

Novel doubly-promoted catalysts for the lean NO_x reduction by H₂ + CO: Pd(K)/Al₂O₃–(TiO₂)

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Abstract

The reduction of NO by CO + H₂ in the presence of excess O₂ has been studied on dispersed, low loading 0.5 wt.% Pd-based catalysts. Two different methods of promotion were imposed separately and together, in order to investigate the feasibility of their synergy to enhance de-NO_x efficiency of the catalytic system. Therefore, the Pd-catalysed NO + CO + H₂ + O₂ reaction was gradually studied over: (i) Pd/Al₂O₃–(TiO₂) catalysts (support-mediated promotion by modifying the Al₂O₃ support with TiO₂), (ii) K-dosed Pd(K)/Al₂O₃ catalysts (surface-induced promotion by modifying the Pd surface with the addition of K), and (iii) doubly-promoted Pd(K)/Al₂O₃–(TiO₂) catalysts. Both (i) and (ii) methods of promotion were found to significantly promote the system, when acting individually. However, the de-NO_x efficiency and N₂-selectivity of the doubly-promoted Pd(K)/Al₂O₃–(TiO₂) catalysts were found to be better than both of the other two cases, indicating a synergy during the simultaneous imposition of the two methods of promotion. The resulted benefits with the optimal doubly-promoted catalyst were very high, ~85% NO_x conversion in a very wide temperature range (100–400 °C), accompanied by very good N₂-selectivities of ~85%, i.e., 15–30 additional percentage units in comparison to the selectivity of the original un-promoted Pd/Al₂O₃ catalyst.

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1. Introduction

Emissions of nitrogen oxides (NO_x), mainly from automotive engines but also from stationary sources have serious environmental consequences, namely smog formation and acid rain [1,2]. Automotive engines are also related to huge CO₂ emissions. However, lean-burn gasoline and diesel engines that work in excess O₂ (lean conditions) offer significant fuel economy, hence lower CO₂ emissions per kilometer, compared to conventional gasoline engines. Unfortunately, the excess oxygen makes the NO_x removal from the exhaust gases of these engines a significantly difficult problem [2–4].

Although three-way catalytic converters (TWCs) employ a satisfactory technology for emission control of stoichiometric gasoline engines, they cannot effectively remove NO_x at low temperatures or under conditions of excess O₂ [4–6]. On the

other hand, in stationary power sources and chemical plants, the NH₃ SCR process is currently the best choice for the NO_x reduction [7]. In spite of the fact that this process is very effective, problems related to the storage and slip of ammonia suggest the development of a new catalytic system capable of removing the NO_x, using in principle the gases which already exist in the exhaust stream (e.g., hydrocarbons, H₂, CO) as reducing agents.

Extensive research has been done regarding the NO_x reduction by hydrocarbons under lean conditions [8], following the pioneering works of Held et al. [9] and Iwamoto et al. [10]. Among the catalytic systems tested, Pt-based catalyst appears to be the most active, offering simultaneously high stability and durability [11,12]. However, Pt exhibits a considerably narrow window of operation at low temperatures in addition to significant formation of the undesirable N₂O [12–15]; N₂O is one of the most powerful greenhouse gases. Recently, efforts for improving the hydrocarbon-SCR of NO_x (including the particular cases of stoichiometric and lean-burn conditions) on Pt-group metals via electropositive surface promotion with

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alkalies or alkaline earths, have offered substantial beneficial effects [16–24].

Besides hydrocarbons, hydrogen is also one of the gases present in automotive exhaust stream. Hydrogen could also be externally supplied (e.g., by the use of a hydrocarbon reformer or another source of safe *in situ* hydrogen production) for the reduction of NO_x from stationary power sources and chemical plants. This can explain the growing interest for the use of H₂ as a reducing agent of NO_x in the last years [25–49]. Most of these studies have used Pt as the catalyst [25–37]. Pt was generally found to offer good de-NO_x efficiency with N₂-selectivities varying typically between 20 and 60% at low temperatures (100–200 °C). Unfortunately, at higher temperatures the Pt-catalysed NO_x reduction is depressed, since the reaction between H₂ and O₂ to form H₂O dominates.

However, the process of the H₂-SCR over Pt for automotive emissions control exhibits an important disadvantage: carbon monoxide, which also coexists in exhaust stream (typically, H₂:CO ~ 1:3), is strongly adsorbed on Pt surfaces, causing an inhibition of H₂ oxidation by both NO and O₂ and consequently an inhibition on NO_x reduction [33,45]. Lambert and co-workers were the first who showed that in contrast to Pt, Pd-based catalysts overcome this poisoning influence of CO, leading to good NO_x conversions with mixed H₂ + CO feeds [45–49]. Furthermore, they found that the activity of Pd strongly depends on the nature of the support. Specifically, they showed that Pd supported on TiO₂-modified Al₂O₃ support offers significantly higher de-NO_x efficiency in comparison to the Pd/Al₂O₃ catalyst. This synergy of the Al₂O₃ and TiO₂ carriers was found to be maximized at about 10 wt.% of TiO₂ [49]. However, the temperature window in which high NO_x conversion and N₂-selectivity were observed was very narrow (150–200 °C).

Prompted by our studies that concern the promotional effects of alkalies on the de-NO_x Pt-group metals catalytic chemistry [16–21,24], and having in our mind the recent achievements of Lambert's group on the support-mediated promotional effects on de-NO_x efficiency of Pd [45–49], we investigated lean NO_x reduction by H₂ + CO over new formulations of doubly-promoted Pd(K)/Al₂O₃–(TiO₂) catalysts; the substances in brackets indicate the used promoter species. For comparison purposes, singly-promoted via support-mediated effects (i.e.,

Pd/Al₂O₃–(10 wt.% TiO₂)) and via surface-induced effects by potassium addition (i.e., Pd(K)/Al₂O₃) catalysts were also examined under similar conditions. The synergistic effect of these two methods of promotion on the characteristics (de-NO_x efficiency and N₂-selectivity) of the NO + CO + H₂ + O₂ reaction over the doubly-promoted Pd catalyst were investigated in a wide range of temperatures and surface promoter loadings.

2. Experimental methods

2.1. Catalyst preparation

Pd/Al₂O₃ or Pd/Al₂O₃–(TiO₂) catalysts used as basis in this study were prepared by impregnation of the Al₂O₃ or Al₂O₃–TiO₂ supports with an aqueous solution of Pd(NO₃)₂·2H₂O (Fluka) in order to yield 0.5 wt.% Pd loading. The impregnation was followed by drying in air at 110 °C. Then, batches of these catalysts were subsequently impregnated in solutions containing various concentrations of KNO₃, in order to yield a range of potassium loading from 0 to 3 wt.%. The batches were dried at 110 °C, calcined in air at 500 °C for 6 h and finally reduced with 15% H₂ (in He) flow at 200 °C for 1 h. All the catalysts produced and investigated in this study are listed in Table 1, where their constitutions as well as their Pd-dispersions, measured via H₂ chemisorption at 60 °C (H₂ pressure <30 Torr) with a Quantachrome Autosorb-1 instrument, are also included. Dispersions were calculated by assuming a 1:1 hydrogen:metal stoichiometry, where the H₂ uptakes were determined by extrapolation of the “plateau” portion of the isotherms to zero pressure. The samples were initially reduced in H₂ at 200 °C for 1 h, followed by out-gassing at the same temperature for 1.5 h.

The Al₂O₃ and Al₂O₃–(10 wt.% TiO₂) supports used here, were prepared by the sol–gel method as follows: Al(NO₃)₃·9H₂O (Carlo Erba Reagenti) precursor was added into hot distilled water (80 °C) under stirring and kept at this temperature for 1 h. Then, NH₃ was added and the gelation took place. The relative molar amounts of Al(NO₃)₃, distilled water and 25% (v/v) NH₃ of the mixture were 1:33:3, respectively. The formed gel was dried at 110 °C for 24 h and then calcined in air at 600 °C for 2 h. The produced Al₂O₃ sol–gel had a BET

Table 1
Constitution and physical properties of 0.5 wt.% Pd catalysts supported on Al₂O₃ and 10 wt.% TiO₂-modified Al₂O₃

Catalyst code and kind of promotion used	Catalyst constitution	H ₂ uptake (cm ³ STP/g _{cat})	Pd dispersion (%)	Active metal surface area ^a (m ² /g _{cat})
C1 original, unpromoted catalyst	0.5 wt.% Pd/Al ₂ O ₃	0.108	20.5	0.457
C2 promoted by only support-mediated effects (10 wt.% TiO ₂ in Al ₂ O ₃ support)	0.5 wt.% Pd/Al ₂ O ₃ –10 wt.% TiO ₂	0.162	30.8	0.685
C3 promoted by only surface-induced effects (0.25 wt.% K)	0.5 wt.% Pd(0.25 wt.% K)/Al ₂ O ₃	0.100	19.0	0.423
C4 doubly-promoted with 0.1 wt.% K and 10 wt.% TiO ₂	0.5 wt.% Pd(0.1 wt.% K)/Al ₂ O ₃ –10 wt.% TiO ₂	0.142	27.0	0.600
C5 doubly-promoted with 0.25 wt.% K and 10 wt.% TiO ₂	0.5 wt.% Pd(0.25 wt.% K)/Al ₂ O ₃ –10 wt.% TiO ₂	0.115	21.8	0.486
C6 doubly-promoted with 0.5 wt.% K and 10 wt.% TiO ₂	0.5 wt.% Pd(0.5 wt.% K)/Al ₂ O ₃ –10 wt.% TiO ₂	0.118	22.4	0.500
C7 doubly-promoted with 1.0 wt.% K and 10 wt.% TiO ₂	0.5 wt.% Pd(1.0 wt.% K)/Al ₂ O ₃ –10 wt.% TiO ₂	0.097	18.5	0.410
C8 doubly-promoted with 3.0 wt.% K and 10 wt.% TiO ₂	0.5 wt.% Pd(3.0 wt.% K)/Al ₂ O ₃ –10 wt.% TiO ₂	0.082	15.5	0.347

^a Calculations based on a Pd surface atom density of 1.27×10^{19} atoms/m².

surface area of 173 m²/g, as determined by N₂ adsorption at –196 °C. In order to produce the TiO₂-modified Al₂O₃ with 10 wt.% TiO₂, the sol-gel Al₂O₃ was added in a solution of titanium isopropoxide (Aldrich) and propanol-2 (volume ratio Ti(OC₃H₇)₄:propanol-2 = 1:10) at 70 °C under continuous stirring for 6 h. After vaporization of the solvent, the remained gel was dried at 110 °C for 12 h and calcined in air at 500 °C for 6 h.

2.2. Catalysts testing

Catalyst testing experiments were carried out in a fixed-bed, single-pass, plug flow reactor consisting of a 0.4 cm i.d. quartz tube loaded with 70 mg of catalyst, which was retained between two plugs of quartz wool. The catalyst temperature was measured by a K-thermocouple located at the centre of the catalyst bed.

Air liquefied certified gas mixtures of 7.83% NO, 10.1% CO, 20% H₂ and 20.7% O₂, all diluted in He, were used. These were further diluted in ultrapure He (99.999%) and supplied to the reactor at one bar through a series of independent mass flow controllers (MKS type 247). The feed composition employed during *light-off* catalyst testing was He balanced 1000 ppm NO_x + 2500 ppm CO + 7500 ppm H₂ + 6% O₂. The total gas flow rate was 280 cm³/min, corresponding to a reciprocal weight space velocity of w/f = 0.015 g s/cm³.

The reactor inlet and outlet were analyzed using a Thermo Environmental Instr., 42C chemiluminescence NO_x analyzer for the analysis of NO and NO₂ and *on-line* gas chromatography (Shimadzu-14B) for the analysis of CO, CO₂, O₂, H₂, N₂ and N₂O. Chromatographic separation of H₂, N₂, O₂ and CO was achieved in a molecular sieve 5A column, while CO₂ and N₂O were separated using a porapak-N column, both operated at 80 °C. NH₃ was not detected in the reactor effluent gas in the overall temperature interval and for all catalysts investigated.

Because of the large excess of oxygen in the reactor effluent gas (~6%), the separation of nitrogen and oxygen by GC was difficult. Thus, for better accuracy, direct estimation of the produced N₂ via integration of its chromatographic peaks was not performed; it was therefore calculated by the following N-containing gases balance equation:

$$N_2(\text{ppm}) = \frac{[\text{NO}_x]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}} - 2[\text{N}_2\text{O}]_{\text{outlet}}}{2}, \quad (1)$$

where [NO_x]_{inlet}, [NO_x]_{outlet} and [N₂O]_{outlet} were measured with good accuracy via the NO_x-analyzer and the GC.

Since there is a small conversion of NO to NO₂ (~15%) at temperatures < 130 °C, due to a gas phase reaction between NO and O₂, the NO_x conversion rather than the NO conversion was chosen in order to characterize the de-NO_x efficiency of the catalysts:

$$\text{NO}_x \text{ conversion (\%)} = \frac{([\text{NO}] + [\text{NO}_2])_{\text{inlet}} - ([\text{NO}] + [\text{NO}_2])_{\text{outlet}}}{([\text{NO}] + [\text{NO}_2])_{\text{inlet}}} \times 100. \quad (2)$$

The selectivity towards N₂ was calculated by:

$$N_2\text{-selectivity (\%)} = \frac{[\text{N}_2]}{[\text{N}_2] + [\text{N}_2\text{O}]} \times 100. \quad (3)$$

The inlet composition and flow rate were kept constant during the catalyst testing experiments, while the temperature was increased stepwise from 30 to 400 °C and held constant at each temperature for at least 30 min prior taking measurements.

Our catalysts were also studied by *in situ* DRIFTS experiments at certain reaction conditions (1000 ppm NO_x + 2500 ppm CO + 7500 ppm H₂ + 6% O₂, He balance; T = 200 °C and total flow rate of 60 cm³/min). Diffuse reflectance IR spectra were collected using an exalibur spectrometer FTS 3000, equipped with a Mercury–Cadmium–Telluride (MCT) detector cooled by liquid nitrogen and an IR chamber (Specac, Environmental chamber DRIFT model) of ~1 cm³ volume. Considering the total flow rate of 60 cm³/min used in FTIR measurements, a space velocity value of 1 s⁻¹ is calculated. The chamber provides inlet and outlet gas stream lines and a temperature controlled heating system (within 25–600 °C). Infrared spectra were obtained with resolution of 2 cm⁻¹ and accumulation of 64 scans. During IR measurements the external optics were continuously purged by CO₂-free dry air generated in an air purifier system (Claind Italy, CO₂-PUR model). About 80 mg of the catalyst sample in a powder form was loaded into the IR chamber. Its surface was carefully flattened in order to optimize the intensity of the reflected IR beam.

3. Results

3.1. The NO_x + H₂ + CO + O₂ reaction performance over Pd/Al₂O₃–(TiO₂) and Pd(K)/Al₂O₃ catalysts; individual imposition of the support-mediated and the surface-induced promotion methods

The promotion of Pd catalytic chemistry for the NO reduction by H₂ + CO in excess O₂, via support-mediated and via surface-induced effects, were separately examined first. Fig. 1a–c shows the total NO_x conversion (Fig. 1a), the NO_x conversion to N₂O (Fig. 1b) and the corresponding selectivity towards N₂ (Fig. 1c) versus temperature for C1 and C2 catalysts, i.e., Pd supported on Al₂O₃ and on TiO₂-modified alumina (Al₂O₃–10 wt.% TiO₂) carriers, respectively (see Table 1). Fig. 1a–c also show the corresponding data obtained for a Pd(0.25 wt.% K)/Al₂O₃ catalyst dosed with 0.25 wt.% of potassium (catalyst C3, Table 1). This particular catalyst was found to exhibit the best de-NO_x behaviour from a series of singly-promoted (by only K-addition at several loadings between 0 and 3 wt.% K) Pd(K)/Al₂O₃ catalysts tested. However, for the sake of clarity, in Fig. 1 we compare only the representative best from its series, catalyst C3, with the original un-promoted catalyst C1 and the catalyst C2 promoted by support-mediated effects.

Obviously, the un-promoted catalyst C1 (Pd/Al₂O₃) displays very poor de-NO_x activity under the conditions employed with

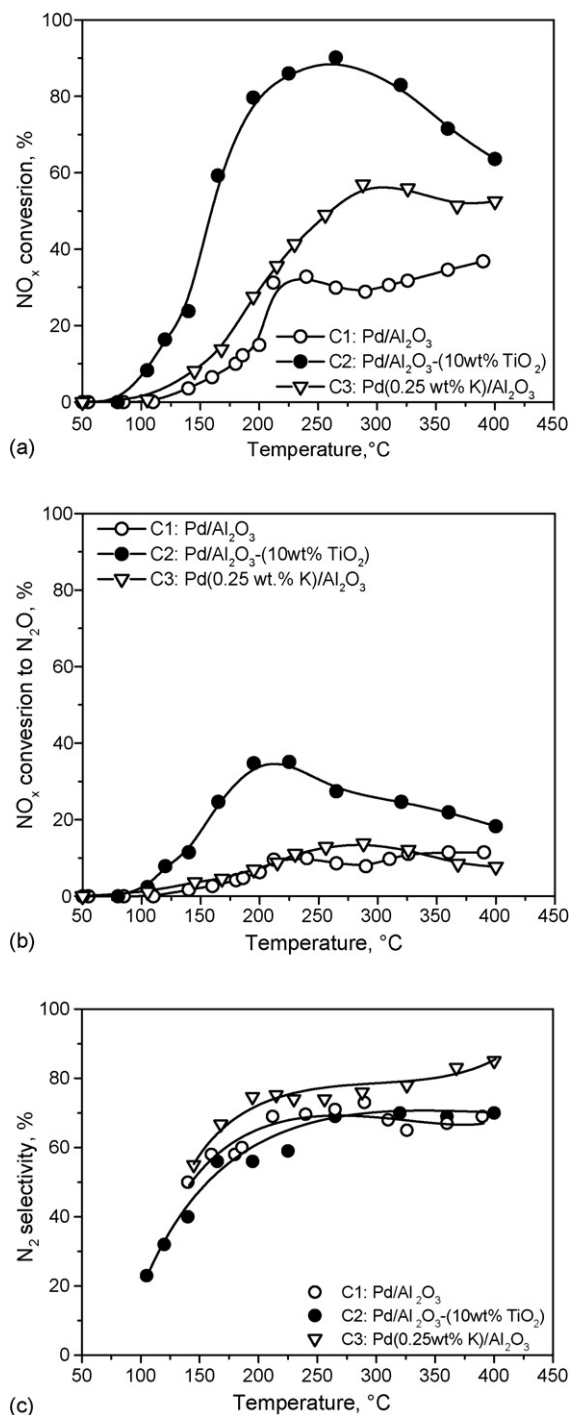


Fig. 1. Total NO_x conversion (a); NO_x conversion to N₂O (b); and the corresponding N₂-selectivity (c), as a function of temperature for the 0.5 wt.% Pd/Al₂O₃, 0.5 wt.% Pd/Al₂O₃–(10 wt.% TiO₂) and 0.5 wt.% Pd(0.25 wt.% K)/Al₂O₃ catalysts. Conditions: feed composition = 1000 ppm NO_x + 2500 ppm CO + 7500 ppm H₂ + 6% O₂, balance He; total flow rate = 280 cm³/min; catalyst weight = 70 mg.

maximum NO_x conversion only at ~35% (Fig. 1a). On the contrary, Pd supported on the mixed Al₂O₃–TiO₂ carrier (catalyst C2) offers much superior de-NO_x activity in the whole temperature interval 50–400 °C, with maximum NO_x conversion value as high as 86%. This, however, is accompanied by a proportional increase in N₂O production rate (Fig. 1b). As a

result, its selectivity towards N₂ was sustained practically unaffected, i.e., similar to that given by catalyst C1, varying between 20 and 70% for $T > 100$ °C (Fig. 1c). Focusing now on the Pd(0.25 wt.% K)/Al₂O₃ catalyst C3, promoted via the method of surface-induced modification, we can see a moderate enhancement in de-NO_x efficiency, i.e., inferior to that obtained with the Pd/Al₂O₃–(TiO₂) catalyst C2 (Fig. 1a). However, this enhancement in NO_x conversion is obviously not followed by any increase in N₂O formation rate (Fig. 1b), resulting in a substantial improvement in N₂-selectivity of catalyst C3 in comparison to the un-promoted catalyst C1 (Fig. 1c).

The superior activities of the Pd/Al₂O₃–(TiO₂) and Pd(K)/Al₂O₃ catalysts C2 and C3, respectively, in comparison to the unpromoted Pd/Al₂O₃ catalyst C1 are also obvious in Figs. 2 and 3, which show the corresponding CO and H₂ conversion profiles versus temperature. Profile shifts of about 30 °C to lower temperatures for both CO and H₂ conversions are achieved by both methods of promotion.

Summarizing the description of the data concerning the individual characteristics of the two methods of promotion, we can note the following: (i) the support-mediated promotion, by itself, offers a very substantial enhancement in NO_x-conversion activity of Pd but not in its N₂-selectivity; (ii) the surface-induced promotion (by K-addition), by itself, offers a moderate enhancement in NO_x-conversion activity of Pd but a substantial improvement of N₂-selectivity.

3.2. The NO_x + H₂ + CO + O₂ reaction performance over the doubly-promoted Pd(K)/Al₂O₃–(TiO₂) catalysts

Fig. 4a depicts the total NO_x conversion as a function of temperature for the five catalysts C4–C8 of Table 1 of the type of Pd(varying wt.% K)/Al₂O₃–(10 wt.% TiO₂), i.e., the catalysts which are simultaneously promoted by support-mediated effects (10 wt.% TiO₂ into Al₂O₃ support) and surface-induced (K addition) effects. It is obvious from Fig. 4a that, although, low or moderate loadings of potassium (typically 0.1–0.5 wt.% K) cause a slight decrease, practically

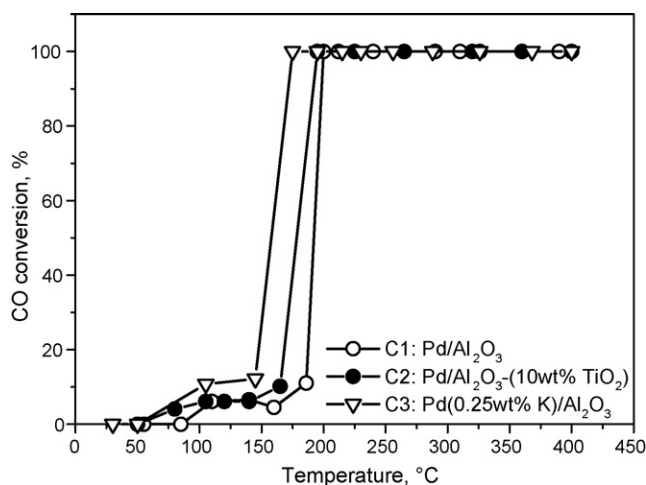


Fig. 2. CO conversion as a function of temperature for 0.5 wt.% Pd/Al₂O₃, 0.5 wt.% Pd/Al₂O₃–(10 wt.% TiO₂) and 0.5 wt.% Pd(0.25 wt.% K)/Al₂O₃ catalysts. Conditions as in Fig. 1.

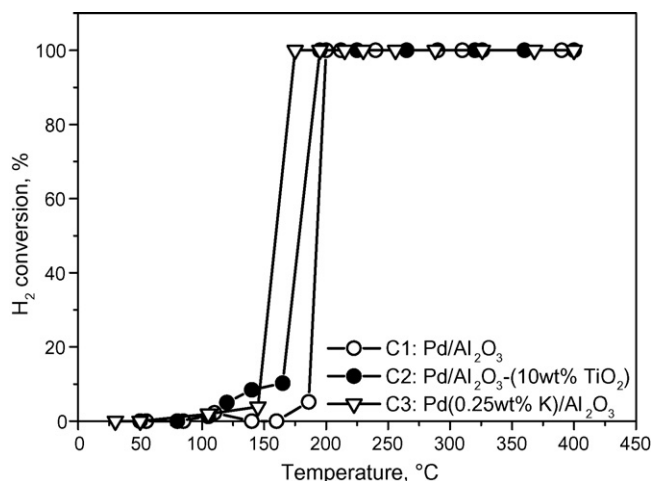


Fig. 3. H_2 conversion as a function of temperature for the 0.5 wt.% $\text{Pd}/\text{Al}_2\text{O}_3$, 0.5 wt.% $\text{Pd}/\text{Al}_2\text{O}_3$ –(10 wt.% TiO_2) and 0.5 wt.% Pd (0.25 wt.% $\text{K})/\text{Al}_2\text{O}_3$ catalysts. Conditions as in Figs. 1 and 2.

they retain the elevated de- NO_x efficiency of $\text{Pd}/\text{Al}_2\text{O}_3$ –(TiO_2) catalyst C2 promoted by only TiO_2 addition in the support. Recall that the activity of C2 was found (Section 3.1, Fig. 1a) to be much superior to that of the un-promoted catalyst C1 ($\text{Pd}/\text{Al}_2\text{O}_3$). In contrary, K-loadings higher than 0.5 wt.% induce severe suppression on the NO_x conversion profiles. This inhibition is being worse as the K-loading is increased (Fig. 4a).

Fig. 4b shows the corresponding conversion of NO_x to N_2O . It is interesting that N_2O formation rate is monotonically depressed by increasing K-loading in the catalyst, thus resulting in a significant influence on the system selectivity towards N_2 .

Fig. 4c shows the N_2 -selectivity behaviour of the doubly-promoted catalysts C4–C8 listed in Table 1. Obviously, the improved N_2 -selectivity values offered by K-dosed catalysts is always superior to the selectivity values obtained with the K-free $\text{Pd}/\text{Al}_2\text{O}_3$ –(TiO_2) catalyst C2 in the whole temperature range investigated and for all K-loadings used (0.1–3 wt.%). Even the catalysts with K-loadings >0.5 wt.%, which actually have inferior NO_x conversion to that of the K-free catalyst C2 (Fig. 4a), still have superior N_2 -selectivity performances compared to the K-free catalyst C2; their magnitudes, however, are not as substantial as with catalysts with low or moderate K-loadings (Fig. 4c). In particular for catalysts with 0.1 and 0.25 wt.% K (catalysts C4 and C5, respectively) this superiority in N_2 -selectivity is up to 30 additional percentage units in comparison to the K-free catalyst in the whole temperature window (100–400 °C) investigated, varying between 55 and 85% (Fig. 4c).

The H_2 and CO conversion profiles versus temperature for the doubly-promoted catalysts (C4–C8, Table 1) were found similar in shape to those depicted in Figs. 2 and 3 for the K-free catalysts. It is a very sharp (almost stepwise) ignition which leads H_2 and CO conversions to 100%. We therefore considered that it is better in this circumstance and for the sake of clarity, to alternatively show (Fig. 5) the effect of potassium loading on the temperatures for 100% conversion of CO and H_2 , respectively. As Fig. 5 shows, potassium addition causes a

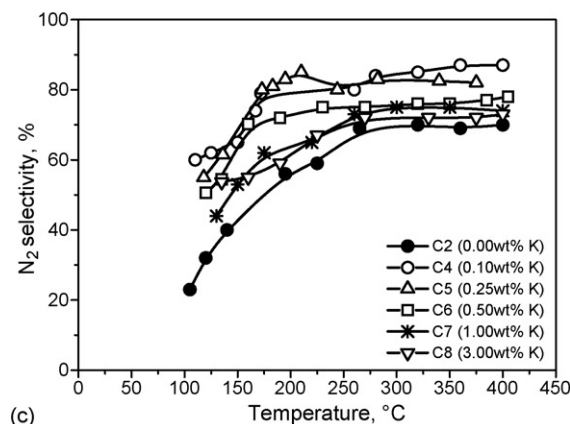
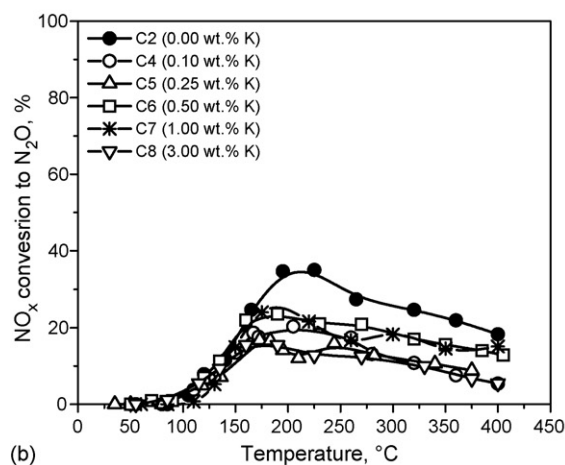
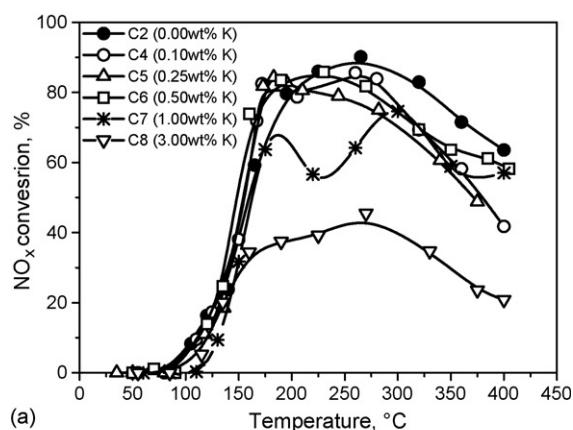


Fig. 4. Total NO_x conversion (a); NO_x conversion to N_2O (b); and the corresponding N_2 -selectivity (c), as a function of temperature for the 0.5 wt.% Pd (K)/ Al_2O_3 –(10 wt.% TiO_2) doubly-promoted catalysts with different potassium loadings. Conditions: feed composition = 1000 ppm NO_x + 2500 ppm CO + 7500 ppm H_2 + 6% O_2 , balance He ; total flow rate = 280 cm^3/min ; catalyst weight = 70 mg.

significant decrease in the temperature required for 100% conversion of CO and H_2 . The K-free catalyst C2 attains 100% CO and H_2 conversions at 194 °C. However, K-dosed catalysts C4–C8 attain 100% CO and H_2 conversions at about 30 °C lower temperatures. For comparison purposes the corresponding values for the original unpromoted catalyst C1 are also depicted in Fig. 5; an overall maximum $\Delta T = 40$ °C is then

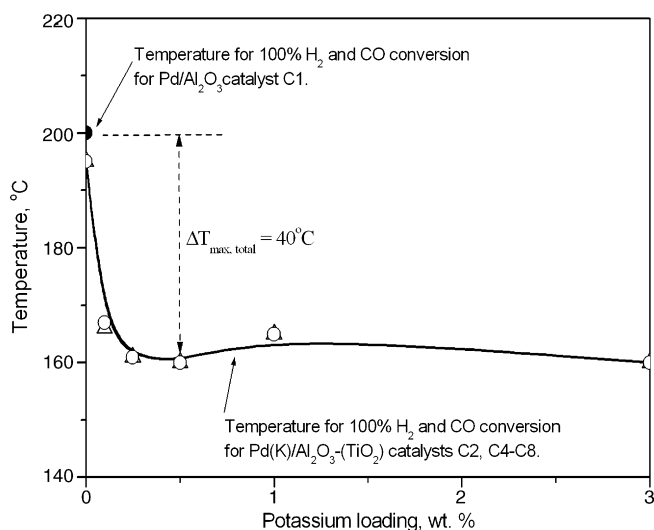


Fig. 5. The effect of potassium loading on the temperature for 100% conversion of CO (Δ) and H₂ (\circ), for the 0.5 wt.% Pd(K)/Al₂O₃–(10 wt.% TiO₂) catalysts with different potassium loadings. The corresponding values for 0.5 wt.% Pd/Al₂O₃ catalyst are also shown. Conditions: feed composition = 1000 ppm NO_x + 2500 ppm CO + 7500 ppm H₂ + 6% O₂, balance He; total flow rate = 280 cm³/min; catalyst weight = 70 mg.

apparent between C1 and the optimal doubly-promoted catalyst C5.

A comparative review of the whole results depicted in Figs. 1–5, clearly shows that the doubly-promoted catalysts are in general superior in de-NO_x performance to that of the catalysts individually promoted by the other two methods. Their catalytic properties combine the benefits offered by the other two individually imposed promotion methods, i.e., the high activity obtained by support-mediated promotional effects together with the improved N₂-selectivity obtained via surface-induced promotion by K. The best catalyst from the whole samples studied here is the doubly-promoted catalyst C4 (or the equivalently performing catalyst C5) that offers ~85% NO_x conversion with ~85% N₂-selectivity in a wide temperature range.

Fig. 6 depicts the *in situ* (under reaction conditions) DRIFT spectra for the following representative catalysts: the original unpromoted Pd/Al₂O₃ catalyst C1, the Pd/Al₂O₃–(10 wt.% TiO₂) catalyst C2 promoted by only support-mediated effects, the Pd(0.25 wt.% K)/Al₂O₃ catalyst C3 promoted by only K-addition, and the doubly-promoted Pd(0.25 wt.% K)/Al₂O₃–(10 wt.% TiO₂) catalyst C5. The feed conditions of the IR chamber were 1000 ppm NO + 2500 ppm CO + 7500 ppm H₂ + 6% O₂, balance He, at a total flow rate of 60 cm³/min. The reaction temperature was kept constant at 200 °C; 200 °C was chosen because at this temperature significant differences in both the activity and selectivity of the catalysts are found (Figs. 1a, c and 4). All spectra were obtained 90 min after the introduction of the gas mixture into the IR chamber.

It is worth emphasizing that the bands we observe in Fig. 6 (in particular those for spectra C1 and C2) are in complete agreement with those observed by Lambert and co-workers for similar catalysts/reaction conditions [47–49]; they have therefore been similarly assigned. Several overlapping bands can be

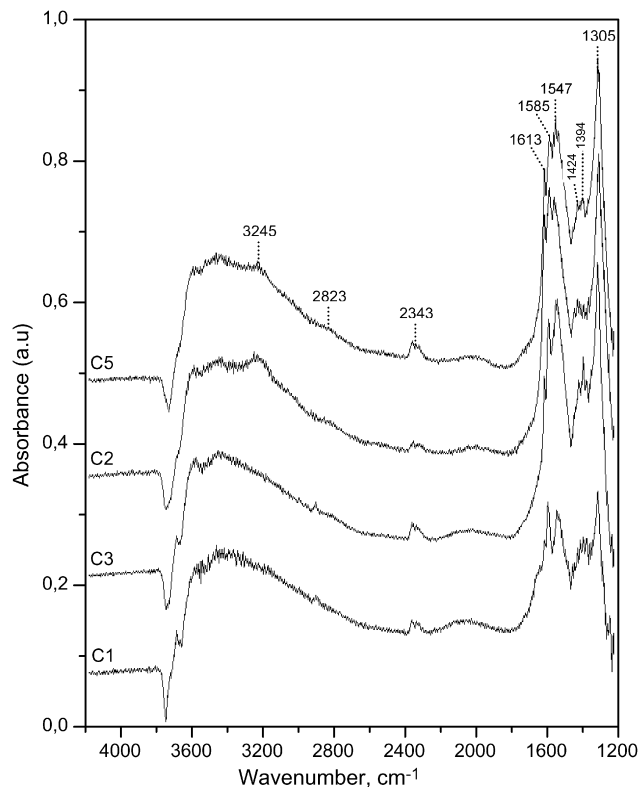


Fig. 6. *In situ* DRIFT spectra for the original unpromoted Pd/Al₂O₃ catalyst C1, the TiO₂-promoted Pd/Al₂O₃–(10 wt.% TiO₂) catalyst C2, the K-promoted Pd(0.25 wt.% K)/Al₂O₃ catalyst C3 and the doubly-promoted Pd(0.25 wt.% K)/Al₂O₃–(10 wt.% TiO₂) catalyst C5. Conditions: 1000 ppm NO_x + 2500 ppm CO + 7500 ppm H₂ + 6% O₂, He balance. *T* = 200 °C, total flow rate *F* = 60 cm³/min.

observed for all samples in the 1650–1250 cm⁻¹ region, which are assigned to various nitrite/nitrate, carbonate and bicarbonate species [48–52]. The band at 1613 cm⁻¹ is attributed to the split ν_3 mode of bridging nitrates whereas the bands in the 1600–1540 cm⁻¹ region to the ν_3 mode of bidentate nitrates. The peak at 1305 cm⁻¹ is assigned to the second ν_3 mode of the bidentate nitrates [49,50].

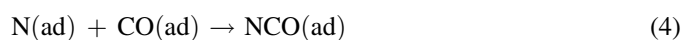
Under the present conditions, carbonate and/or bicarbonate species are also expected to contribute to the intensity of the bands observed in the region below 1650 cm⁻¹. However, a precise assignment of these species is difficult, due to the significant overlap of the bands associated with the different adsorbed species. Thus, the bands at 1585 and 1394 cm⁻¹ can also be due to the $\nu_{as}(\text{COO}^-)$ and $\delta(\text{CH})$ adsorbed formate species, respectively [48,49,52]. Additionally, the overlapping bands at 1613 and 1305 cm⁻¹, can be further assigned to the deformation modes of adsorbed NH₃ [49,53]. This assumption is further supported by the appearance of a wide band at 3245 cm⁻¹, which is characteristic of N–H stretching vibration [49,53]. The shoulder at 2823 cm⁻¹ as well as the band at 1424 cm⁻¹ is consistent with the appearance of NH₄⁺ species [49,53]. The overlapping bands in the middle region (2100–1900 cm⁻¹) can be assigned to various carbonyl species coordinated with Pd sites [48,49,54,55].

Based on the above assignments, we can consider that NH₃ is formed on the surface of all samples. It is worth emphasizing,

however, that the broad band at $\sim 3245\text{ cm}^{-1}$ (N–H stretching mode) is more intense on Pd/Al₂O₃–(TiO₂) and Pd(K)/Al₂O₃–(TiO₂) samples, indicating that the formation of NH₃ is substantially more pronounced in samples that have been modified by TiO₂ addition in the Al₂O₃ support. An interesting feature observed in all spectra, is the absence of isocyanate species (NCO), which are considered as intermediates for NH₃ formation. This simply reflects the rapid hydrolysis of NCO species, by the formed water or hydroxyl groups, as has been considered in similar *in situ* FTIR studies [48,49,56,57].

4. Discussion

First we focus on the behaviour of the singly promoted, by support-mediated modifications, Pd/Al₂O₃–(TiO₂) catalysts. Lambert and co-workers were the first who demonstrated the superior performance of Pd-based catalysts for the lean NO_x reduction with CO + H₂ mixtures [45–49]. Comparing the NO + CO + H₂ + O₂ reaction performance over Pd and Pt catalysts supported on Al₂O₃, they concluded [46] that significantly different SCR-driven channels operate over these two metals since, in complete contrast, the presence of CO, which acts as a poison for Pt, was found to have a pronounced promoting influence on Pd [46]. The authors also showed that the nature of the support is of very critical importance; Pd/Al₂O₃ was found considerably more active than Pd/SiO₂ [46]. As they confirmed by *in situ* DRIFTS studies, the superior de-NO_x performance with CO + H₂ mixtures found for Pd supported on Al₂O₃ is due to *in situ* generation of adsorbed NH₃, a powerful NO_x reductant, which then reduces NO resulting in improved NO_x conversion [47]. The formation and subsequent hydrolysis of isocyanate species (NCO), i.e.:



was considered as the most likely route in NH₃ formation at low temperatures ($< \sim 180\text{ }^\circ\text{C}$), while at higher temperatures the formation of NH₃ was attributed at the direct reaction between H₂ and NO [47,49]. The role of Pd was considered to be very critical for NCO species formation (reaction (4)), while the hydrolysis of NCO (reaction (5)) was considered to take place on Al₂O₃ component of the catalyst after NCO migration to the support [49].

Exploring their studies on this promising metal-support pair (i.e., Pd–Al₂O₃), they showed that TiO₂ doping of the Al₂O₃ support produces yet further significant enhancement in NO_x conversion. This synergy of Al₂O₃ and TiO₂ was attributed to the intrinsic surface chemistry of the pure TiO₂ and Al₂O₃ oxides and not to a mixed oxide formation; the Pd/TiO₂ component of the Pd/Al₂O₃–(TiO₂) catalyst was found to promote the system towards NCO production, whereas, the Al₂O₃ component is then responsible for the subsequent hydrolysis of NCO to form NH₃ [49].

The very substantial enhancement of the Pd/NO + CO + H₂ + O₂ system activity via TiO₂-modification of the Al₂O₃

support found here (Figs. 1–3), confirms the results of Lambert and co-workers. Our *in situ* DRIFT spectra on Pd/Al₂O₃ and Pd/Al₂O₃–TiO₂ catalysts C1 and C2, respectively (Fig. 6), which clearly show the appearance of a sufficiently higher amount of surface NH₃ on the latter catalyst, implies that NH₃ indeed plays a key role in the de-NO_x process over these two catalysts; the TiO₂ induced support-mediated effects apparently follow the mechanism proposed by Lambert and co-workers, which involves the NH₃-SCR channel on enhancing the de-NO_x activity. The absence of ammonia in the reactor effluent gas under steady-state conditions is due to its high reactivity with NO_x [47–49].

We now focus on the behaviour of the singly promoted, by surface-induced effects, Pd(K)/Al₂O₃ catalysts. Concerning the performance of the Pd(K)/Al₂O₃ catalyst C3 (Fig. 1a), our results show that K-addition also causes a significant promoting effect on the de-NO_x activity of Pd. However, in complete contrast to the case of TiO₂-promoted catalyst C2, the presence of K does not cause any detectable influence on the amount of NH₃ intermediate on C3 catalyst surface (Fig. 6). This implies that in the case of K-modified Pd(K)/Al₂O₃ catalysts, most likely another SCR-driven channel is now promoted (different than the NH₃-formation channel considered to be promoted on TiO₂-modified catalysts). The superior N₂-selectivity performance of the Pd(K)/Al₂O₃ catalyst C3 in comparison to that of the Pd/Al₂O₃–(TiO₂) catalyst C2 (the latter exhibits similar N₂-selectivity with Pd/Al₂O₃ catalyst C1, Fig. 1c) is also consistent with this hypothesis.

In order to rationalize the K-promotion on the Pd/NO + CO + H₂ + O₂ system, we recall here the main conclusions emerged from our studies on alkali-promotion of the SCR of NO_x Pt-group metal chemistry [16–21,24]; studying closely similar reaction systems, such as the hydrocarbon- or CO-SCR of NO_x in the absence [16,17,19–21] or in the presence of O₂ [18,24], we have showed that alkalies can substantially promote both activity and selectivity of the NO_x reduction process over Pt and Pd. A model was derived for the way of action of alkali-modifier, which consistently explained all previous experimental findings. According to this model, co-adsorbed alkali on Pt-group metal surfaces enhances the chemisorption of electron acceptor adsorbates (e.g., NO and its dissociation products, CO and O₂), while it weakens the chemisorption of electron donor adsorbates (e.g., hydrocarbons) [17–19,21,24]. Therefore, in respect to NO_x reduction process, the promoting role of alkalies is mainly due to the enhanced dissociative chemisorption of NO (caused by alkali), which is considered as a key reaction initiating step of this process. As predicted theoretically [58], alkali co-adsorbed with NO on Pt-group metal surfaces induces strengthening of the metal–NO bond and hence weakening of the N–O bond in the adsorbed NO molecules. This is due to the effect of electrostatic field of the alkali cation on adjacent co-adsorbed electron acceptors molecules (NO and its dissociation products). Alkali acts to lower the NO π^* orbital energy below the Fermi level, thus populating the former with valence electrons from the metal. This results in strengthening of the metal–N bond and thus weakening the N–O bond, promoting the NO dissociation rate. This feature has also been directly

confirmed by TPD experiments over model (single-crystal) N-dosed Pt{1 1 1} surfaces [59] and more recently via *in situ* DRIFTS studies of NO adsorption over supported Pt/Al₂O₃ catalysts [60].

Therefore, we may conclude that the promotional phenomena observed on the singly promoted, by K-modification, Pd(K)/Al₂O₃ catalysts are mainly due to the enhanced NO dissociative chemisorption on Pd active sites:



The subsequent recombination of two N(ad) atoms to yield N₂ (reaction (7)) and/or reaction of N(ad) with NO(ads) to form N₂O (reaction (8)), then provide the enhanced NO_x reduction rate:



The decreased surface population of molecular NO(ad) and the increased surface population of N(ad) species (due to the promoted reaction (6)), explains the observed enhancement in N₂-selectivity; both factors favor N₂ production at the expense of N₂O production (reactions (7) and (8), respectively).

However, the K-induced Pd–CO bond strengthening, which occurs in parallel with the Pd–NO strengthening, cannot be ignored in the above mechanistic scenario of alkali-promotion (this feature has been directly evidenced by DRIFTS studies of the CO adsorption over alkali-modified supported Pd catalysts [54,61]). An inverse effect due to the competition of CO and NO adsorption on Pd active sites (i.e., CO-poisoning of the surface) is then expected. As we indeed observed, low or moderate K loadings (<0.25 wt.% K) caused promotion, while high K loadings caused significant inhibition of the de-NO_x rate, thus leading to the optimally promoted Pd(0.25 wt.% K)/Al₂O₃ catalyst C3, which has been shown in Fig. 1 as the representative best from its series. This ‘volcano’ behavior of the NO_x reduction rate versus K-loading can be reasonably attributed to the simultaneous action of two factors in competition: enhanced NO dissociative adsorption in competition with the enhanced CO-poisoning of the surface (stronger adsorbed CO). CO-poisoning of Pd/NO + CO + H₂ + O₂ system can also be gas phase driven by increasing the CO/H₂ ratio, as indeed observed by Macleod et al. [49]; they observed volcano dependence of the NO reduction rate upon changing the CO/H₂ gas constitution between the two extreme ends, i.e., absence of CO and absence of H₂. Unfortunately, *in situ* DRIFTS studies (e.g., Fig. 6 data) are of limited use for assignment of bands related to NO or CO due to interferences between gaseous and adsorbed spectra. As a result, *in situ* DRIFT spectra of Fig. 6 cannot be used for extracting information for the overlapping bands in the middle region (2100–1900 cm⁻¹) where the carbonyl species are expected. DRIFT studies on the separate and simultaneous adsorption of CO and NO over our catalyst could give information about the competitive adsorption of CO and NO. However, this is beyond the scope of the present work. Nevertheless, in regard to this point, relevant literature data concerning alkali-induced Pd–CO

bond strengthening on alkali modified catalysts [54,61] and the strengthening of the NO chemisorption bond by alkali-induced effects [59,60] have been already discussed above.

Focusing now on the behaviour of the doubly-promoted Pd(K)/Al₂O₃–(TiO₂) catalysts, their high NO_x reduction activity combined with high selectivity (Fig. 4) can be readily understood in the following terms. Two different NO_x SCR-driven channels are most likely to operate in parallel over these catalysts: (i) the NH₃-formation channel that has its origin on the Pd and Al₂O₃ combined chemistry, which in the present circumstance is further enhanced by TiO₂, and (ii) the NO dissociative chemisorption channel that has its origin on the electronic modification by K of the Pd surface. The former channel provides high NO_x reduction activity but not significant changes in N₂-selectivity (this is easily understood by considering that both Pd/Al₂O₃ and Pd/Al₂O₃–(TiO₂) catalysts operate through the same mechanism, i.e., the NH₃-formation channel). The latter channel provides lower NO_x reduction activity enhancements, due to the competitive role of the Pd–CO bond strengthening, but higher N₂-selectivity values due to the extended NO dissociation on Pd surface. As a result the doubly-promoted catalysts combine the high activity offered by the support-mediated promotional effects of TiO₂ and the elevated selectivity offered by the surface-induced promotional effects of K. In fact, the retained relatively high intensity of surface ammonia intermediate, recorded on the doubly-promoted Pd(K)/Al₂O₃–(TiO₂) catalyst C5 (Fig. 6), confirms that NH₃-formation still plays a key role in the catalytic mechanism of the doubly-promoted catalysts.

However, a more close comparison of the spectra C5 and C2 of Fig. 6, that correspond to the doubly-promoted Pd(K)/Al₂O₃–(TiO₂) catalyst C5 and the K-free TiO₂-promoted Pd/Al₂O₃–(TiO₂) catalyst C2, respectively, clearly indicates that the 3245 cm⁻¹ N–H stretching intensity of the former is less than that of the latter; obviously the presence of K inhibits to some extent the formation of NH₃. This is not surprising considering the increased strengthening of the Pd–CO bond caused by K, a fact that expected to suppress the formation of NCO intermediates (reaction (4)) and consequently NH₃ production (reaction (5)). This interpretation is also in reasonable consistence with the observed suppressed NO_x conversion activities of K-dosed Pd(K)/Al₂O₃–(TiO₂) catalysts C4–C8 in comparison to the K-free catalyst C2 (Fig. 4a). Indeed, low or moderate K-loadings (<~0.5 wt.% K) are found to cause a slight depression in NO_x conversion, this being progressively significant upon increasing K-loadings; the NH₃-formation SCR-driven channel is most likely progressively downgraded upon increasing K-loading, leaving the control of the SCR process to the NO dissociative chemisorption channel.

In summary, we believe that the doubly-promoted Pd(alkali)/Al₂O₃–(TiO₂) catalyst formulation discussed here represents a very promising system for the control of NO_x emissions under oxygen-rich conditions. This novel catalyst delivers both very high NO_x conversion and selectivity towards N₂ under demanding conditions. The temperature window in which NO_x conversion and N₂-selectivity both remain high is very wide, typically 120–400 °C. Their constitution (i.e., TiO₂ and mainly

K loadings) could be optimized in respect to the H₂:CO conditions desired to be used. The method of *electrochemical promotion* could be used as an *in situ*, simple and very effective research tool [62] for such optimization perspectives. Further detailed studies in which use will be made of XPS and HREM are planned for better understanding of the synergy of promotion mechanisms [63]; the development of these systems including the effects of added water could be also considered.

5. Conclusions

1. The activity and N₂-selectivity of Pd-based catalysts for lean NO_x reduction by CO + H₂ can be significantly promoted either via support-mediated effects supplied by TiO₂-modification of the Al₂O₃ support, or via surface-induced effects caused by alkali (K) adatoms on the catalyst surface.
2. When these two methods of promotion are applied simultaneously to the Pd/NO + CO + H₂ + O₂ system the net result is a combination of high NO_x conversion efficiency and high selectivity towards N₂.
3. This synergy of the two methods of promotion derives from the combination of two different SCR channels. The support-mediated (by TiO₂) promotion operates through the NH₃-formation channel, whereas the surface-induced (by potassium) promotion is governed by an extended NO dissociation caused by the electropositive modifier.

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