Novel doubly-promoted catalysts for the lean NO\textsubscript{x} reduction by H\textsubscript{2} + CO: Pd(K)/Al\textsubscript{2}O\textsubscript{3}–(TiO\textsubscript{2})

M. Konsolakis\textsuperscript{a}, M. Vrontaki\textsuperscript{a}, G. Avgouropoulos\textsuperscript{b}, T. Ioannides\textsuperscript{b}, I.V. Yentekakis\textsuperscript{a,*}

\textsuperscript{a}Laboratory of Physical Chemistry and Chemical Processes, Department of Sciences, Technical University of Crete, 73100 Chania, Crete, Greece
\textsuperscript{b}FORTH/ICE-HT, 26500 Patras, Greece

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Abstract

The reduction of NO by CO + H\textsubscript{2} in the presence of excess O\textsubscript{2} 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\textsubscript{x} efficiency of the catalytic system. Therefore, the Pd-catalysed NO + CO + H\textsubscript{2} + O\textsubscript{2} reaction was gradually studied over: (i) Pd/Al\textsubscript{2}O\textsubscript{3}–(TiO\textsubscript{2}) catalysts (support-mediated promotion by modifying the Al\textsubscript{2}O\textsubscript{3} support with TiO\textsubscript{2}), (ii) K-dosed Pd(K)/Al\textsubscript{2}O\textsubscript{3} catalysts (surface-induced promotion by modifying the Pd surface with the addition of K), and (iii) doubly-promoted Pd(K)/Al\textsubscript{2}O\textsubscript{3}–(TiO\textsubscript{2}) catalysts. Both (i) and (ii) methods of promotion were found to significantly promote the system, when acting individually. However, the de-NO\textsubscript{x} efficiency and N\textsubscript{2}-selectivity of the doubly-promoted Pd(K)/Al\textsubscript{2}O\textsubscript{3}–(TiO\textsubscript{2}) 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\textsubscript{x} conversion in a very wide temperature range (100–400°C), accompanied by very good N\textsubscript{2}-selectivities of ~85%, i.e., 15–30 additional percentage units in comparison to the selectivity of the original un-promoted Pd/Al\textsubscript{2}O\textsubscript{3} catalyst.

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1. Introduction

Emissions of nitrogen oxides (NO\textsubscript{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 CO\textsubscript{2} emissions. However, lean-burn gasoline and diesel engines that work in excess O\textsubscript{2} (lean conditions) offer significant fuel economy, hence lower CO\textsubscript{2} emissions per kilometer, compared to conventional gasoline engines. Unfortunately, the excess oxygen makes the NO\textsubscript{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\textsubscript{x} at low temperatures or under conditions of excess O\textsubscript{2} [4–6]. On the other hand, in stationary power sources and chemical plants, the NH\textsubscript{3} SCR process is currently the best choice for the NO\textsubscript{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\textsubscript{x}, using in principle the gases which already exist in the exhaust stream (e.g., hydrocarbons, H\textsubscript{2}, CO) as reducing agents.

Extensive research has been done regarding the NO\textsubscript{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 N\textsubscript{2}O [12–15]; N\textsubscript{2}O is one of the most powerful greenhouse gases. Recently, efforts for improving the hydrocarbon-SCR of NO\textsubscript{x} (including the particular cases of stoichiometric and lean-burn conditions) on Pt-group metals via electropositive surface promotion with
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 NOx from stationary power sources and chemical plants. This can explain the growing interest for the use of H2 as a reducing agent of NOx 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-NOx efficiency with N2-selectivities varying typically between 20 and 60% at low temperatures (100–200 °C). Unfortunately, at higher temperatures the Pt-catalysed NOx 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 NOx 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 NOx 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-NOx 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 NOx 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-NOx 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-NOx efficiency of Pd [45–49], we investigated lean NOx 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-NOx 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 1:3:3, 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 surface area of 380 m2/g.

Table 1

<table>
<thead>
<tr>
<th>Catalyst code and kind of promotion used</th>
<th>Catalyst constitution</th>
<th>H2 uptake (cm3 STP/gcat)</th>
<th>Pd dispersion (%)</th>
<th>Active metal surface areaa (m2/gcat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 original, unpromoted catalyst</td>
<td>0.5 wt.% Pd/Al2O3</td>
<td>0.108</td>
<td>20.5</td>
<td>0.457</td>
</tr>
<tr>
<td>C2 promoted by only support-mediated effects</td>
<td>0.5 wt.% Pd/Al2O3–10 wt.% TiO2</td>
<td>0.162</td>
<td>30.8</td>
<td>0.685</td>
</tr>
<tr>
<td>C3 promoted by only surface-induced effects (0.25 wt.% K)</td>
<td>0.5 wt.% Pd(0.25 wt.% K)/Al2O3</td>
<td>0.100</td>
<td>19.0</td>
<td>0.423</td>
</tr>
<tr>
<td>C4 doubly-promoted with 0.1 wt.% K and 10 wt.% TiO2</td>
<td>0.5 wt.% Pd(0.1 wt.% K)/Al2O3–10 wt.% TiO2</td>
<td>0.142</td>
<td>27.0</td>
<td>0.600</td>
</tr>
<tr>
<td>C5 doubly-promoted with 0.25 wt.% K and 10 wt.% TiO2</td>
<td>0.5 wt.% Pd(0.25 wt.% K)/Al2O3–10 wt.% TiO2</td>
<td>0.115</td>
<td>21.8</td>
<td>0.486</td>
</tr>
<tr>
<td>C6 doubly-promoted with 0.5 wt.% K and 10 wt.% TiO2</td>
<td>0.5 wt.% Pd(0.5 wt.% K)/Al2O3–10 wt.% TiO2</td>
<td>0.118</td>
<td>22.4</td>
<td>0.500</td>
</tr>
<tr>
<td>C7 doubly-promoted with 1.0 wt.% K and 10 wt.% TiO2</td>
<td>0.5 wt.% Pd(1.0 wt.% K)/Al2O3–10 wt.% TiO2</td>
<td>0.097</td>
<td>18.5</td>
<td>0.410</td>
</tr>
<tr>
<td>C8 doubly-promoted with 3.0 wt.% K and 10 wt.% TiO2</td>
<td>0.5 wt.% Pd(3.0 wt.% K)/Al2O3–10 wt.% TiO2</td>
<td>0.082</td>
<td>15.5</td>
<td>0.347</td>
</tr>
</tbody>
</table>

* Calculations based on a Pd surface atom density of 1.27 × 1019 atoms/m2.
surface area of 173 m\(^2\)/g, as determined by N\(_2\) adsorption at -196 °C. In order to produce the TiO\(_2\)-modified Al\(_2\)O\(_3\) with 10 wt.% TiO\(_2\), the sol–gel Al\(_2\)O\(_3\) was added in a solution of titanium isopropoxide (Aldrich) and propanol-2 (volume ratio Ti(OC\(_3\)H\(_7\))\(_4\)–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 liquide certified gas mixtures of 7.83% NO, 10.1% CO, 20% H\(_2\) and 20.7% O\(_2\), 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 for the analysis of NO and NO\(_2\) and \(\text{CO}, \text{CO}_2, \text{O}_2, \text{H}_2, \text{N}_2\) and N\(_2\)O were separated using a porapak-N column, both operated during light-off catalyst testing was He balanced 1000 ppm NO\(_x\) + 2500 ppm CO + 7500 ppm H\(_2\) + 6% O\(_2\). He balance; \(T = 200^\circ\text{C}\) and total flow rate of 60 cm\(^3\)/min. Diffuse reflectance IR spectra were collected using an excalibur 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 \(~1\) cm\(^3\) volume. Considering the total flow rate of 60 cm\(^3\)/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 CO\(_2\)-free dry air generated in an air purifier system (Claind Italy, CO\(_2\)-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\(_x\) + H\(_2\) + CO + O\(_2\) reaction performance over Pd/Al\(_2\)O\(_3–(\text{TiO}_2)\) and Pd(K)/Al\(_2\)O\(_3\) catalysts; individual imposition of the support-mediated and the surface-induced promotion methods

The promotion of Pd catalytic chemistry for the NO reduction by H\(_2\) + CO in excess O\(_2\), 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 N\(_2\)O (Fig. 1b) and the corresponding selectivity towards N\(_2\) (Fig. 1c) versus temperature for C1 and C2 catalysts, i.e., Pd supported on Al\(_2\)O\(_3\) and on TiO\(_2\)-modified alumina (Al\(_2\)O\(_3–10\) wt.% TiO\(_2\)) carriers, respectively (see Table 1). Fig. 1a–c also show the corresponding data obtained for a Pd(0.25 wt.% K)/Al\(_2\)O\(_3\) 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)/Al\(_2\)O\(_3\) 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/Al\(_2\)O\(_3\)) displays very poor de-NO\(_x\) activity under the conditions employed with
maximum NOx conversion only at \( \sim 35\% \) (Fig. 1a). On the contrary, Pd supported on the mixed Al\(_2\)O\(_3\)–TiO\(_2\) 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 N\(_2\)O production rate (Fig. 1b). As a result, its selectivity towards N\(_2\) 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)/Al\(_2\)O\(_3\) 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/Al\(_2\)O\(_3\)–(TiO\(_2\)) catalyst C2 (Fig. 1a). However, this enhancement in NO\(_x\) conversion is obviously not followed by any increase in N\(_2\)O formation rate (Fig. 1b), resulting in a substantial improvement in N\(_2\)-selectivity of catalyst C3 in comparison to the un-promoted catalyst C1 (Fig. 1c).

The superior activities of the Pd/Al\(_2\)O\(_3\)–(TiO\(_2\)) and Pd(K)/Al\(_2\)O\(_3\) catalysts C2 and C3, respectively, in comparison to the un-promoted Pd/Al\(_2\)O\(_3\) catalyst C1 are also obvious in Figs. 2 and 3, which show the corresponding CO and H\(_2\) conversion profiles versus temperature. Profile shifts of about 30 °C to lower temperatures for both CO and H\(_2\) 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 N\(_2\)-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 N\(_2\)-selectivity.

### 3.2. The NO\(_x\) + H\(_2\) + CO + O\(_2\) reaction performance over the doubly-promoted Pd(K)/Al\(_2\)O\(_3\)–(TiO\(_2\)) 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)/Al\(_2\)O\(_3\)–(10 wt.% TiO\(_2\)), i.e., the catalysts which are simultaneously promoted by support-mediated effects (10 wt.% TiO\(_2\) into Al\(_2\)O\(_3\) 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
they retain the elevated de-NO$_x$ efficiency of Pd/Al$_2$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 (Pd/Al$_2$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$_2$O. It is interesting that N$_2$O 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 Pd/Al$_2$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 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
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-\text{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; total flow rate = 280 cm3/min; catalyst weight = 70 mg.

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 + 2500 ppm CO + 7500 ppm H2 + 6% O2, He balance. T = 200°C, total flow rate F = 60 cm3/min.
however, that the broad band at ~3245 cm\(^{-1}\) (N–H stretching mode) is more intense on Pd/Al\(_2\)O\(_3\)–(TiO\(_2\)) and Pd(K)/Al\(_2\)O\(_3\)–(TiO\(_2\)) samples, indicating that the formation of NH\(_3\) is substantially more pronounced in samples that have been modified by TiO\(_2\) addition in the Al\(_2\)O\(_3\) support. An interesting feature observed in all spectra, is the absence of isocyanate species (NCO), which are considered as intermediates for NH\(_3\) 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/Al\(_2\)O\(_3\)–(TiO\(_2\)) 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 + H\(_2\) mixtures [45–49]. Comparing the NO + CO + H\(_2\) + O\(_2\) reaction performance over Pd and Pt catalysts supported on Al\(_2\)O\(_3\), 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/Al\(_2\)O\(_3\) was found considerably more active than Pd/SiO\(_2\) [46]. As they confirmed by *in situ* DRIFTS studies, the superior de-NO\(_x\) performance with CO + H\(_2\) mixtures found for Pd supported on Al\(_2\)O\(_3\) is due to *in situ* generation of adsorbed NH\(_3\), 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.:

\[
\text{N(ad) + CO(ad) → NCO(ad)} \quad (4)
\]

\[
\text{NCO(ad) + H}_2\text{O → NH}_3 + \text{CO}_2 \quad (5)
\]

was considered as the most likely route in NH\(_3\) formation at low temperatures (<~180 °C), while at higher temperatures the formation of NH\(_3\) was attributed at the direct reaction between H\(_2\) 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 Al\(_2\)O\(_3\) component of the catalyst after NCO migration to the support [49].

Exploring their studies on this promising metal-support pair (i.e., Pd–Al\(_2\)O\(_3\)), they showed that TiO\(_2\) doping of the Al\(_2\)O\(_3\) support produces yet further significant enhancement in NO\(_x\) conversion. This synergy of Al\(_2\)O\(_3\) and TiO\(_2\) was attributed to the intrinsic surface chemistry of the pure TiO\(_2\) and Al\(_2\)O\(_3\) oxides and not to a mixed oxide formation; the Pd/TiO\(_2\) component of the Pd/Al\(_2\)O\(_3\)–(TiO\(_2\)) catalyst was found to promote the system towards NCO production, whereas, the Al\(_2\)O\(_3\) component is then responsible for the subsequent hydrolysis of NCO to form NH\(_3\) [49].

The very substantial enhancement of the Pd/NO + CO + H\(_2\) + O\(_2\) system activity via TiO\(_2\)-modification of the Al\(_2\)O\(_3\) support found here (Figs. 1–3), confirms the results of Lambert and co-workers. Our *in situ* DRIFT spectra on Pd/Al\(_2\)O\(_3\) and Pd/Al\(_2\)O\(_3\)–TiO\(_2\) catalysts C1 and C2, respectively (Fig. 6), which clearly show the appearance of a sufficiently higher amount of surface NH\(_3\) on the latter catalyst, implies that NH\(_3\) indeed plays a key role in the de-NO\(_x\) process over these two catalysts; the TiO\(_2\) induced support-mediated effects apparently follow the mechanism proposed by Lambert and co-workers, which involves the NH\(_3\)-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)/Al\(_2\)O\(_3\) catalysts. Concerning the performance of the Pd(K)/Al\(_2\)O\(_3\) 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 TiO\(_2\)-promoted catalyst C2, the presence of K does not cause any detectable influence on the amount of NH\(_3\) intermediate on C3 catalyst surface (Fig. 6). This implies that in the case of K-modified Pd(K)/Al\(_2\)O\(_3\) catalysts, most likely another SCR-driven channel is now promoted (different than the NH\(_3\)-formation channel considered to be promoted on TiO\(_2\)-modified catalysts). The superior N\(_2\)-selectivity performance of the Pd(K)/Al\(_2\)O\(_3\) catalyst C3 in comparison to that of the Pd/Al\(_2\)O\(_3\)–(TiO\(_2\)) catalyst C2 (the latter exhibits similar N\(_2\)-selectivity with Pd/Al\(_2\)O\(_3\) catalyst C1, Fig. 1c) is also consistent with this hypothesis.

In order to rationalize the K-promotion on the Pd/NO + CO + H\(_2\) + O\(_2\) 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 O\(_2\) [18,24], we have showed that alkali 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 O\(_2\)), 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 alkali 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) Na-dosed Pt(111) 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 phenomenon 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:

\[ \text{NO(ad)} \rightarrow \text{N(ad)} + \text{O(ad)} \quad \text{enhanced by K.} \]  

(6)

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

\[ \text{N(ad)} + \text{N(ad)} \rightarrow \text{N}_2(g) \]  

(7)

\[ \text{NO(ad)} + \text{N(ad)} \rightarrow \text{N}_2\text{O}(g). \]  

(8)

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-NOx 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 NOx 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 NOx reduction activity combined with high selectivity (Fig. 4) can be readily understood in the following terms. Two different NOx 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 NOx 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 NOx 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 NOx 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 NOx 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 NOx emissions under oxygen-rich conditions. This novel catalyst delivers both very high NOx conversion and selectivity towards N2 under demanding conditions. The temperature window in which NOx 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 NOₓ 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) atoms 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 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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