

# Strong promotional effects of Li, K, Rb and Cs on the Pt-catalysed reduction of NO by propene

M. Konsolakis, I.V. Yentekakis\*

*Department of Chemical Engineering, University of Patras and Institute of Chemical Engineering and High Temperature Chemical Processes (ICE/HT-FORTH), 26500 Patras, Greece*

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## Abstract

The catalytic activity and selectivity of Pt dispersed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the reduction of NO by propene is promoted extremely strongly by Li, K, Rb and Cs alkalis in a wide temperature range ca. 450–800 K. Remarkable and unprecedented effects on both activity and selectivity are found. The best promotion effects are achieved by Rb-promotion, for which rate increases as high as 420-, 280- and 25-fold are obtained for the formation rates of N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O, respectively, in comparison with the performance of un-promoted (alkali-free) Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. From the other hand, the selectivity towards N<sub>2</sub> is improved from ~20% over the alkali-free unpromoted Pt catalyst, to >90% over the optimally alkali-promoted catalyst. These effects are understandable in terms of the effect of alkali promoter on the relative adsorption strengths of reactant species. Alkali promotes the adsorption, and consequently the dissociation, of electronegative adsorbates (NO) and inhibits the adsorption of electropositive adsorbates (propene), on a catalyst surface predominantly covered by propene and its fragments. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Alkali; Lithium; Potassium; Rubidium; Cesium; Platinum; NO; Propene; Promotion

## 1. Introduction

Promotion of the catalytic properties of Pt-group metals for reactions of high environmental significance, such as the reduction of NO by hydrocarbons or by CO has been a long sought goal in environmental catalysis. Recent reviews of the field reveal the importance of the subject and the urgency with which advances are sought [1–3]. The targets of these promotion strategies are primarily (i) the reduction of noble metal loading required in three-way catalytic converters (TWC) and industrial catalytic systems which are currently used to control the emissions

of automotive and stationary combustion processes, respectively, (ii) the reduction or the replacement of the usage of Rh because of its scarcity in comparison with Pt and Pd, (iii) the development of new catalyst formulations sufficiently active and selective for the proposed process capable to meet the continuously increased requirements for a clean environment. Selectivity towards N<sub>2</sub> formation rather than N<sub>2</sub>O is an important index of catalyst performance, since N<sub>2</sub>O is a powerful greenhouse gas, which also contributes to stratospheric ozone depletion [4]. Although N<sub>2</sub>O emission is not yet regulated by legislation, this is unlikely to remain the case.

Efforts thus far on improving the catalytic properties of Pd and Pt for reactions relevant to three-way catalytic chemistry can be summarized as follows:

\* Corresponding author. Fax: +30-61-993255.  
E-mail address: yyentek@iccht.forth.gr (I.V. Yentekakis).

1. Doping the catalyst supporting material with additives (e.g. MoO<sub>3</sub> or WO<sub>3</sub> [5,6], CeO<sub>2</sub>, Na<sub>2</sub>O or K<sub>2</sub>O [7], La<sub>2</sub>O<sub>3</sub> [8–10]) or by using supports other than  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (e.g. YSZ, TiO<sub>2</sub>, doped-TiO<sub>2</sub> [11,12]). These efforts have indeed improved significantly the activity and selectivity of Pd and Pt for NO reduction to N<sub>2</sub>.
2. Using direct promoters, i.e. materials in direct contact and thus, in direct interaction with the catalyst active phase. These catalysts are usually prepared by simultaneous or subsequent impregnation of the catalytic active phase and of the promoter. Alkalis and alkaline earth are the first in the list of such promoting efforts [13–20].
3. Applying electrochemical promotion (EP) on catalyst films interfaced with solid electrolytes [21–23]. This method of promotion is based on the use of solid electrolytes as reversible in situ promoter donors or poison acceptors to affect the catalytic properties of metals interfaced with them [24–26]. The usage of EP overcomes some existed limitations on the understanding the exact role of promoters in heterogeneous catalysis since it provides a novel in situ reversible and highly controllable means of catalyst promotion [25,26]. These limitations are primarily due to the need of using ultra high vacuum conditions for investigating the role of promoters in chemisorption on catalyst surfaces [27].

Recently, we used EP to investigate the efficacy of Na as a promoter of Pt for reactions of environmental importance, such as CO oxidation [21] and NO reduction by CO [22] and by propene [23]. Most recently EP was also demonstrated on a base metal catalyst (Na-promoted Cu) for the NO+CO reaction [28]. It was shown in all these studies that Na supplied electrochemically from a  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> solid electrolyte, a Na<sup>+</sup> ion conductor, strongly affects both catalytic activity and selectivity of all the above reactions [21–23,28]. In addition to this practical importance we gain further basic knowledge regarding the understanding of the role and the way of action of alkalis on Pt-group metal surfaces. These findings were then applied to the design conventional dispersed catalysts. The achievements were more striking:

1. *For Palladium:* Na-induced increases in reaction rate of the reduction of NO by propene *by up to an order of magnitude*, as well as significant enhancement in N<sub>2</sub> selectivity from a value of about

70% over Na-free (unpromoted) Pd/YSZ to values as high as 95% over optimally promoted Pd/YSZ catalyst [18].

2. *For Platinum:* Remarkable and unprecedented effects on both activity and selectivity induced by Na during the NO+C<sub>3</sub>H<sub>6</sub> reaction over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Activity enhancement *of two orders of magnitude* and large increases in N<sub>2</sub> selectivity from ~20% over the un-promoted Pt to values >95% over optimally Na-promoted Pt was achieved. In effect Pt and Pd was induced by Na promotion to behave like Rh for the dissociation of NO molecules.

Close similarities were found between EP promoted catalysts and conventionally promoted highly dispersed catalysts [19,23,29]. These findings enabled us to propose a specific model for Na-promotion involving Na-induced increase in the strength of Pt-NO chemisorption bond accompanied by a weakening of the N–O bond, thus, facilitating NO dissociation. A similar basis for the present investigation has been laid.

Here we report on the promotional effect of all the rest alkalis, i.e. Li, K, Rb and Cs, on the catalytic performance of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the reduction of NO by propene. All alkalis induce dramatic enhancements on both activity and selectivity, the superior behaviour, however, exhibited by Rb-promotion.

## 2. Experimental

The catalyst used in this study was Pt highly dispersed over a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier, dosed by several loadings of alkali (Li, K, Rb or Cs) promoter. The preparation procedure involved two subsequent impregnation steps as follows. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (Alfa Products) was first impregnated in a solution of H<sub>2</sub>PtCl<sub>6</sub> (Alfa Products) with appropriate concentration so as to yield 0.5% Pt metal loading. After drying, but before thermal decomposition of the active metal precursor, the suspension was impregnated in appropriate solutions of LiNO<sub>3</sub>, KNO<sub>3</sub>, RbNO<sub>3</sub> or CsCl to produce samples with a range of alkali loadings. The suspensions were initially dried at 353 K and then overnight at 383 K. The resulting samples were heated for 1 h in flowing He (100 cm<sup>3</sup>/min) at 673 K, followed by H<sub>2</sub> reduction for 1 h at 673 K in a hydrogen flow of 100 cm<sup>3</sup>/min.

Table 1  
Properties of the alkali-promoted 0.5 wt.% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts<sup>a</sup>

Promotion	Catalyst code	Alkali-loading (wt.%)	H <sub>2</sub> uptake (cm <sup>3</sup> STP/g)	Dispersion (%)
No promotion	Alkali-free unpromoted Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0	0.085	30
Li	Li-0.16	0.16	0.130	45
	Li-0.47	0.47	0.115	40
	Li-0.78	0.78	0.230	80
	Li-1.25	1.25	0.040	14
	Li-1.6	1.6	0.060	20
	Li-4.7	4.7	0.040	14
K	K-0.9	0.9	0.280	98
	K-2.7	2.7	0.220	77
	K-4.4	4.4	0.055	19
	K-7.1	7.1	0.037	13
	K-8.8	8.8	0.037	13
Rb	Rb-1.9	1.9	0.055	19
	Rb-5.8	5.8	0.300	100
	Rb-9.7	9.7	0.043	15
	Rb-15.5	15.5	0.026	9
Cs	Cs-3	3.0	0.205	71
	Cs-9	9.0	0.090	31
	Cs-15	15.0	0.076	26
	Cs-24	24.0	0.082	29

<sup>a</sup> All the above surface characterization measurements refer to used catalysts (i.e. catalysts treated for 5 days at reaction conditions).

Twenty Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different Li, K, Rb, or Cs loadings were produced by this route (Table 1).

Before measurements were taken, the catalysts were operated for 1 day in air and 5 days in a reactive gas mixture at 723 K to eliminate possible residue from the metal precursor and to ensure stable operation (i.e. metal crystallite stabilization resulting from reaction or thermal sintering). Then, active Pt areas were measured via H<sub>2</sub> chemisorption at 298 K, after reduction in H<sub>2</sub> at 623 K for 1 h and degassing at 673 K for 1 h. The hydrogen to metal ratio (H/M) was calculated by assuming a 1:1 hydrogen metal stoichiometry. The H<sub>2</sub> uptakes were determined by extrapolation of the 'plateau' portion (~10–40 Torr) of the isotherms, as described by Benson and Boudart [30]. The BET surface area of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was measured by N<sub>2</sub> adsorption at 77 K and found to be 90 m<sup>2</sup>/g. Relevant data are summarised in Table 1. It is worth noting that catalysts prepared by the above procedure exhibit a great variation in dispersion with respect to alkali loading. These effects are discussed in Section 3.

Reactants were Air Liquide certified standards of 10% NO in He and 10% propene in He. These

were further diluted in ultrapure He (99.999%) and supplied to the reactor at 1 bar. Catalyst testing was performed in a fixed bed, single pass, plug flow reactor, consisting of a 0.4 cm i.d. quartz tube. The total gas flow rate was high, typically 80–300 cm<sup>3</sup>/min, in order to minimize conversion of reactants and to eliminate mass and heat transfer effects during acquisition of the kinetic (turnover frequency) data. The absence of intraparticle and interparticle diffusional effects was experimentally confirmed by variation of catalyst particle size and gas flow rate. NO and C<sub>3</sub>H<sub>6</sub> conversions were typically in the range 10–15% in experiments where kinetic data were acquired, although in a few cases conversions up to 25% were used. Catalyst loadings were typically about 8 mg (grain size 180–250  $\mu$ m), the sample being diluted further by admixture with ~80 g 100–325 mesh  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (alpha products). The catalyst bed was held between plugs of quartz wool and a K-thermocouple was located in the centre of the bed. No reaction was observed over quartz wool for temperatures up to 773 K.

The apparatus consisted of a feed unit and an analysis unit utilizing a combination of on-line gas

chromatography (Shimadzu-14B) with on-line CO<sub>2</sub>-NDIR spectroscopy (Fisher–Rosemount, Binos-100 NDIR CO<sub>2</sub> Analyzer) for the analysis of reactants and products. Separation of N<sub>2</sub> and NO was achieved in a molecular sieve 5A column at 353 K while CO<sub>2</sub>, N<sub>2</sub>O, and C<sub>3</sub>H<sub>6</sub> were separated using a porapak-N column at the same temperature.

### 3. Results

#### 3.1. Effect of alkali loading on turnover activity of Pt

Fig. 1 depicts the effect of Li (Fig. 1a), K (Fig. 1b), Rb (Fig. 1c) and Cs (Fig. 1d) loading on N<sub>2</sub>, CO<sub>2</sub>

and N<sub>2</sub>O turnover formation rates (TOF: molecules of product per surface Pt atom per second), as well as the corresponding behaviour of the selectivity towards N<sub>2</sub>, defined as

$$S_{N_2} = \frac{TOF_{N_2}}{TOF_{N_2} + TOF_{N_2O}} \quad (1)$$

For reasons of comparison the [NO]=1.3% and [C<sub>3</sub>H<sub>6</sub>]=0.6% concentration values chosen here mimic the conditions used in our earlier work including that on electrochemical promotion by sodium.

The results very clearly show a pronounced promotion by all four alkalis of both activity and selectivity, the extent of which is strongly dependent on the alkali loading. Promotion is maximized for a Li content

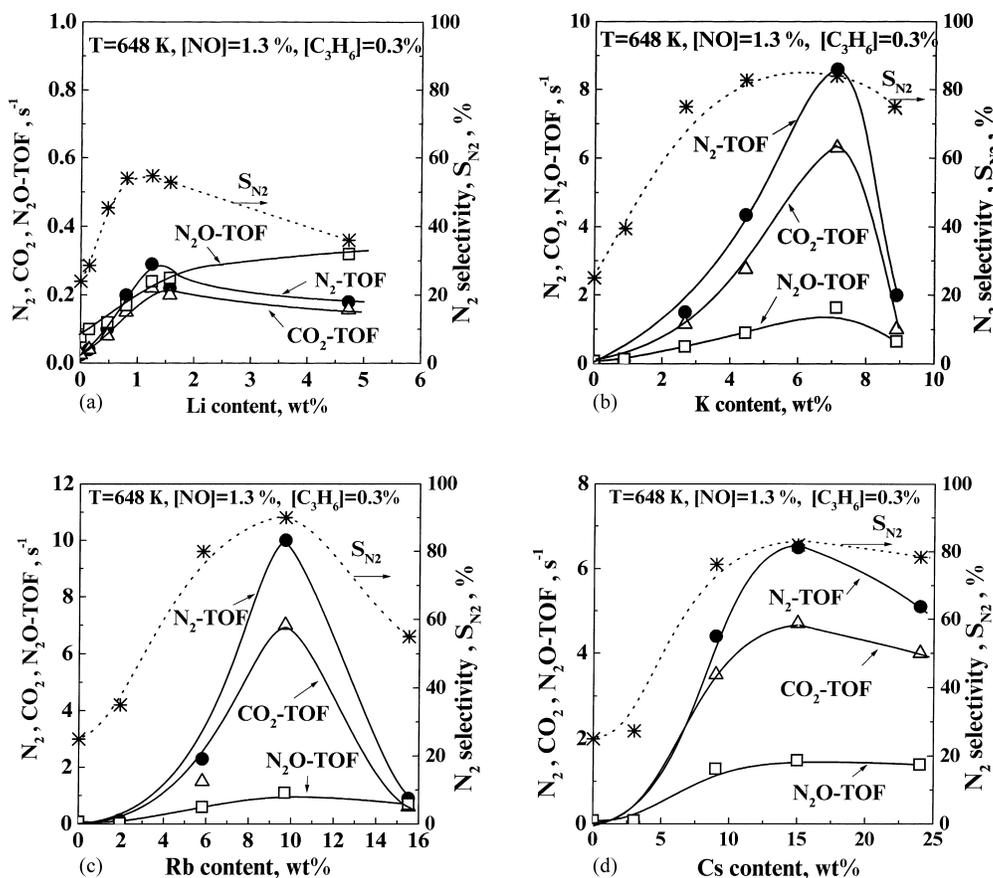


Fig. 1. The effect of Li (a), K (b), Rb (c) and Cs (d) content of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst on the turnover (TOF) formation rates of N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O and on N<sub>2</sub>-selectivity, for fixed temperature and reactant concentrations. T=648 K, [NO]=1.3%, [C<sub>3</sub>H<sub>6</sub>]=0.3%; concentrations refer to reactor outlet. For reasons of comparison, the alkali-free (unpromoted) Pt turnover rates are  $TOF_{N_2}^0=0.024\text{ s}^{-1}$ ,  $TOF_{CO_2}^0=0.025\text{ s}^{-1}$ ,  $TOF_{N_2O}^0=0.077\text{ s}^{-1}$ .

Table 2

Maximum  $\rho$  values achieved for alkali-promoted 0.5 wt.%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts at [NO]=1.3%, [C<sub>3</sub>H<sub>6</sub>]=0.3% and T=648 K

Catalyst code	Max $\rho_{\text{N}_2}$ value	Max $\rho_{\text{CO}_2}$ value	Max $\rho_{\text{N}_2\text{O}}$ value	References value
Li-1.25	11	9	4	This work
Na-4.2	290	200	7	[19]
K-7.1	358	252	21	This work
Rb-9.7	417	280	26	This work
Cs-15	250	188	30	This work

of 1.25 wt.% (catalyst Li-1.25, Table 1), a K content of 7.1 wt.% (catalyst K-7.1, Table 1), a Rb content of 9.7 wt.% (catalyst Rb-9.7, Table 1) and a Cs content of 15.0 wt.% (catalyst Cs-15, Table 1). We designate hereafter the above catalysts as the ‘optimally promoted’ catalysts because they maximize both activity and selectivity. Further increase in the alkali loading (beyond to its optimal value) leads to an inhibition of the rates, thus, producing a ‘volcano’ type behaviour as a function of the alkali content of the catalyst.

The rate enhancement ratio,  $\rho$ , defined as

$$\rho = \frac{\text{TOF}(\text{on alkali - promoted Pt})}{\text{TOF}^0(\text{on alkali - free unpromoted Pt})} \quad (2)$$

exhibits maximum values as high as  $\rho_{\text{N}_2} \sim 420$ ,  $\rho_{\text{CO}_2} \sim 280$ ,  $\rho_{\text{N}_2\text{O}} \sim 25$  for the formation rates of N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O, respectively, in the case of Rb-promotion. K and Cs-promotion offer a similar up to two orders of magnitude enhancement in reaction rates, while Li-promotion is less pronounced (up to one order of magnitude enhancement in rates). Maximum  $\rho$  value data are summarized in Table 2.

The unpromoted alkali-free catalyst exhibits a very low selectivity towards N<sub>2</sub> of the order of 25% (Fig. 1) under the conditions used. This illustrates the relatively poor activity of Pt for the dissociative chemisorption of NO. However, small addition of alkalis causes extensive NO dissociation, leading N<sub>2</sub> selectivity to very high (up to 90%) values (Fig. 1). There is again an optimum loading for each alkali promoter which maximizes the selectivity and which coincide with the loading exhibited the optimal rate enhancement (Fig. 1). However, catalysts with alkali loadings beyond to the observed optimal levels continue to exhibit high N<sub>2</sub> selectivity in comparison with the unpromoted alkali-free Pt.

### 3.2. Effect of NO concentration

Fig. 2 shows the effect of NO concentration on the N<sub>2</sub> (a), CO<sub>2</sub> (b), N<sub>2</sub>O (c) and turnover formation rates

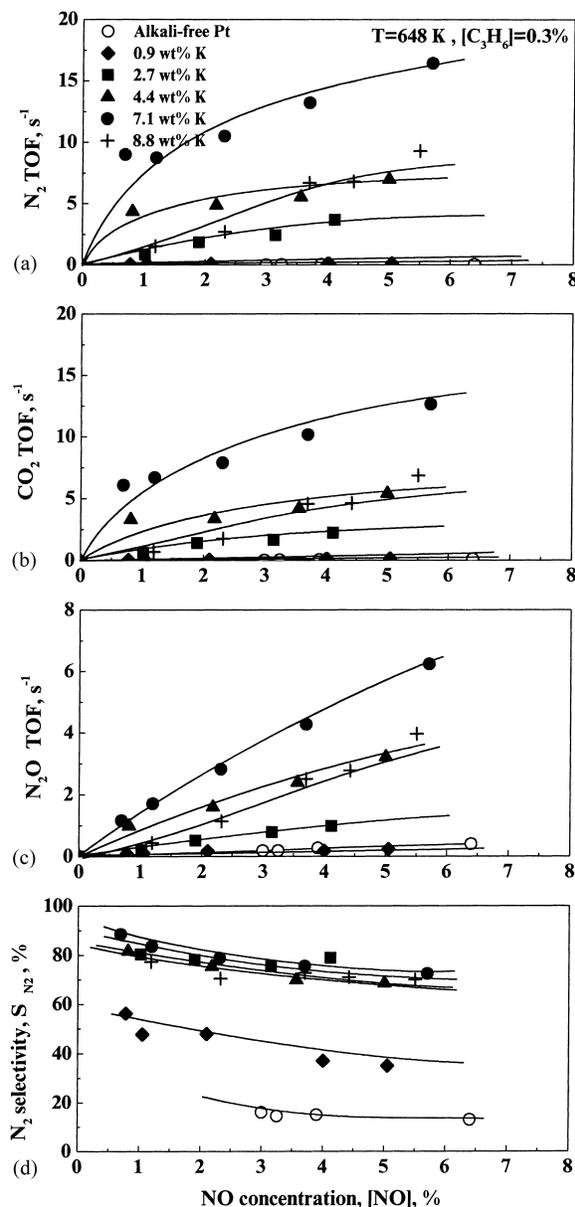


Fig. 2. The effect of NO concentration on the turnover (TOF) formation rates of N<sub>2</sub> (a), CO<sub>2</sub> (b) and N<sub>2</sub>O (c) and on N<sub>2</sub>-selectivity (d) for K-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. T=648 K, [C<sub>3</sub>H<sub>6</sub>]=0.3%; concentrations refer to reactor outlet.

and on  $N_2$ -selectivity (d) for the case of K-promoted catalysts. Similar results were found for Li, Rb and Cs promotion. However, for the sake of brevity, these data are not depicted here. The alkali-induced enhancement on reaction rates and on selectivity is occurred over the whole range of NO concentrations investigated, the extent of enhancement is strongly dependent on the alkali loading. Under all NO concentrations, the best performance is again achieved with optimally promoted catalysts K-7.1 (Fig. 2), Li-1.25, Rb-9.7 and Cs-15 for the case of K, Li, Rb and Cs promotion, respectively.

It is also worth-noticing that the reaction exhibits positive-order dependence on  $[NO]$  and no rate maxima are found within the range of accessible experimental conditions (Fig. 2). For a reaction of Langmuir–Hinshelwood nature, as the  $NO + C_3H_6$  on Pt is [23], this trend strongly supports the view that under all conditions used in this study, the adsorption of propene and its fragments on the catalyst is much stronger than that of NO.

### 3.3. Effect of temperature

Fig. 3 shows the effect of catalyst temperature on NO conversion ( $X_{NO}$ ) for the case of Li (a), K (b), Rb (c) and Cs (d) promotion, whereas Fig. 4 illustrates the corresponding behaviour of the selectivity towards  $N_2$ . The reactor inlet conditions were kept constant, i.e. 1000 ppm NO, 1000 ppm propene at a total flow rate of  $80 \text{ cm}^3 \text{ STP/min}$ . These concentrations are close to those encountered in practical applications and commonly used in the literature as reference conditions. In every case, the amount of catalyst used was  $8(\pm 0.2) \text{ mg}$ . It can be seen (Fig. 3) that the alkali-free Pt never exceeds  $\sim 5\%$  NO conversion and is almost inactive over the whole temperature range. However, K, Rb and Cs-promotion very substantially improved the conversion performance of Pt. For the case of Li-promotion this effect is less pronounced. In particular, the optimally K-promoted catalyst (K-7.1) exhibits a 50% NO conversion temperature,  $T_{50}$ , of  $\sim 550 \text{ K}$  and reaches 100% NO conversion at  $T_{100} \geq \sim 600 \text{ K}$ . Corresponding  $T_{50}$  and  $T_{100}$  values for Rb and Cs promotion are  $T_{50} \sim 580 \text{ K}$  and  $T_{100} \geq \sim 650 \text{ K}$  (catalyst Rb-9.7), and  $T_{50} \sim 580 \text{ K}$  and  $T_{100} \geq \sim 700 \text{ K}$  (catalyst Cs-15), respectively.

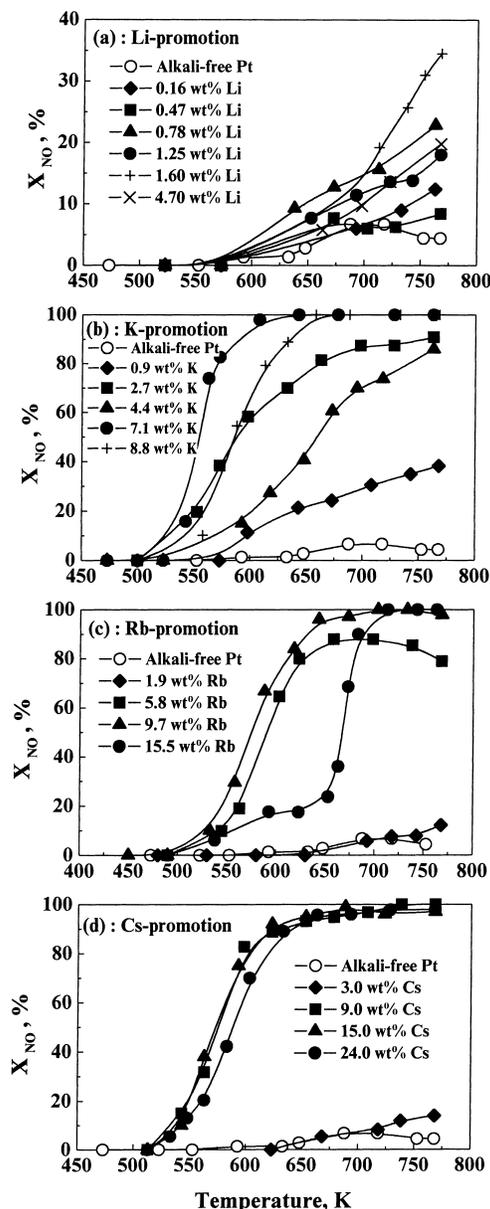


Fig. 3. The conversion of NO to various products for (a) Li-, (b) K-, (c) Rb- and (d) Cs-promoted Pt/ $\gamma$ - $Al_2O_3$  catalysts, as a function of temperature at constant reactor inlet conditions:  $[NO]=1000 \text{ ppm}$  and  $[C_3H_6]=1000 \text{ ppm}$ ; total flow rate  $F=80 \text{ cm}^3/\text{min}$ ; catalyst weight  $8(\pm 0.2) \text{ mg}$ .

Among other things, conversion is significantly affected by the dispersion of the catalyst. As noted in Section 2, the variation in dispersion with alkali loading is quite striking. In general, low or moderate load-

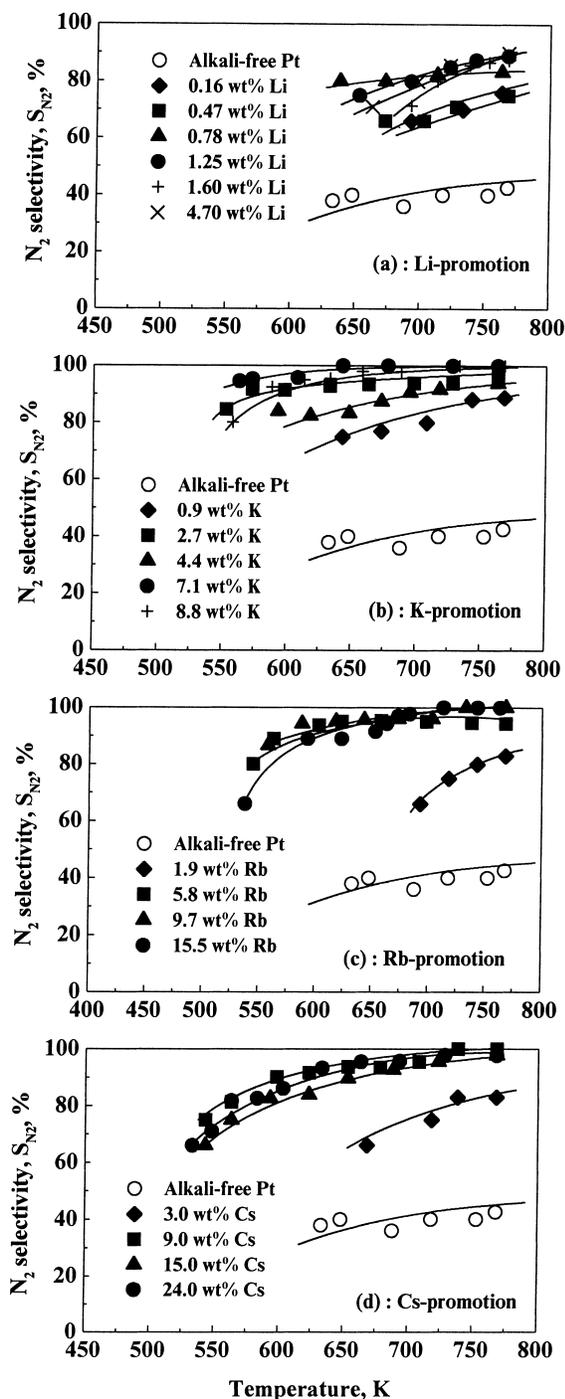


Fig. 4. The selectivity towards  $N_2$  for (a) Li-, (b) K-, (c) Rb- and (d) Cs-promoted  $Pt/\gamma-Al_2O_3$  catalysts, as a function of temperature. Conditions as in Fig. 3.

ings of alkali lead to substantial increase in Pt dispersion (Table 1). There are earlier reports in which reference is made to the effect of alkalis in increasing the dispersion of supported Pt-group metal catalysts [31,32]. In neither case were the authors able to offer any convincing explanation for the origin of this effect. We agree with these earlier workers that further study is necessary in order to elucidate this phenomenon. However with respect to turnover frequency, the optimally loaded catalysts, namely, Li-1.25, K-7.1, Rb-9.7 and Cs-15, also offer (in most cases) the optimal conversion (Fig. 3). In particular, the optimally promoted K-7.1, Rb-9.7 and Cs-15 catalysts indeed offer the best conversion in comparison to the remaining catalysts in their group (Fig. 3b–d), although the profiles of Rb-5.8 and Cs-9 are close to that of the corresponding optimally promoted catalysts (Fig. 3c and d). In the case of Li-promotion the situation is more complex. Although the optimally promoted catalyst (Li-1.25) exhibits significantly higher conversion in comparison to the unpromoted catalyst, Li-0.78 and Li-1.6 appear to have slightly better performance at low and high (>700 K) temperatures, respectively. Such anomalies in conversion relative to turnover frequency are due to the significantly different dispersions of the various catalysts depicted in Fig. 3. However, taking into account that the optimally loaded catalysts exhibit similar or lower dispersion in comparison to the unpromoted catalyst, we can conclude that the principal effect of alkali on conversion performance may again attributed to modification by the promoter of the surface chemistry of the metal.

In accord with Figs. 1 and 2, the alkali-free catalyst exhibits very low  $N_2$ -selectivity over the whole temperature range studied, whereas all the rest alkali promoted catalysts attain very high  $S_{N_2}$  (Fig. 4).

#### 4. Discussion

The present results show that Li, K, Rb and Cs addition on Pt can markedly affect its catalytic properties during the  $NO+C_3H_6$  reaction. Similar behaviour has been reported for the  $Pt/NO+C_3H_6$  system when Na was used as the promoter species [19]. Although, each alkali appears its own promotion characteristic values, i.e. enhancement ratio ( $\rho$ ) and optimal loading, it is obvious that the overall promotion picture is

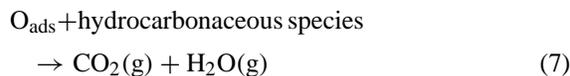
similar. The similarities include the overall kinetic behaviour and the dependence of activity and selectivity on alkali loading as summarized below:

1. In all cases a rapid exponential increase in reaction rates with alkali content is followed by inhibition (Fig. 1). This ‘volcano’ type behaviour of the promotion indicates an optimal promoter loading for each alkali for the catalyst-reaction system under investigation.
2. All alkalis very strongly enhance the formation rates of  $N_2$  and  $CO_2$ , while the effect on the  $N_2O$  formation rate is much less pronounced (Figs. 1 and 2). Thus, the addition of alkali has always a beneficial effect on the selectivity towards  $N_2$ .
3. In all cases the selectivity follows a similar to rate ‘volcano’ behaviour passing through a maximum which corresponds to the optimally promoted catalyst (Fig. 1).

It therefore seems reasonable to propose that similar phenomena control the promotion mechanism induced by each alkali, so that the mode of action of alkali modifier may be justified under the same considerations, similar to those proposed in our earlier work [23]. Alkali addition to the catalyst results from acceleration of the key reaction-initiating step, i.e. dissociation of adsorbed NO. As the catalyst is dosed by alkali, the electronic effect of the latter on co-adsorbed NO strengthens the Pt–NO bond and weakens the N–O bond. This interpretation has been substantiated by the theoretical model of Lang et al. [33] as well as by the experimental work of Harkness and Lambert [34] on the chemisorption of NO on Na-dosed Pt{1 1 1} single crystal model catalysts. They are caused by the electric field of the alkali which lowers the energy of the  $\pi^*$  orbital in the adjacent diatomic molecule (NO). Increased electron density in the  $\pi^*$  orbital strengthens the Pt–NO bond, thus, increasing NO coverage and facilitates dissociation of the N–O bond.

We may rule out the possibility that alkali acts ‘tying up’ residual chlorine based on our earlier detailed studies of this very point [18]. In that work, we demonstrated convincingly that the use of chlorine containing precursors produced results that were essentially identical to those obtained when chlorine-free precursors were used. Therefore, we can argue that the observed effects of alkali are indeed due to electronic effects on the platinum chemistry and not simply due to mopping-up of residual chlorine.

In accord, the formation of nitrogen containing products, and the variations in  $N_2/N_2O$  selectivity may be rationalised in terms of the following reaction scheme:



Rate enhancement is therefore due to (i) increased coverage of NO (reaction 3) in the presence of strongly adsorbing propene and (ii) triggering of NO dissociation, which is the reaction-initiating step (reaction 4). The enhancement of NO adsorption (an electronegative adsorbate) and the inhibition of propene adsorption (an electropositive adsorbate) by alkalis is the key point. These effects act to increase both the NO coverage and its degree of dissociation (reactions 3 and 4). Once  $O_{ads}$  is produced it is scavenged by adsorbed hydrocarbonaceous species (reaction 7), accompanied by  $N_{ads}$  recombination or reaction with  $NO_{ads}$  to yield  $N_2$  and  $N_2O$ , respectively (reactions 5 and 6).

The rates of production of  $N_2$  and  $N_2O$ , and consequently  $N_2$ -selectivity (Eq. (1)) depend on the extent of NO dissociation (reaction 4) which is followed by the elementary reactions (5) and (6). The observed increase in the  $N_2$ -selectivity upon alkali addition is a consequence of increased NO dissociation (due to alkali) i.e. a decreased amount of molecular NO, and an increased amount of atomic N on the surface. Both factors favour reaction (5) over reaction (6), leading to higher  $N_2$ -selectivity (Figs. 1, 2 and 4).

An alternative route for nitrogen formation is via  $N_2O_{ads}$  decomposition. However, most authors consider that this reaction is relatively slow under typical conditions, and that the process, therefore, makes only a negligible contribution to the nitrogen formation rate [35,36].

In a recent detailed kinetic study of the  $NO + C_3H_6$  reaction over Pt films [23], we have shown that under similar conditions, the reaction obeys Langmuir–Hinshelwood (L–H) type kinetics with characteristic

rate maxima reflecting competitive adsorption of the two reactants. These rate maxima occurred at very low  $[C_3H_6]:[NO]$  ratios, typically  $<0.08$ . That is very high partial pressures of NO relative to  $C_3H_6$  are necessary in order to achieve a comparable coverage of both reactants on the Pt surface, thus, maximising the rate [23]. This points to a weaker adsorption of NO on the metal surface relative to  $C_3H_6$ . As a consequence, the Pt surface is predominantly covered by propene and propene-derived species under a wide range of reaction conditions. Since the conditions used here refer to relatively high values of  $[C_3H_6]:[NO]$  ratio, we argue that the chemisorption of propene is much more pronounced than that of NO under all experimental conditions of this study. This is further corroborated by the positive order variation of the reaction rates upon increasing NO concentration, illustrated in Fig. 2. The above consideration is in accord with the adsorption enthalpy of propene on Pt [37] and the results of Burch and Watling [38], which show (in agreement with the present results) that unpromoted Pt/ $\gamma$ - $Al_2O_3$  is almost ineffective for the reduction of NO by propene. Propene and its dissociation products are strongly adsorbed reducing the number of catalytically active sites.

Very recently we demonstrated [39] that the beneficial effects of alkali promotion persists in the presence of oxygen. Specifically we showed that very substantial gains in both activity and selectivity were achievable when a Na-promoted Pt/ $\gamma$ - $Al_2O_3$  catalyst was operated in simulated exhaust gas containing 1% oxygen [39].

At sufficiently high alkali loadings (beyond to the observed optimal levels), Pt/ $\gamma$ - $Al_2O_3$  catalyst exhibits inhibition of its performance (Fig. 1). This is entirely analogous to the corresponding electrochemical promotion data for NO+propene [23] and maybe reflects the accumulation of alkali surface compounds which blocks the surface to adsorption of reactants. Previous XPS studies involving in situ transfer of promoted and poisoned ex-reactor electrochemically promoted catalysts to the spectrometer analysis chamber showed [23] that in the case of NO+ $C_3H_6$  the Na-containing promoting (or poisoning) phase consists principally of a mixture of  $NaNO_2$ ,  $NaNO_3$  and  $NaCO_3$ . Most recently, Lambert and co-workers [28,40] attributed the rate inhibition primarily to the formation of thick (three-dimensional) films of

alkali carbonate that cover the surface and are stable at elevated reaction temperatures. They shown that such alkali carbonates are easily formed in the present of carbon-rich molecules, e.g. propene [40]. On the other hand they showed [28] that when the promoter phase consists exclusively of alkali nitrates, submonolayer films of this component would be expected to be stable [41] at used reaction temperatures. In contrary, thick films of alkali nitrates cannot be built up at the used reaction temperatures because of their volatility. As a result the authors concluded that strong poisoning of alkali nitrates does not occur and that submonolayer quantities of such components survive at reaction temperature promoting the catalyst [28].

In view of the above, and given the marked similarities in behaviour of the electrochemically and classically promoted systems, we propose that under reaction conditions formation of alkali nitrates and carbonates also occurs in the present case. If too much alkali is present in the catalyst formulation it is reasonable to suppose that active sites become covered with these alkali compounds, thus, poisoning the system.

It is interesting to note that in the case of all four alkalis, the optimally promoted catalysts correspond to approximately the same molar loading of alkali. In particular, 1.8, 1.82, 1.14 and 1.13 mmol of alkali/g of catalyst for Li, K, Rb and Cs, respectively. Note however, that the loading of the heavier alkalis although similar and significantly lower than that of the lighter alkalis. If one makes the assumption that the distribution of alkali between the metal and support phases is essentially the same in every case, the following tentative conclusions may be drawn.

1. The results support our view that it is the electronic effect of the alkali ions which is responsible for NO dissociation. To first approximation the extent of this effect depends on the number density of the alkalis species on the metal surface and not on the their chemical identity.
2. However the chemical identity of the alkali does appear to make some difference. The fact that the heavier alkalis appear to be somewhat more effective than the lighter alkalis is fully consistent with the theoretical model of Lang et al. [33] which predicts exactly this. The larger the alkali cation the greater the effect its electric field has on an adsorbed NO molecule.

In a recent study, we showed no beneficial effects of Na addition on the Pd-catalyzed reduction of NO by an alkane (CH<sub>4</sub>) [42]. Indeed, we found that for all loadings, Na induces only poisoning for the NO+CH<sub>4</sub> reaction. Although these results stand in revealing contrast to the present results, i.e. to the strong promotional effect of alkalis in the reduction of NO by propene, they received a consistent explanation [42]. The weak interaction of alkanes with the metal surface in contrast to the strong of alkenes was the key point for the interpretation [42]. Vannice and co-workers showed that other nonmetallic catalytic systems are promising for the NO+CH<sub>4</sub> reaction [43–46]. They also showed that Li-promotion of such materials (e.g. MgO) has a beneficial effect (up to five fold increase) on the rate of NO+CH<sub>4</sub> reaction [43]. A combination of the base materials of our catalysts with the materials proposed by Vannice and co-workers may produce new catalyst formulations capable for the effective simultaneous control of both kind of hydrocarbons (alkanes and alkenes) and nitric oxide form emissions of combustion processes.

## 5. Conclusions

1. The catalytic reduction of NO by propene over Pt exhibits strong promotion by alkalis. Superior behaviour is offered by Rb-promotion for which rate enhancement ratios as high as  $\rho_{\text{N}_2} \sim 420$ ,  $\rho_{\text{CO}_2} \sim 280$ ,  $\rho_{\text{N}_2\text{O}} \sim 25$  for the formation rates of N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O, respectively, are achievable. Rate promotion is followed by severe increase in selectivity towards N<sub>2</sub> which is improved from  $\sim 20\%$  over the alkali-free unpromoted Pt to  $>90\%$  over the optimally alkali-promoted Pt.
2. Promotion is due to the effects of alkalis on the relative adsorption strengths of reactant species. Alkali addition to the catalyst strengthens the Pt–NO bond (thus, increasing NO coverage) and weakens the N–O bond (thus, promoting NO dissociation). From the other hand it inhibits the adsorption of propene on a catalyst surface predominantly covered by propene and its fragments. These factors cause an increase of the probability of the L–H nature surface reaction and consequently lead to very pronounced promotion.

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