

NO reduction by propene or CO over alkali-promoted Pd/YSZ catalysts

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Abstract

The catalytic activity and selectivity of Pd dispersed on 8 mol% yttria stabilized zirconia (YSZ) support for the reduction of NO by propene or CO is strongly promoted by alkalis in a wide temperature range 200–500 °C. Rate increases by *up to one order of magnitude* are achievable, accompanied with significant improvement in N₂-selectivity for the alkali promoted catalysts. The promoting effect of alkalis on both the activity and selectivity can be understood in terms of the effect of alkali promoter on the relative adsorption strengths of reactant species. These achievements could be very useful for the formulation of modern lower cost automotive catalytic converters, capable of controlling automotive emissions more efficiently.

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Keywords: Promotion; Alkalis; NO reduction; Palladium; CO; Propene

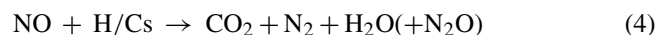
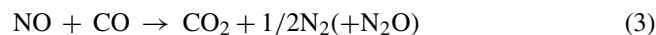
1. Introduction

Nitrogen oxide (NO_x) emissions produced primarily in elevated temperature combustion processes (e.g. automotive engines) contribute significantly to a variety of environmental problems, including among others the photochemical smog and acid rain. On the other hand N₂O is a powerful greenhouse gas, which also contributes to stratospheric ozone depletion [1]. That is why, strict regulations have been imposed for the vehicles NO_x emissions, since automotive exhaust gases are the primary source of these pollutants. In respect to vehicles, a well-established technology for NO_x, CO and hydrocarbons emissions control is the three-way catalytic chemistry (TWC) [2]. The product of this technology, the well known three-way catalytic converter (TWC) is based on the catalytic properties of Pt, Pd and Rh to catalyze efficiently reactions such as:

- Oxidation reactions:



- Reduction reactions:



that convert the three main pollutants CO, NO and H/Cs to CO₂, H₂O and N₂.

Although Pt and Pd are very effective in oxidizing CO and hydrocarbons they are substantially less effective in reducing NO_x [3], in contrast to Rh [4], which is therefore the key component in TWCs, responsible for NO_x reduction. In addition, due to their low NO dissociation activity [3,5], Pd and Pt produce the undesirable N₂O as a byproduct of the reactions (3) and (4).

As a result, numerous environmental catalysis research groups have recently focused on enhancing the activity and N₂-selectivity of Pd (and Pt) in de-NO_x reactions, for which Rh is the currently preferred catalyst, by means of promoters (e.g. [6–12]).

During the last years a systematic study of the above environmentally important reactions (1)–(4), is in progress in our laboratory in order to discover means of enhancing the catalytic properties of Pt-group metals for all these reactions and in particular for the reactions (3) and (4), which concern the simultaneous removal of all pollutants, and the enhancement in the selectivity

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Table 1
Properties of alkali promoted 0.5 wt% Pd/YSZ catalysts

Catalyst code	Alkali-loading (wt%)	Pd/alkali (atoms/atom)	H ₂ uptake (cm ³ STP/g)	Dispersion (%)	Active surface area (m ² /g)
Na-promoted catalysts for the study of NO + CO reaction					
A1	0	∞/1	0.106	20.1	0.448
A2	Na-0.017	6/1	0.105	20.0	0.444
A3	Na-0.034	3/1	0.131	24.9	0.554
A4	Na-0.068	1.5/1	0.123	23.4	0.520
A5	Na-0.102	1/1	0.127	24.1	0.537
Alkali-promoted catalysts for the study of NO + C ₃ H ₆ reaction					
B1	0	∞/1	0.078	15	0.33
B2	Li-0.020	1.5/1	0.055	10.4	0.23
B3	Na-0.068	1.5/1	0.052	10	0.22
B4	K-0.115	1.5/1	0.063	12	0.27
B5	Cs-0.392	1.5/1	0.063	12	0.27

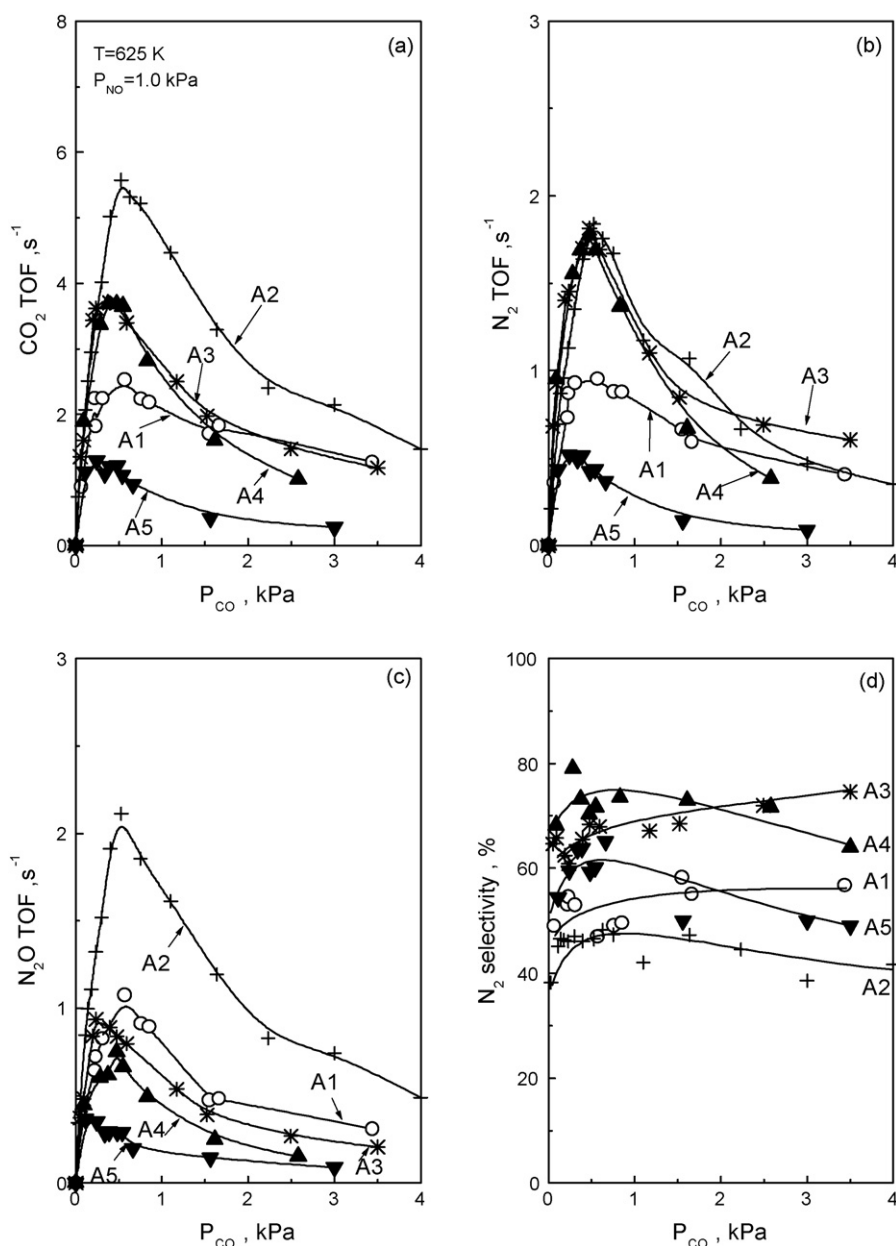


Fig. 1. NO + CO reaction at constant $P_{NO} = 1$ kPa. The effect of P_{CO} on CO₂ (a), N₂ (b) and N₂O (c) TOFs, and on the corresponding N₂ selectivity (d), for Na-promoted Pd/YSZ catalysts.

towards N_2 (instead of N_2O) is an important factor. Achievements of significant practical and theoretical importance have been already reported: we have shown that both de- NO_x activity and N_2 -selectivity of Pt-group metals can be substantially, and in some cases extraordinarily, enhanced by electropositive promotion of these metals with alkalis or alkaline earths. In particular, Pt is the noble metal mostly studied during this project, for which we have shown that NO reduction rate increases by *up to two orders of magnitude* accompanied by large increases of N_2 -selectivity can be obtained over optimally promoted Pt-catalysts by Li, Na, K, Rb, Cs or Ba, under reactions (3) or (4) [13–16] or under simulated exhaust conditions [17]; depending on the active metal/promoter pair and the applied conditions, there is always a promoter loading that optimizes catalyst per-

formance [14]. For palladium, we have shown that it also exhibits strong promotion by Na under the $NO + C_3H_6$ reaction, where rate enhancements up to *one order of magnitude* and significant improvements in N_2 -selectivity were attained [18].

Although the overall picture of the electropositively promoted Pt has been extensively studied up to now, this is not the case for Pd, another potential three-way chemistry noble metal [19,20]. Here, we complete the picture regarding Pd by reporting on the promotional effects of Li, Na, K and Cs alkalis on the catalytic performance (activity and selectivity) of Pd/YSZ during the $NO + C_3H_6$ reaction, as well as on the promotional effect of Na on the catalytic performance of Pd/YSZ during the $NO + CO$. The choice of the YSZ support for Pd was dictated by recent studies, which show that YSZ maximises the turnover

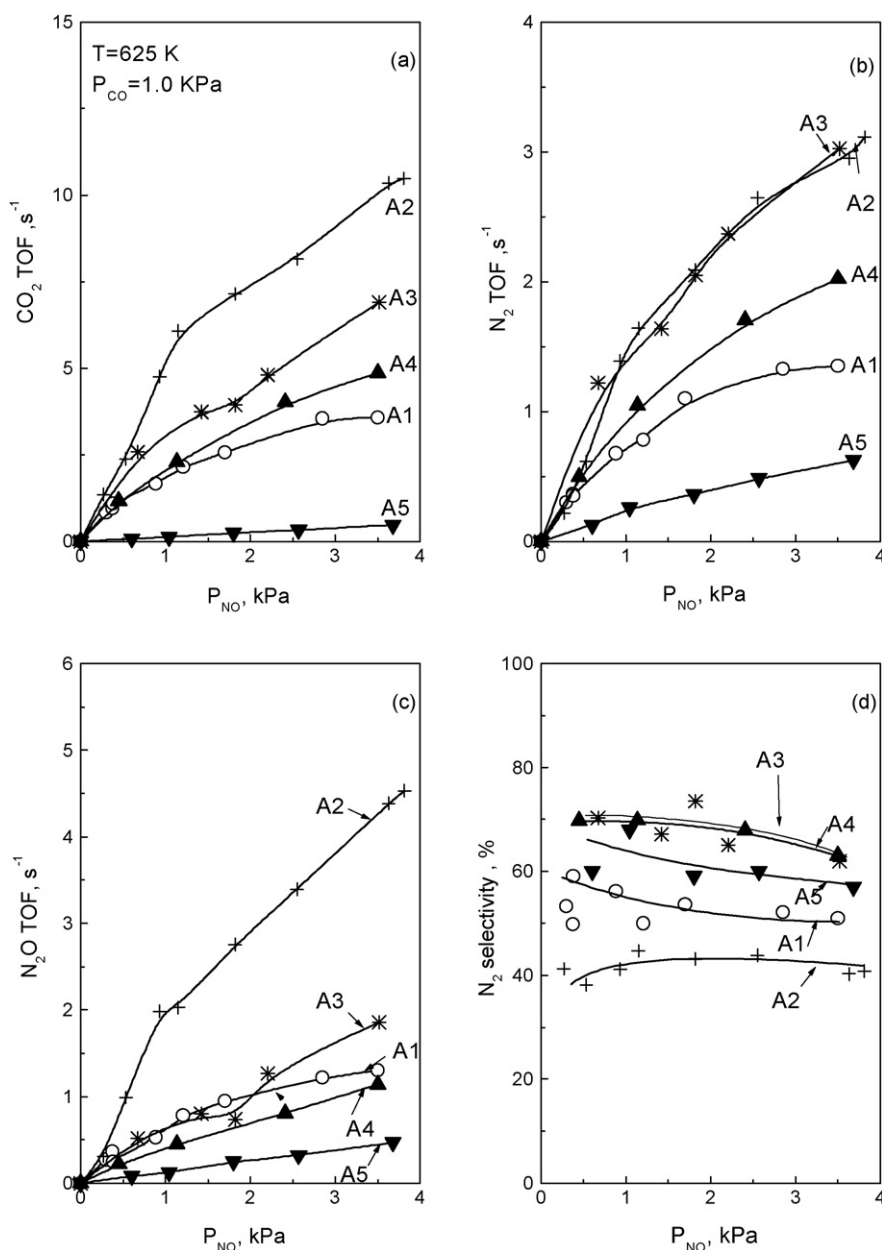


Fig. 2. $NO + CO$ reaction at constant $P_{CO} = 1$ kPa. The effect of P_{NO} on CO_2 (a), N_2 (b) and N_2O (c) TOFs, and on the corresponding N_2 selectivity (d), for Na-promoted Pd/YSZ catalysts.

activity of Pd for reactions of relevance to three-way catalytic chemistry [21].

2. Experimental

The basic catalyst used in this study was 0.5 wt% Pd dispersed over 8 mol% yttria stabilized zirconia (YSZ, 7 m²/g) carrier, prepared by wet impregnation of YSZ support in a solution of Pd(NO₃)₂ (or PdCl₂). After drying, the suspension was subsequently impregnated in appropriate solutions of LiNO₃, NaNO₃, KNO₃, or CsCl to produce one group of samples with different Na loadings (for the study of NO + CO reaction) and another group of samples with different alkalis but at constant ratio of Pd/alkali (Li, Na, K or Cs) atoms, equal to 1.5/1 (for the study of NO + C₃H₆ reaction). This atomic ratio is close to the optimum alkali loading, as it was indicated in a previous study concerning the effect of Na on the catalytic properties of Pd/YSZ during the NO + C₃H₆ reaction [18]. 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 at 673 K, followed by H₂ reduction for 1 h at the same temperature. The properties of alkali promoted catalysts produced by this method are listed in Table 1, where their dispersions and active surface areas (measured via H₂ chemisorption at 333 K) are also included. Catalyst testing was performed in a flow apparatus consisting of a feed unit, a quartz tubular reactor loaded typically with ~8.0 mg of catalyst, and an analysis unit supported by on-line gas chromatography and NO_x continuous chemiluminescence analysis.

3. Results and discussion

The differences in catalysts' dispersion observed between series A and B (Table 1), even for catalysts of the same constitution (e.g. catalysts A4 and B3), are most likely due to the different preparation procedure of these two series: Catalysts A1–A5 have been produced by using PdCl₂, while catalysts B1–B5 by Pd(NO₃)₂ precursor. It is also well known in the literature that residual chloride affects (poisons) the behaviour of catalysts for reactions similar to that studied here. The effects of residual chloride on catalyst performance before and after alkaline earth dosing of the catalysts have been extensively discussed elsewhere [22].

3.1. NO + CO reaction over Pd(Na)/YSZ catalysts

Figs. 1 and 2 depict the effects of CO and NO partial pressures, respectively, on the CO₂ (a), N₂ (b) and N₂O (c) turnover formation rates (TOF: molecules of product per surface Pd atom per second) as well as on N₂-selectivity (d), defined as $S_{N_2} = \text{TOF}_{N_2} / (\text{TOF}_{N_2} + \text{TOF}_{N_2O})$.

It is obvious from the results, that Na has a pronounced effect on both activity and selectivity, the extent of which strongly depends on Na-loading (see also Fig. 3). Under the experimental conditions of the present study, superior N₂ and CO₂ rate performances are achieved by the catalyst A2 with 0.017 wt% Na, but unfortunately its N₂-selectivity is inferior to all the other catalysts including the unpromoted A1 catalyst as well.

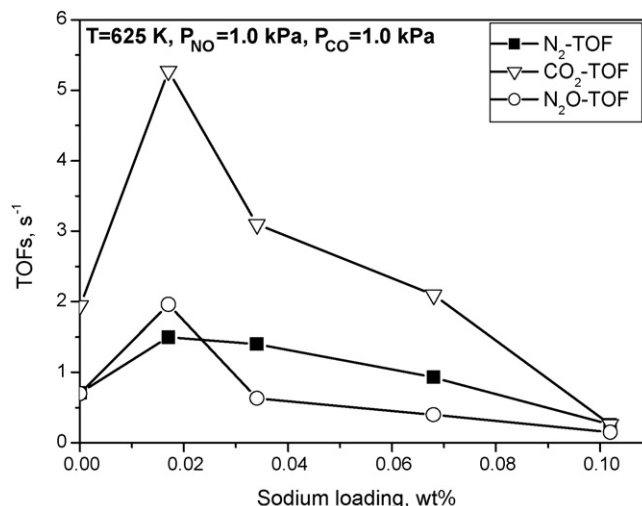


Fig. 3. The effect of Na-loading on CO₂ (a), N₂ (b) and N₂O (c) TOFs. $P_{CO} = P_{NO} = 1$ kPa and $T = 625$ K.

Nevertheless, catalyst A3 with Na loading 0.034 (and catalyst A4 as well, with 0.068 wt% Na) exhibits good performances in both activity and selectivity, that are significantly better compared to the unpromoted catalyst A1. Hereafter, we call this catalyst “*optimally promoted*” catalyst, the achievements of which are N₂ and CO₂ turnover rate enhancements up to 200% (Figs. 1a and b, 2a and b and 3), with insignificant effects on the N₂O formation rate (Figs. 1c, 2c and 3), which lead to a significant selectivity improvement of about 20–30 additional percentage points in comparison to the unpromoted catalyst A1.

It is also worth mentioning the characteristic rate maxima in Fig. 1, which reflects competitive adsorption of NO and CO on the Pd surface. These maxima occur at [NO]/[CO] molar ratios >1, indicating weaker adsorption of NO, relative to CO, on Pd surface. This weaker adsorption of NO is also confirmed by the positive-order dependence of N₂ and CO₂ TOFs on [NO] and the absence of rate maxima over a wide range of NO partial pressures (Fig. 2).

3.2. NO + C₃H₆ reaction over Pd(alkali)/YSZ catalysts

Fig. 4 depicts the effect of NO partial pressure on the CO₂ (a), N₂ (b) and N₂O (c) turnover formation rates as well as on N₂-selectivity over the optimally promoted (by Li, Na, K and Cs) palladium catalysts.

The results very clearly show the promotional effect of all alkalis on both the activity and selectivity. All the alkali-promoted catalysts exhibit better catalytic performance than that of the alkali-free Pd, although, the best performance is obtained by the Na-promoted catalyst, for which N₂ and CO₂ rates enhancements up to one order of magnitude are achievable, in comparison to the alkali-free Pd catalyst, while the selectivity towards N₂ reached values as high as 95%. Another important observation, immersed from Fig. 4, is the appearance of rate maxima for alkali promoted catalyst as the NO concentration is varied, in contrast to the unpromoted catalyst, indicating the pronounced effect of alkalis on the NO chemisorption bond.

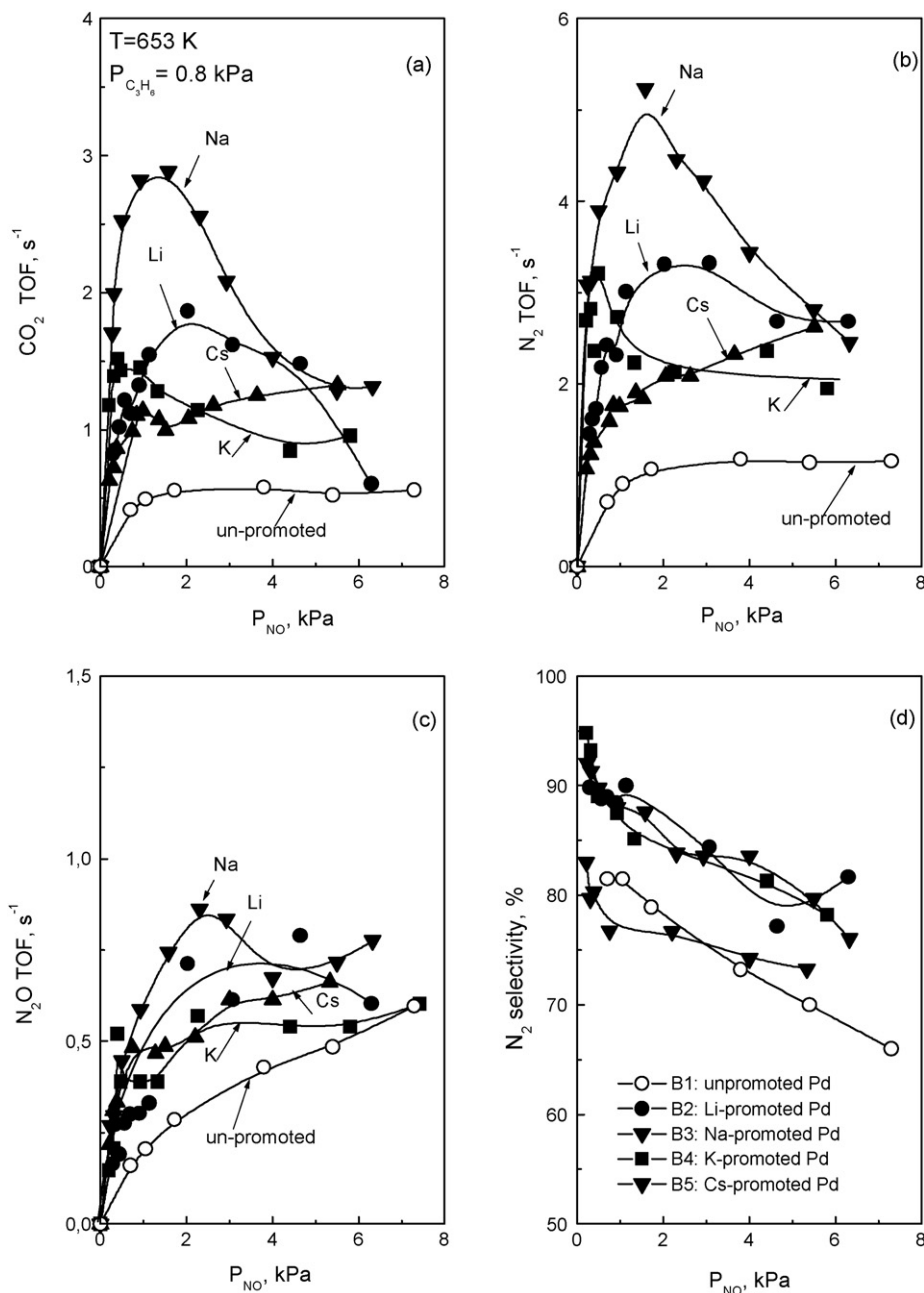


Fig. 4. The effect of NO partial pressure on CO_2 (a), N_2 (b) and N_2O (c) turnover formation rates and on the corresponding N_2 selectivity (d), for (Li, Na, K and Cs)-promoted Pd/YSZ catalysts during the $NO + C_3H_6$ reaction, at constant partial pressure of C_3H_6 ($P_{C_3H_6} = 0.8\text{ kPa}$).

In summary, the present results show that Li, Na, K and Cs addition on Pd can remarkably affect its catalytic properties during reactions related to automotive emissions control, such as $NO + C_3H_6$ or $NO + CO$. The shape of the kinetic curves in Figs. 1 and 3 implies that both reactions exhibits Langmuir–Hinshelwood behaviour with competitive adsorption of the NO and CO (or C_3H_6). Moreover, the kinetic results indicate a weaker adsorption of NO compared to CO (or C_3H_6), which is more pronounced on the unpromoted catalyst. Thus, the alkali-free surface is predominantly covered by CO (or C_3H_6), therefore resulting in a moderate activity and selectivity over the un-promoted Pd.

However, when the Pd surface is modified by alkalis, both the activity and selectivity are significantly enhanced. This promotion can be attributed to the effect of alkalis on the chemisorption bonds of reactant species, and more specifically on the enhancement of NO chemisorption bond compared to CO or propene. This is exactly what someone would expect with electropositive promoters, such as alkalis: the chemisorption bond strength of electron acceptor adsorbates (NO) should be enhanced, whereas the chemisorption bond strength of electron donor adsorbates (propene) should be decreased. The net result is an increased NO population on a catalyst surface initially covered mainly from propene or CO, thus an enhanced

reaction probability (these effects on the chemisorption bonds have been predicted theoretically [23] and directly approved by TPD experiments [24]). The enhancement of the Pd–NO bond strength on the alkali modified surface is accompanied by weakening of the N–O bond in the adsorbed NO molecule, thus facilitating NO dissociation. The observed increase in the N₂-selectivity is a consequence of the increased NO dissociation ($\text{NO}_{\text{ads}} \rightarrow \text{N}_{\text{ads}} + \text{O}_{\text{ads}}$), i.e., the decreased amount of molecular NO and the increased amount of atomic N on the surface. Both factors favour N₂ production through the recombination of two adsorbed N atoms ($\text{N}_{\text{ads}} + \text{N}_{\text{ads}} \rightarrow \text{N}_2(\text{g})$), rather than the N₂O production ($\text{N}_{\text{ads}} + \text{NO}_{\text{ads}} \rightarrow \text{N}_2\text{O}(\text{g})$), leading to higher N₂ selectivity.

It is well known that the presence of oxygen competes the NO reduction during the CO or hydrocarbon SCR of NO [25]. Our recent studies over a similar alkali-promoted catalyst (namely, Na-dosed Pt/ γ -Al₂O₃) have shown that the promotional effects of alkalis remain even in the presence of stoichiometric [17] or excess [26] oxygen conditions. Similarly, Na-induced promotional effects have been reported by Macleod et al. [27] over Pd/ γ -Al₂O₃ catalysts under TWC conditions around to the stoichiometric point.

4. Conclusions

The catalytic reduction of NO by propene or CO over Pd exhibits strong promotion by alkalis. Rate enhancements *up to one order of magnitude* are achievable over alkali promoted catalysts, while the selectivity towards N₂ is significantly improved to values as high as 95%. Promotion is due to the effects of alkalis on the relative adsorption strengths of reactant species. Alkali addition: (i) strengthens the Pd–NO bond (thus increasing NO coverage) and (ii) weakens the N–O bond (thus promoting NO dissociation) on a catalyst surface predominantly covered by propene or CO. Both factors increase the probability of surface reactions, leading to a very pronounced promotion on Pd catalytic performance.

Acknowledgments

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