

## Optimal promotion by rubidium of the CO + NO reaction over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts

M. Konsolakis<sup>a</sup>, I.V. Yentekakis<sup>a,b,\*</sup>, A. Palermo<sup>c</sup>, R.M. Lambert<sup>c</sup>

<sup>a</sup> ICE/HT-FORTH, and Department of Chemical Engineering, University of Patras, 26500 Patras, Greece

<sup>b</sup> Laboratory of Physical Chemistry and Chemical Processes, Department of Sciences, Technical University of Crete, 73100 Chania, Greece

<sup>c</sup> Department of Chemistry, University of Cambridge, CB2 1EW, Cambridge, UK

Received 28 January 2001; received in revised form 10 April 2001; accepted 15 April 2001

### Abstract

The reduction of NO by CO over Rb-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts has been investigated over a wide range of temperature (ca. 200–500°C), partial pressures of reactants and promoter loadings. For purposes of comparison, K- and Cs-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were tested under the same conditions. Rubidium strongly enhanced both catalytic activity and N<sub>2</sub>-selectivity. Rate increases by factors as high as 110 and 45 for the production of N<sub>2</sub> and CO<sub>2</sub>, respectively, relative to unpromoted Pt were obtained, accompanied by substantial increase in N<sub>2</sub>-selectivity (e.g. from 24 to 82% at 350°C and [CO] = 0.5%, [NO] = 1%). Under stoichiometric conditions, Rb-promoted catalysts gave 100% conversion of both reactants with 100% selectivity towards N<sub>2</sub> at  $T \sim 350^\circ\text{C}$  and at an effective reactant contact time of only  $\sim 0.5$  s. In contrast, under the same conditions unpromoted Pt delivered  $<30\%$  conversion and poor N<sub>2</sub>-selectivity (approximately  $<40\%$ ); even at 480°C the conversion was only  $\sim 60\%$ . The observed promotional effects are ascribed to alkali-induced changes in the chemisorption bond strengths of CO, NO and NO dissociation products which lead to the observed activity enhancement and dependence of N<sub>2</sub>-selectivity on promoter loading. The effects of K-promotion mirror those of Rb-promotion, but are significantly less pronounced. Rb is the best alkali promoter. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Platinum; Rubidium-promotion; Potassium; Caesium; NO reduction; CO

### 1. Introduction

Three-way catalytic converters (TWCs) employ formulations based on Pt, Pd and Rh for the simultaneous removal of NO<sub>x</sub>, CO and hydrocarbons from automotive emissions [1–3]. Pt and Pd are very effective in oxidising CO and hydrocarbons, but substantially less effective in reducing NO<sub>x</sub> emission. Conversely, Rh is highly effective for NO dissociative chemisorption [3] and is therefore, the key component responsible for NO reduction in TWCs. On the

other hand, Pt is relatively ineffective for NO dissociation [4,5], whereas Pd exhibits strong structure and temperature sensitivity for this process [6,7].

Future legislation will require further improvements in catalytic converters especially in regard to improved light-off characteristics and more stringent NO<sub>x</sub> abatement, which accounts for the continued strenuous research activity in this field (e.g. [8–17]).

We recently, demonstrated that the catalytic performance of Pt in NO<sub>x</sub> reduction can be dramatically improved by means of electrochemical promotion (EP). Specifically, it was shown that Na supplied electrochemically from  $\beta''$ -Al<sub>2</sub>O<sub>3</sub>, a Na<sup>+</sup> ion conductor, strongly enhanced both the catalytic activity and

\* Corresponding author. Fax: +30-61-993255.

E-mail address: yentek@iceht.forth.gr (I.V. Yentekakis).

selectivity of Pt for the reduction of NO by CO [8] and by propene [9,10]. These results led us to propose a general hypothesis for the mode of promotion by alkalis of the catalytic reduction of NO. The hypothesis is based on well-understood physical principles and is supported by both independent experiments and theoretical calculations, as discussed below. In addition, our EP results led us to synthesise analogous conventional dispersed metal catalyst formulations with which we sought to deliberately exploit the effects of alkali-promotion. Using NO + C<sub>3</sub>H<sub>6</sub> as the test reaction, we showed that alkali-promotion of conventional dispersed platinum metal catalysts results in very large enhancements of both activity and N<sub>2</sub>-selectivity [11–15]: in effect Pt and Pd could be induced to behave like Rh.

Here, we show that even greater benefits can be achieved by Rb-promotion of Pt in the NO + CO reaction. The choice of rubidium as promoter was guided by a recent study, which showed that of all the alkalis Rb is the best promoter for the NO + C<sub>3</sub>H<sub>6</sub> reaction over Pt [13], with K the next most effective. Therefore, in the present case, comparison experiments with K and Cs were also carried out — these establish that Rb is the best promoter in this case too, and the implications of this are discussed.

## 2. Experimental

Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with a range of Rb loadings were prepared by a two step process as follows.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Alfa products, BET surface area  $\sim$ 90 m<sup>2</sup>/g) was first impregnated with a solution containing the appropriate concentration of H<sub>2</sub>PtCl<sub>6</sub> (Alfa products) so as to yield 0.5 wt.% Pt metal loading. The mixture

was then heated while vigorously stirred so as to achieve a paste and subsequently dried in air for 12 h at 110°C. Batches of this material were impregnated with solutions containing different concentrations of RbNO<sub>3</sub> (Alfa products). The resulting samples, after evaporation and drying, were heated for 1 h in flowing He (100 cm<sup>3</sup>/min) at 600°C, followed by H<sub>2</sub> reduction for 1 h at 400°C in a hydrogen flow of 100 cm<sup>3</sup>/min. Four Pt (Rb)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst samples were produced with 0.5 wt.% Pt and 0, 1.9, 9.7 and 15.5 wt.% of Rb (or equivalently 0, 0.23, 1.13, 1.82 mmol Rb/g<sub>cat</sub>). This will be referred to as catalysts C1, C2, C3 and C4, respectively (Table 1). By following an identical procedure, but using the relevant promoter precursor salts instead of RbNO<sub>3</sub>, three K-promoted and other three Cs-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were also prepared for comparison purposes. Finally, a control catalyst consisting of 0.5 wt.% Rh on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared by the same procedure.

Before testing and characterisation, the catalysts were pre-treated for 1 day in air and 5 days in reaction gas mixture at 450°C to ensure stable operation. Metal area measurement was then carried out by H<sub>2</sub> chemisorption at 25°C. The procedure involved reduction in H<sub>2</sub> at 300°C for 1 h followed by degassing at 400°C for 1 h prior to hydrogen chemisorption. The hydrogen to metal ratio (H/M) was calculated by assuming a 1:1 hydrogen:metal stoichiometry. H<sub>2</sub> uptakes were determined by extrapolation of the “plateau” portion ( $\sim$ 10–40 Torr) of the isotherms and relevant data for catalysts C1–C4 are summarised in Table 1. The K-promoted 0.5 wt.% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with 2.7, 4.4 and 8.8 wt.% K loadings (or equivalently 0.69, 1.13 and 2.25 mmol K/g<sub>cat</sub>) had dispersions of 77, 19 and 13% with active metal surface areas 0.77, 0.19 and 0.13 m<sup>2</sup>/g<sub>cat</sub>, respectively. The

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

Catalyst	Rb loading		H <sub>2</sub> uptake (cm <sup>3</sup> STP/g <sub>cat</sub> )	Dispersion (%)	Active metal surface area <sup>b</sup> (m <sup>2</sup> /g <sub>cat</sub> )
	(wt.%)	(mmol/g <sub>cat</sub> )			
C1	0	0	0.085	30	0.30
C2	1.9	0.22	0.055	19	0.19
C3	9.7	1.13	0.043	15	0.15
C4	15.5	1.82	0.026	9	0.09

<sup>a</sup> All measurements refer to catalysts pre-treated for 5 days at reaction conditions.

<sup>b</sup> Active metal surface area calculations based on a Pt surface atom density of  $1.53 \times 10^{19}$  atoms/m<sup>2</sup>.

Cs-promoted catalysts with 9.0, 15.0 and 24.0 wt.% Cs loadings (or 0.68, 1.12 and 1.81 mmol Cs/g<sub>cat</sub>) had dispersions of 31, 26 and 29% with active metal surface areas 0.31, 0.26 and 0.29 m<sup>2</sup>/g<sub>cat</sub>, respectively. The 0.5 wt.% Rh/γ-Al<sub>2</sub>O<sub>3</sub> catalyst had a dispersion of 48% with an active metal surface area of 1.05 m<sup>2</sup>/g<sub>cat</sub>.

A 0.4 cm internal diameter quartz tube was used as a fixed bed, atmospheric pressure reactor for catalyst testing. Catalyst loadings in the reactor were typically ~8 mg (grain size 180–250 μm), the sample being diluted further by admixture with ~80 mg 100–325 mesh α-Al<sub>2</sub>O<sub>3</sub>. Reactor output was analysed by on-line gas chromatography (Shimadzu-14B), separation of N<sub>2</sub>, NO, and CO being achieved in a molecular sieve 5 Å column, while CO<sub>2</sub> and N<sub>2</sub>O were separated using a Porapak-N column, with both columns operated at 80°C.

A high total gas flow rate was maintained during acquisition of kinetic data (100–500 cm<sup>3</sup> STP/min) in order to minimise reactants conversion and to eliminate mass and heat transfer effects. By this means, NO and CO conversions were kept below 10–15%. The absence of intraparticle and interparticle diffusional effects was confirmed by varying catalyst particle size and gas flow rate. During the measurement of conversion performance, the temperature was increased stepwise from 200 to 500°C and at each step all conditions (temperature, flow rate and inlet composition) were kept constant for 30 min before recording the data point.

### 3. Results

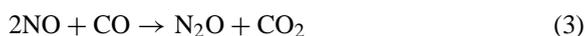
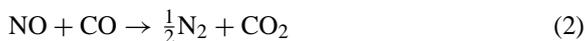
#### 3.1. Kinetic measurements

Data for N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O formation rates are expressed in terms of turnover frequencies (TOF: molecules of product per surface Pt atom per second) based on the measured active surface areas given in Table 1. Particular attention is given to the N<sub>2</sub>-selectivity S<sub>N<sub>2</sub></sub> (%), defined as

$$S_{N_2} (\%) = \frac{r_{N_2}}{r_{N_2} + r_{N_2O}} \times 100 \quad (1)$$

where  $r_{N_2}$  and  $r_{N_2O}$  are the rates of N<sub>2</sub> and N<sub>2</sub>O formation, respectively. N<sub>2</sub> and N<sub>2</sub>O were the only N containing products observed.

Based on the stoichiometry of the two parallel overall reactions that are expected to occur



the material balances implies the following relation between the rates of NO and CO consumption ( $r_{NO}$  and  $r_{CO}$ , respectively) and S<sub>N<sub>2</sub></sub>:

$$r_{NO} = r_{CO} \frac{2}{1 + (S_{N_2}/100)} \quad (4)$$

Note also that the following balance equations should hold:

$$\begin{aligned} r_{NO} &= 2(r_{N_2} + r_{N_2O}) \quad \text{and} \\ r_{CO} &= r_{CO_2} = 2r_{N_2} + r_{N_2O} \end{aligned} \quad (5)$$

All the above relationships were satisfied to within 5% by the data presented here.

#### 3.1.1. Effect of gas phase CO concentration on turnover rates for Rb-promoted catalysts

Fig. 1(a)–(c) show the kinetics of N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O formation, for the four catalysts C1–C4 as a function of CO concentration, for fixed NO concentration ([NO] = 1%) and temperature ( $T = 352^\circ\text{C}$ ). Fig. 2 shows the corresponding behaviour of the N<sub>2</sub>-selectivity. The characteristic rate maxima reflect competitive adsorption of NO and CO on the Pt surface. These maxima occur at [NO]/[CO] molar ratios > 1, indicating weaker adsorption of NO on the metal surface relative to CO under the conditions used here. Similar kinetic behaviour was pointed out by Palermo et al. [8] in an EP study of the NO + CO reaction over polycrystalline Pt-film catalysts. Note that for all catalysts, the N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O rates follow similar (Langmuir–Hinshelwood type) behaviour as [CO] is varied, with a pronounced enhancement in catalytic activity resulting from Rb addition. Note also that the [NO]/[CO] ratios at which the rate maxima occur vary significantly with Rb loading, shifting to lower values as Rb loading is increased.

The data in Fig. 2 show that in general N<sub>2</sub>-selectivity declines with increasing CO concentration. The unpromoted (Rb-free) catalyst exhibits very low selectivity towards N<sub>2</sub> in the order of 20–30% at all CO concentrations, illustrating the relatively poor activity

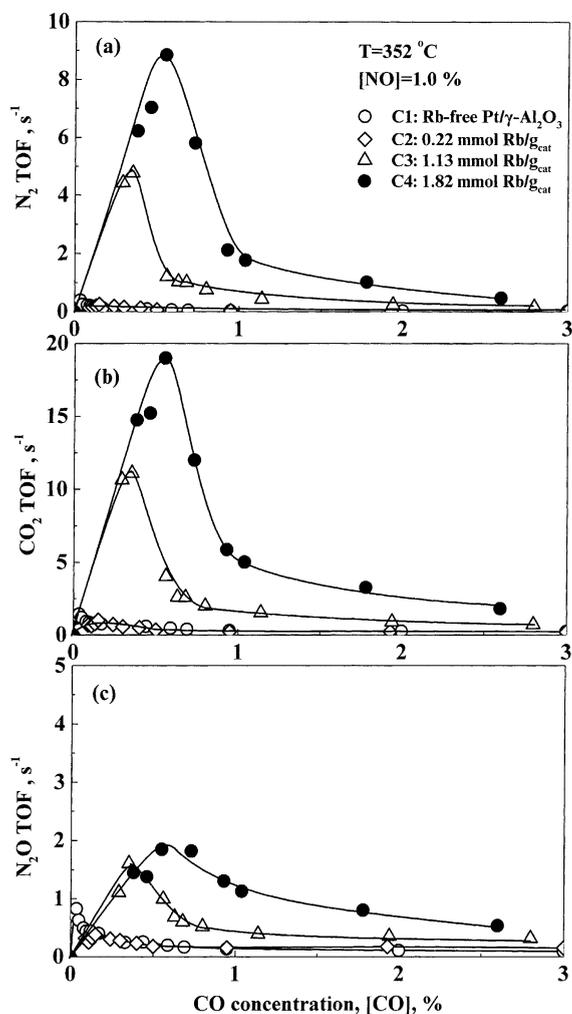


Fig. 1. Effect of CO concentration on the turnover (TOF) formation rates of  $N_2$  (a),  $CO_2$  (b), and  $N_2O$  (c), at fixed temperature and NO concentration for the four Pt/ $\gamma$ - $Al_2O_3$  catalysts of Table 1 promoted with different loadings of Rb. Conditions:  $T = 352^\circ C$ ,  $[NO] = 1\%$ . Concentrations refer to reactor outlet.

of Pt for the dissociative chemisorption of NO. Addition of Rb acts to strongly promote  $N_2$ -selectivity, yielding a gain of up to 60 percentage units for the catalyst with the highest promoter loading (catalyst C4: 1.82 mmol Rb/g<sub>cat</sub> or 15.5 wt.% Rb, Table 1).

### 3.1.2. Effect of gas phase NO concentration on turnover rates for Rb-promoted catalysts

Fig. 3(a)–(c) depict analogous results for the dependence of  $N_2$ ,  $CO_2$  and  $N_2O$  turnover rates and

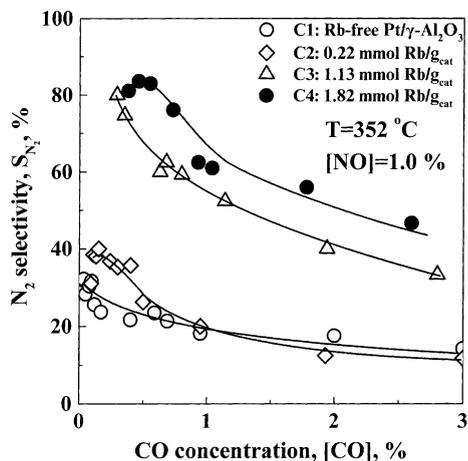


Fig. 2. Effect of CO concentration on  $N_2$ -selectivity at fixed temperature and NO concentration for the four Pt/ $\gamma$ - $Al_2O_3$  catalysts of Table 1. Conditions as in Fig. 1.

$N_2$ -selectivity at fixed  $[CO] = 1\%$  and  $T = 352^\circ C$ , as a function of NO concentration. In this case, the reaction exhibits positive-order dependence on  $[NO]$  and no rate maxima are found within the experimentally accessible range of conditions. Under all NO concentrations, the best performance is again achieved with catalyst C4 (1.82 mmol Rb/g<sub>cat</sub>). Fig. 4 shows the corresponding behaviour of  $N_2$ -selectivity with varying  $[NO]$  for the various promoter loadings. The unpromoted Rb-free catalyst exhibits the lowest selectivity towards  $N_2$  ( $\sim 20\%$ ), whereas the best selectivity is achieved by catalyst C4 which delivers  $S_{N_2} > 60\%$  over the whole range of NO concentrations studied. Comparison of the trends apparent in Figs. 1 and 3 strongly supports the view that under the conditions of this study, CO adsorption is always stronger than that of NO.

### 3.1.3. Effect of alkali loading on turnover rate and selectivity of Pt

Fig. 5a shows the effect of Rb loading on  $N_2$ ,  $CO_2$  and  $N_2O$  turnover rates and on  $N_2$ -selectivity for a fixed temperature ( $352^\circ C$ ) and reactor effluent NO and CO concentrations. The behaviour of the K-promoted catalysts is also depicted (dashed lines, open symbols). Although, promoter loading is frequently given on a wt.% basis, here we express promoter loading in terms of mmol of alkali/g of catalyst in order to facilitate comparison between Rb and K. It is apparent

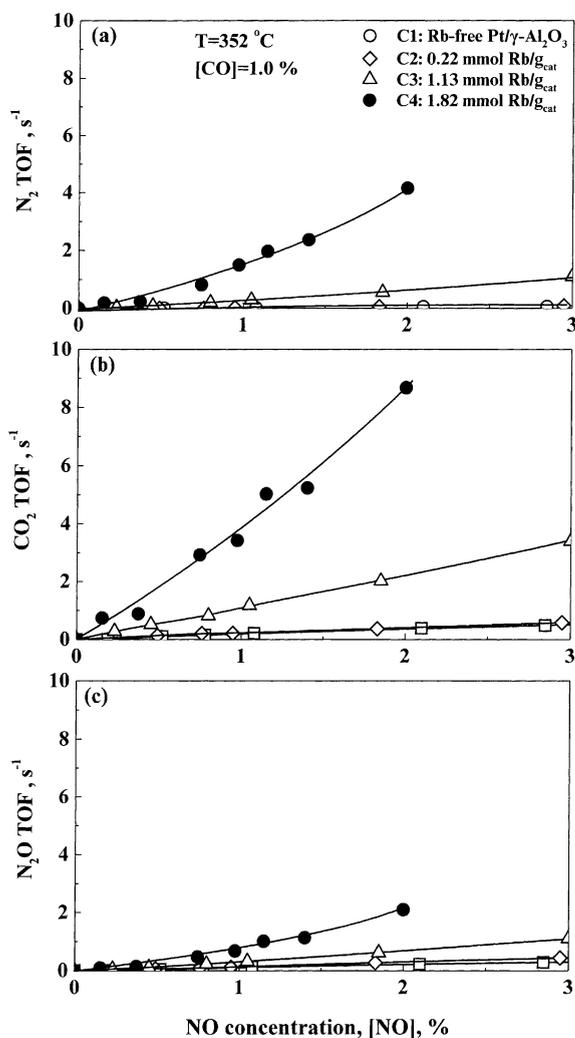


Fig. 3. Effect of NO concentration on the turnover (TOF) formation rates of  $N_2$  (a),  $CO_2$  (b), and  $N_2O$  (c), at fixed temperature and NO concentration for the four Pt/ $\gamma$ - $Al_2O_3$  catalysts of Table 1. Conditions:  $T = 352^\circ C$ ,  $[CO] = 1\%$ . Concentrations refer to reactor outlet.

from Fig. 5a, that although both alkalis exert a pronounced beneficial effect on rates and  $N_2$ -selectivity, Rb is superior to K. For a given alkali loading, Rb always outperforms. To achieve a given TOF or selectivity requires a higher molar loading of K than Rb.

It is useful to define a rate enhancement ratio  $\rho$ , as

$$\rho = \frac{\text{TOF}(\text{on alkali-promoted Pt})}{\text{TOF}^0(\text{on alkali-free Pt})} \quad (6)$$

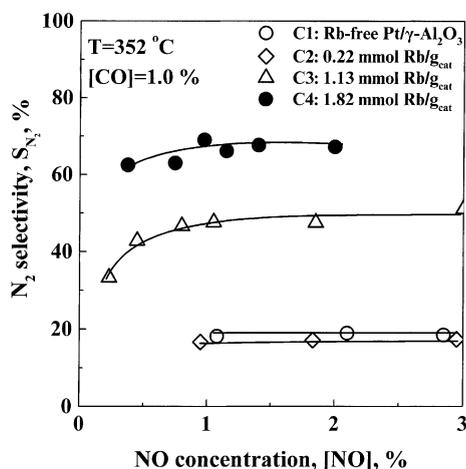


Fig. 4. Effect of NO concentration on the  $N_2$ -selectivity, at fixed temperature and NO concentration for the four Pt/ $\gamma$ - $Al_2O_3$  catalysts of Table 1. Conditions as in Fig. 3.

Fig. 5b depicts  $\rho$ -values as a function of alkali loading. In the case of Rb-promotion, the maximum  $\rho$ -values were obtained with catalyst C4:  $\rho_{N_2} \sim 110$ ,  $\rho_{CO_2} \sim 45$ , and  $\rho_{N_2O} \sim 7$  for the production of  $N_2$ ,  $CO_2$  and  $N_2O$ , respectively. The superior effect of Rb-promotion relative to K is again apparent.

### 3.2. Conversion performance

In these experiments, the reactor inlet concentrations and total gas flow rate were kept constant. Reactant concentrations were 1000 ppm(v) NO and 1000 ppm(v) CO which are close to those encountered in practical applications and commonly used in the literature as reference conditions. The amount of catalyst loaded in the reactor was  $8 (\pm 0.2)$  mg and the total gas flow rate was fixed at  $80 \text{ cm}^3 \text{ STP/min}$ , corresponding to a reciprocal weight time velocity  $w/f = 6 \times 10^{-3} \text{ g s/cm}^3$ . Taking account of the measured catalyst dispersions (Table 1), we calculate an effective contact time [11,12] of the reactants given by surface Pt atoms/(reactant molecules fed/s) in the range of only 0.3–1 s.

Conversions were calculated using following relations:

$$\begin{aligned} \text{Total NO conversion (\%), } X_{NO} \\ = 100 \times \left\{ \frac{[NO]^{in} - [NO]^{out}}{[NO]^{in}} \right\} \quad (7) \end{aligned}$$

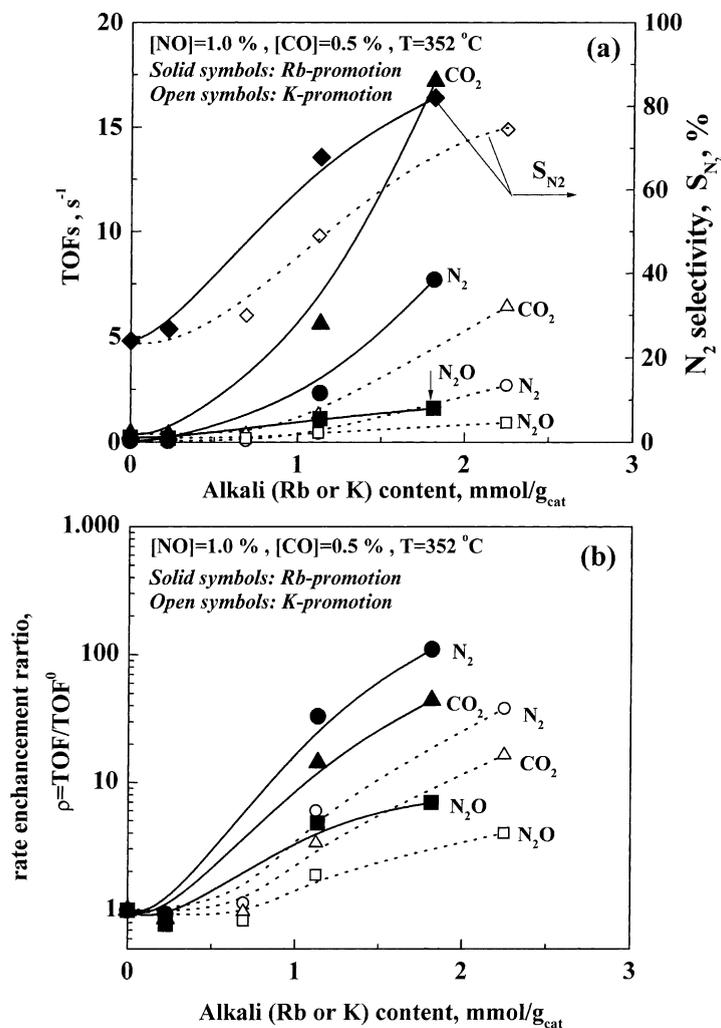


Fig. 5. (a) Effect of Rb or K content of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst on the turnover (TOF) formation rates of N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O and on N<sub>2</sub>-selectivity, at fixed temperature and reactant concentrations. (b) Effect of Rb or K content of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst on the rate enhancement ratio  $\rho = \text{TOF}/\text{TOF}^0$  for N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O formation ( $\text{TOF}_{\text{N}_2}^0 = 0.07 \text{ s}^{-1}$ ,  $\text{TOF}_{\text{CO}_2}^0 = 0.39 \text{ s}^{-1}$ ,  $\text{TOF}_{\text{N}_2\text{O}}^0 = 0.23 \text{ s}^{-1}$ ). Conditions:  $T = 352^\circ\text{C}$ , [NO] = 1%, [CO] = 0.5%. Concentrations refer to reactor outlet. Solid lines and symbols refer to Rb-promotion. Dashed lines and open symbols refer to K-promotion. Triangles: CO<sub>2</sub> formation data; cycles: N<sub>2</sub> formation data; squares: N<sub>2</sub>O formation data.

CO conversion (%),  $X_{\text{CO}}$

$$= 100 \times \left\{ \frac{[\text{CO}]^{\text{in}} - [\text{CO}]^{\text{out}}}{[\text{CO}]^{\text{in}}} \right\} \quad (8)$$

where [NO]<sup>in</sup> and [CO]<sup>in</sup> or [NO]<sup>out</sup> and [CO]<sup>out</sup> are the reactor inlet or outlet NO and CO concentrations, respectively.

N<sub>2</sub>-selectivity is now calculated by an expression equivalent to Eq. (1):

$$S_{\text{N}_2}(\%) = \frac{2[\text{N}_2]}{X_{\text{NO}}} \times 100 = \frac{[\text{N}_2]}{[\text{N}_2] + [\text{N}_2\text{O}]} \times 100 \quad (9)$$

where [N<sub>2</sub>] and [N<sub>2</sub>O] are the concentrations of N<sub>2</sub> and N<sub>2</sub>O, respectively in the reactor effluent gas. The nitrogen and carbon mass balances, i.e. [NO]<sup>in</sup> –

$[\text{NO}]^{\text{out}} = 2([\text{N}_2] + [\text{N}_2\text{O}])$  and  $[\text{CO}]^{\text{in}} - [\text{CO}]^{\text{out}} = [\text{CO}_2]$  always closed to within 2%, implying that there was no significant production of  $\text{NO}_2$  under any of the conditions used.

### 3.2.1. Effect of temperature on NO and CO conversion and $\text{N}_2$ -selectivity of Rb, K or Cs-promoted catalysts

Fig. 6(a)–(c) show the effect of catalyst temperature on NO and CO conversions as well as on the corresponding  $\text{N}_2$ -selectivity for catalysts C1–C4. In the interests of clarity, the conversion of NO to  $\text{N}_2$  or to  $\text{N}_2\text{O}$  are not depicted separately. However, since  $\text{N}_2$  and  $\text{N}_2\text{O}$  are the only N containing products,  $\text{N}_2$  and  $\text{N}_2\text{O}$  yields are readily calculated from the data of Fig. 6(a) and (c) by use of Eq. (9). For comparison purposes, the corresponding behaviour of the 0.5 wt.% Rh/ $\gamma\text{-Al}_2\text{O}_3$  catalyst is also shown in Fig. 6. Similar data were acquired for the K- and Cs-promoted catalysts. These results are not shown in Fig. 6, but are discussed explicitly in connection with Fig. 7.

As apparent from Fig. 6, Rb-promotion substantially improves the performance of Pt, increasing NO and CO conversion as well as  $\text{N}_2$ -selectivity. Note that the NO and CO conversions achieved with unpromoted Pt are relatively poor and do not exceed ~60% up to 480°C. In marked contrast, all the Rb-promoted catalysts achieve 100% conversions at significantly lower temperatures. For catalysts with Rb loadings higher than 1.13 mmol/g<sub>cat</sub> (9.7 wt.% Rb), complete conversion of reactants was obtained at  $\geq 350^\circ\text{C}$  with  $\text{N}_2$ -selectivity close to 100%. At any given temperature, although the Rh/ $\gamma\text{-Al}_2\text{O}_3$  catalyst showed higher conversion than any of the Pt(Rb) catalysts (Fig. 6(a) and (b)), it exhibits selectivity behaviour similar to that of catalyst C4.

### 3.2.2. Light-off temperature ( $T_{50}$ ) for NO conversion

Fig. 7 shows the NO light-off temperature (the temperature for 50% conversion of NO)  $T_{50}$ , for all the catalysts examined in this study. The alkali-free Pt/ $\gamma\text{-Al}_2\text{O}_3$  catalyst gives  $T_{50} = 463^\circ\text{C}$  with a corresponding  $\text{N}_2$ -selectivity at this temperature of 53%. On the other hand, although the Rh/ $\gamma\text{-Al}_2\text{O}_3$  catalyst shows a significantly lower light-off temperature ( $T_{50} = 238^\circ\text{C}$ ) the corresponding  $\text{N}_2$ -selectivity is only 31%. This latter behaviour is due to the much lower light-off temperature that favours formation of

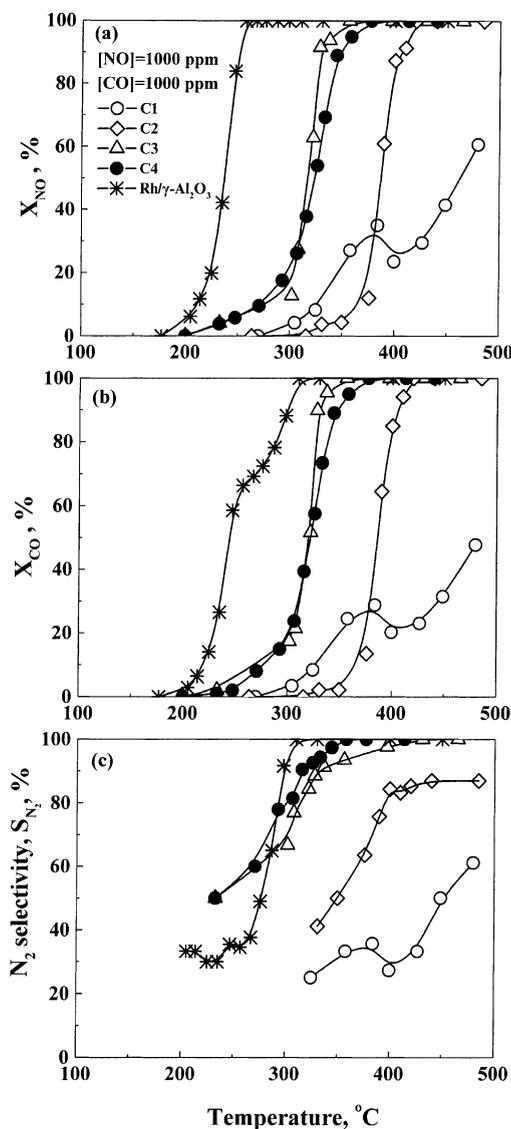


Fig. 6. Conversion of NO (a), and CO (b) and the corresponding  $\text{N}_2$ -selectivity (c), for Rb-promoted Pt/ $\gamma\text{-Al}_2\text{O}_3$  catalysts as a function of temperature at constant reactor inlet conditions:  $[\text{NO}] = 1000 \text{ ppm(v)}$ ,  $[\text{CO}] = 1000 \text{ ppm(v)}$ , total gas flow rate  $80 \text{ cm}^3\text{STP/min}$ ; catalyst weight  $8(\pm 0.2) \text{ mg}$ . ( $w/f = 6 \times 10^{-3} \text{ g s/cm}^3$ ). Comparison with the behaviour of 0.5 wt.% Rh/ $\gamma\text{-Al}_2\text{O}_3$  catalyst.

$\text{N}_2\text{O}$ . It is very apparent that Rb- and K-promotion of Pt cause very significant decreases in  $T_{50}$  (NO) resulting in NO reduction performance that approaches that of Rh. In particular Rb-promotion gives a reduction in  $T_{50}$  by  $\sim 150^\circ\text{C}$  for loadings approximately

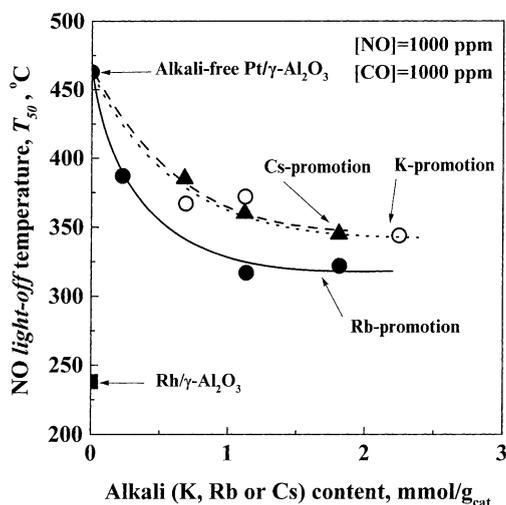


Fig. 7. Effect of K-, Rb- or Cs-promotion on the NO light-off temperature for Pt/NO + CO system. Conditions as in Fig. 6.

>1.13 mmol Rb/g<sub>cat</sub> (approximately >9.7 wt.% Rb). Thus, catalyst C4 (1.82 mmol Rb/g<sub>cat</sub>, 15.5 wt.% Rb) delivers  $T_{50} = 322^{\circ}\text{C}$  with  $\text{N}_2$ -selectivity as high as 93% at this temperature. K-promotion produced similar effects, although in all cases, these were smaller than in the case of Rb-promotion (Fig. 7). In comparison with Rb, larger molar loadings of K were needed to produce similar reductions in light-off temperature (Fig. 7). Finally, as a control, a limited number of measurements were carried out with the corresponding Cs-promoted catalysts. The results (see Fig. 7) clearly indicate that although, Cs is an effective promoter, it is not as good as Rb. Thus, the best Cs-promoted catalyst gave a  $T_{50}$  of  $345^{\circ}\text{C}$  and a selectivity of 89%.

#### 4. Discussion

Our results show that Rb can markedly improve the catalytic properties of Pt in the reduction of NO by CO. Rate enhancement ratios ( $\rho$ ) increased monotonically with Rb loading, the best results being obtained with catalyst C4 with the highest Rb loading. Moreover, the effect of Rb on the rate of  $\text{N}_2\text{O}$  formation is much lower than on the rates of  $\text{CO}_2$  and  $\text{N}_2$  production, thus, resulting in a significant increase in  $\text{N}_2$ -selectivity of the from ~20–30% over unpromoted Pt to >80% over catalyst C4. Potassium and caesium

exert similar though distinctly less pronounced beneficial effects, a difference that will be discussed below in terms of a general model for the mode of action of alkali promoters in the catalytic reduction of NO. This model was originally developed in the context of our work on electrochemical promotion by alkalis of NO reduction: it applies equally in the present case.

The Langmuir–Hinshelwood nature of the Pt-catalysed NO + CO reaction involving competitive adsorption of the reactants is well established [5,16]. The present results are in line with this view (Figs. 1 and 3) and a plausible reaction pathway may be written in terms of the following elementary steps:



It is also widely accepted [5,16] that NO dissociation is rate determining for the overall reaction. On this basis, an explicit rate expression has been derived [16], which implies a monotonically declining rate with increasing CO concentration, exactly as observed in Fig. 1, except at low CO concentrations. At low CO concentrations, the equation derived by Granger et al. [16] does not hold, as one must obtain a zero rate in the limit of vanishing [CO]. The result should be a rate maximum at some intermediate value of [CO], as we observe. Our data indicate that at sufficiently low [CO]/[NO] ratios CO adsorption must become rate limiting, and the rate should exhibit positive order in [CO] as indeed we find. On the other hand, the results shown in Fig. 3 for the dependence of rate on [NO] are fully in accord with the behaviour predicted by Granger et al. [16].

How do K, Rb and Cs promoters work to promote NO reduction? As noted above, we have already proposed a detailed general model to explain this behaviour [9]. The essence of this model is summarised below.

It is well established [17] that alkali adatoms on the Pt{111} surface cause substantial dissociation of

co-adsorbed NO molecules. The electric field of the positively charged alkali acts to depress the energy of the NO  $\pi^*$ -orbital below the metal Fermi level. The resulting metal  $\rightarrow$  adsorbate charge transfer weakens the N–O bond and strengthens the metal–N bond, thus, acting to increase NO coverage while at the same time promoting NO dissociation. Direct experimental verification of this alkali-induced perturbation of the bonding in chemisorbed NO has also been obtained [18]. These effects of electropositive adatoms on co-adsorbed diatomic molecules have received a detailed theoretical interpretation by Lang et al. [19]. One is dealing with an example of the Stark effect, with the electric field being supplied by the adsorbed alkali ion. It is a short-range phenomenon, acting over distances of the order of one or at most two lattice parameters, due to the screening effect of the metal's valence electrons. This is in good accord with experimental observations [20] which show that alkali coverages in the order of 0.01 to 0.1 monolayers are necessary for appreciable promotion to occur. In the present case, the promotional effects of alkalis on both reaction rate and N<sub>2</sub>-selectivity may readily be understood in these terms, as discussed below.

Unpromoted Pt is a poor catalyst because NO adsorption is relatively weak and NO dissociation is inefficient [5]. In the presence of alkali, two important effects occur due to influence of the alkali in (i) strengthening the Pt–N bond, and (ii) weakening the N–O bond. Specifically, the first acts to increase the coverage of NO and the second increases the degree of dissociation of NO. These two effects favour reactions (10), and (12) and hence the overall rate of conversion of NO. Promotion of NO dissociation also favours reaction (13) at the expense of reaction (14), thus, resulting in increased selectivity. The principal features of the alkali-promoted NO + CO reaction are therefore very satisfactorily accounted for.

Consider now, the kinetic data obtained with the best catalyst, C4, which delivers the highest specific activity and selectivity. Under differential conditions, a rate maximum is observed at a [NO]/[CO] ratio of 1/0.5 (Fig. 1). At this point, the surface coverage by CO and by NO, N, O is optimised with respect to overall rate of conversion of NO. Fig. 2 shows that increasing CO concentration causes a decrease in N<sub>2</sub>-selectivity and reaction rate. This is to be expected,

since NO dissociation requires bare sites adjacent to the adsorbed NO; increasing the CO coverage, therefore leads to self-poisoning of both activity and selectivity by inhibiting the NO dissociation rate.

At lower Rb loadings both reaction rate and N<sub>2</sub>-selectivity are attenuated relative to catalyst C4. This is understandable in terms of a reduction in the proportion of Pt surface sites that are subjected to the beneficial effects of alkali-promotion, which is a short-range effect [19]. Interestingly, the [NO]/[CO] ratio at which the rate maximum occurs now shifts to a higher value ( $\sim 1/0.3$ ), and this upshift continues as the Rb loading is decreased further. That is, as the Rb coverage decreases, a higher NO gas phase concentration is required in order to obtain the optimum surface coverages of NO and its dissociation products thereby maximising the reaction rate. Thus, the systematic effect of alkali on the kinetic behaviour is also understandable.

Why is Rb apparently a more effective promoter than both K and Cs? We may offer a plausible tentative answer in the case of Rb versus K as follows. Assuming that for a given molar amount of alkali Rb and K are similarly dispersed on the Pt surface, we may rationalise the greater efficiency of Rb in terms of its ionic size. The calculations of Lang et al. [19] clearly show that the larger the alkali cation, the greater the electric field experienced by a co-adsorbed species located at an adjacent site. Thus, Rb<sup>+</sup> should perturb the Pt–N and N–O bonding more strongly than does K<sup>+</sup>, leading to the observed relative effectiveness. This is in line with our earlier work on the Li-, Na-, K-, Rb- and Cs-promoted Pt/(NO + C<sub>3</sub>H<sub>6</sub>) system [12,13] which also showed that heavier alkalis were more effective than lighter alkalis, with Rb best. Clearly, this argument does not account for the relative efficiency of Rb and Cs so one would have to invoke additional phenomena. For example, the large size of the Cs ion may induce site switching in the co-adsorbed NO (e.g. from a bridge site to an atop site), thus, increasing the distance between the two adsorbates and reducing the alkali-induced electric field experienced by the NO. Such site switching effects are well known from single crystal studies of NO adsorption on transition metals [21]; to invoke them here is admittedly speculative. In this connection, it is interesting to note that Alexandrou et al. [22] found that for the Pt-catalysed NO + CO reaction,

Na decreased  $T_{50}$  by only  $\sim 60^\circ\text{C}$ , which supports the view that Rb is the optimal alkali promoter for this reaction.

Why do we not observe poisoning at some sufficiently high loading of alkali? No doubt such effects due to blocking of active sites would eventually become apparent if the alkali loading were to be increased indefinitely. For our purposes, the interesting point is that in the case of the Pt/(NO + C<sub>3</sub>H<sub>6</sub>) reaction promoted by Li, Na, K, Rb or Cs, poisoning was observed at alkali loadings corresponding to the highest loadings used here [12,13]. Post-reaction XPS studies of EP NO<sub>x</sub> reduction catalysts provide a clue to the origin of this difference in behaviour. In the case of the Cu-catalysed NO + CO reaction electrochemically promoted by Na [23], the promoter phase consisted mainly of submonolayer films of alkali nitrate. On the other hand, EP studies in the presence of hydrocarbons [9,24] show that over-promotion by alkali promoter poisons activity due to site blocking by multilayers of alkali carbonate. This could perhaps account for the absence of poisoning in the present case: bulk alkali nitrates are less thermally stable than the corresponding carbonates so that multilayers are less likely to accumulate on the metal surface.

## 5. Conclusions

1. The catalytic reduction of NO by CO over Pt exhibits very strong promotion by Rb. Rate gains by two orders of magnitude can be achieved, accompanied by a large increase in selectivity (up to 60 percentage units). K and Cs, though highly effective, are significantly inferior.
2. Promotion is due to alkali-induced increase in the strength of NO chemisorption relative to that of CO. This is accompanied by weakening of the N–O bond, which facilitates NO dissociation, which is the critical reaction-initiating step. These two effects act to increase both the overall activity and the selectivity towards N<sub>2</sub> formation. The superior effect of rubidium may be associated with the larger size of the Rb ion as compared to the K ion. The lower efficiency of Cs relative to Rb may reflect a change in the adsorption site of NO due to the very large Cs ion.

## Acknowledgements

The authors acknowledge support from the Greek Ministry of Development GSRT and the Athens British Council under the British-Greece Joint R&T Programs 1999–2000 (Grant no. ATH/882/2/ATPOL). IVY also thanks ICE/HT-FORTH and the Department of Chemical Engineering, University of Patras, for partial support of this project.

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