 at [O<sub>2</sub>]/[C<sub>2</sub>H<sub>4</sub>] = 2.0, T = 340 °C</li> </ul>	[20]

Table 2. Cont.

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and optimal achievements	Ref.
C <sub>3</sub> H <sub>6</sub> , O <sub>2</sub>	Pt film over NaSiCon (Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> ) solid electrolyte (EPOC)	Na	T = 300 °C, $\theta_{Na}$ = 0–6% - C <sub>3</sub> H <sub>6</sub> /O <sub>2</sub> = 0.04%/0.2% (stoich.) - C <sub>3</sub> H <sub>6</sub> /O <sub>2</sub> = 0.04%/8.3% (O <sub>2</sub> -rich)	<ul style="list-style-type: none"> <li>✓ Strong promotion by Na under near-stoichiometric C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub> conditions; no promotion or moderate poisoning under oxygen excess (lean-burn) conditions. Under reaction conditions promoter phase exists as Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>.</li> <li>➤ <math>\rho = 3.5</math> with <math>\theta_{Na} = 3.6\%</math> at [C<sub>3</sub>H<sub>6</sub>]/[O<sub>2</sub>] = 0.04/0.2, T = 300 °C; <math>\rho = 0.8</math> with <math>\theta_{Na} &gt; \sim 2\%</math> at [C<sub>3</sub>H<sub>6</sub>]/[O<sub>2</sub>] = 0.04/8.3, T = 300 °C</li> </ul>	[43] [44]
C <sub>3</sub> H <sub>6</sub> , O <sub>2</sub>	Pt film over (K) $\beta$ -Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	K	T = 190–310 °C [C <sub>3</sub> H <sub>6</sub> ] = 2000 ppm, [O <sub>2</sub> ] = 1–7%	<ul style="list-style-type: none"> <li>✓ Strong promotion by K (better than that of Na) under both near-stoichiometric and oxygen-rich conditions.</li> <li>✓ Formation of stable and more effective promoter phases (potassium oxides and superoxides).</li> <li>➤ <math>\rho = 7</math>, propene conversion increased from 10% to 70%, at 200 °C and [C<sub>3</sub>H<sub>6</sub>]/[O<sub>2</sub>] = 2000ppm/7% (O<sub>2</sub>-rich)</li> <li>➤ <math>\rho = 3</math> at 220 °C and [C<sub>3</sub>H<sub>6</sub>]/[O<sub>2</sub>] = 2000ppm/1% (near-stoichiometric).</li> </ul>	[45] [46]
C <sub>3</sub> H <sub>6</sub> , O <sub>2</sub>	0.5 wt% Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Na	T = 100–500 °C [C <sub>3</sub> H <sub>6</sub> ] = 1000 ppm, [O <sub>2</sub> ] = 5% Na-loadings: 0, 1.6, 2.6, 4.2 wt%	<ul style="list-style-type: none"> <li>✓ Volcano type promotion under excess oxygen conditions (optimal Na-loading at <math>\sim 2.6</math>wt% Na).</li> <li>✓ C<sub>3</sub>H<sub>6</sub> oxidation is inhibited for higher Na loadings; poisoning becomes even worse in case of NO co-feed.</li> <li>➤ <math>\Delta T_{50} = -60</math> °C at [C<sub>3</sub>H<sub>6</sub>]/[O<sub>2</sub>] = 0.1%/5% (O<sub>2</sub>-rich conditions) with 2.6wt% Na (<math>\theta_{Na} \sim 23\%</math>); <math>\rho \sim 10</math> at T = 120–200 °C.</li> </ul>	[47]

Table 2. Cont.

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and optimal achievements	Ref.
Alkanes oxidation (alkane + O <sub>2</sub> )					
C <sub>3</sub> H <sub>8</sub> , O <sub>2</sub>	Pt film over (Na)β''Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	Na	T = 320–440 °C [C <sub>3</sub> H <sub>8</sub> ] = 0.2%, [O <sub>2</sub> ] = 1% θ <sub>Na</sub> = 0–3%	<ul style="list-style-type: none"> <li>✓ Na addition to the catalyst causes only poisoning of the rate. Low θ<sub>Na</sub> = 1–3% are enough to cause up to 3 orders of magnitude rate poisoning (ρ~0.002). Under reaction conditions Na forms carbonate, bicarbonate and oxide phases.</li> <li>➤ Strong poisoning: ρ~0.002 for θ<sub>Na</sub>&gt;~2.5% at T = 440 °C.</li> </ul>	[48] [49]
CH <sub>4</sub> , O <sub>2</sub>	5 (or 2.5) wt% Pd/γ-Al <sub>2</sub> O <sub>3</sub> (CCP)	Na, K, Ba, Ca	T = 250–600 °C; [CH <sub>4</sub> ] = 500 ppm, [O <sub>2</sub> ] = 8%, [H <sub>2</sub> O] = 5%, [CO <sub>2</sub> ] = 5% Loadings: Ca: 0.38, 0.76, 1.5 wt%; Ba = 5 wt%; K = 1.48 wt%; Na = 0.87 wt%	<ul style="list-style-type: none"> <li>✓ Both beneficial and detrimental effects on CH<sub>4</sub> oxidation were found depending on the promoter, catalyst composition and pre-treatment. Promotion was achieved with Ca-doping and after cooling in inert atmosphere.</li> <li>✓ No promotion (even inhibition) was observed by Na and K addition at the specific loadings used.</li> <li>➤ Highest activities for 2.5wt%Pd/γ-Al<sub>2</sub>O<sub>3</sub> and 5wt%Pd/γ-Al<sub>2</sub>O<sub>3</sub> were obtained with 0.38 and 0.76 wt% Ca addition, respectively, that is, at a weight ratio Ca:Pd equal to 0.15 in both cases.</li> </ul>	[50]



Olsson and co-workers [50] studied the effect of the addition of alkalis (Na, K) and alkaline earths (Ba, Ca) on Pd/Al<sub>2</sub>O<sub>3</sub> catalyst for methane combustion (CCP). Both beneficial and detrimental effects on methane oxidation were observed. High loadings of alkaline modifiers caused reaction inhibition. No promotion was induced by Na and K modifiers, while Ba- and Ca- doping caused reaction inhibition. However, when using a specific catalyst pre-treatment, which leads to the removal of surface hydroxyl species, promotional effects of Ca were recorded at Ca loadings where they previously observed reaction inhibition. The Ca/Pd ratio was found to be critical for the aforementioned promotion. A Ca/Pd ratio of 0.15 was favourable. The modification of the redox properties of palladium and the formation of PdO were considered the origin of this promotion, which overcomes the alkaline-induced inhibition of methane adsorption (activation) on increased electronic density catalyst particles surfaces which occurs in parallel.

Comparatively overviewing the literature findings of Section 3.1.2 summarized in Table 2, the following general features and conclusions can emerge.

Alkali addition on PGMs-based catalyst is detrimental for alkanes oxidation reactions that was attributed to the low adsorption propensity of alkanes on PGMs surfaces which becomes worse due to the alkali induced promotion of oxygen adsorption and the concomitant O-poisoning of the surfaces.

On the opposite, alkenes oxidation on PGMs is substantially promoted by electropositive promoters, attributed to the opposite trend of their adsorption compared to alkanes: The alkali-induced enhancement on oxygen adsorption counterbalances its coverage on a PGM surface, predominantly covered by the alkene molecules on the unpromoted surface, resulting to an enhancement on reaction probability (promotion).

The alkenes oxidation followed volcano type promotion upon increasing promoter loading, resulting from the competitive adsorption of the reactants (Langmuir-Hinshelwood type reaction) and the formation of 3D alkali carbonates and their excessive accumulation on the surface at high promoter loadings.

The main promotion characteristics were qualitatively similar between EPOC and CCP studies, although the intensity of the promotion was larger in the latter case: maximum rate enhancement ratios ( $\rho$ ) obtained were 3.5 and 10 by using EPOC and CCP, respectively. An ultimate contact between nanodispersed active phase particles and promoter species, which is favoured in CCP, is most probably responsible for this superiority.

### 3.1.3. NO Reduction by CO

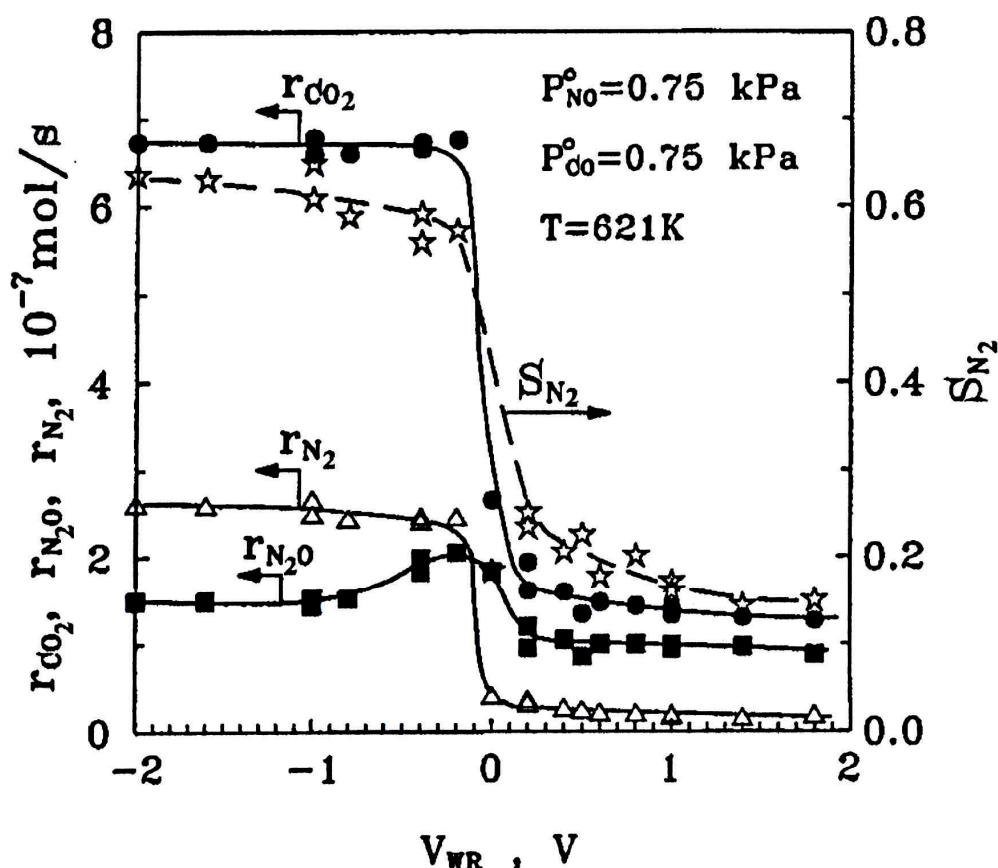
The first study of the effect of electropositive promoters on the Pt-catalysed NO reduction by CO was reported by Palermo et al. [17]. The EPOC was applied by means of a Pt/Na<sup>+</sup>-conducting  $\beta''$ -Al<sub>2</sub>O<sub>3</sub>/Au cell. The promotional effect of Na on the Pt/NO + CO system was strongly dependent on the reaction temperature, gas composition and Na coverage. For instance, at high CO/NO ratios the effect of Na was marginal and according to the authors this was attenuated by CO island formation and limited availability of chemisorbed NO. At low CO/NO ratios the effect of Na was also relatively small, because, as authors conclude, the CO + O reaction is limited by the low CO coverage. However, at the intermediate CO/NO regime, where the above constraints do not apply, Na strongly accelerates the reaction: rate gains of up to  $\rho = 13$  for N<sub>2</sub> production compared to the unpromoted Na-free Pt rate were achieved (Table 3). Significant increases to N<sub>2</sub> selectivity of the system (up to 30%) were also obtained (Figure 9). Significant progressive changes in the apparent activation energy of the NO + CO reaction upon varying the promoter coverage, similar to that obtained with the Pt/O<sub>2</sub> + CO catalytic system [16], were also recorded in this study. The observed promotional phenomena, on both rate and selectivity, were attributed to the enhanced NO versus CO chemisorption and the extended dissociation of the chemisorbed NO molecules, both induced by Na-promoter.

**Table 3.** Electropositive promotion of PGMs-catalysed NO reduction by CO (NO + CO).

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and maximum achievements	Ref.
NO, CO	Pt film over (Na) $\beta''$ Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	Na	T = 300–400 °C [CO] = 0–1.5%, [NO] = 0–1.5% [NO]/[CO] = 0.75%/0.75% $\theta_{Na}$ = 3–20%	<ul style="list-style-type: none"> <li>✓ The promotional effects of Na are maximized at intermediate CO/NO values, while at high and low CO/NO values promotion was attenuated due to the formation of CO islands and the low CO coverage, respectively.</li> <li>✓ Significant Na-induced changes on the reaction apparent activation energy recorded.</li> <li>➤ <math>\rho_{N_2} \sim 13</math>, <math>\rho_{CO_2} \sim 4.8</math>, <math>\Delta S_{N_2} \sim +45\%</math> at T = 348 °C for <math>\theta_{Na} = 3</math>–20%</li> </ul>	[17]
NO, CO	Rh film over (Na) $\beta''$ Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	Na	T = 307 °C [CO] = [NO] = 1%	<ul style="list-style-type: none"> <li>✓ Sodium coverage (<math>\theta_{Na}</math>), catalyst work function (<math>\Delta\Phi</math>) and catalyst potential (<math>V_{WR}</math>) are directly correlated; <math>\theta_{Na}</math> and <math>\Delta\Phi</math> varying linearly with <math>V_{WR}</math>. Low sodium coverages ca. 1–2% are able to create significant promotion of the Rh-catalysed NO+CO (but less than that obtained on Pt catalysts).</li> <li>➤ <math>\rho_{N_2} \sim 3.1</math>, <math>\rho_{CO_2} \sim 1.4</math>, <math>\rho_{N_2O} = 0.3</math>, <math>\Delta S_{N_2} \sim +50\%</math> (24%→80%) at T = 307 °C, for <math>\theta_{Na} \sim 1</math>–2%</li> </ul>	[51] [52]
NO, CO	0.5 wt% Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	K, Rb, Cs	T = 150–500 °C [CO] = 0–3%, [NO] = 0–3% Promoter loadings used: wt% Rb: 1.9, 9.7, 15.5 wt% Cs: 9.0, 15.0, 24.0 wt% K: 2.7, 4.4, 8.8	<ul style="list-style-type: none"> <li>✓ All K, Rb, Cs alkalis exert a pronounced promotion; however, Rb promotion is superior to K and Cs.</li> <li>✓ In comparison with Rb, larger molar loadings of K were needed to produce similar reductions in light-off temperature. In both cases promotional effects increased monotonically with increasing alkali loading.</li> <li>➤ <math>\rho_{N_2} \sim 110</math>, <math>\rho_{CO_2} \sim 45</math>, <math>\rho_{N_2O} = 7</math>, <math>\Delta S_{N_2} = +58\%</math> (24%→82%) at T = 350 °C, [CO] = 0.5%, [NO] = 1%; 15.5 wt% Rb</li> <li>➤ <math>\rho_{N_2} \sim 45</math>, <math>\rho_{CO_2} \sim 15</math>, <math>\rho_{N_2O} = 4</math>, <math>\Delta S_{N_2} = +51\%</math> (24%→75%) at T = 350 °C, [CO] = 0.5%, [NO] = 1%; 8.8 wt% K</li> <li>➤ <math>\Delta T_{50} = -150</math> °C with Rb loading &gt;9.7 wt%; <math>\Delta T_{50} = -115</math> °C with K loading &gt; 4.4 wt%; <math>\Delta T_{50} = -115</math> °C with Cs loading &gt; 15 wt%, at [NO] = [CO] = 1000 ppm.</li> </ul>	[53]

Table 3. Cont.

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and maximum achievements	Ref.
NO, CO	0.5wt%Pd/YSZ (CCP)	Na	T = 352 °C [CO] = 0–4%, [NO] = 0–4% Na loadings: 0.017, 0.034, 0.068 and 0.102 wt% (or 6/1, 3/1, 1.5/1 and 1/1 Pd/Alkali)	<ul style="list-style-type: none"> <li>✓ Volcano type promotion was obtained with an optimal Na-loading equal to 0.034wt% Na (i.e., Pd/alkali molar ratio = 3/1), taking into account both activity and N<sub>2</sub>-selectivity.</li> <li>➤ <math>\rho_{N_2} \sim 2</math>, <math>\rho_{CO_2} \sim 1.5</math>, <math>\rho_{N_2O} = 1</math>, <math>\Delta S_{N_2} = +20\%</math> (from ~50% to ~70%) at T = 352 °C, [CO] = [NO] = 1% for 0.034 wt% Na.</li> </ul>	[54]
NO, CO, O <sub>2</sub>	1 wt% Pd/( $\gamma$ -Al <sub>2</sub> O <sub>3</sub> or CZ) (CCP)	Ba	T = 50–300 °C [CO] = 2.2%, [NO] = 0.2% [O <sub>2</sub> ] = 1% Ba-loadings: 0, 1, 5 and 15 wt% Ba	<ul style="list-style-type: none"> <li>✓ Ba-induced promotional effects on Pd/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub>; progressively increased activity with increasing Ba-loading.</li> <li>✓ Ba-induced poisoning effects on Pd/CZ; progressively decreased activity with increasing Ba-loading.</li> <li>➤ <math>\Delta T_{50(CO)} = -40</math> °C and <math>\Delta T_{50(NO)} = -33</math> °C with 15wt% Ba on Pd/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub> (promotion)</li> <li>➤ <math>\Delta T_{50(CO)} = +97</math> °C and <math>\Delta T_{50(NO)} = +99</math> °C with 10wt% Ba on Pd/CZ (strong poisoning)</li> </ul>	[55]

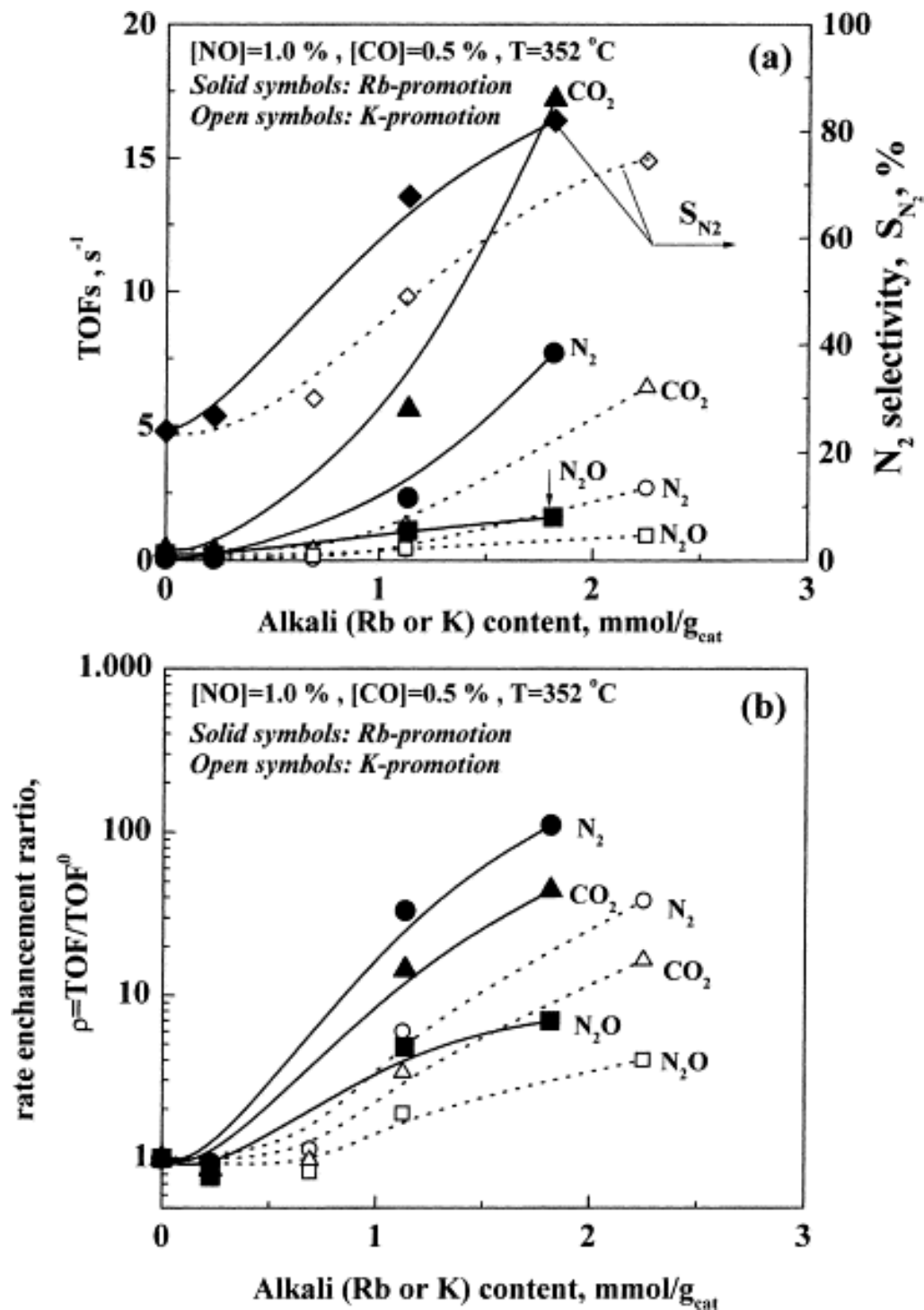


**Figure 9.** Effect of catalyst potential on the  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{N}_2\text{O}$  formation rates and the selectivity towards  $\text{N}_2$  during the EPOC by Na of the Pt-catalysed  $\text{NO} + \text{CO}$  reaction. Conditions:  $[\text{NO}] = [\text{CO}] = 0.75\%$ ,  $T = 348^\circ\text{C}$ . Data was acquired in a  $\text{Pt}/(\text{Na})\beta''\text{Al}_2\text{O}_3/\text{Au}$  galvanic cell. (Reprinted with permission from Ref. [17]; Copyright 2005, Elsevier).

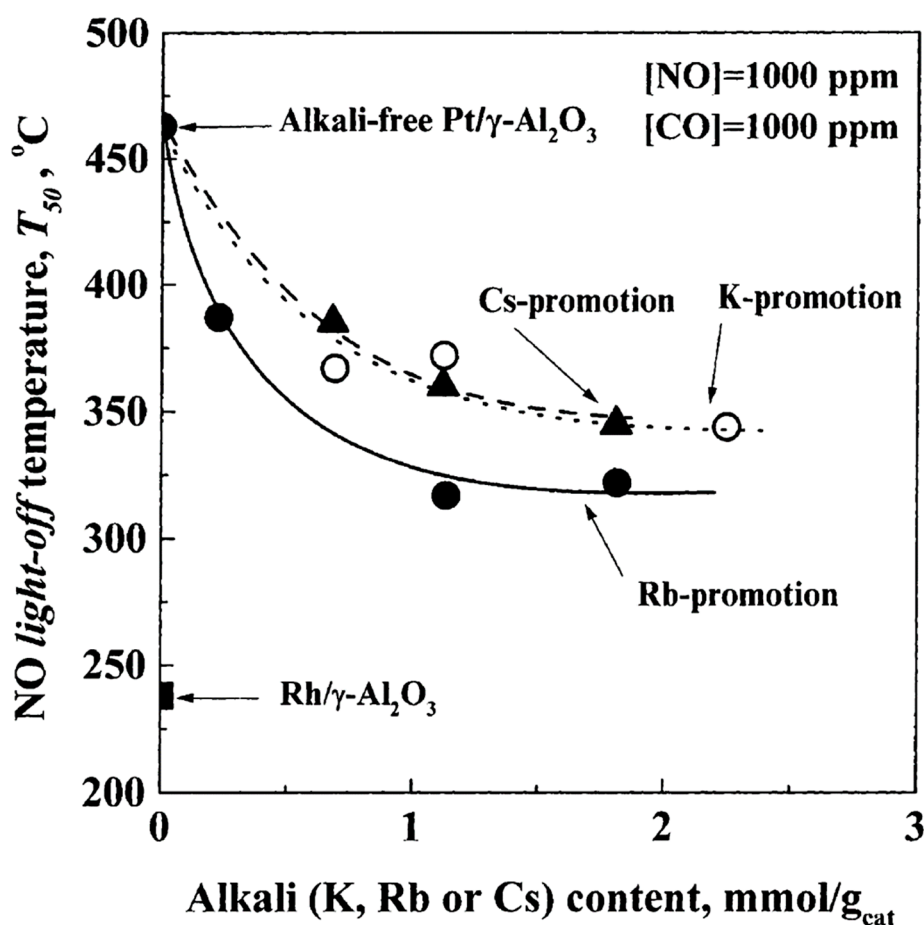
Another EPOC (by Na) study using a  $\text{Rh}/(\text{Na})\beta''\text{Al}_2\text{O}_3/\text{Au}$  galvanic cell was performed by Williams et al. [51,52]. They showed that the  $\text{NO}$  reduction by  $\text{CO}$  can also be promoted over  $\text{Rh}$  catalyst. Rate enhancement ratios of  $\rho_{\text{N}_2} = 3.1$ ,  $\rho_{\text{CO}_2} = 1.4$  and  $\rho_{\text{N}_2\text{O}} = 0.3$  were observed at  $T = 307^\circ\text{C}$  and stoichiometric  $\text{CO}/\text{NO}$  gas reaction conditions ( $[\text{NO}] = [\text{CO}] = 1\%$ ) for a sodium coverage as low as 2% (Table 3), together with a large increase in  $\text{N}_2$ -selectivity: from 24% on the electrochemically cleaned Na-free  $\text{Rh}$  to 80% on  $\text{Rh}$  electrochemically dosed with  $\theta_{\text{Na}} = 2\%$ . These promotional effects were attributed to the Na-induced  $\text{NO}$  dissociation, which was considered as the rate limiting step for the  $\text{NO}$  reduction by  $\text{CO}$  process. Using XPS and work function ( $\Delta\Phi$ ) measurements the authors also demonstrated that the Na coverage on the catalyst surface can be controlled through the externally imposed catalyst potential; a linear relationship of catalyst work function and  $\theta_{\text{Na}}$  with catalyst potential was experimentally demonstrated in this study [51,52].

Konsolakis et al. [53] studied the  $\text{NO} + \text{CO}$  reaction on (K, Rb and Cs)-promoted, conventional (CCP), highly dispersed  $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  catalysts, over a wide range of temperature (ca.  $150\text{--}500^\circ\text{C}$ ), partial pressures of reactants and promoter loadings (Table 3). All these alkalis were found to be very active promoters for the reaction, however, optimal promotion was achieved by rubidium: rate increases by factors as high as  $\rho_{\text{N}_2} = 110$  and  $\rho_{\text{CO}_2} = 45$  for the production of  $\text{N}_2$  and  $\text{CO}_2$ , respectively, relative to alkali-free  $\text{Pt}$  were obtained, accompanied by substantial increases in  $\text{N}_2$ -selectivity by up to  $\sim 60\%$  (Figure 10) [53]. The effects of K and Cs-promotion mirror those of Rb-promotion but they were less pronounced. Light-off measurements in the temperature range of  $150\text{--}500^\circ\text{C}$  and under stoichiometric conditions (1000 ppm  $\text{NO} + 1000$  ppm  $\text{CO}$ ) showed that the  $\text{NO}$  conversion performance of alkali-free  $\text{Pt}$  is very poor (never exceeding 60%), whereas the  $0.5\text{wt}\%\text{Pt}(\text{Rb})/\gamma\text{-Al}_2\text{O}_3$  catalyst

promoted with 9.7wt% Rb (optimally promoted catalyst), exhibited 100% NO and CO conversions with 100% N<sub>2</sub>-selectivity at ~350 °C. In addition, 115 °C decrease on the NO light-off temperature (T<sub>50</sub>) was obtained for K and Cs, while a larger decrease in T<sub>50</sub> by ~150 °C was obtained by Rb-promotion (Figure 11).



**Figure 10.** (a) Effect of Rb or K content of Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst on the turnover (TOF) formation rates of N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O and on N<sub>2</sub>-selectivity at T = 352 °C, [NO] = 1%, [CO] = 0.5%. (b) Corresponding enhancement ratio  $\rho = \text{TOF}/\text{TOF}^0$  values. Solid lines and symbols refer to Rb-promotion, dashed lines and open symbols refer to K-promotion. (Reprinted with permission from Ref. [53]; Copyright 2001, Elsevier).



**Figure 11.** Effect of K-, Rb- or Cs-promotion on the NO light-off temperature ( $T_{50}$ ) for Pt/NO + CO system. Conditions: [NO] = 1000 ppm, [CO] = 1000 ppm, total gas flow rate  $F_t = 80 \text{ cm}^3\text{STP}/\text{min}$ ; catalyst weight  $8(\pm 0.2) \text{ mg}$ . ( $w/F_t = 6 \times 10^{-3} \text{ g s}/\text{cm}^3$ ). (Reprinted with permission from Ref. [53]; Copyright 2001, Elsevier).

The observed promotional effects were ascribed to alkali-induced changes in the chemisorption bond strengths of CO, NO and NO dissociation products. The superior promotion of Rb compared to that of K was attributed to its larger size and thus to the greater electric field experienced by co-adsorbed species located at an adjacent site. On the other hand, the unexpected lower efficiency of Cs promotion compared to that of Rb was attributed to a change in the adsorption site of NO due to the very large Cs ion [53].

More recently Konsolakis and Yentekakis [54] reported on the promotional effect of Na on the Pd-catalysed NO + CO reaction (CCP). A series of Na-promoted Pd catalysts were prepared on yttria-stabilized zirconia (YSZ; 10mol%  $\text{Y}_2\text{O}_3/\text{ZrO}_2$ ) carrier (i.e., Pd(Na)/YSZ), with different loadings of alkali-promoter. Both promoting and poisoning effects, regarding the Na-loading, were found in a wide range of CO/NO ratios. For example at equimolar CO/NO composition ( $[\text{CO}] = [\text{NO}] = 1\%$ ) and  $T = 352 \text{ }^\circ\text{C}$ , the optimal promoter loading was found to be between 0.02–0.03wt% of Na (corresponding to a nominal sodium coverage of  $\theta_{\text{Na}} \sim 3\%$ ; Equation (4) with  $d_{\text{Na}} = 3.314 \times 10^{19} \text{ atoms}/\text{m}^2$ ) which leads to  $\text{N}_2$  and  $\text{CO}_2$  formation rate enhancements by up to  $\sim 200\%$ , accompanied by a significant improvement in  $\text{N}_2$ -selectivity of about 20% in comparison to the un-promoted Pd/YSZ catalyst (Table 3). The promotional effects were interpreted in a similar manner to the aforementioned studies [17,51–53].

Tanikawa and Egawa [55] studied the effect of Ba-promoter on NO + CO reaction in the presence of  $\text{O}_2$  over Pd dispersed on  $\gamma\text{-Al}_2\text{O}_3$  and ceria-zirconia supports (CCP). They found that the activity of Pd/ $\gamma\text{-Al}_2\text{O}_3$  was gradually enhanced by increasing the Ba loading up to 15wt%; the light-off



temperatures ( $T_{50}$ ) for CO oxidation and NO reduction were decreased by 40 and 33 °C, respectively, over the optimally modified Pd(15%Ba)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. However, Ba addition on Pd/CZ catalyst decreased its activity for both NO reduction and CO oxidation reactions (Table 3).

Finally, Lepage et al. [56] studied the effect of electropositive promoters (monovalent H<sup>+</sup>, Na<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> or divalent Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> cations) over Rh nanoparticles supported on a series of Y zeolites for the NO reduction by CO by means of infrared spectroscopy of NO adsorption to monitor the electronic modifications of Rh nanoparticles. The observed decrease in NO reduction ignition temperature ( $T_{10}$ ) with increasing ionic radius-to-charge ratio was related to the degree of electron transfer from Rh particles to the adsorbed NO molecules. The shift of the IR band of linearly adsorbed NO to lower wavenumbers with increasing the radius/charge ratio of promoter elements substantiated this argument.

A comparative overview of the literature involved in this section and in Table 3 gives prominence to the following general features: (i) Promotion either induced by EPOC or by CCP is substantial and has qualitatively similar characteristics, although CCP leads to much larger rate enhancements;  $\rho$  values in the region of 45–110 and around 13 were obtained by using CCP and EPOC, respectively. The ultimate contact and thus the higher interaction of the well dispersed active phase particles with the promoter species may be the cause of the mentioned differences on promotion intensity. (ii) Heavier alkalis were typically more effective than lighter alkalis, with Rb being the best. (iii) Among Pt, Pd and Rh precious metals, alkali promotion was significantly more effective on Pt than on Rh and Pd. (iv) Alkali-induced enhancement of the dissociative chemisorption of NO was considered as a key factor for the interpretation of the aforementioned pronounced promotion.

### 3.1.4. NO Reduction by Hydrocarbons or H<sub>2</sub>

#### (i) NO reduction by alkenes

NO reduction by hydrocarbons under in situ electrochemical promotion (EPOC) by alkalis was firstly demonstrated by Harkness and Lambert [57] and Yentekakis et al. [58]. Using ethylene as reductant, Harkness and Lambert [57] showed that the rate of the NO + ethylene reaction over a Pt film interfaced with Na<sup>+</sup>-conducting  $\beta''$ -Al<sub>2</sub>O<sub>3</sub>, linearly increased with  $\theta_{Na}$  at low and intermediate sodium coverages (typically  $\theta_{Na} < 0.3$ ), achieving a plateau for higher values. Rate enhancement values  $\rho$  up to 15 were obtained (Table 4).

On the other hand Yentekakis et al. [58] showed very pronounced NO reduction rate enhancements (using propene as the reductant) for the Pt-catalysed NO+propene reaction upon Na promotion over similar Pt/(Na) $\beta''$ -Al<sub>2</sub>O<sub>3</sub> electrocatalyst. This effect was studied at 375 °C in a wide range of  $P_{NO}$  (0–7 kPa) and  $P_{C_3H_6}$  (0–0.4 kPa) partial pressures. The promotional effect of Na was found to be significant in the whole range of conditions studied. The coverage of the promoting species was determined via galvanostatic transients. These transients showed that the promotional effects maximized at a Na coverage of  $\theta_{Na} \sim 0.4$ , for which value the maximum enhancements in CO<sub>2</sub> and N<sub>2</sub> rates were  $\sim 7$  times larger than the rate of the unpromoted Pt, while the N<sub>2</sub>-selectivity increased from 60% on the clean Pt surface to 80% on the optimal Na-promoted Pt surface (Table 4). Higher sodium coverages ( $\theta_{Na} > 1$ ) caused a gradual decrease of the promoting phenomena. This suggests that nominal sodium coverages greater than one exhibit activity much higher than clean Pt because a substantial amount of Na is present as 3D crystallites, as demonstrated by XPS. A Na-induced strengthening of the NO chemisorbing bond relative to propene was indicated by the kinetic data. The accompanied weakening of the N–O bond and the concomitant extended NO dissociation were considered for the interpretation of the observed promotional effects. XPS data confirmed that under reaction conditions the promoter phase consists of a mixture of NaNO<sub>2</sub> and NaNO<sub>3</sub> 3D crystallites. At high Na loadings these surface promoter compounds inhibit reaction due to active sites blocking phenomena.

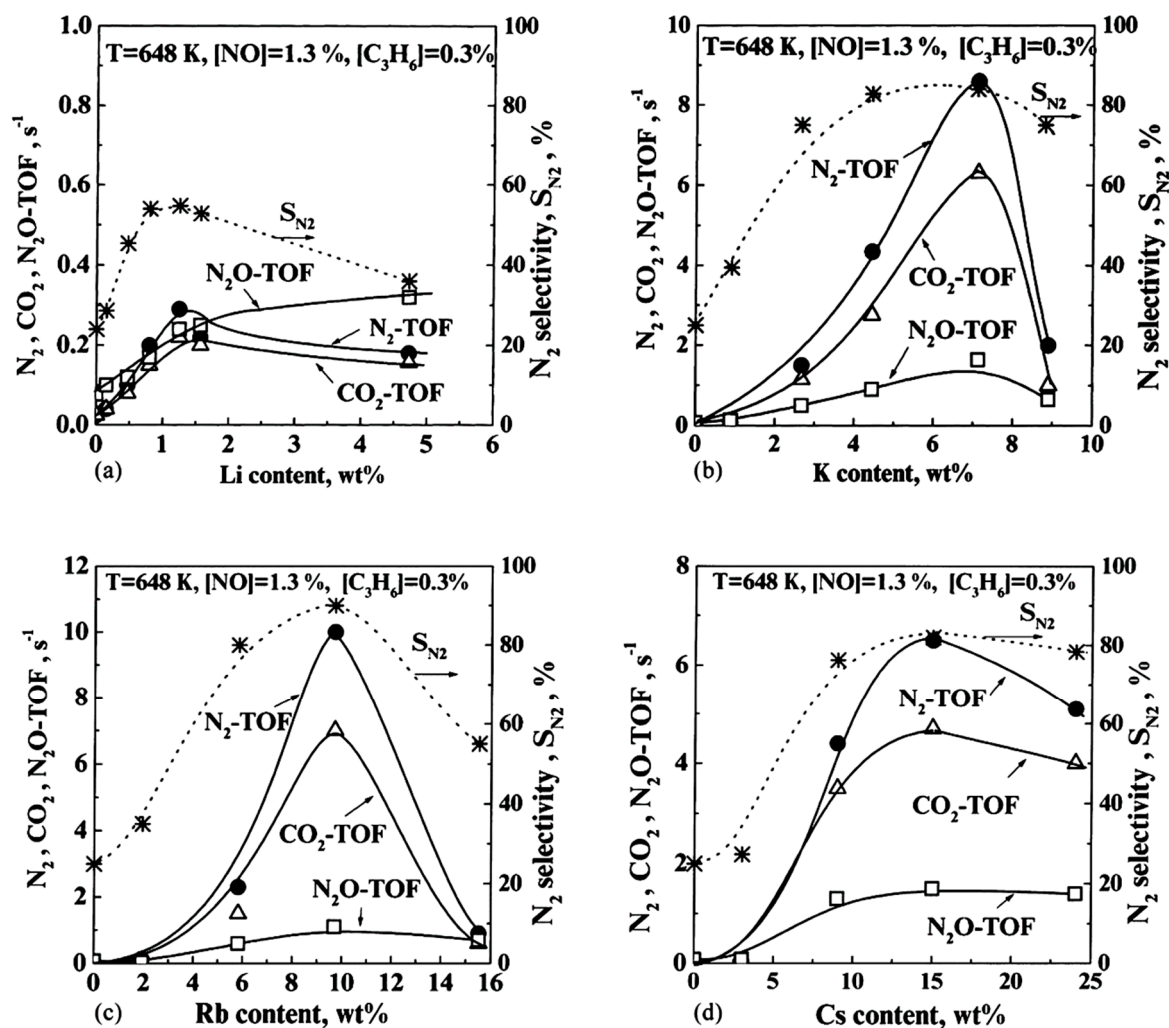
EPOC was also used by Williams et al. [59] for the study of NO reduction by propene over Rh film catalyst interfaced with (Na) $\beta''$ -Al<sub>2</sub>O<sub>3</sub>. They found that Na pumping onto Rh surface at a coverage

as low as ~2% causes a very large increase in the N<sub>2</sub>-selectivity from 45% on the Na-free Rh surface to 82% on the Na-promoted surface together with beneficial effects on the reaction rate: rate enhancement ratio values of  $\rho = 2.4$ , 1.7 and 0.4 were recorded for the N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O productions, respectively (Table 4). In a subsequent publication [60] the authors examined the impact of O<sub>2</sub> co-feed. It was found that upon increasing [O<sub>2</sub>], the promotional effects of Na were progressively attenuated and finally reversed to poisoning for [O<sub>2</sub>] = 2%. Similar considerations as in Reference [57] and [58] were used for the interpretation of the promotional effects, as well.

Using CCP, the group of Yentekakis [14,54] showed that the NO + propene reaction over Pd dispersed on 8mol% Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub> support (YSZ) can be substantially promoted by dosing the catalyst with alkalis. In Reference [14], the rate increased by an order of magnitude accompanied by selectivity increases from ~75% over the Na-free Pd/YSZ catalyst to >95% over the optimally Na-promoted Pd/YSZ catalyst in the temperature interval of 250–450 °C. The promotional effects were found to be optimized at a sodium content of 0.06wt% (corresponding to nominal sodium coverage of ~7%; Equation (4)), while over-promotion attenuated the rate (volcano type behaviour). These promotional effects caused a decrease in the NO light-off temperature (T<sub>50</sub>) of about 110 °C between the optimally promoted and unpromoted Pd catalyst (Table 4). A strengthening of the chemisorption bond of NO relative to propene that facilitates weakening of the N–O bond of the adsorbed NO molecules and thus their dissociative chemisorption was considered as the origin of the promotional effects. In ref. [54] the effects of Li, Na, K and Cs alkalis on Pd-catalysed NO + C<sub>3</sub>H<sub>6</sub> reaction were comparatively studied: Four catalysts dosed with the same alkali/Pd = 1/1.5 atom/atom loading were prepared and their behaviour was compared in a wide range of [NO] at constant [C<sub>3</sub>H<sub>6</sub>] = 0.8% and T=380 °C. All these catalyst were found significantly better in terms of activity and selectivity in comparison to the unpromoted Pd/YSZ, in the whole range of conditions investigated; Na provided the most significant promotional effects (Table 4).

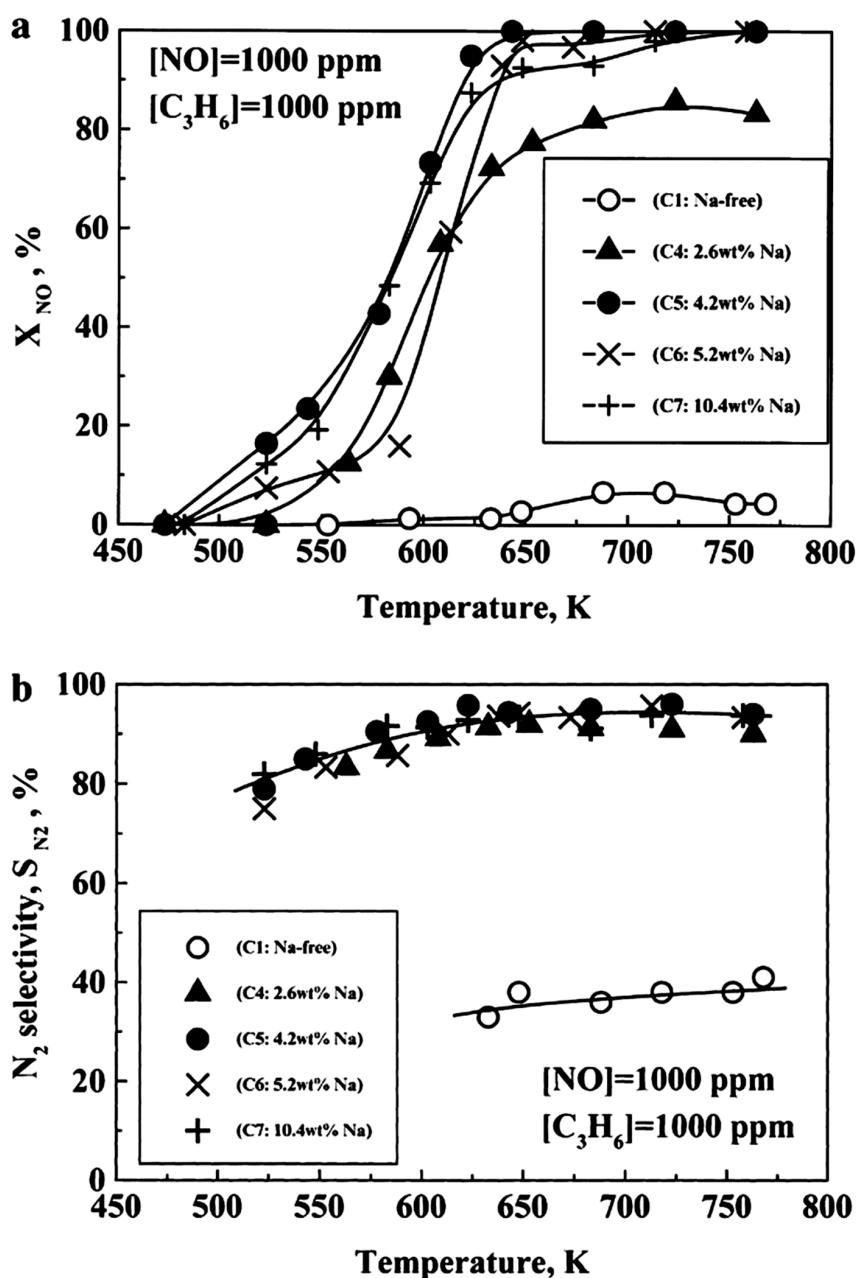
Systematically expanding their studies on conventional promoted catalysts (CCP), Yentekakis and co-workers showed that Pt nanoparticles dispersed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are subjected to extraordinarily effective promotion by alkalis (Li, Na, K, Rb and Cs) [15,61] and alkaline earths (Ba) [62,63] in both activity and N<sub>2</sub>-selectivity during the NO+propene reaction in the temperature interval of TWCs interest (ca. 200–550 °C). In References [15,61] rate increases by two orders of magnitude were achieved, while the selectivity towards N<sub>2</sub> was improved from ~20% over the alkali-free unpromoted Pt catalyst, to >95% over the optimally alkali-promoted catalysts. Best promotional effects were achieved by Rb-promotion, for which rate increases as high as 420-, 280- and 25-fold were obtained for the formation rates of N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O, respectively, in comparison to the performance of the unpromoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (Table 4). Volcano type behaviour was found to be followed upon increases of promoter loadings for all cases. Thus, promotion was found to be maximized for a Li content of 1.25wt%, a K content of 7.1wt%, a Rb content of 9.7 wt% a Cs content of 15wt% (Figure 12) [61] and a Na content of 4.18wt% [15].

This very spectacular promotion in light-off diagrams (see for example Figure 13) showed that the marginal (~10%) NO conversion efficiency of un-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can be readily proved by alkalis to values up to 100% in the temperature window of TWCs interest, offering at the same time selectivities towards N<sub>2</sub> >95% [15,61]. However, besides temperature, NO<sub>x</sub> removal efficiency of automotive catalytic converters is greatly affected by the presence of oxygen in the exhausts gases, in particular under excess O<sub>2</sub> conditions. Therefore, the NO + C<sub>3</sub>H<sub>6</sub> + excess O<sub>2</sub> reaction is of higher practical significance than the NO + C<sub>3</sub>H<sub>6</sub> one. Hence, it was decided to analyse this reaction and the effect of O<sub>2</sub> in a distinguishable section of the article (Section 3.2).



**Figure 12.** The effect of Li (a), K (b), Rb (c) and Cs (d) content of 0.5wt%Pt/ $\gamma$ - $Al_2O_3$  catalyst on the turnover (TOF) formation rates of  $N_2$ ,  $CO_2$  and  $N_2O$  and on  $N_2$ -selectivity. Conditions:  $T = 375\text{ }^\circ\text{C}$ ,  $[NO] = 1.3\%$ ,  $[C_3H_6] = 0.3\%$  (Reprinted with permission from Ref. [61]; Copyright 2001, Elsevier).

In the case of Ba-promotion the optimal Ba-loading was found to be 15.2wt% Ba (Table 4) [62]. Using a 1000 ppm NO + 1000 ppm  $C_3H_6$  feed composition (these concentrations are close to those encountered in practical applications and commonly used in the literature as referred conditions) the authors showed that the very poor NO light-off behaviour of Ba-free Pt/ $\gamma$ - $Al_2O_3$  catalysts, which gave a lower than 10% NO conversion in the whole 200–550  $^\circ\text{C}$  temperature interval, can be dramatically improved (in a similar manner to alkali-promotion [15,61]), achieving 100% NO conversion at relatively low temperatures accompanied by  $N_2$ -selectivities near to 100%. Further studying the Ba-promoted Pt/ $\gamma$ - $Al_2O_3$  system, the authors focussed on the effect of residual chloride, which concerns catalysts prepared from chlorine-containing precursors [63]; the detrimental effect of residual chloride on deNO<sub>x</sub> catalysis is well known. Very strikingly, it was found that when Ba is used to promote catalysts prepared from chloride-containing precursors, all the original chloride is retained, yet the catalysts exhibit very strong promotion and in every aspect their behaviours are identical to that of the chloride-free Ba-promoted catalyst [63]. This significant from the practical point of view attenuation of the inhibiting effect of chloride was rationalized in terms of formation of a stable 2D  $BaCl_2$  phase on the catalysts surface, where the promoting effect of Ba overwhelms the poisoning effect of Cl and a large net promotion is resulted.



**Figure 13.** The conversion of NO (a) and the corresponding selectivity towards N<sub>2</sub> (b) for Na-promoted 0.5wt%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, as a function of temperature at constant reactor inlet conditions: [NO] = 1000 ppm, [C<sub>3</sub>H<sub>6</sub>] = 1000 ppm; total flow rate  $F_t = 80 \text{ cm}^3\text{STP/min}$ ; catalyst weight  $8(\pm 0.2) \text{ mg}$ . (Reprinted with permission from Ref. [15]; Copyright 1999, Elsevier).

Macleod et al. [64] studied the NO + C<sub>3</sub>H<sub>6</sub> reaction over dispersed Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (CCP). Rh is one of the noble metals used in TWCs and its use is related to the effective NO reduction in the three-way catalytic chemistry. They found that NO reduction chemistry on Rh can also be improved by alkalis. For instance, at 375 °C, a 7.3wt% Na content in the catalyst was found to be optimal promoter loading, leading to a ~3-fold increase in Rh activity (Table 4). Significant increases in N<sub>2</sub>-selectivity, up to 90% were also obtained, when the unpromoted Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> appeared to have only 53%. In addition, Na was found to suppress de formation of CO and HCN. Higher Na loadings were poisoning the catalyst below to its initial Na-free performance. However, it is worth noticing the substantially lower degree of promotional effect of alkalis on the NO reduction chemistry of Rh compared to that observed for Pt and Pd.

## (ii) NO reduction by alkanes

Yentekakis and co-workers [65,66] studied the reduction of NO by methane over Na-dosed Pd catalyst (CCP) dispersed on yttria stabilized zirconia (YSZ) at temperatures between 350–500 °C and a wide range of reactants concentrations ( $[\text{NO}] = 0\text{--}1.5\%$ ,  $[\text{CH}_4] = 0\text{--}25\%$ ). It was observed that the reaction clearly exhibits Langmuir-Hinshelwood type kinetics over Pd with characteristic rate maxima reflecting competitive adsorption of NO and methane; NO adsorption however was found to be much more pronounced than that of  $\text{CH}_4$  within the temperature range investigated. Sodium was found to cause strong poisoning of the reaction at any loading due to a Na-induced oxygen poisoning of the catalyst (derived by NO decomposition) (Table 4). The very different response of alkali promotion for the NO reduction by alkanes (strong poisoning effects) and by alkenes (strong promotional effects) is attributed to the different trends of the adsorption of the two kinds of hydrocarbons (alkanes and alkenes) on the Pt-group metal surfaces [67,68].

It is worth noting the similarities on the effect of electropositive promotion of Pt-group metals (PGM) between the alkanes or alkenes oxidation by dioxygen (Section 3.1.2) and by NO (Section 3.1.4): In both cases when the oxidation process involves alkenes, electropositive promoters induce strong promotion, whilst when the reductant agent is an alkane, electropositive promoters lead to poisoning. This is understandable in view of the different trend of alkenes and alkanes adsorption on the PGM surfaces (strong and weak, respectively [67,68]) and the influence of the promotion on it [15,20,47,61,65,66] and the fact that in both cases the oxidant species are mainly based on adsorbed atomic oxygen derived by the dissociative chemisorption of molecular oxygen or NO [47].

(iii) NO reduction by  $\text{H}_2$  or  $\text{CO} + \text{H}_2$ 

Besides hydrocarbons, hydrogen is also one of the gases present in automotive exhaust stream. It could also be externally supplied, by the use of a hydrocarbon reformer or another source of safe in situ hydrogen generator, for the reduction of  $\text{NO}_x$  from stationary power sources and chemical plants. Notably, the  $\text{NH}_3$ -Selective Catalytic Reduction process ( $\text{NH}_3$ -SCR) which is currently one of the most performing technologies for  $\text{deNO}_x$  processes in stationary power applications and chemical plants, experiences drawbacks related to the storage and slip of ammonia, although it may be pointed out that urea (as an  $\text{NH}_3$  carrier) is now commercially available for use on diesel truck and some lighter vehicles. These issues can explain the growing interest and efforts for the use of  $\text{H}_2$  as a reducing agent of  $\text{NO}_x$  in the last years (e.g., [69–72]). Most of these studies have used Pt-group metals as catalysts.

The first EPOC work in this field was performed by Marina et al. [19], who studied the effect of Na on the Pt-catalysed NO reduction by  $\text{H}_2$  with  $(\text{Na})\beta''\text{Al}_2\text{O}_3$  as a source of Na promoter species. Rate enhancement ratio values up to  $\rho_{\text{N}_2} = 30$  were achieved for the formation of  $\text{N}_2$ , accompanied by significant increases in  $\text{N}_2$ -selectivity. At 375 °C, Na coverage of only 6% increased the  $\text{N}_2$ -selectivity from ~36% on the clean Na-free Pt surface to ~75% on the Na-promoted Pt surface (Table 4). The promotional effects of Na were applicable in a wide range of  $\text{H}_2/\text{NO}$  gas phase compositions (ca. 0.1–3.0) and temperature (ca. 300–450 °C).

Burch and Coleman [73] studied the effect of sodium for the selective catalytic reduction of NO by hydrogen in the presence of excess oxygen (lean-burn conditions) over  $\text{Na}_2\text{O}$ -modified conventional, highly dispersed Pt/ $\text{Al}_2\text{O}_3$  and Pt/ $\text{SiO}_2$  catalysts (CCP), at temperatures representative of automotive “cold-start” conditions (<200 °C). They found that small sodium loadings significantly increased the NO conversion rate while larger sodium loadings led to severe poisoning. Under oxygen excess and low temperatures (<~140 °C) the selectivity to  $\text{N}_2$  was practically unaffected by the addition of sodium, while an adverse effect was found at higher temperatures (Table 4).

Machida et al. [74] investigated the effect of alkalis (Na, K, Cs) and alkaline earths (Mg, Ca, Ba) on Pt/ZSM5 catalysts (CCP) for the selective reduction of NO by  $\text{H}_2$  under  $\text{O}_2$  excess (0.08% NO, 0.08–0.56%  $\text{H}_2$ , 10%  $\text{O}_2$ ). The optimum promotional effects were obtained with Na promoter at loadings of 10–15wt%, which exhibited  $\text{NO}_x$  conversion higher than 90% and  $\text{N}_2$  selectivity of ~50%. Based on in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) studies,



it was suggested that Na promotes the adsorption of NO as NO<sub>2</sub>-type species, which would be an intermediate towards N<sub>2</sub> formation.

The H<sub>2</sub>-SCR process over Pt for automotive emissions control, however, exhibits an important disadvantage: CO, which also coexists in exhaust stream, is strongly adsorbed on Pt surface causing inhibition of NO<sub>x</sub> reduction. Pioneer CCP work by Lambert and co-workers [75–78] showed that Pd overcomes this poisoning effect of CO leading to good NO<sub>x</sub> conversions at mixed H<sub>2</sub> + CO feeds. In addition, they found that Pd dispersed on 10wt% TiO<sub>2</sub>-modified Al<sub>2</sub>O<sub>3</sub> offers even more improved deNO<sub>x</sub> efficiency in comparison to the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. The effective temperature window of these new catalyst formulations was however relatively narrow (ca. 150–200 °C). In a similar manner, Yentekakis and co-workers [79] studied the lean NO<sub>x</sub> reduction by H<sub>2</sub> + CO over potassium-modified Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts. They found that potassium is a very active promoter of the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst for H<sub>2</sub>-SCR process leading to significant enhancements of both NO<sub>x</sub> conversion activity and N<sub>2</sub>-selectivity of Pd. A potassium loading of ~0.25 wt% was found to optimize the catalyst performance in both activity and selectivity, leading to a catalyst formulation that offered up to ~90% NO<sub>x</sub> conversion with a N<sub>2</sub>-selectivity of the order of >85% for the temperature range of 180–300 °C (Table 4).

#### (iv) Direct NO decomposition

Limited studies can be found on this topic, probably due to the necessity of high temperatures for the direct NO decomposition. Wang et al. [80] studied the direct decomposition of NO into nitrogen and oxygen over Na-modified Pd/Al<sub>2</sub>O<sub>3</sub> catalysts (CCP) in a flow reactor. They found that the NO reduction activity of Pd was significantly promoted by pre-coating the Al<sub>2</sub>O<sub>3</sub> support with NaOH before the impregnation with Pd. A loading of 13wt% NaOH on a 4.8wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst enhanced the nitrogen yield from 15% up to 60% at T = 627 °C (Table 4). The observed NO decomposition rate enhancement was attributed to the strengthening of the NO adsorption bond on Pd sites.

Overviewing the literature included in Section 3.1.4 and Table 4 the following general remarks can emerge:

- Alkanes oxidation, either using dioxygen (Section 3.1.2) or NO (this section) behaves similarly under electropositive promotion by alkalis: addition of alkali on PGM surfaces causes only poisoning. Interpretations given are similar in both cases, based on the low adsorption propensity of alkanes on PGM surfaces and on the O-poisoning of the surfaces resulted by the alkali-induced enhancement of NO dissociative chemisorption.
- On the opposite, electropositive promotion of the NO + alkenes reactions is very pronounced; apparently it is the greater observed, for emissions control catalysis model reactions reviewed in the present work, offering  $\rho$  values as high as  $\rho_{N_2} = 420$  and  $\rho_{CO_2} = 280$ .
- Some studies performing one-by-one comparison of EPOC and CCP by means of Na promoted Pt/NO + C<sub>3</sub>H<sub>6</sub> system have demonstrated the very close similarities on the promotion output characteristics of the two methods and have convincingly argued for the similar origin of promotion in both cases.
- Once again (see Section 3.1.3) the intensity of CCP was superior to that of EPOC, indicating that an intimate contact between active phase and promoter particles succeeded by nanostructured catalysts seems to play a significant role on the promotion intensity.
- Heavier alkalis were again (see Section 3.1.3) more effective than the lighter ones; Rb was the best promoter.
- Among Pt, Pd and Rh, alkali promotion was more effective on Pt, lower on Pd and even lower on Rh. As we shall see (Section 3.3) this is related to the initial, unpromoted propensity of each metal on the dissociative adsorption of NO.
- Promotion by alkalis was also found to be substantial on the NO reduction by H<sub>2</sub> as well as on the direct NO decomposition reaction, although only few studies appeared in the open literature so far.
- Catalytic activity promotion was always accompanied by substantial increases on the system selectivity towards N<sub>2</sub>.

**Table 4.** Electropositive promotion of PGMs-catalysed NO reduction by hydrocarbons (alkenes or alkanes), H<sub>2</sub> or H<sub>2</sub> + CO.

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and maximum achievements	Ref.
<b>NO reduction by alkenes (NO + Alkene)</b>					
NO, C <sub>2</sub> H <sub>4</sub>	Pt film over (Na)β''Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	Na	T = 275–450 °C [NO] = 0.5–1%, [C <sub>2</sub> H <sub>4</sub> ] = 1–3% θ <sub>Na</sub> = 0–40%	<ul style="list-style-type: none"> <li>✓ Significant promotion in a wide range of gas compositions (C<sub>2</sub>H<sub>4</sub>/NO = 1–6); in all compositions promotion was monotonically increased by increasing θ<sub>Na</sub> up to 40%. Significant changes in apparent activation energy by varying θ<sub>Na</sub>.</li> <li>➤ ρ<sub>CO<sub>2</sub></sub> = 15 for θ<sub>Na</sub> = ~30% and [C<sub>2</sub>H<sub>4</sub>] = 1.5%, [NO] = 0.65% at T = 402 °C</li> </ul>	[57]
NO, C <sub>3</sub> H <sub>6</sub>	Pt film over (Na)β''Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	Na	T = 330–400 °C [NO] = 0–6%, [C <sub>3</sub> H <sub>6</sub> ] = 0–0.4% θ <sub>Na</sub> = 0–100%	<ul style="list-style-type: none"> <li>✓ Significant volcano type promotion observed with rate increases by an order of magnitude; optimal promotion achieved at θ<sub>Na</sub> ~30%. Significant changes in apparent activation energy upon varying θ<sub>Na</sub> were found. Under reaction conditions, the promoter phase consists of a mixture of NaNO<sub>2</sub>/NaNO<sub>3</sub>, which at high Na- loadings cause poisoning.</li> <li>➤ ρ<sub>N<sub>2</sub></sub> ~ ρ<sub>CO<sub>2</sub></sub> = 7, ρ<sub>N<sub>2</sub>O</sub> = 3, ΔS<sub>N<sub>2</sub></sub> = +20% (60%→80%), for θ<sub>Na</sub> = ~30%, [C<sub>3</sub>H<sub>6</sub>] = 0.6%, [NO] = 1.3%, T = 375 °C</li> </ul>	[58]
NO, C <sub>3</sub> H <sub>6</sub>	Rh film over (Na)β''Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	Na	T = 350 °C [NO] = 1–9%, [C <sub>3</sub> H <sub>6</sub> ] = 1%, [O <sub>2</sub> ] = 0–2%	<ul style="list-style-type: none"> <li>✓ Na promotes the Rh-catalysed NO+propene reaction, especially its selectivity towards N<sub>2</sub>. The impact of [NO]/[C<sub>3</sub>H<sub>6</sub>] ratio was studied: promotion was superior for [NO]/[C<sub>3</sub>H<sub>6</sub>] = 1%/1%. The impact of O<sub>2</sub> co-feed was also tested: upon increasing [O<sub>2</sub>] the promotional effects of Na were progressively decreased, reversing to poisoning at [O<sub>2</sub>] = 2%. Under promoted conditions the promoter phase consists of carbonate, nitrate or both.</li> <li>➤ ρ<sub>N<sub>2</sub></sub> = 2.4, ρ<sub>CO<sub>2</sub></sub> = 1.7, ρ<sub>N<sub>2</sub>O</sub> = 0.4, ΔS<sub>N<sub>2</sub></sub> = +37% (45%→82%), for θ<sub>Na</sub> = ~20%, [C<sub>3</sub>H<sub>6</sub>] = [NO] = 1%, T = 350 °C.</li> </ul>	[59] [60]



Table 4. Cont.

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and maximum achievements	Ref.
NO, C <sub>3</sub> H <sub>6</sub>	0.5 wt% Pd/YSZ (CCP)	Na, Li, K, Cs	T = 250–450 °C [NO] = 0–8%, [C <sub>3</sub> H <sub>6</sub> ] = 0–8% Na loadings: 0–0.102 wt% (nominal $\theta_{Na}$ = 0–30%)	<ul style="list-style-type: none"> <li>✓ Rate increases by an order of magnitude were achieved. Promotion followed volcano type behaviour (optimal promotion at ~20% <math>\theta_{Na}</math>). In respect to Li, Na, K, Cs alkalis studied Na was superior promoter. Significant variation of the apparent activation energy with Na loading; the promoted induced isokinetic effect was demonstrated.</li> <li>➤ <math>\rho_{N_2} \sim \rho_{CO_2} \sim 7</math>, <math>\rho_{N_2O} \sim 1.5</math>, <math>\Delta S_{N_2} = +20\%</math> (75%→95%), for <math>\theta_{Na} = \sim 20\%</math>, [NO] = 1%, [C<sub>3</sub>H<sub>6</sub>] = 0.8%, T = 380 °C</li> <li>➤ <math>\Delta T_{50} = -110</math> °C at [C<sub>3</sub>H<sub>6</sub>] = [NO] = 0.8% with the optimally promoted catalyst, <math>\theta_{Na} = 20\%</math> (0.068 wt% Na).</li> </ul>	[14] [54]
NO, C <sub>3</sub> H <sub>6</sub>	0.5 wt% Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Na, Li, K, Rb, Cs	T = 200–500 °C [NO] = 0–7%, [C <sub>3</sub> H <sub>6</sub> ] = 0.3, 0.6% Alkali loadings: Li: 0–4.7 wt%; Na: 0–10.4 wt%; K: 0–8.8 wt%; Rb: 0–15.5 wt%; Cs: 0–24 wt%.	<ul style="list-style-type: none"> <li>✓ Extraordinarily effective promotion, by up to two orders of magnitude, with all alkalis (the highest found so far in emissions control catalysis: 420-fold rate increases). Volcano type behaviour; the optimal alkali loading depends on its entity. Among Li, Na, K, Rb, Cs alkalis studied superior promotion was offered by Rb.</li> <li>➤ <math>\rho_{N_2} = 420</math>, <math>\rho_{CO_2} = 280</math>, <math>\rho_{N_2O} = 25</math>, <math>\Delta S_{N_2} &gt; +75\%</math> (20%→&gt; 95%), with 9.7wt%Rb at [NO] = 1.3%, [C<sub>3</sub>H<sub>6</sub>] = 0.3%, T = 375 °C</li> <li>➤ Optimal alkali loadings: Li: 1.25 wt%, Na: 4.16 wt%, K: 7.1 wt%, Rb: 9.7 wt%, Cs: 15 wt%.</li> </ul>	[15] [61] [21] [22]

Table 4. Cont.

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and maximum achievements	Ref.
NO, C <sub>3</sub> H <sub>6</sub>	0.5 wt% Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Ba	T = 200–500 °C [NO] = 0–5%, [C <sub>3</sub> H <sub>6</sub> ] = 0–2% Ba loadings: 0, 3.5, 9.7, 15.2, 22.3wt%	<ul style="list-style-type: none"> <li>✓ Significant, volcano type promotion with rate increase by up to two orders of magnitude; optimal promoter loading at 9.7wt% Ba.</li> <li>✓ Significant changes in apparent activation energy upon varying Ba loading.</li> <li>➤ <math>\rho_{N_2} = 165</math>, <math>\rho_{CO_2} = 110</math>, <math>\rho_{N_2O} = 9</math>, <math>\Delta S_{N_2} = +49\%</math> (45%→94%) with 9.7wt% Ba at [NO] = 1.3%, [C<sub>3</sub>H<sub>6</sub>] = 0.3%, T = 450 °C. <math>\Delta T_{50} = -124</math> °C for NO conversion</li> </ul>	[62] [63]
NO, C <sub>3</sub> H <sub>6</sub>	0.5 wt% Rh/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Na	T = 200–550 °C [NO] = 0–1%, [C <sub>3</sub> H <sub>6</sub> ] = 0.1% Na loadings: 0, 1.8, 3.0, 7.3, 11.3 wt%	<ul style="list-style-type: none"> <li>✓ Significant, volcano type promotion -but not such impressive as in the case of Pt [15,61–63]; optimal promoter loading: 7.3wt% Na.</li> <li>✓ The formation of CO and HCN by-products was also suppressed by Na-promotion.</li> <li>➤ <math>\rho_{N_2} = 3.3</math>, <math>\rho_{CO_2} = 2.7</math>, <math>\rho_{N_2O} = 2</math>, <math>\Delta S_{N_2} = +29\%</math> (43%→72%) with 7.3wt% Na at [NO] = [C<sub>3</sub>H<sub>6</sub>] = 0.3%, T = 375 °C</li> </ul>	[64]
<b>NO reduction by alkanes (NO + Alkane)</b>					
NO, CH <sub>4</sub>	0.5 wt% Pd/YSZ (CCP)	Na	T = 350–450 °C [NO] = 0–1.5%, [CH <sub>4</sub> ] = 0–20% Na loadings: 0, 0.017, 0.034, 0.068, 0.102 wt%	<ul style="list-style-type: none"> <li>✓ Pd by itself is an effective catalyst for NO reduction by CH<sub>4</sub>. Na induced only poisoning in the whole region of [NO] and [CH<sub>4</sub>] concentrations studied; the weak adsorption of CH<sub>4</sub> compared to that of O<sub>2</sub> and the O-poisoning of Pd surface due to the strengthening of the Pd-O bond induced by Na, readily explains this behaviour.</li> <li>➤ Only Na-induced poisoning on the system was obtained.</li> </ul>	[65] [66]

Table 4. Cont.

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and maximum achievements	Ref.
NO reduction by H <sub>2</sub> and/or CO (NO + H <sub>2</sub> , NO + H <sub>2</sub> + CO) in the absence or presence of O <sub>2</sub>					
NO, H <sub>2</sub>	Pt film on (Na)β''Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	Na	T = 300–450 °C [NO] = 0–1.6%, [H <sub>2</sub> ] = 0–1% θ <sub>Na</sub> = 0–12%	<ul style="list-style-type: none"> <li>✓ Significant, volcano type, promotion effects of Na to NO+H<sub>2</sub>/Pt catalytic system; optimal promoter coverage θ<sub>Na</sub>~6%</li> <li>✓ Significant variations in the apparent activation energy of the reaction.</li> <li>➤ ρ<sub>N<sub>2</sub></sub> = 30, ρ<sub>N<sub>2</sub>O</sub> = 6, ΔS<sub>N<sub>2</sub></sub> = +40% (36→75%) with θ<sub>Na</sub>~6% at [NO] = 0.63% [H<sub>2</sub>] = 0.3%, T = 375 °C</li> </ul>	[19]
NO, H <sub>2</sub> , O <sub>2</sub>	1 wt% Pt/γ-Al <sub>2</sub> O <sub>3</sub> 1 wt% Pt/SiO <sub>2</sub> (CCP)	Na (Mo)	T = 50–200 °C [NO] = 0.1%, [H <sub>2</sub> ] = 0.4%, [O <sub>2</sub> ] = 6% Na <sub>2</sub> O-loadings: 0, 0.27, 1, 5 and 10 wt%	<ul style="list-style-type: none"> <li>✓ The study conducted at lean conditions and at temperatures representative of automotive “cold-start” conditions.</li> <li>✓ Volcano type promotion, optimized at a Na<sub>2</sub>O loading = 0.27 wt%. Addition of MoO<sub>3</sub> as co-promoter enhances Pt performance for all the loadings tested (2.5, 10, 23, 46 wt% MoO<sub>3</sub>)</li> <li>➤ ΔX<sub>NO</sub> = 20% (75%→90%) with 0.27 wt% Na<sub>2</sub>O-loading at T = 125 °C.</li> <li>➤ Best catalyst: 1 wt% Pt/10 wt% MoO<sub>3</sub>/0.27 wt% Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> offered X<sub>NO</sub> = 95% at 100 °C and a ΔT<sub>50</sub> = −50 °C.</li> </ul>	[73]
NO, H <sub>2</sub> , O <sub>2</sub>	1 wt% Pt/ZSM-5 (CCP)	Na, K, Cs, Mg, Ca, Ba	T = 40–110 °C [NO] = 0.08%, [H <sub>2</sub> ] = 0.08–0.56%, [O <sub>2</sub> ] = 10% O <sub>2</sub> Na loadings: 0, 3, 5, 10, 15 and 20 wt%	<ul style="list-style-type: none"> <li>✓ Optimum promotion achieved by Na. Optimal promoter loading: 10–15 wt% Na.</li> <li>➤ NO<sub>x</sub> conversion &gt; 90% with a selectivity towards N<sub>2</sub>~50%.</li> </ul>	[74]

Table 4. Cont.

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and maximum achievements	Ref.
NO, H <sub>2</sub> , CO, O <sub>2</sub>	0.5 wt% Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> 0.5 wt% Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> (CCP)	K	T = 50–400 °C [NO] = 0.1%, [CO] = 0.25%, [H <sub>2</sub> ] = 0.75%, [O <sub>2</sub> ] = 6% O <sub>2</sub> K loadings: 0, 0.1, 0.25, 0.5, 1.0 and 3.0 wt% K	<ul style="list-style-type: none"> <li>✓ Synergy between support-mediated (modification of Al<sub>2</sub>O<sub>3</sub> with TiO<sub>2</sub>) and surface-induced (K-addition) promotions providing very pronounced <i>de</i>NO<sub>x</sub> performance.</li> <li>✓ K-promotion over the doubly-promoted catalyst appeared volcano type behaviour with optimal K-loading=0.25wt%.</li> <li>➤ 90% NO<sub>x</sub> conversion with &gt;85% N<sub>2</sub>-selectivity in a wide range of temperatures (180–300 °C) were achieved on the optimally doubly-promoted catalyst: 0.5 wt% Pd(0.25 wt% K)/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub>-10 wt% TiO<sub>2</sub>. Also, <math>\Delta T_{50} = -40</math> °C</li> </ul>	[79]
<b>Direct NO decomposition</b>					
NO	(0.6–10 wt%)Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Na	T = 550–900 °C [NO] = 4% in He Na loadings (as NaOH): 0, 1.3, 4.3, 6.5 and 13 wt% NaOH	<ul style="list-style-type: none"> <li>✓ Pre-coadding of <math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub> with NaOH causes significant promotion of the direct NO decomposition activity of Pd/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub> catalyst.</li> <li>✓ Promotion was progressively increased with increasing promoter loading.</li> <li>➤ <math>\Delta X_{NO} = 45\%</math> (15%→60%) at T = 625 °C over the 13 wt% NaOH-promoted 4.8 wt% Pd/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub> catalyst.</li> </ul>	[80]

### 3.1.5. N<sub>2</sub>O Decomposition and/or Reduction

It is well known that nitrous oxide (N<sub>2</sub>O) is absent in automotive engines exhausts gases, although this can be a by-product (in low concentrations) of the NO reduction reactions taking place in the after-treatment devices of cars (catalytic converters), primarily formed during the “cold start” and “intermediate temperature” periods. However, N<sub>2</sub>O is a powerful greenhouse gas (global warming potential ~310) and also the dominant stratospheric ozone-depleting gas nowadays. These account for the currently devoted high attention on the N<sub>2</sub>O emissions control. Besides mobile sources, other anthropogenic sources of N<sub>2</sub>O emissions involve stationary fuels combustion processes, agricultural activities and industrial plants (e.g., adipic and nitric acid plants) where it is produced in fairly high concentrations; the latter rationalizes why a major portion of deN<sub>2</sub>O studies concerns gas mixtures with relatively high N<sub>2</sub>O concentrations (ca. 0.1–1 vol.%; Table 5), not actually mirror cars emissions.

#### (i) Direct N<sub>2</sub>O decomposition

No studies of electrochemical catalyst promotion (EPOC) were found in literature regarding the direct N<sub>2</sub>O decomposition. In the next paragraphs we summarize some examples of the CCP studies for this reaction.

The pronounced effect of electropositive promoters on the direct N<sub>2</sub>O decomposition performance (de-N<sub>2</sub>O) of noble metals supported catalysts was demonstrated by several groups [81–85] (Table 5). In particular, Haber et al. [81] investigated the effect of Li, Na, K and Cs on N<sub>2</sub>O decomposition over Rh catalysts supported on alkali-modified Al<sub>2</sub>O<sub>3</sub> carrier. They found that the deposition of alkali metals on Al<sub>2</sub>O<sub>3</sub> support results in a notable increase of Rh dispersion, which improved de-N<sub>2</sub>O efficiency. In almost all cases the optimum promotional effects were obtained at ~0.078 mol% alkali (Table 5).

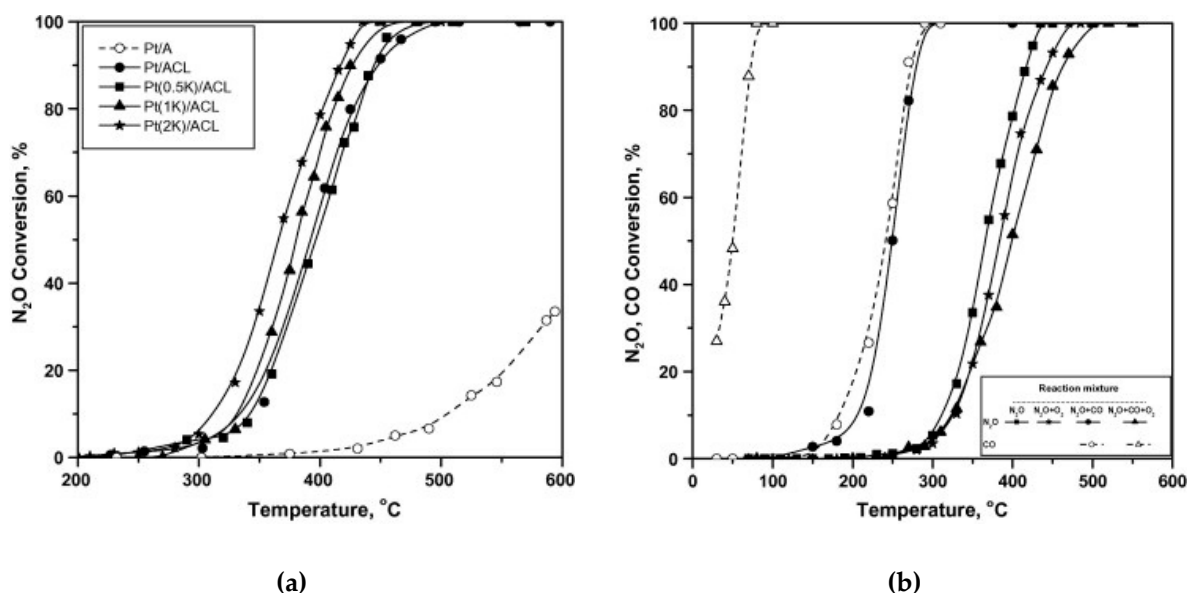
Parres-Escaped et al. [82] studied the N<sub>2</sub>O decomposition over Rh catalysts supported either on bare  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or on alkaline earth modified alumina (5 wt% Mg- and Sr-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). Enhanced deN<sub>2</sub>O performance was obtained with Rh/(Sr)Al<sub>2</sub>O<sub>3</sub> catalysts, which achieved total N<sub>2</sub>O conversion at 300 and 350 °C, in the absence and presence of O<sub>2</sub>, respectively, compared to 375 and 450 °C over un-promoted catalysts (Table 5). However, Mg addition was not beneficial to deN<sub>2</sub>O Rh/Al<sub>2</sub>O<sub>3</sub> activity. The latter was attributed to the formation of magnesium aluminate, while the former was attributed to the enhanced Rh dispersion (determined by TEM) on account of the Sr-modifier.

Combined structural and surface promotion was applied by Konsolakis et al. [83] to facilitate the deN<sub>2</sub>O performance of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. To this end, rare earth oxides (CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>) were used as structural promoters of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support and potassium (K) as surface promoter of Pt, providing a doubly-promoted Pt(K)/Al<sub>2</sub>O<sub>3</sub>-(CeO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub>) catalyst composite. The study was conducted on macro-structured, cordierite honeycomb monolith washcoated catalytic arrangements, suitable for practical implementations. The effect of K-promoter was studied in the range of 0–2 wt% K loadings, while the impact of O<sub>2</sub>, CO and H<sub>2</sub>O in the feed stream was also investigated (Table 5). It was found that incorporation of 20 wt% CeO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub> in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (ACZ) results in dramatic enhancement of the deN<sub>2</sub>O catalyst activity which is further improved by potassium addition. The promotional effects of K were found to monotonically increase upon increasing its loading on the structurally promoted Pt/ACZ catalyst in the range of 0–2 wt% studied. As a result, the final doubly-promoted catalyst with 2 wt% K loading achieved 100% N<sub>2</sub>O conversion at a temperature of only 440 °C; notably the bare Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> did not exceed ~35% N<sub>2</sub>O conversion even at 600 °C (Figure 14a). In respect to the impact of CO, O<sub>2</sub>, H<sub>2</sub>O co-feed, the authors found the following deN<sub>2</sub>O efficiency sequence in all promoted or non-promoted catalysts: N<sub>2</sub>O + CO >> N<sub>2</sub>O > N<sub>2</sub>O + O<sub>2</sub> > N<sub>2</sub>O + O<sub>2</sub> + CO (Figure 14b). Water co-feed was detrimental to deN<sub>2</sub>O performance but in a partially reversible manner after its removal from the feed stream; the catalytic efficiency was totally restored by adding H<sub>2</sub> into N<sub>2</sub>O + H<sub>2</sub>O feed.

Papista et al. [84] studied the promoting impact of potassium addition to Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst on N<sub>2</sub>O decomposition under both deficient and O<sub>2</sub> excess conditions. Varying K loading in the range of 0–1 wt%, the authors found poisoning effect on the deN<sub>2</sub>O performance of iridium in the absence of oxygen in the feed. The opposite was true in the case of oxygen excess conditions; a

pronounced promotion was recorded showing that K prohibits the oxygen-poisoning of the catalysts; the latter self-poisoning is a typical problem in deN<sub>2</sub>O catalytic chemistry, since the removal of the N<sub>2</sub>O decomposition-derived adsorbed oxygen on the catalyst surface is a key reaction step of the process. The alkali promotion found in the case of oxygen excess conditions follows volcano behaviour providing therefore an optimal promoter loading of 0.5 wt% K, that resulted in a significant decrease of T<sub>50</sub>, equal to  $\Delta T_{50} = -80$  °C (Table 5). The effect of alkali on the adsorption properties of Ir involving strengthening of the Ir–O bond of adsorbed O species with concomitant changes on the oxidation state of the metal was considered upon interpretation of the promotional and/or poisoning effects observed.

Finally, Goncalves and Figueiredo [85] studied the effect of potassium on the catalytic activity of Pt supported on activated carbon (ROX 0.8) for the simultaneous reduction of NO + N<sub>2</sub>O mixtures. They found a synergistic effect between K and Pt which led to high activity at relatively low temperatures. For instance, at 350 °C, a very stable and close to 100% conversion of both reactants was recorded over a 5wt% K/0.1wt% Pt catalyst, in opposite to the monometallic 0.5wt% K or 0.1wt% Pt counterparts (Table 5). The latter showed significantly lower conversion activity of about 25% for NO and 90% and 0% for N<sub>2</sub>O, respectively. The improved redox properties of the bimetallic K/Pt formulation was responsible for this synergy on enhancing both deNO and deN<sub>2</sub>O reactions [85].



**Figure 14.** (a): N<sub>2</sub>O conversion profiles as a function of temperature (light-off curves) for bare Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, structurally promoted Pt/ACL and doubly-promoted Pt(K)/ACL catalysts under direct decomposition of N<sub>2</sub>O; Feed: 0.1% N<sub>2</sub>O, balance He; GHSV = 10,000 h<sup>−1</sup>. (b): N<sub>2</sub>O (and CO) conversion profiles obtained over the optimally doubly-promoted Pt(2wt%K)/ACL catalyst under direct N<sub>2</sub>O decomposition or N<sub>2</sub>O + CO reactions in the absence or presence of O<sub>2</sub>, that is, under the feeds: 0.1% N<sub>2</sub>O, balance He; 0.1% N<sub>2</sub>O + 2% O<sub>2</sub>, balance He; 0.1% N<sub>2</sub>O + 0.1% CO, balance He; 0.1% N<sub>2</sub>O + 0.1% CO + 2% O<sub>2</sub>, balance He. GHSV = 10,000 h<sup>−1</sup>. (Reprinted with permission from Ref. [83]; Copyright 2013, Elsevier).

## (ii) N<sub>2</sub>O reduction by hydrocarbons

Very recently, the effect of alkali modifiers on another very important reaction related both to the TWC chemistry and N<sub>2</sub>O abatement, that is, the N<sub>2</sub>O reduction by hydrocarbons, was extensively studied by Pekridis et al. [25,86]. In particular, the role of potassium (K) promoter on the surface and catalytic properties of Pd/Al<sub>2</sub>O<sub>3</sub> (CCP) catalysts for N<sub>2</sub>O reduction by alkanes (CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>) or alkenes (C<sub>3</sub>H<sub>6</sub>) was investigated [86]. Potassium strongly enhanced the N<sub>2</sub>O reduction by propane or propene, resulting in notably lower N<sub>2</sub>O light off temperatures (~100 °C) compared to the un-promoted catalyst (Table 5). However, a slight inhibition upon K-promotion was obtained when CH<sub>4</sub> was used

as a reducing agent, implying that the extent of K-promotion is strongly related with the nature of the reducing agent. A comprehensive surface characterization study, involving XPS, in situ DRIFT spectroscopy of CO adsorption and FTIR-pyridine adsorption, was undertaken to correlate the de-N<sub>2</sub>O performance with the catalyst surface characteristics. The results revealed that the electronic, acidic and structural properties of Pd/Al<sub>2</sub>O<sub>3</sub> catalyst can be substantially modified by potassium, which in turn affects the reactants chemisorption bonds and as a consequence the overall surface activity. Specifically, addition of K on Pd/Al<sub>2</sub>O<sub>3</sub> decreases the adsorption strength of electron-donor adsorbates, such as C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub>, enhancing the N<sub>2</sub>O adsorption through an electron transfer from metal sites to N<sub>2</sub>O antibonding orbitals. Both factors act synergistically towards increasing active sites for N<sub>2</sub>O adsorption/decomposition. However, in the case of CH<sub>4</sub>, K enhances the adsorption strength of N<sub>2</sub>O and its dissociation products (O<sub>ads</sub>), at the expense of weakly bonded CH<sub>4</sub>, leading to poisoning by strongly bonded oxygen atoms.

In correlation with the above study, the EPOC concept (through a Pd-film electrocatalyst interfaced with (K)β''Al<sub>2</sub>O<sub>3</sub> solid electrolyte) was also used as a probe technique for exploring in detail the response of Pd metal to alkali (K) promotion in the same reaction [25]. The obtained results matched very well the promotion characteristics of the previous CCP study that involved conventional highly dispersed catalysts, demonstrating experimentally again that electrochemical promotion is an efficient tool for a rapid investigation of the promoter effect on a catalytic system. The obtained information could be further used to design and optimize efficient and “smart” catalysts formulations.

The N<sub>2</sub>O reduction by propene was also studied by de Lucas-Consuegra et al. [87,88], over Pt-based electro-catalysts, electrochemically promoted by potassium by the use of a (K)β''Al<sub>2</sub>O<sub>3</sub> solid electrolyte. The authors found significant rate enhancement ratios ( $\rho_{\max} \sim 10$ ) at temperatures between 400–450 °C and a reaction mixture composition of N<sub>2</sub>O/C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub> = 1000 ppm/2000 ppm/2000 ppm (Table 5). Potassium coverages (estimated by appropriate galvanostatic transients) higher than  $\theta_K \sim 70\%$  were necessary in order to achieve such large rate enhancements. They also found that these pronounced promotional effects are similar for a wide range of O<sub>2</sub> concentration in the reaction mixture (2000–7000 ppm), while at larger O<sub>2</sub> concentrations (>9000 ppm) the promoting phenomena were practically vanished. A very significant observation of this work was also the demonstration that potassium addition strongly decreased the inhibiting effect of water vapor on the Pt-catalysed N<sub>2</sub>O/C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub> catalytic system.

Overviewing the literature findings included in Section 3.1.5 and Table 5 the following general conclusions can emerge:

- Alkali addition on PGM catalysts typically promotes the direct N<sub>2</sub>O decomposition reaction (in the absence or presence of O<sub>2</sub> in the feed stream) or its reduction by reducing agents.
- Among Pt, Rh and Ir catalysts, alkali-promotion of the N<sub>2</sub>O decomposition reaction was found to be very effective and superior on Pt, less effective on Rh and detrimental (poisoning) on Ir; in the case of Ir, alkali-induced promotion was obtained only under excess oxygen conditions, which was attributed to changes on the oxidation state of the metal.
- Comparative EPOC and CCP studies of alkali promotion on the N<sub>2</sub>O reduction by the use of several reducing agents (CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub>) demonstrated the great similarities on the output promotional characteristics of the two methods.



**Table 5.** Electropositive promotion of PGMs-catalysed N<sub>2</sub>O decomposition and/or reduction reactions.

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and maximum achievements	Ref.
N <sub>2</sub> O	0.1 wt %Rh/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Li, Na, K, Cs	T = 250–450 °C [N <sub>2</sub> O] = 1% Alkali loadings (as alkali oxides): 0.033, 0.066, 0.078, 0.099 wt%	<ul style="list-style-type: none"> <li>✓ Alkali addition enhanced Rh dispersion and thus deN<sub>2</sub>O catalytic activity. Best promoter was Cs.</li> <li>✓ Volcano type promotion for all alkalis used; optimal promoter loading ~0.078wt% of alkali oxide.</li> <li>➤ <math>\Delta T_{50} = -60</math> °C for Li and Na promotion; <math>\Delta T_{50} = -70</math> °C for K promotion; <math>\Delta T_{50} = -90</math> °C for Cs promotion</li> </ul>	[81]
N <sub>2</sub> O, presence or absence of O <sub>2</sub>	0.5 wt% Rh/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Mg, Sr	T = 250–450 °C [N <sub>2</sub> O] = 0.1%; [N <sub>2</sub> O] = 0.1% + [O <sub>2</sub> ] = 5%. Mg- or Sr-loading: 5 wt%	<ul style="list-style-type: none"> <li>✓ Significant promotion by Sr either in the absence or in the presence of O<sub>2</sub>.</li> <li>✓ Small inhibition and marginal promotion by Mg in absence and presence of O<sub>2</sub>, respectively.</li> <li>➤ <math>\Delta T_{50} = -45</math> and <math>-50</math> °C in the absence and presence of O<sub>2</sub>, respectively, with a Sr-loading = 5wt%.</li> <li>➤ <math>\Delta T_{50} = +10</math> and <math>-15</math> °C in the absence and presence of O<sub>2</sub>, respectively, with a Mg-loading = 5wt%.</li> </ul>	[82]
N <sub>2</sub> O, presence or absence of O <sub>2</sub> , CO, H <sub>2</sub> O	0.5 wt% Pt/Al <sub>2</sub> O <sub>3</sub> -(CeO <sub>2</sub> -La <sub>2</sub> O <sub>3</sub> ) (CCP)	K	T = 200–600 °C [N <sub>2</sub> O] = 0.1%; [N <sub>2</sub> O] = 0.1% + [O <sub>2</sub> ] = 2%; [N <sub>2</sub> O] = 0.1% + [CO] = 1%; [N <sub>2</sub> O] = 0.1% + [CO] = 1% + [O <sub>2</sub> ] = 2%. K-loadings: 0, 0.5, 1.0 and 2.0 wt%	<ul style="list-style-type: none"> <li>✓ K was found to be an effective promoter of the Pt-catalysed N<sub>2</sub>O decomposition under both reducing and oxidizing conditions. H<sub>2</sub>O in the feed caused detrimental but to a great extent reversible (upon removal) influence on deN<sub>2</sub>O efficiency over both K-free and K-promoted catalysts.</li> <li>✓ Promotion was monotonically enhanced with increasing K-loading.</li> <li>➤ <math>\Delta T_{100} = -60</math> °C under N<sub>2</sub>O feed; <math>\Delta T_{100} = -50</math> °C under N<sub>2</sub>O + O<sub>2</sub> feed; <math>\Delta T_{100} = -45</math> °C under N<sub>2</sub>O + CO + O<sub>2</sub> feed</li> </ul>	[83]
N <sub>2</sub> O presence or absence of O <sub>2</sub>	0.5 wt% Ir/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	K	T = 300–600 °C [N <sub>2</sub> O] = 0.1%; [N <sub>2</sub> O] = 0.1% + [O <sub>2</sub> ] = 2%. K-loadings: 0, 0.25, 0.5 and 1.0wt%	<ul style="list-style-type: none"> <li>✓ K induces poisoning effects on the Ir-catalysed N<sub>2</sub>O decomposition at O<sub>2</sub>-deficient conditions.</li> <li>✓ In opposite, K is an effective promoter under O<sub>2</sub> excess conditions; volcano type promotion with an optimal K-loading equal to 0.5 wt% K.</li> <li>➤ <math>\Delta T_{50} = -80</math> °C under [N<sub>2</sub>O] = 0.1% + [O<sub>2</sub>] = 2% and 0.5 wt% K loading.</li> </ul>	[84]

Table 5. Cont.

Reactants	Catalyst and (Promotion method applied)	Promoter	Reaction conditions	Promotion highlights and maximum achievements	Ref.
N <sub>2</sub> O, NO	(0.1 and 0.5 wt%)Pt/(ROX 0.8) (CCP)	K	T = 50–500 °C [NO] = 0.1%; [N <sub>2</sub> O] = 0.05%; and [N <sub>2</sub> O] = 0.05% + [NO] = 0.1% K-loading: 3 and 5 wt%	<ul style="list-style-type: none"> <li>✓ K addition simultaneously promotes the conversions of NO and N<sub>2</sub>O at relatively low temperatures.</li> <li>➤ 100% conversion of both N<sub>2</sub>O and NO over 5 wt% K/0.1 wt% Pt/Al<sub>2</sub>O<sub>3</sub> under [N<sub>2</sub>O] = 0.05% + [NO] = 1% at T = 350 °C.</li> </ul>	[85]
N <sub>2</sub> O + CH <sub>4</sub> , N <sub>2</sub> O + C <sub>3</sub> H <sub>8</sub> , N <sub>2</sub> O + C <sub>3</sub> H <sub>6</sub> , presence or absence of O <sub>2</sub>	2 wt% Pd/γ-Al <sub>2</sub> O <sub>3</sub> , and Pd film on (K)β''Al <sub>2</sub> O <sub>3</sub> solid electrolyte (CCP vs EPOC)	K	T=100–500 °C [N <sub>2</sub> O] = 0.15% [CH <sub>4</sub> ] = 0.6% [C <sub>3</sub> H <sub>8</sub> ] = 0.2% [C <sub>2</sub> H <sub>6</sub> ] = 0.2% ([O <sub>2</sub> ] = 3%) K-loadings: 0, 2.5, 4.5, 7.0, 9.0 wt%	<ul style="list-style-type: none"> <li>✓ Both structural and electronic properties of Pd particles were modified by K addition.</li> <li>✓ K addition strongly promotes N<sub>2</sub>O reduction by both C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub>.</li> <li>✓ K addition slightly inhibits N<sub>2</sub>O reduction by CH<sub>4</sub>.</li> <li>✓ CCP and EPOC induced K-promotion behaviours were found to match well each other.</li> <li>➤ ΔT<sub>50</sub> = +25 °C under [N<sub>2</sub>O] = 0.15% + [CH<sub>4</sub>] = 0.6% and 9 wt% K loadings</li> <li>➤ ΔT<sub>50</sub> = −100 °C under [N<sub>2</sub>O] = 0.15% + [C<sub>3</sub>H<sub>8</sub>] = 0.2% and 9 wt% K loadings</li> <li>➤ ΔT<sub>50</sub> = −135 °C under [N<sub>2</sub>O] = 0.15% + [C<sub>2</sub>H<sub>6</sub>] = 0.2% and 7–9 wt% K-loadings.</li> </ul>	[25] [86]
N <sub>2</sub> O, C <sub>3</sub> H <sub>6</sub> , O <sub>2</sub>	Pt film on (K)β''Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	K	T = 180–580 °C [N <sub>2</sub> O] = 0.1%, [C <sub>2</sub> H <sub>6</sub> ] = 0.2%, [O <sub>2</sub> ] = 0.2–1.0% θ <sub>K</sub> = 0–90%	<ul style="list-style-type: none"> <li>✓ Strong K-induced promotion was observed. This was progressively attenuated and finally reversed to poisoning upon increasing O<sub>2</sub> in the feed stream. K-promotion prevented deN<sub>2</sub>O activity of Pt from the poisoning effect of H<sub>2</sub>O.</li> <li>➤ ρ<sub>N<sub>2</sub>O</sub> = 38.5, ρ<sub>C<sub>3</sub>H<sub>6</sub></sub> = 1.2 under [N<sub>2</sub>O] = 0.1% + [C<sub>2</sub>H<sub>6</sub>] = 0.2% + [O<sub>2</sub>] = 0.2%, T = 450 °C, θ<sub>K</sub> ~40% (V<sub>WR</sub> = −1 V)</li> </ul>	[87] [88]

### 3.2. Electropositive Promotion of PGMs Operated Under Simulated Practical Conditions

#### 3.2.1. Simulated TWC Conditions

Given that alkalis and alkaline earths were found to strongly promote reactions related with the three-way catalytic (TWC) chemistry, testing of these new catalyst formulations at conditions that simulate automotive exhaust conditions was a reasonable consequence. To this end, Konsolakis et al. [89] studied the promotional effects of Na on Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts operated under simulated exhaust conditions at the stoichiometric point (SP), that is, at the value equal to 1 of the stoichiometric number (S), calculated as:

$$S = (2[\text{O}_2] + [\text{NO}]) / ([\text{CO}] + 9[\text{C}_3\text{H}_6]) \quad (8)$$

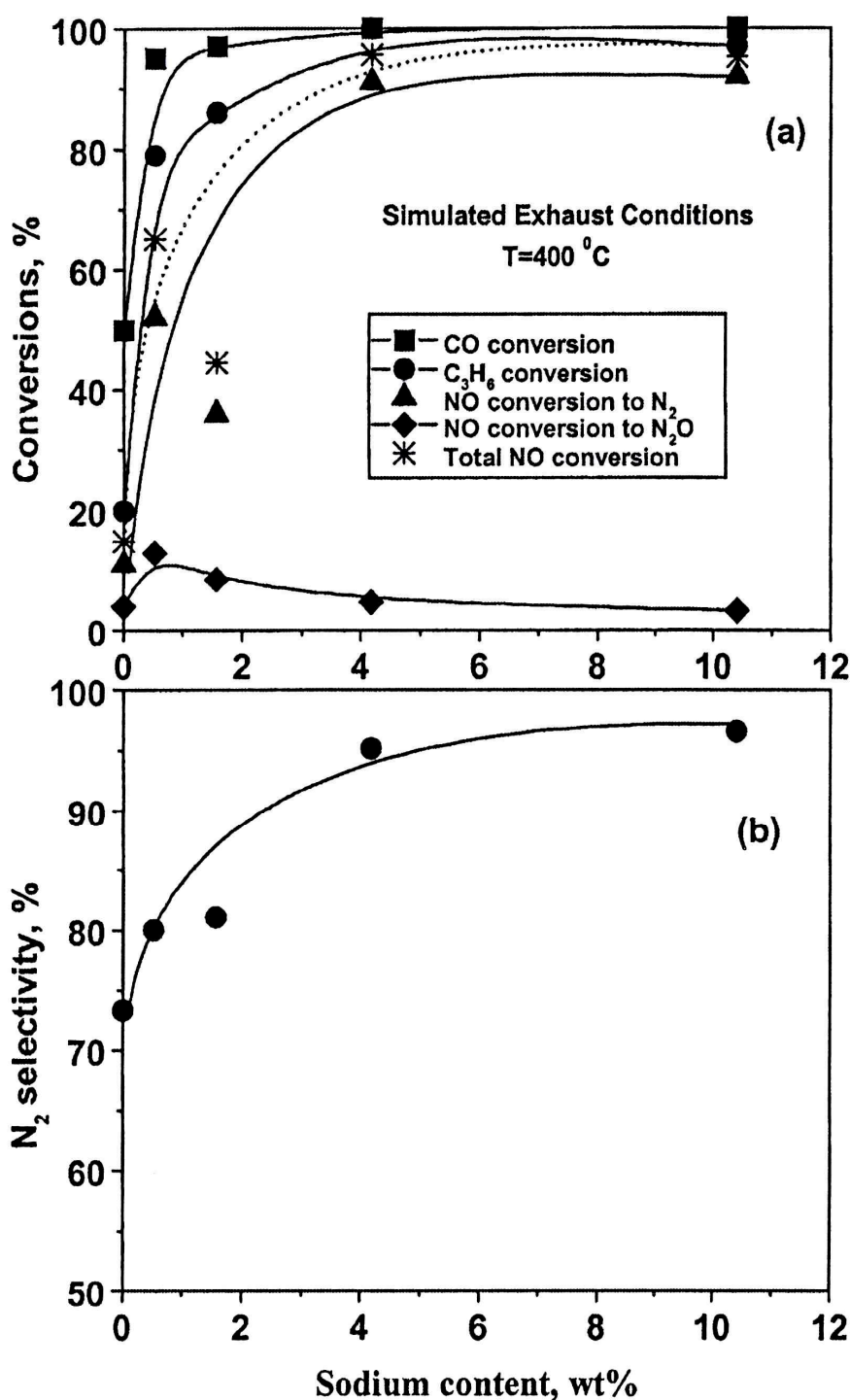
using a feed mixture consisting (v/v) 1000 ppm NO + 1067 ppm C<sub>3</sub>H<sub>6</sub> + 7000 ppm CO + 7800 ppm O<sub>2</sub>.

A series of Na-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were tested under these conditions at temperatures from 200–500 °C typical of TWCs. Typical results of the promoter effect on the overall NO, CO and C<sub>3</sub>H<sub>6</sub> conversions and selectivity obtained at 400 °C, are shown in Figure 15. The conversions of all three pollutants, NO, CO and C<sub>3</sub>H<sub>6</sub>, reach 100% at sodium contents > 4.2wt%. In addition, Na promoter causes a significant decrease in the light off temperature of ~100 °C, together with significant improvements (~75%) in N<sub>2</sub>-selectivity (Table 6). The promotional effect was attributed to the modified relative adsorption strengths of reactants and reaction intermediates, as explained above in the previous sections [89].

In a similar motive, Macleod et al. [90,91] studied the Na promotion of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts operated under simulated TWC conditions over a range of stoichiometries from fuel rich to fuel lean conditions (0.90 < S < 1.1). They observed significantly different responses of Na addition in the two cases (Table 6). Na addition to Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> significantly improves its overall performance: although the recorded promotional effects were not as high as those observed in Reference [89] for Na-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, results were again very spectacular.

A 7wt% Na loading (optimal promoter loading for the conditions used) offered a ~50 °C lower light off temperature than the unpromoted Pd when tested under stoichiometric feed conditions (1000 ppm NO + 1067 ppm C<sub>3</sub>H<sub>6</sub> + 7000 ppm CO + 7800 ppm O<sub>2</sub>). Beneficial effects of sodium addition were also recorded under both fuel rich and fuel lean conditions (Table 6). In the former case, Na was found to prevent catalyst poisoning by carbon deposition therefore maintaining high NO conversions, while in the latter case Na reduced the formation of N<sub>2</sub>O therefore leading to enhanced selectivities toward N<sub>2</sub>. However, the authors found that Na addition to Rh has a detrimental effect causing severe activity poisoning and N<sub>2</sub>-selectivity reduction over the greater part of the temperature interval of 200–400 °C investigated [92]. It was attributed to the enhanced oxygen adsorption on the Rh active sites at the expense of the hydrocarbon, whilst in the case of Pd the beneficial effects were considered as a consequence of Na-promoted NO dissociation, together with inhibition of self-poisoning due to excessive propene adsorption [91]. It is worth noting that NO dissociative chemisorption takes place spontaneously on Rh but not on Pd.

Tanaka et al. [92] have also reported the beneficial effects of the addition of a small amount of Na<sub>2</sub>O to (1.67wt%Pt)(12.3wt%MoO<sub>3</sub>)/SiO<sub>2</sub> catalysts investigated under simulated exhaust from automobile engine and three-way behaviour around the stoichiometric point (SP). They found that the active window of SP for the Na-promoted PtMoNa/SiO<sub>2</sub> catalyst is wider than that of the Na-free counterpart, that is, PtMo/SiO<sub>2</sub> and Pt/SiO<sub>2</sub> catalysts (Table 6). The observed improvements were attributed to the wider redox ratio window and to the depressed (by Mo and Na) oxidation of Pt, even under oxygen excess.



**Figure 15.** Testing Na-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts at simulated exhaust conditions of conventional stoichiometric gasoline engines (T=400 °C, 1000 ppm NO, 1067 ppm CO and 7800 ppm O<sub>2</sub>; F<sub>t</sub> = 80 cm<sup>3</sup>STP/min; m<sub>cat</sub> = 8 mg). Effect of Na loading on reactants conversions (a) and selectivity towards N<sub>2</sub> (b). (Reprinted with permission from Ref. [89]; Copyright 2000, Elsevier).

Shinjon et al. [93] have investigated the effect of an alkaline earth (Ba) modifier on the catalytic activity of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts under simulated automotive exhaust conditions at the stoichiometric point (1% CO, 0.3% H<sub>2</sub>, 0.1% C<sub>3</sub>H<sub>6</sub>, 0.1% NO, 0.75% O<sub>2</sub>, 3% H<sub>2</sub>O, 12% CO<sub>2</sub>). They found that the TWC-performance of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts was improved by Ba, offering ~30 °C lower light off temperatures compared to those for the un-promoted catalysts (Table 6). However, the overall

performance of Rh catalysts was deteriorated with Ba addition. It was attributed to the fact that Ba addition to Pt catalysts suppressed the strong hydrocarbon chemisorption, enhancing simultaneously the oxygen adsorption. On the other hand, Ba addition to Rh catalysts results in strong adsorption of oxygen species, suppressing hydrocarbon chemisorption and thus the reaction between them.

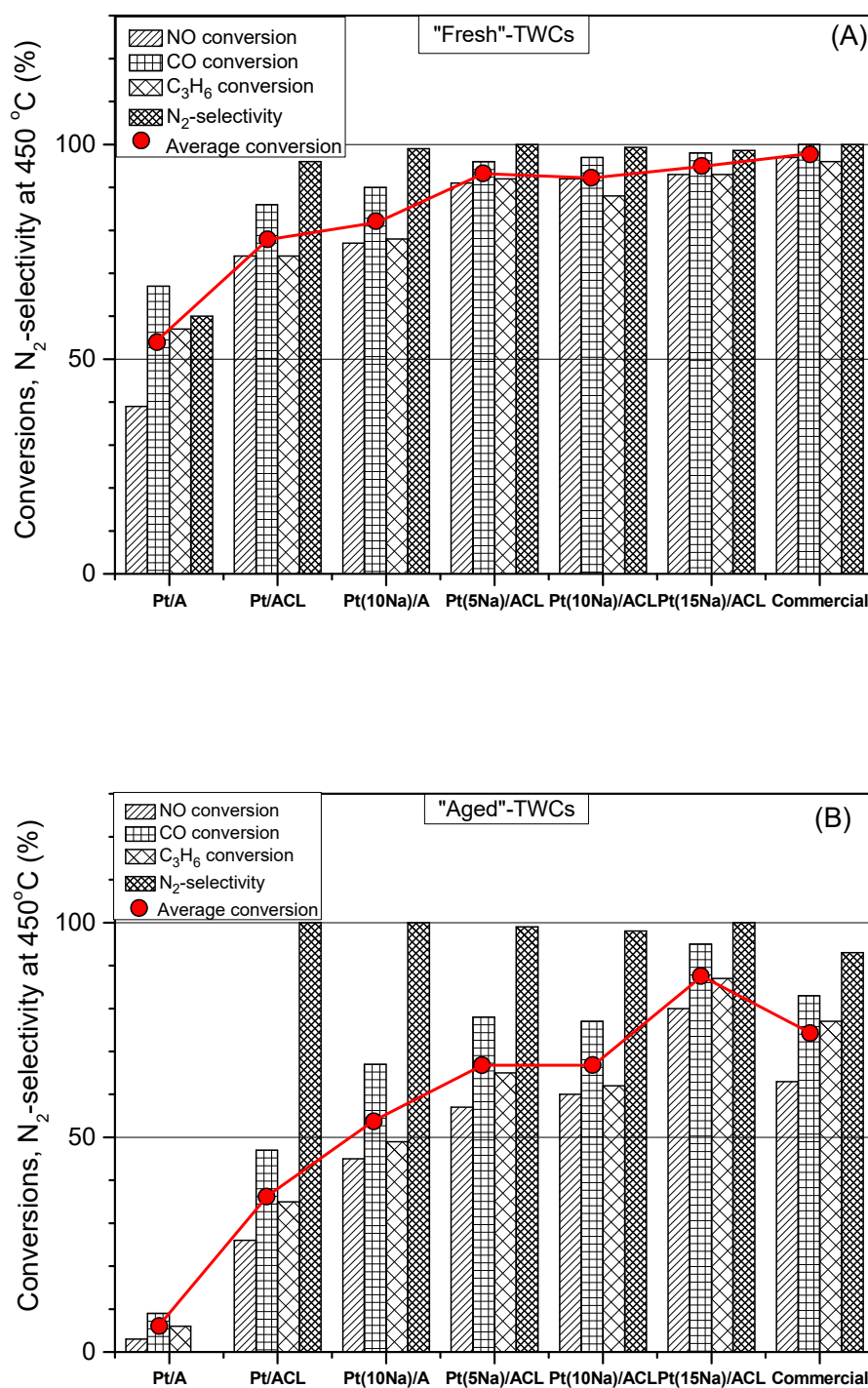
Kobayashi et al. [94] investigated the influence of Ba and Sr alkaline earth metals on a commercial Pd-only TWC catalyst (Pd/Al<sub>2</sub>O<sub>3</sub>-based TWC catalyst of N.E. ChemCat Corp.). Improved three-way catalytic performance was obtained regarding CO and NO<sub>x</sub> conversions (Table 6). The enhanced basicity and the electron-donation ability of these basic elements were considered to play significant role in the improvement of TWC performance. A higher electron density around Pd<sup>(III)</sup> was revealed by XPS measurements in the Ba-promoted Pd/Al<sub>2</sub>O<sub>3</sub> catalyst in comparison with the Ba-free counterpart. The stabilization of PdO that may suppress palladium species sintering and the electron enrichment palladium particles that endows Pd to behave like Rh were concluded as the main promoting factors in this study [94].

A NO-free gas mixture of CO, C<sub>3</sub>H<sub>6</sub>, H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O, simulating two-stroke motorcycle emissions (Table 6), was considered by Lee and Chen [30] for the investigation of the impact of Na<sub>2</sub>O and K<sub>2</sub>O addition on a 0.4wt% Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst operated at 150–450 °C under stoichiometric and oxygen-deficient conditions (by varying the oxygen to reductants stoichiometric number; S = 1, 0.31 and 0.17). Significant enhancements on the CO and C<sub>3</sub>H<sub>6</sub> conversions were achieved by the addition of both alkalis under operation at the stoichiometric point (S = SP = 1); superior promotion was the one induced by potassium. Under O<sub>2</sub>-deficient conditions alkalis addition enhanced CO conversion but not that of propene, which was reduced. The presence of water in the gas mixture was found to have a strong positive impact on catalyst performance, in particular on K-promoted catalyst and for CO conversion (Table 6).

Yentekakis and co-workers [95,96] developed monolithic type catalytic converters with a washcoat containing only one precious metal (Pt-only TWC), which was optimally promoted by Na. Catalytic performance tests of this novel TWC under simulated exhaust conditions in a wide temperature range (150–500 °C) exhibited similar performance and even better N<sub>2</sub> selectivity (~100% in the whole temperature range) compared to that of a commercial bimetallic (Pt/Rh)-TWC catalyst (Figure 16A, Table 6); notably, the aforementioned TWC had a 4.5-fold lower noble metal loading in comparison to the commercial one. These novel material formulation and design for TWCs is subjected to much lower production cost (use of only one noble metal at much lower loading, without the necessity of scarce Rh in their constitution) and cost-effective recycling.

Most recent tests of these novel TWCs at more severe temperature conditions (>800 °C) have also shown a significant resistance to deactivation (Figure 16B) [97,98], implying that the promoter phase (Na) does not practically escape from the catalyst composite even at very high temperatures, due to its stabilization via the formation of new β' and β'' sodium-alumina phases as verified by TEM and XRD studies [97,98]. These phases, in direct interaction with the active phase (Pt), then act as a spontaneous (thermal diffusion driven) Na promoter source during TWC operation causing permanent promotion [97,98].

Overviewing the literature findings presented in this section and in Table 6, one can readily conclude that electropositive promotion of PGM-catalysts under simulated automotive exhaust conditions follows, in general terms, the promotional characteristics corresponding to the simple (model) reactions of the complex reactions scheme taking place into the converter. However, other possible synergistic or competitive interactions between the reactants and reactions' intermediates on a densely populated surface with all these competitive species can be at work affecting the overall performance.



**Figure 16.** Three-way catalytic performance at 450 °C of “fresh” (A) and “aged” (B) TWC samples at simulated stoichiometric gasoline engines exhaust conditions (0.1% NO + 0.7% CO + 0.1067% C<sub>3</sub>H<sub>6</sub> + 0.78% O<sub>2</sub>, balanced with He at 1 bar; F<sub>t</sub> = 3200 cm<sup>3</sup> (STP)/min). (Reproduced with permission from Ref. [98]; Copyright 2011, Elsevier).



**Table 6.** Electropositive promotion of PGM-catalysts operated under simulated automotive exhaust conditions.

Reactants	Catalyst and (promotion method applied)	promoter	Conditions	Promotion highlights and achievements	Ref.
NO, C <sub>3</sub> H <sub>6</sub> , CO, O <sub>2</sub>	0.5wt%Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Na	T = 200–500 °C (at simulated TWC conditions) [NO] = 1000 ppm, [CO] = 7000 ppm, [C <sub>3</sub> H <sub>6</sub> ] = 1067 ppm, [O <sub>2</sub> ] = 7800 ppm; (at S = SP = 1) w/F = $6 \times 10^{-3}$ g·s/cm <sup>3</sup> Na loadings: 0, 0.52, 1.57, 4.18 and 10.4 wt% Na	<ul style="list-style-type: none"> <li>✓ Na promotes simultaneously the conversions of all three pollutants, CO, C<sub>3</sub>H<sub>6</sub> and CO and enhances the N<sub>2</sub>-selectivity at all promoter loadings used.</li> <li>➤ CO, C<sub>3</sub>H<sub>6</sub> and NO conversions reached 100%, 100% and &gt; 91% at T = 400 °C and for Na-loadings &gt;4.18wt%; the corresponding values on the unpromoted Pt/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub> were only 50, 20 and 11%.</li> <li>➤ <math>\Delta T_{50}(\text{CO}) = -79^\circ\text{C}</math>, <math>\Delta T_{50}(\text{C}_3\text{H}_6) = -77^\circ\text{C}</math>, <math>\Delta T_{50}(\text{NO}) = -93^\circ\text{C}</math> and <math>\Delta S_{\text{N}_2} = +81\%</math>.</li> </ul>	[89]
NO, C <sub>3</sub> H <sub>6</sub> , CO, O <sub>2</sub>	0.5 wt% Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> and 0.5 wt% Rh/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Na	T = 100–340 °C (at simulated TWC conditions) [NO] = 1000 ppm, [CO] = 7000 ppm, [C <sub>3</sub> H <sub>6</sub> ] = 1067 ppm, $6970 \leq [\text{O}_2] \leq 8630$ ppm (around SP: $0.9 \leq S \leq 1.1$ ) w/F = $15 \times 10^{-3}$ g·s/cm <sup>3</sup> Na loadings for Pd/Al <sub>2</sub> O <sub>3</sub> : 0, 1.8, 3.5, 7.0, 12.0 wt% Na loadings for Rh/Al <sub>2</sub> O <sub>3</sub> : 0, 3.0 and 7.3 wt%.	<ul style="list-style-type: none"> <li>✓ The studies involve the Na impact on Pd and Rh operated at TWC conditions over a range of the stoichiometric number (S) values from fuel-rich to lean.</li> <li>✓ Na promotion was beneficial under both oxidizing and reducing conditions for Pd catalysts. Optimal loadings &gt;3.5wt% Na:</li> <li>➤ <math>\Delta T_{50}(\text{CO}) = -48^\circ\text{C}</math>, <math>\Delta T_{50}(\text{C}_3\text{H}_6) = -35^\circ\text{C}</math>, <math>\Delta T_{50}(\text{NO}) = -38^\circ\text{C}</math> (at SP = 1) and <math>\Delta S_{\text{N}_2} = +35\%</math> (at S &gt; 1.04: oxidizing conditions).</li> <li>✓ In opposite to Pd, Na addition on Rh was detrimental.</li> </ul>	[90] [91]
NO, C <sub>3</sub> H <sub>6</sub> , CO, O <sub>2</sub> , H <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> O	1.67 wt% Pt/12.3wt% MoO <sub>3</sub> -SiO <sub>2</sub> (CCP)	Na <sub>2</sub> O	T = 100–600 °C w/F = $9.91 \times 10^{-3}$ g·s/cm <sup>3</sup> Na <sub>2</sub> O loadings: 0.05, 0.1, 1.0 wt%. Simulated oxidizing feed, S = 9.91:4.3% O <sub>2</sub> , 0.12% NO, 800ppm C <sub>3</sub> H <sub>6</sub> , 0.12% CO, 400ppm H <sub>2</sub> , 12.3% CO <sub>2</sub> , 3% H <sub>2</sub> O. Simulated exhaust feed, S-scan: 0.40–1.21%O <sub>2</sub> , 0.12% NO, 490–62 ppm C <sub>3</sub> H <sub>6</sub> , 0.45–1.50% CO, 0.15–0.50% H <sub>2</sub> , 10.0% CO <sub>2</sub> , 3.0% H <sub>2</sub> O.	<ul style="list-style-type: none"> <li>✓ Under nearly stoichiometric conditions, a wider redox ratio window of NO<sub>x</sub> conversion was obtained with PtMoNa/SiO<sub>2</sub> catalyst compared to Pt/SiO<sub>2</sub>.</li> <li>✓ Under oxidizing conditions PtMoNa/SiO<sub>2</sub> catalyst resulted to a shift of all CO, C<sub>3</sub>H<sub>6</sub> and NO<sub>x</sub> conversion profiles to higher temperatures. However, a wider temperature window with higher NO<sub>x</sub> conversion was obtained.</li> </ul>	[92]



Table 6. Cont.

Reactants	Catalyst and (promotion method applied)	promoter	Conditions	Promotion highlights and achievements	Ref.
NO, C <sub>3</sub> H <sub>6</sub> , CO, O <sub>2</sub> , H <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> O	1.67 wt% Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> 0.9 wt% Rh/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Ba	T = 100–400 °C (at simulated TWC conditions) [NO] = 1000 ppm, [C <sub>3</sub> H <sub>6</sub> ] = 334 ppm, [CO] = 1%, [H <sub>2</sub> ] = 0.3%, [CO <sub>2</sub> ] = 12%, [H <sub>2</sub> O] = 3%, [O <sub>2</sub> ] = 0.75% GHSV = 200000 h <sup>−1</sup> Ba-loading: 5.8, 11.5, 23 and 46 wt% Ba	<ul style="list-style-type: none"> <li>✓ Ba addition significantly promotes Pt/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub> activity under simulated exhaust conditions. The opposite is true for Rh/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub>.</li> <li>➤ <math>\Delta T_{50(\text{NO}_x)} = -30</math> °C over 46wt% Ba-promoted Pt/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub></li> <li>➤ <math>\Delta T_{50(\text{NO}_x)} = +15</math> °C over 46wt% Ba-promoted Rh/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub></li> </ul>	[93]
Exhaust gas from an automotive engine	5wt% Pd-commercial TWC catalyst supplied by N.E. ChemCat Corp. (CCP)	Ba, Sr, La	T=300–600 °C Real stoichiometric automotive engine exhaust gas GHSV = 68000 h <sup>−1</sup> Ba, Sr od La-loading: 5wt%	<ul style="list-style-type: none"> <li>✓ The TWC performance of the Pd-based commercial catalyst was significantly improved by the addition of Ba, Sr or La.</li> <li>✓ The performance improvements followed the order: Ba &gt; Sr &gt; La.</li> <li>✓ Alkaline earths promotion was related with the stabilization of PdO phase and its electron enrichment, which endows Pd to behave like Rh.</li> </ul>	[94]
C <sub>3</sub> H <sub>6</sub> , CO, H <sub>2</sub> , O <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> O (NO-free)	0.4 wt% Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Na, K	T = 150–450 °C (simulated two-stroke motorcycle emissions). [CO] = 1–4.14%, [C <sub>3</sub> H <sub>6</sub> ] = 0.08–0.7%, [O <sub>2</sub> ] = 0.96–0.9%, [H <sub>2</sub> ] = 0.2%, [CO <sub>2</sub> ] = 10%, [H <sub>2</sub> O] = 0 or 10%. Stoichiometric numbers studied S = 1, 0.31, 0.17 Na-loading: 4.5 wt%; K-loading: 7.6 wt%	<ul style="list-style-type: none"> <li>✓ Significant promotion by both Na<sub>2</sub>O and K<sub>2</sub>O; superior that of K<sub>2</sub>O.</li> <li>✓ Under oxygen-deficient conditions (S = 0.17 and 0.31), H<sub>2</sub>O addition enhances both CO and C<sub>3</sub>H<sub>6</sub> conversions (in particular X<sub>CO</sub> and over K-promoted catalyst)</li> <li>➤ <math>\Delta T_{50(\text{CO})} = -90</math> °C <math>\Delta T_{50(\text{C}_3\text{H}_6)} = -110</math> °C at S = SP = 1 and absence of H<sub>2</sub>O.</li> <li>➤ <math>\Delta X_{\text{CO}} = 51</math> and 48 at S = 0.31, without and with H<sub>2</sub>O, respectively.</li> <li>➤ <math>\Delta X_{\text{CO}} = 22</math> and 48 at S = 0.17, without and with H<sub>2</sub>O, respectively.</li> </ul>	[30]

Table 6. Cont.

Reactants	Catalyst and (promotion method applied)	promoter	Conditions	Promotion highlights and achievements	Ref.
NO, C <sub>3</sub> H <sub>6</sub> , CO, O <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> O	0.1 wt% Pt/( $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> -La <sub>2</sub> O <sub>3</sub> -cordierite monolith) versus a Commercial 0.37Pt/0.08Rh-TWC(CCP)	Na	T = 150–500 °C (simulated TWC conditions) [NO] = 0.1%, [CO] = 0.7%, [C <sub>3</sub> H <sub>6</sub> ] = 0.1067%, [O <sub>2</sub> ] = 0.78%, [H <sub>2</sub> O] = 10%, [CO <sub>2</sub> ] = 10% GHSV = 50500 h <sup>-1</sup> Na-loading: 1 and 2 wt% Na (i.e., 5 and 10 wt% in the washcoat)	<ul style="list-style-type: none"> <li>✓ The Na-promoted monometallic (Pt-only) TWC, with 4.5-fold less PGMs loading compared to bimetallic commercial one, exhibits similar performance with the commercial and better N<sub>2</sub> selectivity (~100% in the whole temperature range 150–500 °C).</li> <li>✓ Marginal impact of H<sub>2</sub>O and CO<sub>2</sub> on the performance of Na/Pt-TWC.</li> <li>✓ A synergy between surface promoter (Na) and structural promoters (CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>) was resulted, leading to this attractive promotion.</li> <li>✓ Significant resistant to deactivation, even upon severe aging (&gt;800 °C).</li> <li>✓ Na promotion remains at work even after aging due to the formation of <math>\beta'</math>, <math>\beta''</math> sodium alumina phases, which act as permanent spontaneous sources of Na promoter species during TWC operation.</li> </ul>	[95] [96] [97] [98]

### 3.2.2. Oxygen Excess Conditions (Simulated Lean-Burn and Diesel Exhausts Gases)

Some other EPOC studies regarding the electrochemical activation of Pt-based electrochemical catalysts for NO<sub>x</sub> reduction by propene under oxygen excess were performed by the groups of Vernoux and de-Lucas Consuegra. In this sense, Vernoux et al. observed a significant promotional effect of Na promoters electrochemically supplied from a NASICON solid electrolyte support [99]. The study was carried out under lean-burn conditions (oxygen excess, typical of Diesel engines). In such a system, electrochemical promotion is shown to strongly enhance both the catalytic activity and the selectivity to N<sub>2</sub> (from 41% to 61%) using very low overpotentials (−100 mV) at 300 °C (Table 7).

In the same line, the group of de Lucas Consuegra performed several EPOC studies by using Na and K promoters by means of (Na<sup>+</sup>)β'Al<sub>2</sub>O<sub>3</sub> and (K<sup>+</sup>)βAl<sub>2</sub>O<sub>3</sub> solid electrolytes, respectively. First, they studied the effect of reaction temperature and O<sub>2</sub> concentration in the feed stream on Pt catalysts promoted with Na species. Under lean burn conditions, at low reaction temperatures (220 °C), rate enhancement ratios up to 1.4 were observed for the NO reduction rate (Table 7) [100,101]. Nevertheless, as the reaction temperature increased, the promotional effect decreased, even resulting in a transition to a regime where the alkali metal induced poisoning. This progressive suppression of the promotional effect was due to an increase of the oxygen coverage on the Pt surface with the temperature, which led to a C<sub>3</sub>H<sub>6</sub> adsorption inhibition. However, at all explored reaction temperatures, the presence of sodium ions induced a large increase of the N<sub>2</sub> selectivity (up to 90%), minimizing the N<sub>2</sub>O formation.

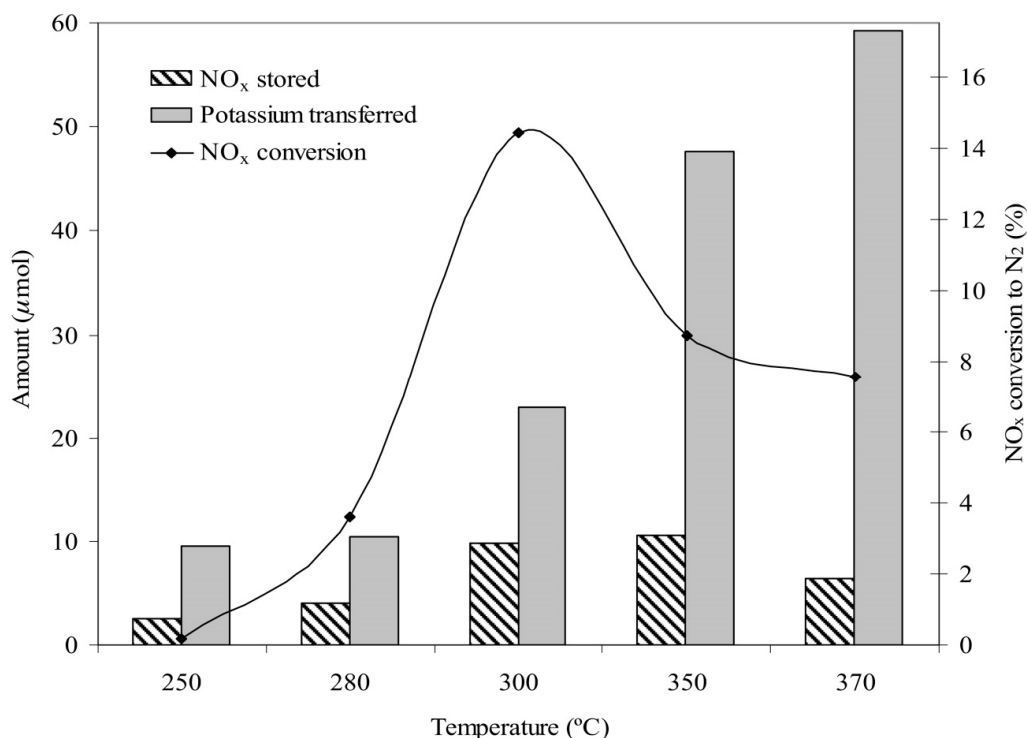
Regarding the effect of the O<sub>2</sub> concentration, a study was performed at low temperatures (240 °C) under O<sub>2</sub> concentrations ranging from 0.5% to 5%. The promotional effect of sodium on the overall catalytic activity for NO removal was progressively lowered with increasing oxygen concentrations, as a result of a strong inhibition of propene adsorption and a relative increase of the oxygen coverage. In all cases, the presence of sodium ions induced an increase in the nitrogen selectivity by promoting the NO adsorption and subsequent dissociation.

In a new investigation, de Lucas Consuegra et al. [102] studied for the first time the promotional effect of K (EPOC) under the presence of steam in the feed stream under lean burn conditions, as a new approach to the development of efficient catalysts under real working conditions of combustion engines. In this study, they demonstrated that the presence of K promoters could be practically used to decrease the inhibitory effect of water for the reduction of NO by propene. In addition, as previously demonstrated in other studies, they verified that the K species form stable nitrate species on the Pt surface. This discovery led to a new series of studies performed by the same research team, leading with the NO<sub>x</sub>-storage and Reduction technology (NSR) by means of alkali-based Pt electrochemical catalysts.

Briefly, the NSR process was developed in the early 1990s by Toyota. It is based on the ability of alkali and alkali earth elements to store NO<sub>x</sub> in form of nitrites/nitrates under lean burn conditions (oxygen excess). Then, by the injection of extra fuel, the stored NO<sub>x</sub> are released and reduced with hydrocarbons, CO or H<sub>2</sub>, to produce N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O. The alkali promoters function in two ways in these “smart” materials: first, they act as electronic promoters to enhance the NO oxidation to NO<sub>2</sub> (which has been identified as the rate determining step of the overall process) and to store the NO<sub>2</sub> produced in form of nitrites/nitrates (as previously demonstrated).

In these studies, de-Lucas Consuegra et al. demonstrated, for the very first time, the possibility to perform the NSR process via EPOC, by the use of Pt catalysts supported on K<sup>+</sup>-βAl<sub>2</sub>O<sub>3</sub> solid electrolytes (to supply the K promoter species) [103,104]. The studies were performed under lean burn conditions and even under the presence of steam. The 2 main conclusions from these studies were:

- Potassium ions electrochemically transferred to the Pt catalyst play a double role in the NSR process, as a promoter for the NO oxidation reaction and as storage sites through the formation of potassium nitrates.
- The maximum yield of Pt/(K)βAl<sub>2</sub>O<sub>3</sub> to effectively reduce NO<sub>x</sub> to N<sub>2</sub> was obtained at T = 300 °C (Figure 17). This temperature is suitable for both, gasoline and diesel engines working under lean burn conditions.



**Figure 17.** Influence of the reaction temperature on the amount of NO<sub>x</sub> stored, potassium transferred and on the NO<sub>x</sub> conversion to N<sub>2</sub> during NO<sub>x</sub> storage/reduction experiments. Lean phase (NO/C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub>:1000 ppm/1000 ppm/5% O<sub>2</sub>), 6 min of duration, V<sub>cell</sub> = −1.5 V. Rich phase (NO/C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub>:1000 ppm/1000 ppm/0.5% O<sub>2</sub>), 5 min of duration, V<sub>cell</sub> = 3V. Data was acquired in a Pt/(K)βAl<sub>2</sub>O<sub>3</sub>/Au galvanic cell (Reprinted with permission from Ref. [103]; Copyright 2011, Elsevier).

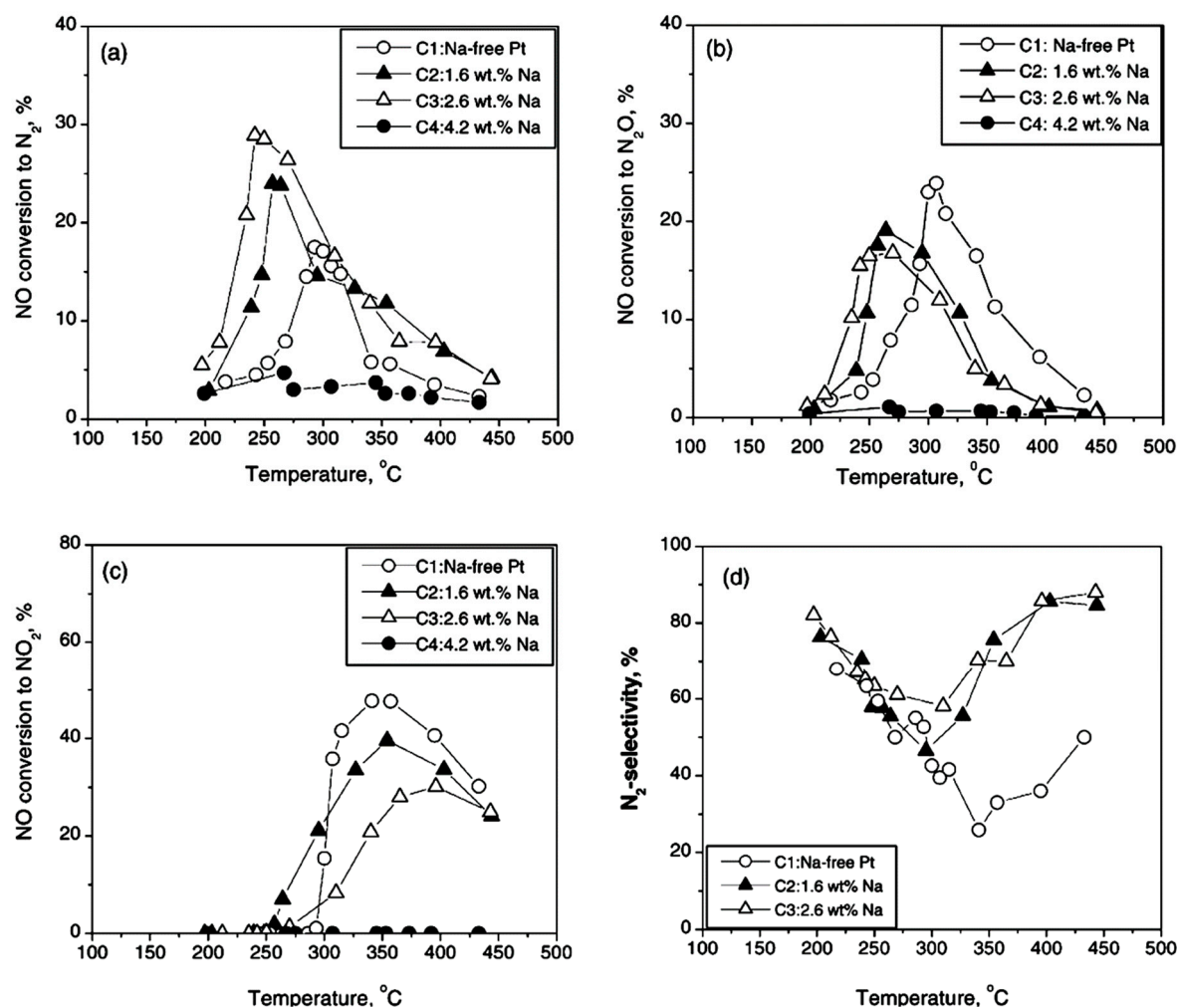
In respect to conventional highly dispersed catalysts and using CCP, early studies by Burch and Watling that involved the influence of a number of promoters, including alkalis (namely K and Cs) and alkaline earths (namely La, Mg, Ba), on the Pt-catalysed propene-SCR of NO<sub>x</sub> under lean-burn conditions have showed that addition of one of the following: 2.42wt% K<sub>2</sub>O, 7.25wt% Cs<sub>2</sub>O, 7.93wt% BaO, 2.07wt% MgO and 8.35wt% La<sub>2</sub>O<sub>3</sub> in 1wt%Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst results in suppression of the catalytic activity of Pt (NO<sub>x</sub> conversion efficiency) and to marginal effects on N<sub>2</sub>/N<sub>2</sub>O selectivity (Table 7) [105]. However, later studies of the de-Nox activity of supported Pt catalysts under lean burn conditions have shown very pronounced promotional effects by alkalis or alkaline earths: Vernoux et al. [106] and Yentekakis et al. [47], systematically investigated the resulted promotional effects of Na addition on supported Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalysts (CCP) during NO + propene + excess O<sub>2</sub> as a function of the Na-loading, have shown significant beneficial effects of the alkali on both de-Nox activity and N<sub>2</sub>/N<sub>2</sub>O selectivity at low and intermediate Na-loadings (Table 7). In both studies, the effects (promoting or poisoning, depending on promoter loading) were understandable in terms of the influence of the alkali promoter on the relative adsorption strengths of reactants and intermediates on a highly populated surface with electrophilic and electrophonic adsorbates. In particular, Yentekakis et al. [47] demonstrated that Na acts beneficially to de-Nox process in a narrow window of Na loading (ca. 0–2.6wt% Na), while overpromotion to the optimal value of ~2.6wt% Na causes significant inhibition of the catalyst performance. The recorded promotional effects can be summarized as follows: Na widened the temperature window of the C<sub>3</sub>H<sub>6</sub> + NO + O<sub>2</sub> reaction towards lower temperatures by ~50 °C, accompanied by an enhancement in N<sub>2</sub>-selectivity by ~40 additional percentage points; the promotion is optimized at a sodium loading of 2.6wt% Na on the 0.5wt%Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst (Figure 18). Obviously, the promoter loadings chosen by Burch and Watling were out from this optimal window, explaining the poisoning effects observed by the authors [105].

**Table 7.** Electropositive promotion of PGMs-catalysed lean-NO<sub>x</sub> reduction by C<sub>3</sub>H<sub>6</sub> (the so-called simulated lean-burn or diesel exhaust conditions).

reactants	Catalyst and (promotion method applied)	Promoter	Conditions	Promotion highlights and achievements	Ref.
NO, C <sub>3</sub> H <sub>6</sub> , O <sub>2</sub> excess	Pt film on NASICON solid electrolyte (EPOC)	Na	T = 200–400 °C [NO] = 0.2%, [C <sub>3</sub> H <sub>6</sub> ] = 0.2%, [O <sub>2</sub> ] = 5% Na coverage: non estimated (catalyst potential V <sub>WR</sub> is given)	<ul style="list-style-type: none"> <li>✓ Na promotion induced strong enhancements on both activity and N<sub>2</sub>-selectivity under lean-burn conditions at quite low T.</li> <li>➤ <math>\rho_{N_2} \sim \rho_{CO_2} \sim 1.7</math>, <math>\rho_{N_2O} \sim 1.1</math>, <math>\Delta S_{N_2} = +20\%</math> (41%→61%) at T = 295 °C, <math>\Delta V_{WR} = -200</math> mV.</li> </ul>	[99]
NO, C <sub>3</sub> H <sub>6</sub> , O <sub>2</sub> excess	Pt impregnated on (Na)β''Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	Na	T = 220–300 °C [NO] = 0.2%, [C <sub>3</sub> H <sub>6</sub> ] = 0.2%, [O <sub>2</sub> ] = 0.5, 1 and 5%. $\theta_{Na} = 0-8\%$	<ul style="list-style-type: none"> <li>✓ Na significantly promotes the low temperature (T = 220 °C) lean-burn activity and N<sub>2</sub>-selectivity of Pt impregnated catalyst on Na<sup>+</sup> conducting solid electrolyte. At higher T (&gt;240 °C) Na supply to the catalyst can lead even to poisoning of the activity but not of the selectivity which is increased (reaching ~90%).</li> <li>➤ Promotion : <math>\rho_{N_2} \sim \rho_{CO_2} \sim 1.4</math>, <math>\Delta S_{N_2} = +20\%</math> (60→75%) at T = 220 °C, [O<sub>2</sub>] = 5%, <math>\theta_{Na} = 7-8\%</math></li> <li>➤ Poisoning: <math>\rho_{N_2} \sim 0.3</math>, <math>\rho_{CO_2} \sim 0.02</math>, <math>\Delta S_{N_2} = +50\%</math> (40→90%) at T = 300 °C and <math>\theta_{Na} = 7-8\%</math></li> </ul>	[100] [101]
NO, C <sub>3</sub> H <sub>6</sub> , O <sub>2</sub> excess, H <sub>2</sub> O	Pt impregnated on (K)βAl <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	K	T = 180–400 °C [NO] = 0.2%, [C <sub>3</sub> H <sub>6</sub> ] = 0.2%, [O <sub>2</sub> ] = 5%, [H <sub>2</sub> O] = 5% $\theta_K$ : varying, non-estimated	<ul style="list-style-type: none"> <li>✓ K promotion depresses the inhibitory effect of H<sub>2</sub>O on the lean NO<sub>x</sub> reduction by C<sub>3</sub>H<sub>6</sub>.</li> <li>✓ K promoter species form stable nitrates on Pt surface, thus can operate as a NO<sub>x</sub>-Storage Reduction (NSR) species.</li> </ul>	[102]
NO, C <sub>3</sub> H <sub>6</sub> , O <sub>2</sub> excess	Pt film on (K)βAl <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	K	T = 250–370 °C [NO] = 0.1%, [C <sub>3</sub> H <sub>6</sub> ] = 0.1%, [O <sub>2</sub> ] = 5% $\theta_K$ : varying, non-estimated	<ul style="list-style-type: none"> <li>✓ The electrochemically assisted NO<sub>x</sub>-Storage Reduction (NSR) process by a Pt/(K)βAl<sub>2</sub>O<sub>3</sub>/Pt electrochemical cell is demonstrated.</li> <li>✓ Electrochemically transferred K play a double role: promoter of the lean NO<sub>x</sub> reduction and NO<sub>x</sub>-storage/release species.</li> <li>➤ Maximum deNO<sub>x</sub> to N<sub>2</sub> yield was obtained at T = 300 °C.</li> </ul>	[103] [104]

Table 7. Cont.

reactants	Catalyst and (promotion method applied)	Promoter	Conditions	Promotion highlights and achievements	Ref.
NO, C <sub>3</sub> H <sub>6</sub> , O <sub>2</sub> excess	1 wt% Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	K, Cs, La, Mg, Ba	T = 200–500 °C [NO] = 0.1%, [C <sub>3</sub> H <sub>6</sub> ] = 0.1%, [O <sub>2</sub> ] = 5% Alk-loadings: A/Pt = 10/1 molar ratio	✓ Performance inhibition effects of alkaline materials addition were found at the specific loading used for each alkaline (2.42, 7.25, 7.93, 2.07 and 8.35wt% of K <sub>2</sub> O, Cs <sub>2</sub> O, BaO, MgO and La <sub>2</sub> O <sub>3</sub> , respectively).	[105]
NO, C <sub>3</sub> H <sub>6</sub> or C <sub>3</sub> H <sub>8</sub> , O <sub>2</sub> excess	0.9 wt% Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Na	T = 200–650 °C [NO] = 0.2%, [HC] = 0.2% (HC: C <sub>3</sub> H <sub>6</sub> or C <sub>3</sub> H <sub>8</sub> ), [O <sub>2</sub> ] = 5% GHSV = 20,000h <sup>−1</sup> Na-loadings: 0.12, 1 and 5 wt%	✓ Under C <sub>3</sub> H <sub>6</sub> /NO/O <sub>2</sub> reaction strong Na-induced promotion was obtained (optimal Na-loading 5wt%). In opposite, under C <sub>3</sub> H <sub>8</sub> /NO/O <sub>2</sub> reaction severe inhibition was induced by Na addition. ➤ Promotion : $\Delta T_{50(C_3H_6)} = -39$ °C under C <sub>3</sub> H <sub>6</sub> /NO/O <sub>2</sub> reaction on the 5 wt% Na – modified catalyst; $\Delta S_{N_2} \sim +20\%$ for T > 280 °C. ➤ Poisoning: $\Delta T_{50(C_3H_8)} = 191$ °C under C <sub>3</sub> H <sub>8</sub> /NO/O <sub>2</sub> reaction on the 5wt%Na-modified catalyst.	[106]
NO, C <sub>3</sub> H <sub>6</sub> , O <sub>2</sub> excess	0.5 wt% Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (CCP)	Na	T = 200–450 °C [NO] = 0.1%, [C <sub>3</sub> H <sub>6</sub> ] = 0.1%, [O <sub>2</sub> ] = 5% Na-loadings: 0, 1.6, 2.6 and 4.2 wt%	✓ Strong promotion by Na with an optimal loading of 2.6wt% Na. Higher Na-loadings caused strong inhibition (volcano behaviour; over-promotion). NO <sub>x</sub> conversion window is widened and moved to lower temperatures. ➤ $\Delta T_{50(C_3H_6)} \sim \Delta T_{50(NO_x)} = -65$ °C; $\Delta S_{N_2} = +40\%$ at T > 320 °C for 2.6wt% Na loading	[47]
NO, C <sub>3</sub> H <sub>6</sub> , CO, H <sub>2</sub> O, CO <sub>2</sub> , O <sub>2</sub> excess	Ir-black (CCP)	Na	T = 150–450 °C [NO] = 300 ppm, [C <sub>3</sub> H <sub>6</sub> ] = 1800 ppm, [CO] = 450 ppm, [O <sub>2</sub> ] = 8%, [H <sub>2</sub> O] = 10%, [CO <sub>2</sub> ] = 10.7% Na-loadings: 0–10wt%	✓ Na-loadings > ~1 wt% enhanced the selectivity towards N <sub>2</sub> in the whole temperature range (150–450 °C) but not affected the activity. ✓ Na-loadings > 3 wt% caused rate inhibition for all CO, NO <sub>x</sub> , C <sub>3</sub> H <sub>6</sub> conversions.	[107]
NO, C <sub>3</sub> H <sub>6</sub> , (O <sub>2</sub> )	Ir film on (K) $\beta''$ -Al <sub>2</sub> O <sub>3</sub> solid electrolyte (EPOC)	K	T = 250–400 °C [NO] = 0.2%, [C <sub>3</sub> H <sub>6</sub> ] = 0.2%, [O <sub>2</sub> ] = 0–5% $\theta_K = 0$ –100%	✓ Marginal effects of K addition on the Ir surface at reducing (absence of O <sub>2</sub> ) conditions. Strong K-induced poisoning at oxidizing conditions for both propene oxidation and NO <sub>x</sub> reduction with significant decreases in N <sub>2</sub> -selectivity, as well.	[108]



**Figure 18.**  $\text{C}_3\text{H}_6 + \text{NO} + \text{O}_2$  reaction on Na-promoted Pt/ $\gamma\text{-Al}_2\text{O}_3$  catalysts. The effect of temperature on the conversion of NO to various N-containing products and the corresponding  $\text{N}_2$ -selectivity: (a) NO conversion to  $\text{N}_2$ ; (b) NO conversion to  $\text{N}_2\text{O}$ ; (c) NO conversion to  $\text{NO}_2$ ; (d)  $\text{N}_2$ -selectivity. Conditions: 1000 ppm NO, 1000 ppm  $\text{C}_3\text{H}_6$ , 5%  $\text{O}_2$ ; reactant contact time 4 s. (Reprinted with permission from Ref. [47]; Copyright 2005, Elsevier).

The performance of another noble metal, iridium, the three-way catalytic chemistry of which has several promising characteristics, have been studied under Na-promotion by Wogerbauer et al. [107]. A simulated exhaust gas mixture consisted of 300 ppm NO, 0.18% propene, 450 ppm CO, 8%  $\text{O}_2$ , 10%  $\text{H}_2\text{O}$ , 10.7%  $\text{CO}_2$ , balance  $\text{N}_2$  was used, while the temperature and Na promoter loading were varied between 150–450 °C and 0–10wt%, respectively. They found that under the conditions used and for Na loadings higher than ~3wt%, Na caused an inhibition on the Ir-black catalytic activity for CO, propene and  $\text{NO}_x$  conversions (Table 7). However, the selectivity towards  $\text{N}_2$  was significantly improved up to 100% for samples with Na content > ~1wt% in the whole temperature range.

More recently, Goula et al. studied the effect of electrochemically supplied potassium on a porous Ir-film catalyst under the  $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$  reaction at a variety of oxygen concentrations [108]. In this EPOC study the Ir-film was interfaced with a (K) $\beta''\text{-Al}_2\text{O}_3$  solid electrolyte on which the catalyst was supported by sputtering. It was found that K addition on the Ir surface is detrimental on catalyst performance (propene oxidation, NO reduction efficiency and  $\text{N}_2$ -selectivity) for all oxygen concentrations investigated. Only at zero  $\text{O}_2$  concentration, that is,, at net reducing conditions of the reactive mixture, a slight promoting effect of potassium on the  $\text{N}_2$ -selectivity but not on the rates was observed (Table 7). This very different effect of alkali-promotion, compared to that observed on Pt



and Pd noble metals under similar conditions (on which strong promotional effects were recorded), was understandable in terms of the electronic influence of co-adsorbed potassium on the adsorption strengths of the neighbour reactants on the Ir surface: the excessive enhancement of oxygen adsorption on Ir sites in the expense of the hydrocarbon adsorption caused O-poisoning of the surface.

Overviewing Section 3.2.2 and the involved literature listed in Table 7, it is apparent that as we have seen in Section 3.1.4, alkali-promotion of the reduction of NO by propene remains very effective even under excess O<sub>2</sub> conditions, at concentrations > ~5% which simulate lean-burn and diesel engines exhaust gases. However, at excess oxygen conditions promotional effects on both activity and selectivity are significantly attenuated and also limited in quite narrow temperature and/or promoter loading windows. Volcano type behaviour of promotion is once again recorded upon increasing alkali loading and EPOC or CCP promotion characteristics were qualitatively similar.

### 3.3. Mechanistic Implications: The mode of Action of Electropositive Promoters

#### 3.3.1. Main Promotion Characteristics and Mechanistic Implications

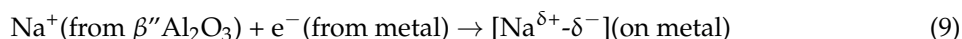
The above described results show that electropositive promoters (alkalis and alkaline earths) can markedly affect the catalytic properties of Pt-group metals during CO or hydrocarbons oxidation and NO reduction by CO or hydrocarbons in the absence or presence of oxygen, as well as of other environmentally important reactions (see Tables 1–7). The promotional benefits on the catalytic performance (activity, selectivity) achieved were similar, independently of the promotion method used, that is, the electrochemical promotion of catalysis (EPOC) or the conventional catalyst promotion one (CCP). The intensity of promotion, the optimal promoter loading and other characteristics of the induced promotional effects are subjected to the specific reaction/catalyst system and the individual reaction conditions applied (Tables 1 and 2).

This electropositive promotion (by alkalis and alkaline earths) of PGMs for emissions control catalysis reaction was found to be very pronounced not only when applied to model reaction systems (Tables 1–5) but also under complex reaction systems that mirror practical applications, that is, stoichiometric gasoline, lean-burn and diesel engines exhaust conditions (Tables 6 and 7). The latter boosts the practical importance of the subject and direct implementations on practical systems appear attractive and promising.

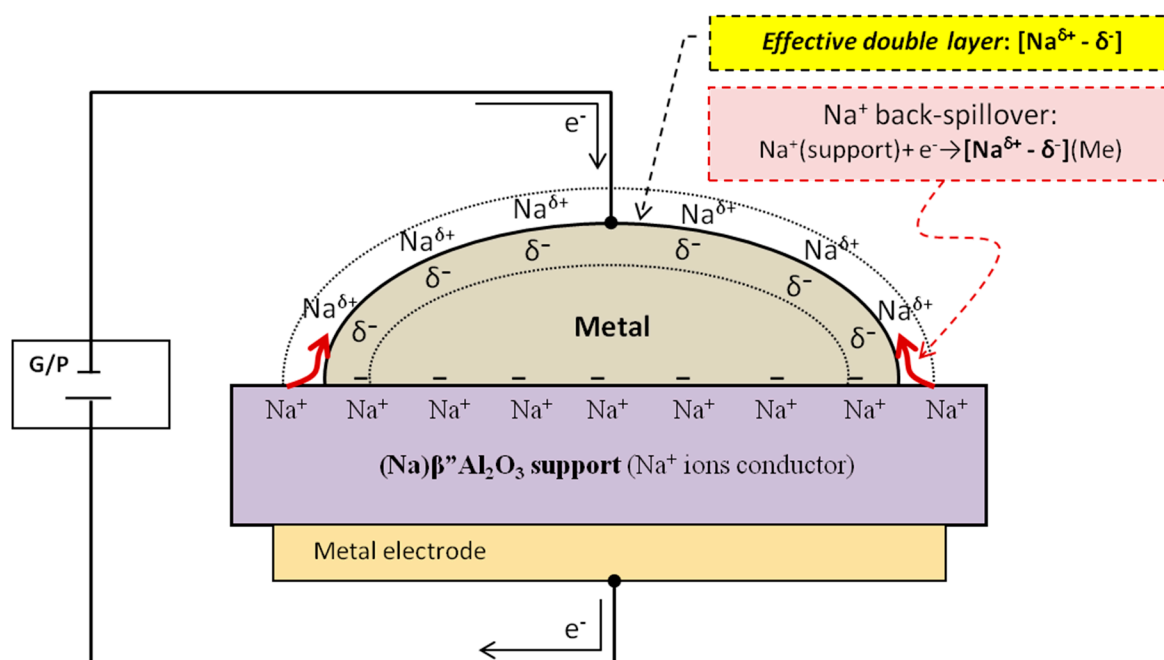
Model reactions studies and their individual characteristics (Section 3.1) enabled us to better understand the mechanism of the promoters' action. EPOC has also a significant role on this issue, since it gave us the opportunity of in situ adjustment of the promoter loading, recording at the same time its influence on the catalytic performance. Recall that some studies were explicitly focussed on experimentally establishing that EPOC and CCP are similar in origin and are subjected to the same physicochemical rules; the only practical different is the procedure used for the promoter supply [21,22,25]. To this end, Yentekakis and co-workers [21,22] have first shown that the promotional effects of sodium, electrochemically induced (via EPOC) on the NO + C<sub>3</sub>H<sub>6</sub>/Pt catalytic system, mirror those obtained on a highly dispersed Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, promoted by means of CCP method at similar conditions. Therefore, EPOC and CCP will be hereafter considered as identical phenomena; the mechanistic model described below that interprets the mode of action of electropositive promoters, may be considered identical valid for both promotion methods. The vast majority of the publications reviewed here have been based on this model to consistently interpret individual promotional phenomena appeared at the specific reaction systems investigated. The main body of the model is described below and several direct spectroscopic evidences supporting its consistency are presented.

Using EPOC (via a galvanic cell as it was described by the formula (1) and Figure 1) one can electrochemically control (Faraday law) the migration of promoting species (e.g., Na<sup>+</sup>, Figure 19) from the solid electrolyte onto the catalyst/gas interface, where an effective and overall neutral double layer is formed through this ions back-spill over imposed electrochemically (Figure 19).

Actually, the electrocatalytic reaction taking place at the three-phase-boundary metal-solid electrolyte-gas that leads to the formation of the effective double layer is [6,7,16,109]:



where  $[\text{Na}^{\delta+}-\delta^-]$  denotes the overall neutral Na species present at the metal-gas interface (effective double layer): the Na adatom on the metal surface carries a charge  $\delta^+$  and  $\delta^-$  is the image charge in the metal; the charge  $\delta$  is about 0.8–0.5, decreasing with increasing Na coverage [7].



**Figure 19.** Schematic of the effective double layer approach of catalyst promotion [6,7,110]. An electron enriched (lower work function) catalyst surface is developed due to the uniformly dispersed  $\text{Na}^{\delta+}$  adatoms.

It is worth noting that an identical configuration is expected on the metal catalyst surface when Na is introduced to the catalyst by conventional methods (e.g., impregnation, vapor deposition, etc.), as recently demonstrated by Lambert and co-workers [110,111] who showed using XPS that the electrochemically-supplied sodium is identical with gas-supplied (by evaporation) of  $\text{Na}^{\delta+}$  cations on the catalyst surface.

Since alkali ad-atoms are imposed on the catalyst surface, they are spread over the entire metal surface due to strong repulsive dipole-dipole interactions, establishing a homogeneous, neutral, effective double layer. This double layer corresponds to an electrically modified metal surface, practically an electron enriched (lower work function) metal surface due to the  $\delta^-$  charge located at the metal side interface half-layer. This electrically modified surface interacts with the co-adsorbed reactants, reaction intermediates and products, changing their binding energies (in respect to those on a promoter-free metal surface), producing pronounced alterations in catalytic performance. Therefore, the main feature of the electropositive promotion of PGM by alkalis and alkaline earths is the resulted electron enriched, lower work function, PGM surface.

Therefore, the concomitant alterations on the adsorption characteristics of the co-adsorbed reactants on such a modified metal surface are of course subjected to the electronic properties of the reactants: electrophilic (electron acceptor) or electrophobic (electron donor): both theory [112] and experiment (e.g., [106,113]) have shown that electropositively promoted (by alkalis) Pt-group metal (PGM) surfaces appear strengthening in the bonds of the metal—electron acceptor (electrophilic)

adsorbates, for example, PGM–NO, PGM–O<sub>2</sub>, PGM–N, PGM–O, PGM–CO and weakening in the bonds of the metal–electron donor (electrophobic) adsorbates, for example, PGM–hydrocarbons and their fragments, PGM–CO. Donation and/or backdonation issues of electron charge between adsorbates and metal surfaces during the formation of a chemisorptive bond and their impact on the bond strength have been thoroughly explained by Vayenas and Brosda in Ref. [114] and in brief summarized in the following statements: “Electron backdonation to bonding singly occupied orbitals of an electron acceptor reactant lying below the metal Fermi level ( $E_F$ ) results in strengthening of the metal–adsorbate bond, while electron backdonation to antibonding orbitals, leads to weakening of the chemisorptive bond and destabilization of the adsorbate. Also electron donation to a metal from a singly occupied orbital on an electron donor adsorbate lying above Fermi level of the metal leads in general to strengthening of the chemisorptive bond. There are cases, such as the CO chemisorption on transition metals, where both donation of electrons (from the adsorbate to the metal) and backdonation of electronic charge (from the metal to the adsorbate) play an important role in the chemisorptive bond formation (e.g., Blyholder model for CO chemisorption [115])”; (The latter explains why someone can find CO to be considered as an electron-acceptor or even as an electron-donor adsorbate). These modifications on the reactants chemisorptive bonds are accompanied by alterations in the activation energies of the catalytic reactions and in some cases on their mechanism (e.g., on the rate determination step), resulted to dramatic changes on their intrinsic activity and/or selectivity. The specific features of the promotion are subjected to the specific catalytic systems under consideration and to the reaction conditions imposed.

Taking into account that the vast majority of the reactions involved in emission control catalysis processes obey Langmuir–Hinshelwood mechanism (competitive adsorption of the reactants), the following example could be of usefulness for a better understanding of the mechanism of action of the promoters under the concept of the effective double layer approach. Let’s suggest a starting rate at point 1 on the rate versus [A] curve I (Figure 20), as determined by the applied reaction conditions on the unpromoted reaction  $A + B$ , that are considered to follow a typical Langmuir–Hinshelwood (LH) mechanism with the well-known characteristic rate maximum (point 2) due to the competitive adsorption of the reactants. The reaction rate is proportional to the product of the reactants’ coverages,  $\theta_A \cdot \theta_B$  (Equation (10)), maximized at equilibrated coverages  $\theta_A$  and  $\theta_B$  on the catalyst surface:

$$r = k_0 \exp(-E_a/RT) \theta_A \cdot \theta_B \quad (10)$$

where  $k_0 \exp(-E_a/RT) = k$  is the temperature dependence of the rate constant  $k$  with a pre-exponential factor  $k_0$  and an apparent activation energy  $E_a$ .

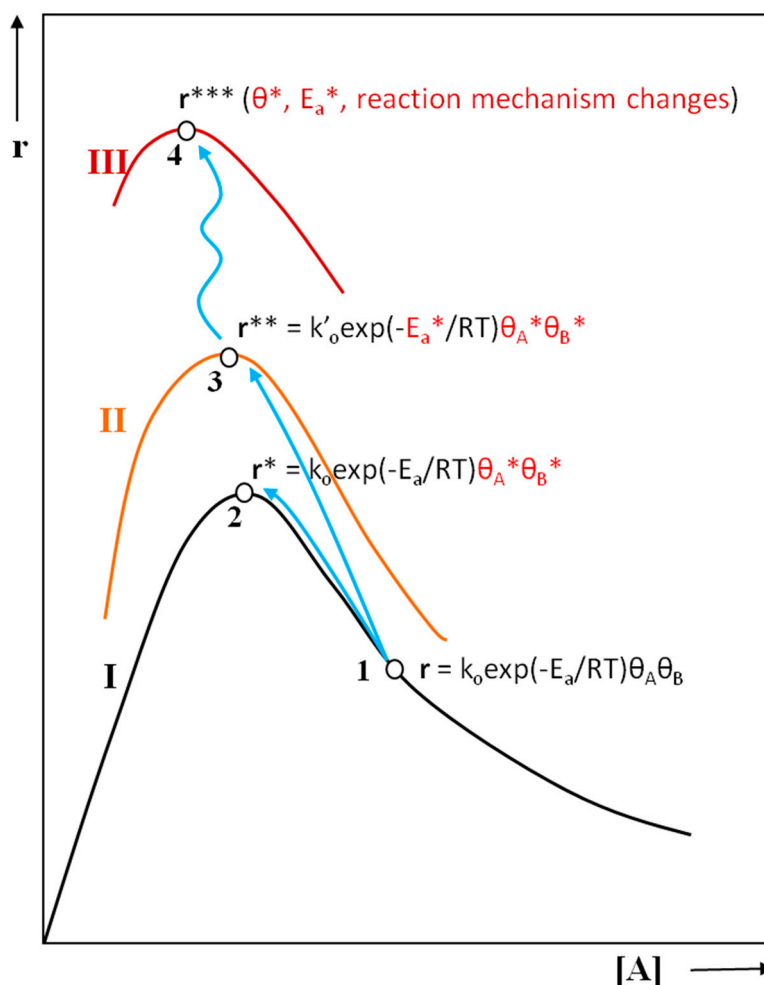
Applying (chemically or electrochemically) a promoter, the created effective double layer (Figure 19) causes alterations on the adsorption strengths of the reactants, modifying their coverages  $\theta_A$  and  $\theta_B$  thus giving the possibility of their adjustment at the equilibrated values  $\theta_A^*$  and  $\theta_B^*$  that minimizes reaction probability and consequently rate (point 2):

$$r^* = k_0 \exp(-E_a/RT) \theta_A^* \cdot \theta_B^* \quad (11)$$

However, this is the minimum effect that can be offered by this course and actually Equation (11) and consequently path 1→2 are not real: Due to the induced changes on the chemisorptive bonds of the reactant, alteration on the apparent activation energy of the reaction is also expected from the unpromoted value  $E_a$  to a modified value  $E_a^*$ , leading the reaction rate to follow a new substantially enhanced behaviour (curve II, Figure 20, for example, point 3), following Equation (12):

$$r^{**} = k_0 \exp(-E_a^*/RT) \theta_A^* \cdot \theta_B^* \quad (12)$$

Notably, in the cases where reaction mechanism modifications are induced by the promoter as well (e.g., change of the rate determination step), promotion can receive unprecedented enhancements (promoted rate  $r^{***}$  on curve III, Figure 20, e.g., point 4).



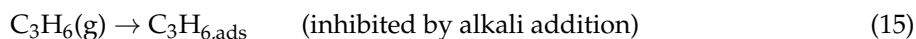
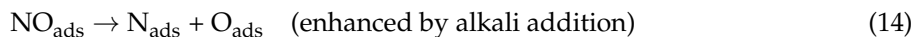
**Figure 20.** Schematic representation of the mechanism of promotion on a Langmuir-Hinshelwood type reaction.

An example which mirrors all the aforementioned issues is the alkali-promoted NO + C<sub>3</sub>H<sub>6</sub> reaction on Pt [15,58,61]; reaction rate enhancements up to 40,000% were achieved accompanied with dramatic changes on the selectivity towards N<sub>2</sub>, as well (Table 4). The promotion mechanism on this system is described as follow (Figure 21):

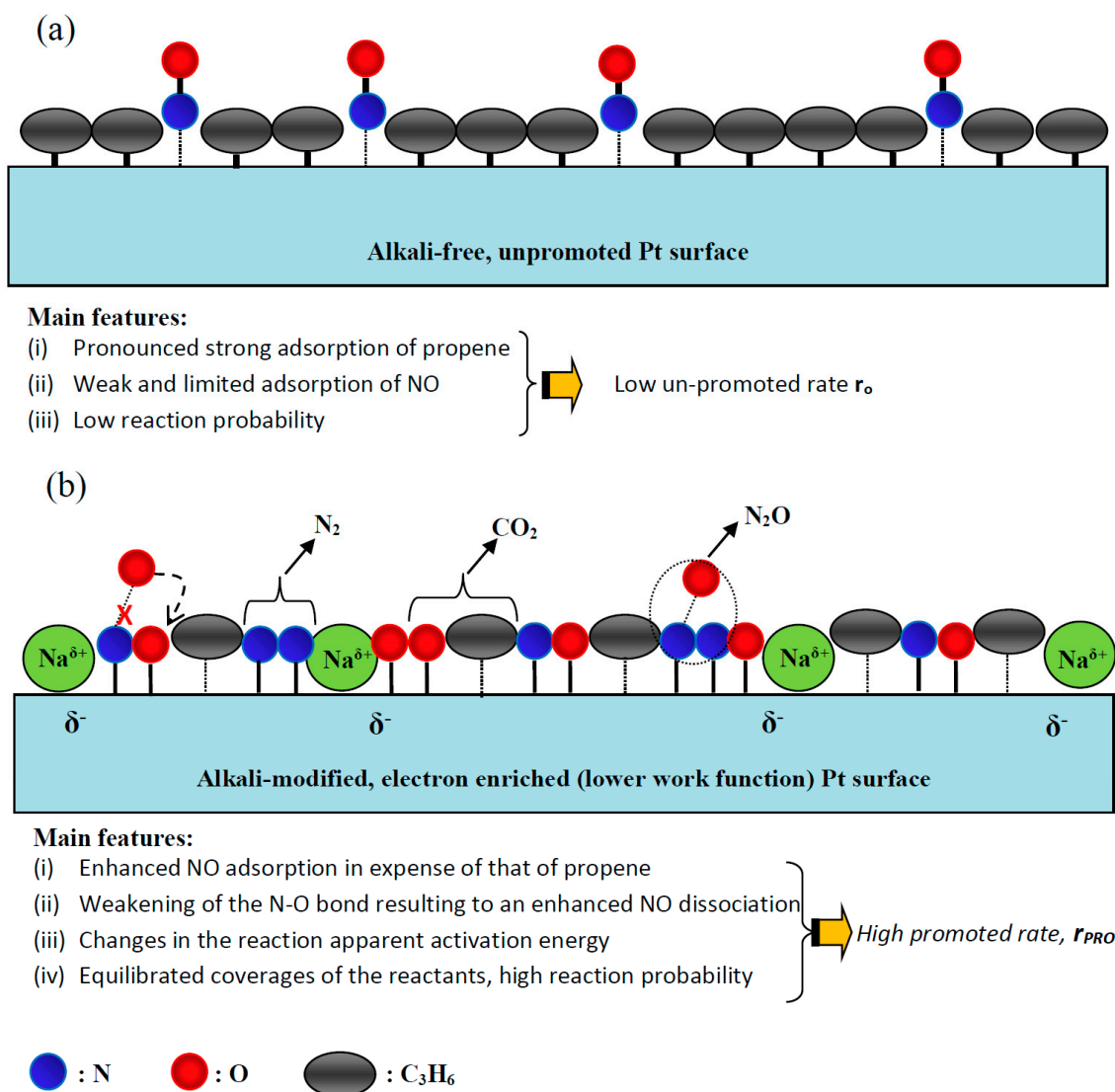
First, it is well established that NO + C<sub>3</sub>H<sub>6</sub> reaction over Pt obeys Langmuir-Hinshelwood type kinetics with characteristic rate maxima reflecting competitive adsorption of the two NO and C<sub>3</sub>H<sub>6</sub> reactants on Pt active sites; these rate maxima occurred at very low C<sub>3</sub>H<sub>6</sub>/NO ratios (<0.08), that is, very high NO concentrations relative to C<sub>3</sub>H<sub>6</sub> are necessary in order to achieve a comparable coverage of both reactants on the Pt surface, thus maximizing the rate [58,62], reflecting a weaker adsorption of NO on Pt sites relative to C<sub>3</sub>H<sub>6</sub> [58,62,67,68] mainly due to the presence of  $\pi$ -electrons in the alkene structure. As a consequence, in a wide range of reactants partial pressures and temperatures conditions the un-promoted (alkali-free) Pt surface is predominantly covered by propene and propene-derived fragments (Figure 21a), therefore the un-promoted reaction rate,  $r_0$ , is quite low.

Addition of alkali, which is accompanied by the formation of the [Alkali <sup>$\delta^+$</sup> – $\delta^-$ ] effective double layer, provides an electron enriched (lower work function) metal surface that in effect favours the adsorption of electrophilic co-adsorbates (NO) and inhibit that of electrophobic co-adsorbates (C<sub>3</sub>H<sub>6</sub> and its fragments). According to the following Reaction (13)–(18) scheme,





the resulted effects are (Figure 21b): (i) strengthening of the Pt–NO bond with a concomitant enhancement population of NO molecules on the alkali-modified surface (Reaction (13)) –the surface populations of NO and propene are therefore equilibrated; (ii) strong enhancement of the dissociative adsorption of NO (Reaction (14)) as a result of the Pt–NO bonds strengthening and the concomitant weakening of the N–O bond in the adsorbed NO molecules—the surface is enriched with very active atomic oxygen species; (iii) weakening of the strength of the Pt–C<sub>3</sub>H<sub>6</sub> bond—an equilibrated population of more active (due to their weaker adsorption) hydrocarbonaceous species is resulted (Reaction (15), Figure 21b).



**Figure 21.** Schematic of the mechanism of action of alkalis as promoters on the Pt-catalysed NO + C<sub>3</sub>H<sub>6</sub> reaction. Expected distribution of reactants and/or intermediates over the unpromoted surface (a) and the Na-promoted surface (b).

All these factors operate together in increasing the reaction probability of NO and propene molecules, leading to an enhanced promoted rate,  $r_p$ , over the alkali-modified surface. These changes on adsorbed species distribution and/or population (coverage), their bond-strengths and activation energies and on reaction rate-determination-step (rds) were successfully used to convincingly interpret the rate enhancement values,  $\rho = r_{CCP}/r_o$ , as high as 420 and 280 for  $N_2$  and  $CO_2$  productions have been reported for this catalytic system under electropositive promotion by alkalis or alkaline earths [15,61,62]. Notably, these gains in catalytic activity did not reflect the maxima of the L-H rate curves, *that is*, were not restricted by the optimal balance of the competitive reactants' coverages. These were extraordinarily larger, due to the synergy of the aforementioned factors.

The observed increase in  $N_2$ -selectivity upon electropositive promotion can be also readily understood in terms of the above considerations. According to the reaction network (13)–(18), the production rates of  $N_2$  and  $N_2O$  depend on the extent of NO dissociation (reaction (14)), which is followed by the elementary Reactions (16) and (17). The observed increase in the  $N_2$ -selectivity upon promoter addition is a consequence of increased NO dissociation, *that is*, less molecular NO and more atomic N on the surface. According to Lang et al. [112], the electrostatic field produced by  $Na^+$  can shift the  $\pi^*$ -orbital energy of NO adsorbed in the vicinity of an alkali ion below the Pt Fermi level. Then, valence electrons from the metal can populate the NO  $\pi^*$ -orbital energy, resulting in weakening of the N–O bond and a strengthening of the Pt–N bond. Both factors favour Reaction (16) over Reaction (17), leading to higher  $N_2$  selectivity.

In the case of  $CO + O_2$  reaction the strong promotion observed under CO-rich reaction conditions (e.g., [16,27]), was understandable by means of the pronounced strengthening of the O adsorption bond, compared to that of CO: at such conditions where CO coverage predominates and the formation of CO islands suppresses reaction probability, the alkali-induced pronounced adsorption of O species causes destruction of CO islands thus increasing reaction probability [16].

In the case of alkanes oxidation, it is well known that alkanes, in particular  $CH_4$ , have low propensity for adsorption (activation) on PGM surfaces. The adsorption of these electrophobic adsorbates is being even worse on alkali-modified electron enriched surfaces. This makes the generally observed alkali-induced poisoning of alkanes oxidation reactions readily understandable, no matter of what oxidant agent (oxygen or NO) used [48,49,65,66].

The opposite was true for alkenes oxidation (by  $O_2$  or NO), due to their strong propensity to adsorb on PGMs. Thus, weakening their adsorption and at the same time strengthening the adsorption of the electrophilic limiting reactant (O) on the alkali modified PGM surfaces are factors that operate synergistically creating ideal promotion conditions (e.g., [18,20,43–47]).

Comparing the alkali promotion of the NO reduction by alkenes, the Ir~Rh < Pd < Pt increasing order can be observed: marginal promoting effects have been obtained during Rh- or Ir-catalysed NO reduction by propene [59,60,64,107,108], in opposite to the very large on Pd [14] and to the extraordinarily large on Pt (e.g., [15,58,61,62,106]) This is related to the different propensity of NO adsorption on these metals: on Ir and Rh, NO has high propensity of adsorption, which is also dissociative; on Pd less and partly dissociative, while on Pt it is even less and non-dissociative. Therefore, enhancing NO adsorption by alkali-promotion on Ir and Rh surfaces has not further practical value (NO adsorption/dissociation is close to ideal on the unpromoted Ir and Rh), while on Pt the non-dissociative and quite limited NO adsorption can become much stronger and fully dissociative, enabling Pt to behave like Rh or Ir (e.g., [15,47,61,62,89]).

Comparing the amount of an alkali necessary to optimize promotion for a certain reaction on different Pt group metals, the general trend is that only few surface concentrations are needed in the case of Rh and Ir (ca.  $\theta_{Alkali} \sim 1\text{--}3\%$ ), quite more for Pd ( $\theta_{Alkali} \sim 5\text{--}10\%$ ) and much more for Pt ( $\theta_{Alkali} \sim 15\text{--}40\%$ ) (e.g., [14,15,18,22,51,57,58,108]). This is readily understandable in similar terms used above: Rh and Ir electron availability (work function, WF) is by its own close to the optimal value for the reactions under consideration and only few amounts of alkalis are necessary for the optimal



promoter loading adjustment. The opposite is true for Pd and in particular for Pt; these two metals showing a higher WF than Rh and Ir.

For a certain catalytic system and operating conditions, the amount of alkali that is needed to optimize promotion depends on the chemical identity of the alkali: heavier alkalis appear to be more effective than the lighter ones (e.g., [61]). This is fully consistent to the effective double layer approach considered and to the theoretical predictions of Lang et al. [112], which have shown that the larger the alkali cation the greater the effect its electric field has on an electron acceptor adsorbate (e.g., NO).

In the cases of more complex reactions systems, as for instance those simulating automotive exhaust gas mixtures, the explanation of the promotional effects is typically more complicated and may involve all the possible effects, synergistic or competitive, induced through the modification of the metal work function on all electrophilic and/or electrophobic reactant species and intermediates on such a densely populated surface with all these competitive species (e.g., [47,79,89,106]).

It is also of worth noting that: (i) Alkalis and alkaline earths are typically permanent promoters as a result of the fact that they do not participate in the reactions networks. This is of high technological importance: since the optimal alkali amount is incorporated on the catalyst and independently of the method used for its supply (EPOC or CCP), its amount remains practically constant for a very long time offering promotion. This explains why Faradaic Efficiency values as large as  $\Lambda > 10^5$  have been measured in EPOC by alkalis studies (e.g., [16–18,42]). (ii) Volcano type behaviour of the promotional effects as a function of the promoter loading was an additional common feature of the titled promotion, that is, outgoing of the optimal amount of the promoter (the so-called over-promotion) the reaction is gradually inhibited rather than promoted (e.g., [15–17,47,58]). Two main factors were considered to be responsible for this behaviour: (a) the extended strengthening of the adsorption bond of the electrophilic adsorbate (electronic effect) and (b) the formation of extended surface complexes of the promoter with the reactant species and/or reaction intermediates that can block active sites (geometric effect). These factors can operate together suppressing the rate in case of over-promoted catalysts. However, it must be noticed that the formation of such 2D or 3D surface alkali complex compounds (alkali nitrites, nitrates, carbonates, oxides or even superoxides, depending on the reaction atmosphere), that can be valid even at low promoter loadings, do not actually cancel the role of alkali as a promoter (e.g., [20,43–46,51,52,57–60]). On the opposite, stabilization on the catalysts surfaces, even at elevated temperatures of catalytic interest, of normally volatile alkali metals is achieved by the formation of such stable surface alkali complex compounds.

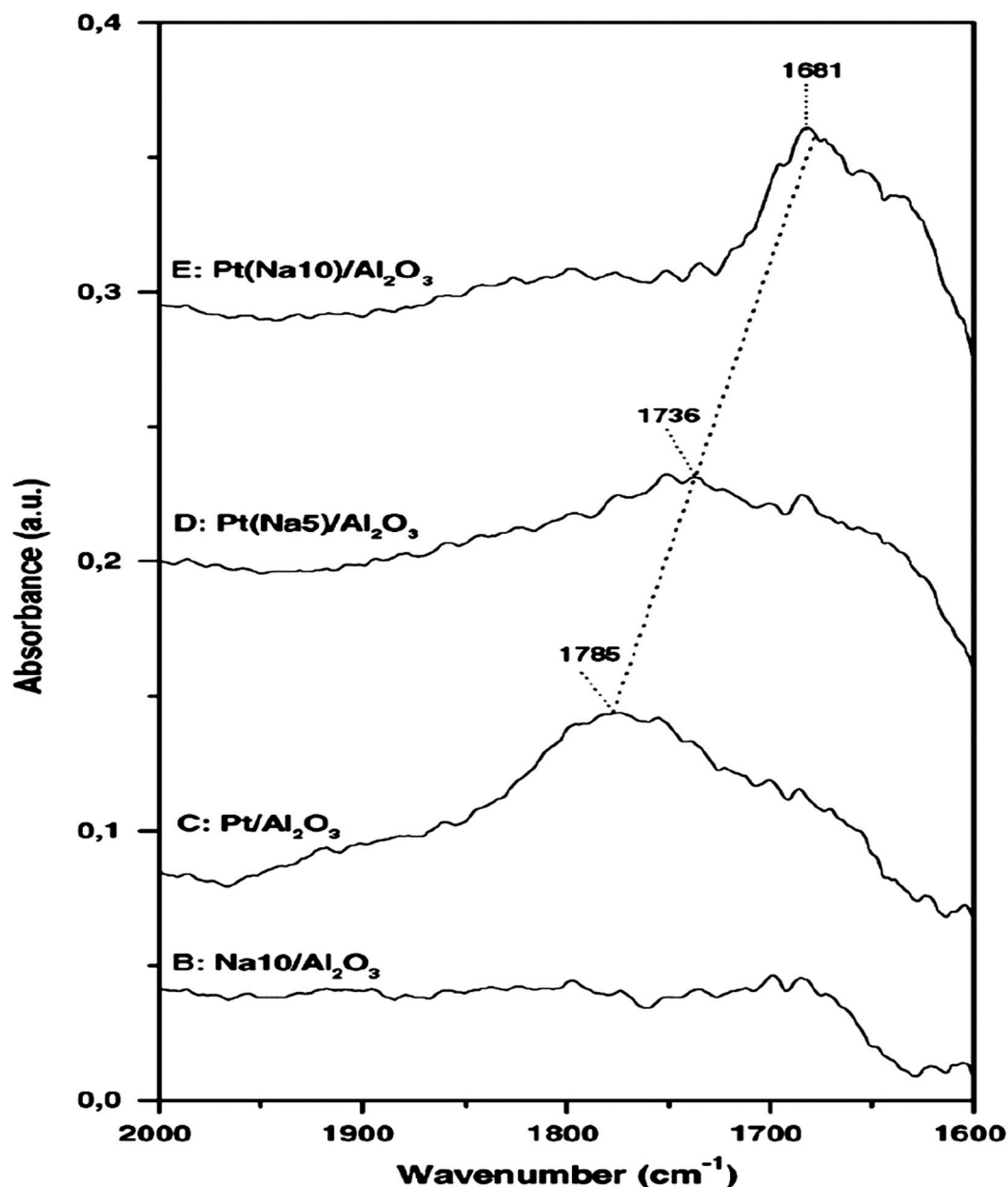
### 3.3.2. Direct Spectroscopic and Other Analytical Technique Evidences

Besides of the numerous kinetic studies demonstrating the usefulness of the electropositive promotion of PGM in emissions control catalysis, particular emphasis to direct evidences for the origin and mechanism of this promotion have been devoted by several research groups using a variety of surface science or other analytical techniques, including: in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [95–98,113], x-ray photoelectron spectroscopy (XPS) (e.g., [51,52,111]), temperature programmed desorption (TPD) [106,116–120], scanning tunnelling microscopy (STM) [121–123] and work function [51,52] measurements.

To this end, Koukiou et al. [113], studying the interaction of NO with Na-modified Pt surfaces over a conventional, highly dispersed, Pt catalyst, namely Pt(Na)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, by means of in situ DRIFTS, have shown that increasing sodium loading causes a pronounced and progressive red shift of the N–O stretching frequency (Figure 19) associated with molecular NO adsorbed on the Pt component of the supported catalyst.

At the highest sodium loading (10wt% Na; corresponding to an upper limit of about  $\theta_{\text{Na}} = 0.5$  nominal sodium fractional coverage on Pt particles [102]) a 1680 cm<sup>−1</sup> species is observed that corresponds to an activated NO<sup>δ−</sup> species with bond order 2, that is, a negatively charged adsorbate with increased electron density in the  $\pi^*$  antibonding orbital. The rigorous model developed by Lang et al. [112] was considered for understanding the effect of alkali on Pt surface. They have shown

that the inhomogeneous electric field associated with adsorbed alkali ions acts to depress the energy of the antibonding  $\pi^*$  orbital of electron-accepting (electrophilic) co-adsorbates (e.g., CO, NO) below the metal Fermi level. Therefore, the red shifts showed in Figure 22, as authors argue [113], are due to the resulting metal  $\rightarrow$  adsorbate charge transfer that acts to weaken the N–O bond, red-shifting its vibration frequency and promoting its dissociation, rather than to alkali-induced changes in the relative populations of various forms of adsorbed NO.



**Figure 22.** DRIFT spectra (expanded scale for the region 2000–1600  $\text{cm}^{-1}$  and subtracting spectrum of pure  $\text{Al}_2\text{O}_3$ ) obtained with 10wt%Na/ $\gamma\text{-Al}_2\text{O}_3$  (B), Pt/ $\gamma\text{-Al}_2\text{O}_3$  (C), Pt(Na5)/ $\gamma\text{-Al}_2\text{O}_3$  (D) and Pt(Na10)/ $\gamma\text{-Al}_2\text{O}_3$  (E) samples after NO adsorption for 1 min at 27 °C. (Reprinted with permission from Ref. [113]; Copyright 2007, Elsevier).

The chemisorption characteristics of NO on Na-dosed Pt{111} surface has been also studied by Harkness and Lambert [116] by means of temperature-programmed desorption (TPD). It was clearly demonstrated that the presence of Na on the Pt{111} single crystal causes an increase in the adsorption energy of NO (i.e., strengthening of the metal–NO bond) accompanied by a monotonically increased

NO dissociation (i.e.,  $N_2$  desorption) as a function of Na coverage. In particular, NO-TPD spectra on Na-dosed Pt{111} (from 0 to 1.2 ML of Na coverage) have showed two characteristic peaks, indicated as features (a) and (b); sodium caused an increase in the desorption peak (a) temperature from 360 K on the clean Pt{111} to 380 K at 0.25 ML Na-dosed Pt{111}. Even at very low Na coverages ( $>0.1$  ML), the second NO desorption feature (b) from sodium affected sites is appeared at  $\sim 520$  K which is grew at the expense of the feature (a) and progressively shifted to higher desorption temperature, up to 610 K, upon increasing Na coverage to 1.2 ML. At the same time, the feature (a) is progressively attenuated to zero (practically vanished at  $\sim 1$  ML of Na); A progressively increased  $N_2$  peak is concomitant to the aforementioned TPD experiment, with the  $N_2$  desorption peak to remain constant at 540 K up to 1 ML of Na, after which it is shifted to 540 K for 1.2 ML (i.e., 100% dissociation of adsorbed NO can be obtained at sufficiently high, ca 1 ML, sodium coverage) [116].

Similar TPD studies by Garfengel et al. [117], involving the interaction of NO with K-dosed Pt{111}, yielded the same evidences: an alkali-induced increase in the Pt–NO bond strength accompanied by alkali-promoted NO dissociation was demonstrated.

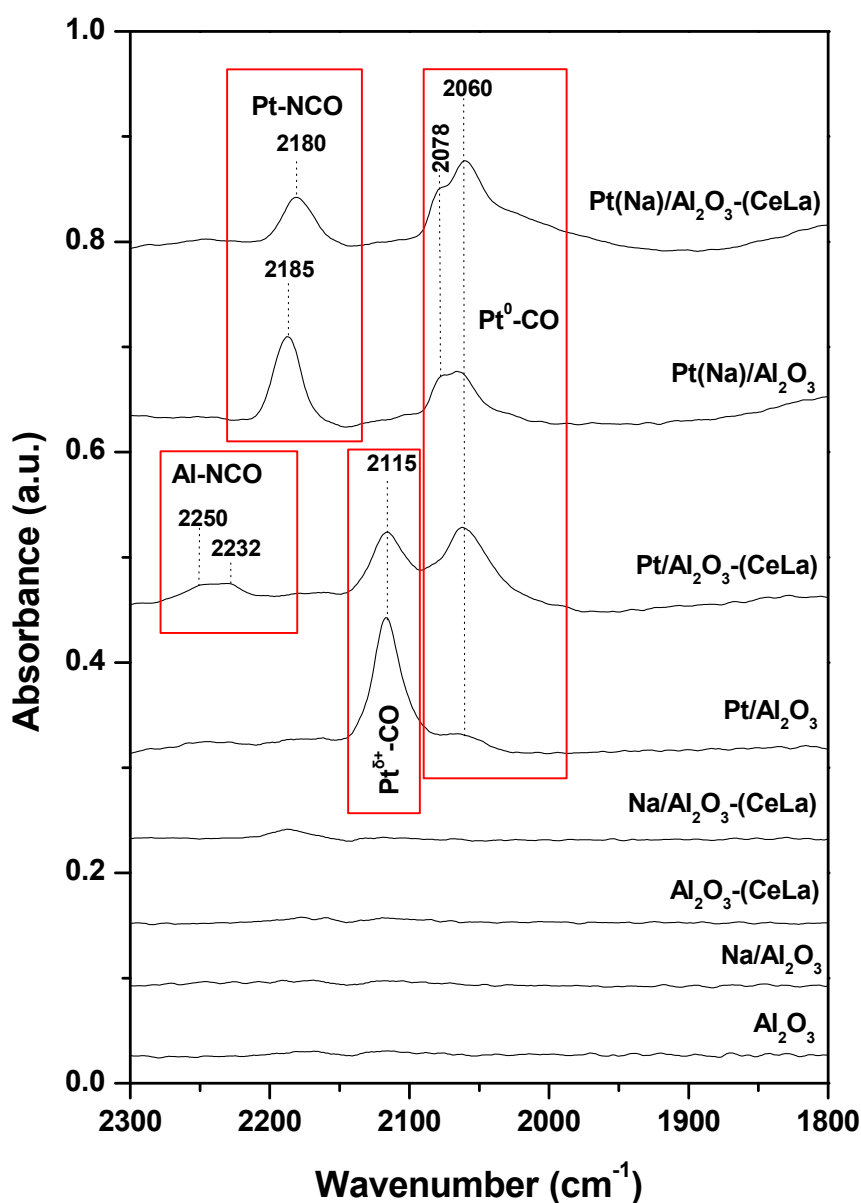
Temperature-programmed desorption (TPD) studies after adsorption of oxygen on Na-dosed Pt/ $Al_2O_3$  catalysts where performed by Vernoux et al. [106] in order to elucidate possible influences of the Na addition on the Pt–O bond strength. They demonstrated that the adsorption strength of the atomic oxygen (an electron acceptor adsorbate) on the Pt component of the catalyst is enhanced by Na addition; their data clearly showed that the temperature of the oxygen desorption peak correspond to Pt–O interaction increases with increasing Na loading of the catalyst, directly evidencing a strengthening of the Pt–O bond [106].

A number of early and recent studies concern the chemisorption of CO on alkali-modified PGM surfaces [95–97,117–120]. To this end, Bertolini et al. [118] studied the chemisorption of CO on K-modified Pt(100) surfaces by means TPD and Auger Electron Spectroscopy (AES). The progressive increase on the CO desorption peak temperature (i.e., strengthening of the Pt–CO) as a function of K coverage, observed at low K coverages  $\theta_K$  (ca. 0–0.4), was attributed to long range uniform electronic modifications, that is, work function changes, due to charge transfer;  $K^{\delta+}$  ( $\delta \approx 1$ ) adspecies appear on the K-dosed surface, uniformly distributed due to repulsion between these charged species. Such an electron enriched (lower work function) Pt surface strengthens the adsorption of CO via substantial charge donation from the K-modified Pt surface into the  $2\pi^*$  orbitals of CO [118]. At high K coverages (ca. 0.45–1) short range interactions between the CO and K adspecies, that is, an even more direct bonding of CO with K (formation of CO–K–Pt surface complexes), were considered.

Pitchon et al. studied the effect of (Li, Na, K and Cs)-dosed Pd/ $SiO_2$  on CO adsorption characteristics [119]. They demonstrated drastic changes in the infrared spectrum of CO adsorbed on Pd sites; a significant weakening on the strength of the C–O bond of adsorbed CO molecules caused the appearance of a new  $\nu_{CO}$  band at low infrared frequency—the extent of the interaction was depended by the nature of the alkali. These influences were assigned to a localized interaction “Pd–CO–alkali” rather than to long range electronic modifications.

Using FTIR spectroscopy, Liotta et al. studied the effect of sodium on the adsorption of CO on Pd-based catalysts supported on two different supports ( $SiO_2$  and model or natural pumices) [120]. Depending on the support used, the appearance of both electronic and geometric effects—that attributed to the different localization of sodium ions in the catalysts—were evidenced; the geometric effects were predominant in the Pd/ $SiO_2$  catalysts, whereas electronic effects were most important than the geometric ones in the Pd/pumise catalysts. It was again considered in this study that an electronic density transfer to Pd is the common effect of the presence of alkali either it is subsequently added to the catalysts or is present as a structural component of the support, although, the authors observed important geometric effects in the former case. The electronic effect, that produces a red shift (towards lower frequencies) of the CO bands of the IR spectra of chemisorbed CO, owing to an enhanced transfer of electron density from the metal to the  $\pi^*$  molecular orbitals of CO, was again invoked [120].

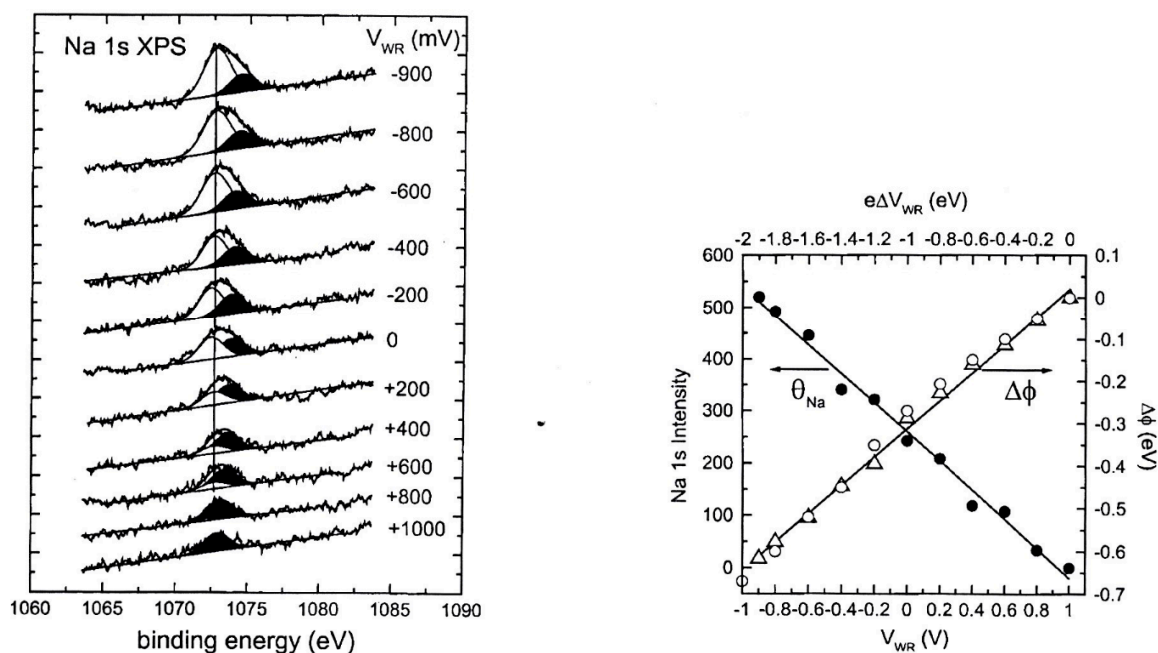
Electron enriched Pt surfaces resulted by combined application of alkali-induced surface promotion and support-mediated promotion by Ce-based mixed oxides were also recently demonstrated via in situ DRIFTS studies by Yentekakis and co-workers [95–97]. Over doubly promoted Pt(Na)/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub> catalysts operated under TWC conditions, the authors demonstrated a substantial population of adsorbed species at 2060 cm<sup>-1</sup> attributed to CO on reduced Pt<sup>0</sup> sites when CeO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub> was incorporated into the Al<sub>2</sub>O<sub>3</sub> support. This feature was substantially exacerbated when Na promoter was also incorporated in the catalyst formulation, while at the same time the formation of active Pt-NCO intermediates at about 2180 cm<sup>-1</sup>, which resulted from an enhanced NO decomposition, was facilitated by alkali-promotion on the Pt(Na)/Al<sub>2</sub>O<sub>3</sub>-CeLa catalyst (Figure 21). On the un-modified Pt/Al<sub>2</sub>O<sub>3</sub> catalyst counterpart, CO species adsorbed on positively charged Pt sites (Pt<sup>δ+</sup>-CO) were assigned (Figure 23). These features, fully compatible with the way of action of alkali promotion analysed so far, were considered as a convincing explanation of the substantially enhanced TWC performance of this complex reactions/catalyst system.



**Figure 23.** In-situ DRIFT spectra during simulated TWC reaction conditions (1000 ppm NO + 1067 ppm C<sub>3</sub>H<sub>6</sub> + 7000 ppm CO + 7800 ppm O<sub>2</sub>; F<sub>t</sub> = 80 cm<sup>3</sup>/min; T = 200 °C). (Reproduced with permission from Ref. [96]. Copyright 2008, Elsevier).

Finally, a number of studies involving x-ray photoelectron spectroscopy (XPS) published by the groups of Lambert and Yentekakis (e.g., [20,51,52,57–60]) have doubtlessly shown that in EPOC studies that concern PGMs films interfaced with an alkali conducting solid electrolyte, the promoting species are indeed alkaline ions reversibly supplied by the external bias onto the catalyst surface.

The authors have also shown that under reaction conditions the electrochemically supplied alkali ions form stable surface compounds (e.g., alkali nitrites, nitrates and carbonates) that can act as promoters even under such formulations and which, in excess (over-promotion), induce geometric, active sites blocking, phenomena and thus poisoning effects on PGMs activity [20,51,52,57–60]. Combining XPS and ultraviolet photoelectron spectroscopy (UPS), the authors demonstrated a linear relationship of the catalyst work function ( $\Delta\Phi$ ) and the alkali coverage ( $\theta_{\text{Na}}$ ) with the catalyst potential overpotential ( $\Delta V_{\text{WR}}$ ) (Figure 24) [51,52] and confirmed that electrochemically supplied alkali ions on the catalyst surface are identical in behaviour (and chemical state) with the alkali supplied by vacuum deposition [21,22]. This makes the close similarities found between EPOC and CCP methodologies of catalyst promotion readily understandable [15,21,22,25,58] and prompts for the use of EPOC as an effective and rapid method for exploring the effects of a range of promoters and for assessing the response of the reaction rate/selectivity to promoter coverage (finding out its optimal loadings at any set of conditions) before applying them to the design of efficient conventional catalyst formulations.



**Figure 24.** Na 1s XPS spectra versus catalyst potential ( $V_{\text{WR}}$ ) for Rh film interfaced with  $(\text{Na})\beta''\text{Al}_2\text{O}_3$   $\text{Na}^+$ -ions conductor, at 307 °C and UHV conditions. The inset shows the integrated Na1s XPS intensity due to sodium on the Rh surface and associated work function change of the Rh film as a function of  $V_{\text{WR}}$ . Data was acquired using a  $\text{Rh}/(\text{Na})\beta''\text{Al}_2\text{O}_3/\text{Au}$  galvanic cell (Reproduced with permission from Ref. [51]. Copyright 2001, American Chemical Society).

A recent review of the literature using surface analysis techniques to shed light on the electropositive promotion via the EPOC concept has recently provided by Gonzalez-Cobos and de Lucas-Consuegra [124].

All the aforementioned in this chapter studies, unambiguously lead to the main conclusion that alkalis adatoms on PGM surfaces provide electron enriched metal sites (lower work function surfaces), which favour the adsorption of electron donor (electrophilic) co-adsorbates and inhibit the adsorption of electron acceptor (electrophobic) co-adsorbates. The formation of alkali-reactants-metal surface complexes and therefore geometric type influences, besides the above electronic ones, can be at work

in cases where the conditions assist such a course. These issues were considered in the vast majority of electropositive promotion studies by alkalis or alkaline earths to explain promotion phenomena observed on PGM-catalysed emissions control catalysis reactions.

#### 4. Conclusions and Perspectives

The electropositive promotion, by alkalis or alkaline earths, has been found to be an effective tool for promoting the catalytic performance of Platinum Group Metals for the vast majority of important reactions involved in emissions control catalysis systems, such as CO and alkenes oxidations, NO reduction by CO, alkenes or H<sub>2</sub>, N<sub>2</sub>O decomposition and/or reduction; the only exceptions were the alkanes oxidation by dioxygen or NO.

Up to two orders of magnitude rate increases were achievable, in particular with electropositive-promoted Pt, while in de-NO<sub>x</sub> reactions the selectivity towards N<sub>2</sub> was simultaneously improved towards values approaching 100% over the “optimally promoted” catalysts.

Promotional achievements were large not only for model reactions but also for gas mixtures that simulate practical systems, such as stoichiometric gasoline, lean-burn or diesel engines exhaust streams.

The intensity of promotion was generally followed the order Pt > Pd > Rh~Ir, thus providing Pt or Pd-based catalysts to operate like Rh or even better in emissions control catalytic reactions. These achievements were lead to the synthesis of novel simple in synthesis and cost-effective monometallic (Pt or Pd-only) with low precious metal loading, extremely active, stable and readily recycling, three-way catalyst formulations that were compared well with commercial bi- or three-metallic (Rh, Pt, Pd)-TWCs for the control of stoichiometric gasoline engines exhaust emissions. The absence of rare and expensive Rh in the formulations of three-way converters has therefore been introduced with the concomitant environmental and economic gains.

Electropositive promotion of PGM was also found to be effective at excess oxygen conditions (e.g., lean-burn of diesel engines exhaust gases), without however in that case to obtain solutions fully satisfying the requirements.

Latterly, doubly promoted catalyst formulations, combining electropositive promotion by alkalis and support-mediated promotion by mixed oxide supports (including combinations of Al<sub>2</sub>O<sub>3</sub> with CeO<sub>2</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub>) have been found to provide even better promotion and stability for emissions control implementations. Such synergistic promotion catalysts’ designs could lead to control systems readily adapted on a number of specific emissions of stationary sources, that have high environmental footprint and their control is an urgent issue.

From the theoretical point of view, electropositive promotion of PGM was successfully understood and interpreted in terms of the effective double layer approach, that is, a homogeneous, neutral, effective double layer established by the alkali (or alkaline earths) adatoms that are spread over the entire PGM surface providing an electron enriched (lower work function) metal surface due to the  $\delta^-$  charge located at the metal side interface half-layer, which interacts with the co-adsorbed reactants, reaction intermediates and products, changing their binding energies producing pronounced alterations in catalytic performance. To this end, strengthening in the bonds of the metal—electron acceptor adsorbates and weakening in the bonds of the metal—electron donor adsorbates are resulted, which are accompanied by alterations in the activation energies of the reactions between them, leading to dramatic changes of the intrinsic catalytic performance (activity and/or selectivity). In particular, in emissions control catalysis processes involving NO<sub>x</sub> reduction, the promotion of the dissociative chemisorption of the NO molecules, which is a key reaction initiating step in deNO<sub>x</sub> processes, facilitated by the alkali-induced strengthening of the PGM–NO and the accompanied weakening of the N–O bond of the adsorbed NO molecules, convincingly interpret the enormous effective promotion of both deNO<sub>x</sub> activity and N<sub>2</sub>-selectivity offered via electropositive promotion of these catalytic systems.

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in the field, publishing a number of papers that are included and analysed in the present review. All authors read and approved the final version of the manuscript.

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