The nature of metal oxide on adsorptive and catalytic properties of Pd/MeOx/Al2O3 catalysts

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Abstract

The role of ceria, niobium and molybdenum oxides on the promotion of the NO reduction by CO was studied. A bifunctional mechanism was discussed as a function of both the nature of interaction between metal oxide and palladium and the redox properties of each metal oxide. The NO dissociation was better on the Pd/MoO3/Al2O3 catalyst than on the Pd/CeO2/Al2O3 and Pd/Nb2O5/Al2O3 catalysts. The explanation for the very high N2 production on Pd–Mo catalyst during the TPD analysis may be attributed to the NO+MoO5 stoichiometric reaction. The promoting effect of a reducible oxide for the NO+CO reaction at low temperature can be ascribed mainly to its easiness for a redox interchange and its interaction with the noble metal particles. This would increase the surface redox ability and favor the dynamic equilibrium needed for high N2 selectivity.

Keywords: Ceria; Catalysts; Redox properties; Redox mechanism

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1. Introduction

Automotive emission control catalysts contain several base metal additives, in addition to the noble metals, which improve greatly the catalytic performance. Ceria is added mainly due to its oxygen storage capacity [1], [2] and [3]. The role of ceria in promoting the NO/CO reaction is based on its ability to create oxygen vacancies through the Ce4+/Ce3+ redox couple [2], [3] and [4]. A bifunctional mechanism has been proposed which includes the participation of both metal and support to explain the promotion of the NO reduction in the presence of a reducible support [2] and [5]. According to Praliaud et al. [5],
these active sites are located at the metal–support interface and are related to the redox properties of the support.

Molybdenum oxide addition on palladium catalysts enhances the selectivity for nitrogen in the NO+CO reaction even under slightly oxidizing conditions[6, 7] and [8]. The high selectivity towards nitrogen has been attributed to Pd–Mo interaction. Recently, Schmal and coworkers [9] and [10] proposed that the catalytic behavior of the Pd–Mo/Al₂O₃ catalysts on the NO+CO reaction could be explained by a bifunctional mechanism. After adsorption and dissociation of NO on Mo⁴⁺, the oxygen dissociated is transferred to the Pd. The CO adsorbed on Pd surface reacts to CO₂.

Such as ceria, niobium oxides can also be reduced/oxidized as function of the atmosphere. After reduction at high temperature, Hu et al. [11] proposed the presence of NbO₂ species on the silica-supported niobia-promoted rhodium catalysts. During temperature-programmed oxidation (TPO), oxygen consumption was attributed to oxidation of partially reduced niobia species to Nb₂O₅. Rasband and Hecker [12] performed the NO reduction by CO on Rh/Nb₂O₅/SiO₂ catalysts. The addition of Nb₂O₅ diminished the reaction rate, which was attributed to the decrease of Rh dispersion. However, the selectivity on these catalysts was not reported.

This work aims to study the effect of the nature of metal oxides on adsorptive and catalytic properties of Pd/MeOₓ/Al₂O₃ catalysts for the NO+CO reaction. Here, we want to present the evidence for the NO dissociation over promoted catalysts reduced oxides (CeO₂, MoO₃ and Nb₂O₅). A bifunctional mechanism is also discussed as a function of both the nature of interaction between metal oxide and palladium and the redox properties of each metal oxide.

2. Experimental

2.1. Catalyst preparation

Alumina (AL-3916P — Engelhard) was calcined in air at 823 K for 16 h (BET area=190 m²/g). Catalysts were prepared by Al₂O₃ impregnation with an aqueous solution of either ammonium heptamolibdate (Riedel), cerium nitrate (Aldrich), or niobium oxalate (CBMM). The samples were dried at 353 K and calcined under flowing air at 773 K, for 2 h. Pd/Al₂O₃ and Pd/MeOₓ/Al₂O₃ samples were obtained by incipient wetness impregnation of Al₂O₃ and MeOₓ/Al₂O₃, respectively, with a solution of palladium chloride (Aldrich). Then, the samples were dried at 373 K, followed by calcination under flowing air at 773 K for 2 h. The prepared catalysts, their notation and composition are presented in Table 1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd (wt.%)</th>
<th>MeOₓ (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al₂O₃</td>
<td>1.25</td>
<td>—</td>
</tr>
<tr>
<td>Pd/Al₂O₃/Al₂O₃</td>
<td>0.85</td>
<td>13.00</td>
</tr>
<tr>
<td>Pd/MoO₃/Al₂O₃</td>
<td>1.02</td>
<td>11.61</td>
</tr>
<tr>
<td>Pd/Nb₂O₅/Al₂O₃</td>
<td>1.10</td>
<td>9.10</td>
</tr>
</tbody>
</table>

2.2. Catalyst characterization

2.2.1. Temperature-programmed reduction (TPR)

TPR experiments were performed in a conventional equipment, as described elsewhere [13]. The catalysts were pretreated at 423 K for 30 min in flowing argon. Then, the samples were heated at 10 K/min from room temperature to 1273 K in a flow of 1.6% H₂ in argon and the H₂ consumption was monitored using a thermal conductivity detector (TCD).

2.2.2. H₂ and CO chemisorption
H₂ and CO uptakes were measured in an ASAP 2000C equipment (Micromeritics). Before the reduction, the catalysts were dehydrated at 423 K for 0.5 h under vacuum. Then, the catalysts were reduced at 773 K (5 K/min) in flowing H₂ (30 cm³/min). Following reduction, the samples were evacuated for 1 h at reduction temperature and cooled down to adsorption temperature under vacuum. Irreversible uptakes were obtained from dual isotherms measured for hydrogen (at 343 K) and carbon monoxide (at 298 K) using the method described by Benson et al. [14] and Yates and Sinfelt [15] for H₂ and CO, respectively.

2.2.3. Infrared spectroscopy of adsorbed carbon monoxide or nitrogen monoxide
Self-supported samples used for infrared study were compressed into thin disk wafers with a 20 mm of diameter. The disk was placed in a sample holder and introduced into a cell, which allowed in situ reduction. All samples were reduced at 773 K with flowing H₂ (30 cm³/min) for 1 h and evacuated for 1 h at the same temperature prior cooling down to room temperature. Then, 10 Torr (1 Torr=133.3 Pa) of CO or NO was adsorbed at 298 K. After evacuation at the same temperature for 1 h, the infrared spectra were recorded on a Fourier transform infrared spectrometer (Perkin Elmer 2000).

2.2.4. CO and NO temperature-programmed desorption (TPD)
TPD of adsorbed CO or NO was carried out in a microreactor coupled to a quadrupole mass spectrometer (Prisma, Balzers). A Quadstar analytical system was used to select a series of masses and to record the signal intensity at each mass as a function of the temperature. The catalysts were purged out under helium flow (50 cm³/min) at a heating rate of 10 K/min, from room temperature to 823 K, prior to TPD experiments. The catalysts were then cooled to room temperature and reduced at 773 K, for 2 h, in a flow of pure H₂ (30 cm³/min). Following reduction, the samples were outgassed with helium at the reduction temperature for 1 h. The adsorption of either CO or NO was performed by pulses of a mixture of 5% CO in helium or 1% NO in helium, respectively, through the catalyst bed until saturation. After adsorption, the catalysts were heated at 20 K/min up to 823 K in a flow of helium (50 cm³/min). The mass spectrometer was calibrated against helium mixtures containing specified concentrations of CO, NO or N₂O and pure CO₂, H₂, N₂ or Ar. The experimental determination of the fragmentation pattern of each product was obtained separately by the mass spectrometer [10]. The distribution of desorbed products was calculated from the TPD spectra of individual mass fragments as follows. For example, the CO signal was calculated from the m/e=28 ratio allowing for the contribution of CO₂ (m/e=44) to this signal using the experimental fragmentation pattern for CO₂. Thus, the raw data signal for the m/e=44 peak was divided by 9.96 to form a signal corresponding to the m/e=28 contribution from CO₂. Then, this contribution was removed from the m/e=28 signal to yield a signal for CO without the contribution of CO₂. The same procedure was applied to the desorption spectra of compounds containing nitrogen atoms. The distribution of desorbed products was based on the number of carbon or nitrogen desorbed atoms.

2.3. Catalytic activity
The catalytic experiments were performed in a microreactor at atmospheric pressure. Catalysts (ca. 100 mg) were pretreated in helium (ml/min) at 823 K for 1 h. Then, the catalysts were reduced at 773 K, for 2 h. The reaction mixture consisted of 1.0% CO/0.6% NO balanced with He flow (150 ml/min; space velocity=100,000 h⁻¹). The effluent products were analyzed by on line gas chromatography, using a TCD detector and a Carbosieve Carboxen 1000 column with Cryogen.

3. Results and discussion
3.1. The Pd–metal oxide interaction

The TPR profile of MoO$_3$/Al$_2$O$_3$, CeO$_2$/Al$_2$O$_3$ and Nb$_2$O$_5$/Al$_2$O$_3$ catalysts are shown in Fig. 1. The TPR profile of MoO$_3$/Al$_2$O$_3$ catalyst showed two peaks at 755 and 1223 K. The peak at lower temperature has been attributed to reduction of Mo$^{6+}$ to Mo$^{4+}$, whereas the one at high temperature is due to removal of oxygen atom in the sublayer [16].

![Figure 1](https://example.com/figure1.png)

**Fig. 1.** TPR profile of MeO$_x$/Al$_2$O$_3$ catalysts.

The TPR profile of CeO$_2$/Al$_2$O$_3$ showed a shoulder at 867 K and a peak at 1160 K. Monteiro et al. [17] showed that the profiles of 3 and 20% CeO$_2$/Al$_2$O$_3$ exhibited several reduction peaks at around 720, 870, 1135 and above 1150 K, which were related to ceria loading. In the literature, these peaks have been ascribed to different ceria species. According to Shyu et al. [18], the peak at around 720 K corresponds to the reduction of ceria capping oxygen. The peaks at 870, 1000 and above 1200 K were assigned to the formation of non-stoichiometric cerium oxides (CeO$_x$), CeAlO$_3$ and Ce$_2$O$_3$, respectively. Recently, Appel et al. [19] studied the influence of the precursor on the distribution of cerium species over alumina. TPR results also revealed the presence of several reduction peaks, which were attributed to the surface reduction of CeO$_2$ and to the formation of CeAlO$_3$ and Ce$_2$O$_3$. Therefore, our results are in good agreement with the literature and the H$_2$ uptake corresponded to the reduction of ceria capping oxygen (867 K) and the formation of Ce$_2$O$_3$ (1160 K).

The Nb$_2$O$_5$/Al$_2$O$_3$ catalysts presented only one peak at around 909 K and small hydrogen consumption above 1000 K. Several surface species have been found on supported niobium oxide. Raman studies showed the presence of NbO$_x$ tetrahedral and NbO$_x$ octahedral structures on Nb$_2$O$_5$/Al$_2$O$_3$ samples [20], [21] and [22]. XANES and EXAFS analysis revealed three surface species on alumina-supported niobium oxide: NbO$_x$ monomer, Nb$_2$O$_5$ dimmer and niobic acid-like polymer [23]. In all cases, the amount of each species was a function of the niobia loading. Thus, our TPR results suggest that the peak at 900 K and the hydrogen uptake at high temperature may be attributed to reduction of octahedral and tetrahedral niobium oxides species, respectively.

The TPR profiles of Pd/Al$_2$O$_3$, Pd/MoO$_3$/Al$_2$O$_3$, Pd/CeO$_2$/Al$_2$O$_3$ and Pd/Nb$_2$O$_5$/Al$_2$O$_3$ catalysts are shown in Fig. 2. The Pd/Al$_2$O$_3$ catalyst showed a peak at 420 K and a broad desorption
peak between 600 and 800 K. This peak has been attributed to PdO\textsubscript{2}Cl\textsubscript{y} reduction [19]. Oxychloride species are easily found on catalysts prepared by PdCl\textsubscript{2} precursor, being formed from chlorine residues under oxidizing treatments, e.g. sample calcination [24].

Fig. 2.
TPR profile of Pd/MeO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts.

The Pd/MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalyst presented three hydrogen uptake regions, namely, at 362, 774 and 1216 K. The hydrogen uptake at 362 K did not only correspond to palladium oxide reduction but also to Mo\textsuperscript{6+} to Mo\textsuperscript{4+} reduction since the H\textsubscript{2} consumption exceeded the stoichiometric H\textsubscript{2} amount for the complete reduction of palladium oxide (Table 2). The palladium addition strongly promoted the molybdenum oxide reduction, explaining the decrease of the peak at 774 K. However, the removal of oxygen atoms in the sublayer (1216 K) was not influenced by the presence of palladium.

Table 2. Hydrogen consumption during TPR

<table>
<thead>
<tr>
<th>Samples</th>
<th>H\textsubscript{2} Consumption (µmoles H\textsubscript{2}/g\textsubscript{cat})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>298K: 5  298–450 K: 479  900–1223 K: 787</td>
</tr>
<tr>
<td>MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>298K: 1  298–450 K: 466  900–1223 K: 1553</td>
</tr>
<tr>
<td>Nb\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>298K: –  298–450 K: –  900–1223 K: 66</td>
</tr>
<tr>
<td>Pd/Al\textsubscript{2}O\textsubscript{3}</td>
<td>298K: 73  298–450 K: –  900–1223 K: –</td>
</tr>
<tr>
<td>Pd/CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>298K: 188  298–450 K: 158  900–1223 K: 157</td>
</tr>
<tr>
<td>Pd/MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>298K: 363  298–450 K: 51  900–1223 K: 748</td>
</tr>
<tr>
<td>Pd/Nb\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>298K: 88  298–450 K: 48  900–1223 K: 52</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Hydrogen consumption at room temperature.

The TPR profile of Pd/CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} displayed three peaks at 352, 631 and 1005 K. The peak at 352 K was ascribed to palladium oxide reduction whereas the peaks at high temperatures were due to reduction of ceria capping oxygen and to the formation of Ce\textsubscript{2}O\textsubscript{3}. However, the
hydrogen consumption at 352 K was higher than that necessary to reduce the palladium oxide (Table 2) suggesting that reduction of ceria species occurred at this region. Furthermore, both peaks corresponding to ceria reduction were shifted to lower temperature in the presence of palladium. Monteiro et al. [17] observed that palladium interacts preferentially with surface ceria species promoting its reduction. XPS results revealed that the valence of ceria is closer to Ce\(^{3+}\) at lower ceria content whereas the presence of palladium did not affect the ceria valence at high loading of ceria.

The Pd/Nb\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalysts showed a peak at 418 K and two broad hydrogen consumption at around 660 and 1260 K. The hydrogen uptake at 418 K was slightly greater than the one observed on Pd/Al\(_2\)O\(_3\) catalyst, indicating that there is a small reduction of niobium oxide at this temperature. Furthermore, the palladium addition shifted the peak at 909 K on the Nb\(_2\)O\(_5\)/Al\(_2\)O\(_3\) sample toward 660 K and increased the amount of hydrogen consumption due to niobium oxide reduction (Table 2). Hu et al. [11] also observed a promoting effect of noble metal addition on niobium oxide reduction on Rh/Nb\(_2\)O\(_5\)/SiO\(_2\) catalysts. According to them, the niobia particles interacted with rhodium since the noble metal was dispersed on those niobia particles. Thus, our results revealed also a strong interaction between palladium and niobium oxide.

3.2. The effect of metal oxide addition on adsorptive properties of Pd

The amount of H\(_2\) and CO irreversibly adsorbed on Pd/Al\(_2\)O\(_3\) and Pd–MeO\(_x\)/Al\(_2\)O\(_3\) catalyst, the CO/H\(_2\) ratio and the dispersion values are presented in Table 3. The metal oxide addition caused suppression of H\(_2\) chemisorption capacity. This effect was more pronounced on Pd/MoO\(_3\)/Al\(_2\)O\(_3\) and Pd/Nb\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalysts. Furthermore, the CO adsorption stoichiometry changed drastically as function of the nature of the metal oxide. The CO/H\(_2\) ratio showed a CO stoichiometry between bridged (CO/H\(_2\)=1) and linear (CO/H\(_2\)=2) for Pd/Al\(_2\)O\(_3\) catalyst. However, the CO/H\(_2\) ratio was higher than 2 on the Pd/MoO\(_3\)/Al\(_2\)O\(_3\) and Pd/Nb\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalysts, whereas CO was bonded almost completely in the bridged form on Pd/CeO\(_2\)/Al\(_2\)O\(_3\).

Table 3. Hydrogen adsorption, palladium dispersion and H\(_2\)/CO ratio obtained from chemisorption

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Consumption (µmoles/mg(_{Pd}))</th>
<th>Dispersion (%)</th>
<th>CO/H(_2) (ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H(_2)</td>
<td>CO</td>
<td>H(_2)</td>
</tr>
<tr>
<td>Pd/Al(_2)O(_3)</td>
<td>2.10</td>
<td>2.94</td>
<td>45</td>
</tr>
<tr>
<td>Pd/CeO(_2)/Al(_2)O(_3)</td>
<td>1.19</td>
<td>1.26</td>
<td>25</td>
</tr>
<tr>
<td>Pd/MoO(_3)/Al(_2)O(_3)</td>
<td>0.43</td>
<td>2.04</td>
<td>9</td>
</tr>
<tr>
<td>Pd/Nb(_2)O(_5)/Al(_2)O(_3)</td>
<td>0.64</td>
<td>2.61</td>
<td>15</td>
</tr>
</tbody>
</table>

The infrared spectrum of the irreversibly adsorbed carbon monoxide on Pd/Al\(_2\)O\(_3\) catalyst displayed two absorption bands at 1945 and 2082 cm\(^{-1}\) (Fig. 3a). These bands correspond to bridged and linear-bonded carbon monoxide on palladium atoms, respectively [25] and [26], in good agreement with the CO/H\(_2\) ratio as determined by H\(_2\) and CO adsorption measurements.
The infrared spectrum of carbon monoxide adsorbed on Pd/MoO$_3$/Al$_2$O$_3$ catalyst was similar to that on the Pd/Al$_2$O$_3$ (Fig. 3b). The band above 2000 cm$^{-1}$ was attributed to linear adsorbed species and below 2000 cm$^{-1}$ to bridged species. However, the relative intensities of these bands changed as compared to Pd/Al$_2$O$_3$ catalyst. The linear/bridged carbon monoxide ratio increased in the presence of MoO$_3$. These results were attributed to dilution effect of Pd among MoO$_3$ and explained the strong decrease of hydrogen adsorption (Table 3). However, this result did not justify the high CO/H$_2$ ratio obtained. On the other hand, the Pd/MoO$_3$/Al$_2$O$_3$ catalyst showed also a band around 2196 cm$^{-1}$. The literature claims that this band was attributed to CO chemisorption on partially reduced molybdenum oxide [6], which supports the observed high CO/H$_2$ ratio (Table 3). Recently, we also reported the presence of a band around 2191 cm$^{-1}$ on the MoO$_3$/Al$_2$O$_3$ catalyst [10].

The Pd/CeO$_2$/Al$_2$O$_3$ catalyst exhibited two CO adsorption bands at 1971 (bridged) and 2077 cm$^{-1}$ (linear). However, the amount of CO bridged bond was larger than the linear bonded species, in a good agreement with the CO/H$_2$ ratio measurements by CO and H$_2$ adsorption.

The IR spectra of CO adsorbed on Pd/Nb$_2$O$_5$/Al$_2$O$_3$ exhibited two bands at 1935 and 2090 cm$^{-1}$, corresponding to bridged and linear forms of CO adsorption (Fig. 3d). As on the PdMoO$_3$/Al$_2$O$_3$ catalyst, the linear/bridge ratio increased on the Pd/Nb$_2$O$_5$/Al$_2$O$_3$ catalyst. At high temperature reduction (HTR) the Pd/Nb$_2$O$_5$ catalyst led to suppression of the bridged CO adsorption band, which was attributed to the blocking effect Pd surface by NbO$_x$ species [27].

Hu and coworkers [11, 28] and [29] studied the Rh–Nb$_2$O$_5$ interaction on the Rh/Nb$_2$O$_5$/SiO$_2$ catalysts and observed strong suppression of H$_2$ chemisorption capacity after HTR. They attributed it to the migration of NbO$_2$ species during the HTR at the surface of Rh atoms. Thus, the increase of the linear/bridged ratio could be explained by the decoration of Pd particles by partially reduced niobium oxide species. In spite of the high CO/H$_2$ ratio measurements by H$_2$ and CO adsorption, it was not observed a band that could be attributed to CO adsorption on partially reduced niobium oxide. Moreover, Pd/Nb$_2$O$_5$/Al$_2$O$_3$ and Pd/MoO$_3$/Al$_2$O$_3$ catalysts showed high values of CO/H$_2$ ratios by chemisorption, suggesting either: (i) a dilution effect of palladium ensembles by reduced MeO$_x$ species, which inhibits both
hydrogen dissociation and CO bridge-bonded on Pd\(^0\) particles or (ii) CO adsorption on partially reduced MeO\(_x\) species.

The profiles of CO desorption are presented in Fig. 4a–d. The TPD curves following carbon monoxide adsorption on Pd/Al\(_2\)O\(_3\) catalyst displayed four peaks at 377, 470, 657 and 823 K. Rieck and Bell [30] and [31] assigned the peaks at low temperatures in the TPD spectra to linearly bonded CO, whereas the peaks at high temperature were attributed to bridge-bonded CO on Pd\((1\ 0\ 0)\) and Pd\((1\ 1\ 1)\) planes. Thus, the desorption peak below 400 K can be related to linear adsorbed CO on Pd\((1\ 0\ 0)\). On Pd/MeO\(_x/\)Al\(_2\)O\(_3\) catalysts, the desorption starts 20 K later, at least, and was ascribed to CO adsorbed on top of Pd\((1\ 1\ 1)\) faces. Indeed, Pd\((1\ 0\ 0)\) is usually present on more disperse catalysts just as observed by hydrogen chemisorption for Pd/Al\(_2\)O\(_3\) sample (Table 3). In addition, TPR profiles showed an easier reduction of palladium on MeO\(_x/\)Al\(_2\)O\(_3\), which is related to a weakening of palladium–Al\(_2\)O\(_3\) interaction, that also favors particles in a Pd\((1\ 1\ 1)\) main orientation.
Desorption peaks above 600 K are also related to CO bridge-bonded on palladium. The addition of Nb$_2$O$_5$ and MoO$_3$ decreased the relative intensity of linear/bridge peaks, which agreed with the CO FTIR spectra (Fig. 4b and d).

Formation of CO$_2$ was observed in all samples, besides releasing carbon monoxide molecules, but hydrogen was produced only on Pd/Al$_2$O$_3$ catalyst. Hydrogen evolved symmetrically to the CO$_2$ formation at high temperature (823 K). Several measurements of CO desorption on alumina supported catalysts has pointed out to simultaneous CO$_2$ and H$_2$ releasing [32] and [33]. In fact, at this temperature, dehydroxilation of alumina takes place in the non-evacuated samples and the presence of hydroxyl groups at the surface allows to the reaction with CO through the water gas shift reaction. However, high MeO$_x$ loading on alumina
minimizes the hydroxyl group density on the modified supports, as evidenced by the negligible formation of hydrogen during CO TPD.

The formation of CO$_2$ molecules in the absence of hydrogen can be explained by the Boudouart reaction, where carbon dioxide plus carbon is produced from the CO disproportionation (2CO → CO$_2$ + C). Recently, Baldanza et al. [10] observed the formation of CO$_2$ during the TPO carried out after the CO TPD analysis on a Pd/Al$_2$O$_3$ catalyst. This CO$_2$ stems from the carbon produced by the Boudouart reaction. Noteworthy is the Pd/CeO$_2$/Al$_2$O$_3$ catalysts that presented an unexpected behavior due to the great amount of CO$_2$ production. This CO$_2$ formation could be attributed to the high storage capacity of cerium oxide and oxygen transfer.

**Fig. 5a** shows the FTIR spectrum of alumina after exposure to NO at room temperature, followed by evacuation at 298 K. The bands at 1297, 1464, 1556, 1590 and 1621 cm$^{-1}$ have been reported for NO adsorption on alumina due to nitrate and nitrite complexes [34].

![High-quality image](76K)

**Fig. 5.** Infrared spectra of NO adsorbed on (a) Al$_2$O$_3$; (b) Pd/Al$_2$O$_3$; (c) Pd/MoO$_3$/Al$_2$O$_3$; (d) Pd/CeO$_2$/Al$_2$O$_3$; (e) Pd/Nb$_2$O$_5$/Al$_2$O$_3$.

The IR spectra of NO adsorption on Pd/Al$_2$O$_3$ catalyst showed basically the same bands present on alumina (**Fig. 5b**). However, a new broad band was observed around 1775 cm$^{-1}$. The literature reported bands for NO adsorption on Pd in the Pd/Al$_2$O$_3$ catalysts around 1753–1750 cm$^{-1}$ (linear), at 1615–1599 cm$^{-1}$ (twofold bridged) and at 1580–1572 cm$^{-1}$ (threefold bridged) [34]. In this work, the linear form was only observed, probably due to the superposition of the bridged forms of NO on reduced Pd by the NO adsorption band on the support. **Fig. 5c** presents the infrared spectra of NO adsorption on Pd/MoO$_3$/Al$_2$O$_3$ catalyst. The molybdenum addition led to a strong suppression of the bands attributed to the adsorption of NO on alumina. This result suggested well dispersed molybdenum over alumina surface. Furthermore, compared to NO adsorption on alumina, there are two new bands at 1723 and 1819 cm$^{-1}$. These bands have been assigned to NO adsorption on partially reduced molybdenum species [35]. Recently, we also performed IR measurements of NO adsorption on
MoO$_3$/Al$_2$O$_3$ sample [10]. The IR spectrum revealed the presence of two bands at 1711 and 1814 cm$^{-1}$, in agreement with the data presented in the literature. Hoost et al. [8] showed decreasing NO adsorption on lanthanum-promoted Pd/Al$_2$O$_3$ catalyst, which was assigned to either the coverage of palladium particles with LaO$_x$ patches or to an increase in the NO dissociation. On the Pd/MoO$_3$/Al$_2$O$_3$ catalyst, the decrease of hydrogen adsorption and the increase of the linear/bridged carbon monoxide ratio agreed well with the dilution or blocking of palladium surface by molybdenum species model. However, the increase of NO dissociation cannot be disregarded.

The IR spectrum of NO adsorption on Pd/CeO$_2$/Al$_2$O$_3$ catalyst is displayed in Fig. 5d. The band at 1776 cm$^{-1}$ was associated to linearly adsorption of NO on Pd. The bands at 1228, 1312, 1466, 1557 and 1616 cm$^{-1}$ corresponded to NO adsorption on alumina. However, the bands at 1228 and 1466 cm$^{-1}$ were more intense in the presence of cerium oxide than on alumina support. This suggested a modification of the alumina support due to the presence of cerium oxide or NO adsorption on partially reduced cerium oxide.

The Pd/Nb$_2$O$_5$/Al$_2$O$_3$ catalyst exhibited bands at 1266, 1292, 1590 and 1622 cm$^{-1}$ and a shoulder at 1558 cm$^{-1}$ (Fig. 5e). In comparison to NO adsorption on pure alumina, the presence of niobium oxide increased strongly the intensity bands of the 1266 and 1622 cm$^{-1}$. Furthermore, the addition of niobium did not suppress the bands corresponding to the NO adsorption on alumina, as observed on Pd/MoO$_3$/Al$_2$O$_3$ catalyst. These results could be related to changes in the distribution of Lewis and Bronsted acid sites, since alumina support exhibits only Lewis acid site [36]. At high loading of niobium oxide on alumina, we observed that the number of Lewis acid sites decreased while the Bronsted acid sites still remain [36]. These Bronsted acid sites were attributed to the bridging M---O$_{\text{support}}$ bonds [21]. The increase of intensity bands at 1266 and 1622 cm$^{-1}$ could explain the appearance of Bronsted acid sites. On the other hand, the bands at 1818 and 1862 cm$^{-1}$ observed on Pd/Nb$_2$O$_5$/Al$_2$O$_3$ catalyst, cannot be attributed to any adsorption mode of NO on Al$_2$O$_3$ or Pd (Fig. 5a and b). We claim these bands corresponding to NO adsorption on partially reduced niobium oxide. They were not observed on the Nb$_2$O$_5$/Al$_2$O$_3$ sample, once high temperatures are needed to reduce niobium oxide.

The TPD spectra of adsorbed NO on Pd/Al$_2$O$_3$ are shown in Fig. 6a. NO, N$_2$O and N$_2$ were the nitrogen-containing products detected during the TPD. The spectrum for NO exhibited a shoulder at 430 K and a narrow peak centered at 542 K. The spectrum for N$_2$ is composed of a single, broad peak centered at 780 K. The N$_2$O signal consisted of a small peak at 540 K and a broad peak around 780 K.
The TPD spectra of NO adsorption on Pd(1 1 1) and Pd(1 0 0) surfaces and Pd/Al₂O₃ catalysts showed two N₂ desorption peaks, which were attributed to atomic nitrogen [37] and [38]. According to Goodman [37] and [38], the one at high temperature corresponds to the inactive adsorbed nitrogen species, which are strongly bounded. These N species inhibited further NO adsorption and dissociation.

On the other hand, the addition of metal oxides changed remarkably the NO TPD profiles. Independent of the nature of metal oxide, the conversion of NO to N₂ and N₂O increased, whereas the NO desorption decreased. However, the extension of the NO dissociation was a function of the nature of the metal oxide.

Important changes were observed on the Pd/MoO₃/Al₂O₃ catalyst (Fig. 6b). Only small amounts of NO desorption were observed in the presence of MoO₃. The adsorbed NO underwent
extensive decomposition during TPD. The primary nitrogen-containing species were \( \text{N}_2 \) and \( \text{N}_2\text{O} \) (Table 4). Two \( \text{N}_2 \) desorption peaks were observed at 538 and 752 K. It is important to stress that on MoO\(_3\)/Al\(_2\)O\(_3\) catalyst it exhibited only a small peak of \( \text{N}_2 \) around 500 K.

Table 4. Yield (carbon or nitrogen basis) of products desorbed during TPD of CO or NO

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%) CO</th>
<th>Yield (%) CO(_2)</th>
<th>Yield (%) NON(_2)ON(_2)</th>
<th>Yield (%) N(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al(_2)O(_3)</td>
<td>25</td>
<td>75</td>
<td>60</td>
<td>9</td>
</tr>
<tr>
<td>Pd/CeO(_2)/Al(_2)O(_3)</td>
<td>16</td>
<td>84</td>
<td>42</td>
<td>12</td>
</tr>
<tr>
<td>Pd/MoO(_3)/Al(_2)O(_3)</td>
<td>40</td>
<td>60</td>
<td>1</td>
<td>21</td>
</tr>
<tr>
<td>Pd/Nb(_2)O(_5)/Al(_2)O(_3)</td>
<td>37</td>
<td>63</td>
<td>43</td>
<td>11</td>
</tr>
</tbody>
</table>

TPR and IR measurements of CO or NO adsorption revealed the presence of partially reduced molybdenum oxide on Pd/MoO\(_3\)/Al\(_2\)O\(_3\) catalysts. In addition, the TPD spectrum of NO adsorption on MoO\(_3\)/Al\(_2\)O\(_3\) catalyst provided clear evidence of NO dissociation over these partially reduced molybdenum oxides. Indeed, palladium promotes the reduction of molybdenum oxide on these catalysts, as seen through TPR and IR results. Therefore, the enhancement of NO dissociation to \( \text{N}_2 \) and \( \text{N}_2\text{O} \) on the Pd–Mo catalysts was directly related to the higher amount of reduced molybdenum species.

The Pd/CeO\(_2\)/Al\(_2\)O\(_3\) and Pd/Nb\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalysts exhibited pronounced NO desorptions (Fig. 6c and d). On Pd/CeO\(_2\)/Al\(_2\)O\(_3\), the NO spectrum exhibited a narrow peak at 445 K. The \( \text{N}_2 \) spectrum showed one peak at 520 K and another broad peak centered at 745 K. The \( \text{N}_2\text{O} \) formation profile showed a broad peak around 733 K. Cordatos and Gorte studied the adsorption properties of CO and NO on ceria supported Pd model catalyst [2]. Their TPD results revealed that the presence of ceria enhanced significantly the NO dissociation. Rao et al. [3] also reported the evidence for NO dissociation over reduced ceria-containing catalysts. The Ce\(^{4+}\)/Ce\(^{3+}\) redox couple promoted the NO reduction over the Ce\(^{3+}\) sites to \( \text{N}_2 \) and \( \text{N}_2\text{O} \).

According to the literature [2] and [3], the higher formation of \( \text{N}_2 \) and \( \text{N}_2\text{O} \) could be attributed to the presence of partially reduced ceria species.

The NO signal on the Pd/Nb\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalyst showed one peak at 415 K and a shoulder at 500 K. The \( \text{N}_2 \) spectrum exhibited a peak around 600 K and a shoulder at 834 K. The \( \text{N}_2\text{O} \) signal was very similar to the \( \text{N}_2 \) profile. Markedly was the addition of niobium oxide by decreasing the NO desorption and increasing \( \text{N}_2 \) and \( \text{N}_2\text{O} \) formation (i(Table 4) and [Table 5]). However, the promoting effect of Nb\(_2\)O\(_5\) on NO dissociation was not so important compared to molybdenum oxide.

Table 5. NO conversion and selectivity toward \( \text{N}_2 \) in NO+CO reaction at 493 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NO conversion (%)</th>
<th>( \text{N}_2 ) selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al(_2)O(_3) (Cl)</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>Pd/CeO(_2)/Al(_2)O(_3)</td>
<td>39.5</td>
<td>41</td>
</tr>
<tr>
<td>Pd/MoO(_3)/Al(_2)O(_3)</td>
<td>12</td>
<td>26</td>
</tr>
<tr>
<td>Pd/Nb(_2)O(_5)/Al(_2)O(_3)</td>
<td>12</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) NO conversion at 493K.

Indeed, the NO dissociation can probably be associated to redox properties of each metal oxide. TPR analysis revealed the promoting effect of palladium on the reduction of the metal oxides, which was more pronounced on the Pd/MoO\(_3\)/Al\(_2\)O\(_3\) catalyst (Table 2). Thus, it suggests that the partially reduced metal oxide contributes to the formation of new site, increasing the NO dissociation, which may be attributed to the following
NO+Me₆⁺ stoichiometric reactions:

\[
\begin{align*}
\text{Mo}^{6⁺} + \text{NO} & \rightarrow \text{Mo}^{5⁺} + \frac{1}{2} \text{N}_2 \\
2\text{Ce}^{3⁺} + \text{NO} & \rightarrow 2\text{Ce}^{4⁺} + \frac{1}{2} \text{N}_2 \\
2\text{Nb}^{4⁺} + \text{NO} & \rightarrow 2\text{Nb}^{5⁺} + \frac{1}{2} \text{N}_2
\end{align*}
\]

It turns out that it is necessary to reduce twofold more cerium or niobium oxides than molybdenum oxide to produce the same amount of N₂ from NO molar unity. Indeed, the degree of reduction to MeOₓ species in the presence of palladium are shown in the TPR profiles and the amounts of reduced Me⁺.species were taken in account in the TPD calculations. Fig. 7 presents the influence of temperature on conversion and selectivity during the CO+NO reaction on Pd/MeOₓ/Al₂O₃ catalysts. Pd/MeOₓ/Al₂O₃ and Pd/MoOₓ/Al₂O₃ showed clearly higher activity and even better selectivity towards N₂ at lower temperatures (473–533 K) as compared to Pd/Al₂O₃ samples. On the other hand, Pd/NbₓO₅/Al₂O₃ was almost inactive and did not produce N₂ at low temperature. According to Goodman and coworkers[37] and [38] it can be explained by the presence of two nitrogen species. At low temperatures this nitrogen species are active. Indeed, the TPD results showed two temperature ranges of N₂ desorption, which were associated to active and inactive N species, respectively. The Mo and Ce-promoted catalysts displayed this behavior while the Nb-promoted samples did not, independent of the presence of palladium. From the TPD results of these samples we obtained 27% of the total N₂ desorption corresponding to the active N species on the Mo-promoted and 32% on the Ce-promoted samples. These species are negligible on the Nb-promoted samples, although the total desorption is almost equal to the Ce-promoted samples. Therefore, most N₂ desorbed on Nb corresponds to the inactive N species, which explains the lower N₂ selectivity below 600 K observed in the catalytic test. In conclusion, the inactive N species do not favor the redox mechanism. Hence, Ce and Mo are very good promoters due to the easier reduction of Ce and Mo favoring the redox mechanism. On the other hand, NbₓO₅, which is more difficult to reduce under these reaction conditions, inhibits the formation of N active species and thus disfavors the redox mechanism.
The differences observed on TPD results of NO and reaction between CO+NO are due to the easiness of reduction and oxidation of the promoters which explains the N$_2$ production by the proposed NO+CO cyclic redox mechanism [2] and [9]. Therefore, the formation of NbO$_x$ species needs higher temperatures than molybdenum or cerium in the presence of palladium to activate the redox behavior. Above 280°C the CO oxidation and NO reduction capacities were very similar to all surface active sites based on thermodynamic backgrounds.

4. Conclusions

The NO dissociation during TPD was better on the Pd/MoO$_3$/Al$_2$O$_3$ catalyst than on the Pd/CeO$_2$/Al$_2$O$_3$ and Pd/Nb$_2$O$_5$/Al$_2$O$_3$ catalysts that was probably associated to redox properties of each metal oxide.

The better performance of the Pd–Mo catalyst during TPD of NO for nitrogen may be attributed to the NO+Me$^{\delta^+}$ stoichiometric reaction. The differences observed on TPD results of NO and reaction between CO+NO are due to the easiness of reduction and oxidation of the promoters which explains the N$_2$ production by the proposed NO+CO cyclic redox mechanism.

Therefore, the palladium particle size and its surface plane orientation on the Pd/MeO$_3$/Al$_2$O$_3$ catalysts seem to play a secondary role. Thus, the promoter effect of a reducible oxide for NO+CO reaction at low temperatures is mainly ascribed to its easiness for the redox interchange and its interaction with the noble metal particles, which can even increase the surface redox ability and co-operate itself to the dynamic equilibrium needed for high N$_2$ selectivity.

Ce and Mo are good promoters due to the easier reduction of Ce and Mo favoring the redox mechanism. On the other side, Nb$_2$O$_5$ is more difficult to reduce under these reaction conditions inhibiting the formation of N active species and thus disfavoring the redox mechanism.

References


