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NO reduction with CO on alumina-modified silica-supported palladium and molybdenum-palladium catalysts

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Abstract

In this work, Pd and Mo-Pd catalysts supported on Al_2O_3 modified SiO_2 and Si-MCM-41 materials were prepared, characterized by H_2 chemisorption and FTIR spectroscopy of adsorbed CO and NO and tested for the reduction of NO with CO. The characterization results indicated that in the bimetallic catalysts, Mo that is loaded first, migrates over the Pd atoms and reduced the fraction of exposed metal atoms. The reduction of NO with CO at 523 K showed that the specific activity for NO conversion increased as a result of the Pd-Mo interaction. In the 523–573 K temperature range NH_3 was produced in addition to CO_2, N_2 and N_2O. This result suggests the reaction of NCO species formed on the Pd surface with OH groups of the support materials to produce isocyanic acid (HNCO) that is hydrolyzed to NH_3. The catalysts exhibited a decreasing selectivity to N_2O and a parallel increase in the production of N_2 and NH_3 as the conversion increases. The effect of Mo on the reaction selectivity was clear for $Pd/Al_2O_3/SiO_2$; at similar NO conversion level the selectivity to N_2O and N_2 decreased with increasing NH_3 formation. FTIR spectra of adsorbed species under reaction conditions demonstrated the absence of isocyanate species and the presence of NH_4^+ ions in accordance with the high Brønsted acidity of the support materials.

Keywords: NO*x*; MCM-41; Pd catalyst; Mo-Pd catalyst; NO reduction with CO

1. Introduction

The modification of the surface of silica has been studied to obtain novel materials with different applications, such as sorbent materials [1], electrochemical sensors [2,3] and catalysts [4]. Canut et al. [5] showed that sol–gel dip coating is a viable route for depositing composite NiO–SiO_2 multilayers of controllable stoichiometry, thickness and density. On the other hand, Iengo et al. [6], have shown the possibility to anchor on the surface of a support rich in hydroxyl groups, such as silica support, different amounts of aluminum and zirconium alkoxides changing the acidic properties of the surface.

In a previous work [7] we have modified the surface of a mesoporous silica (250 $m^2\ g^{-1}$) with alumina using aluminum isopropoxide as alumina precursor. After three successively grafting reactions a homogeneous silica surface coverage was obtained and it was verified that the incorporation of 5.5 wt% alumina was preferentially on the silica surface, since bulk alumina was not observed. Using this method it was possible to combine mechanical, structural and chemical properties of silica and alumina.

Subsequently, SiO_2 and a Si-MCM-41 materials were both modified with alumina, and used to prepare supported mono- [8] and bi- [9] metallic palladium catalysts that were characterized and tested in the direct decomposition of nitric oxide at 723 K. The X-ray diffraction of these materials showed that the structure of the mesoporous supports was not destroyed by metal impregnation or after the catalytic tests performed on them. The better dispersed metal phase was observed in the catalyst supported on MCM-41 due to the high surface area. However, the alumina-modified supports did not improve the performance of the catalysts. On the contrary, there was a slight decrease in activity when the film was present in part due to changes in Pd dispersion. Perhaps, the most significant effect of alumina addition to the SiO_2 support was a marked decrease in N_2O formation. As the analysis of reaction

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products was carried out by FTIR, the production of N_2 was not followed.

A more appropriate reaction to test the Pd catalysts is the reduction of NO with CO that occurs in catalytic converters. The main nitrogen products of this reaction are N_2 and N_2O, but NH_3 (g), HNCO (g) and adsorbed isocyanate species have been observed depending on the presence of H_2 or H_2O.

Cant et al. [10] studied the reaction of NO with excess CO in the presence of water vapor for silica and alumina supported platinum catalysts and observed the formation of gaseous HNCO and NH_3. Pd/SiO_2 also produces HNCO and NH_3, but the concentrations were much lower than with Pt/SiO_2. The same authors [11] studied the $CO + NO + H_2$ reaction over silica-supported Pt, Pd and Rh catalysts and verified that the initial reaction of H_2 generates NH_3 and H_2O that are converted to HNCO at higher temperatures. If water is also present in the feed stream the hydrolysis of HNCO amplifies the production of NH_3. Recently, we have found [12] that both HNCO and NH_3 are formed during the NO + CO reaction on Pd/Al_2O_3 even in the absence of H_2 or H_2O in the feed mixture.

To enhance the activity and the selectivity to N_2 of Pd catalysts, a second metal has been incorporated, promoting a bimetallic interaction. Schmal et al. [13] studied the NO + CO reaction on Pd, Mo and Pd-Mo (0.9% Pd, 7.5% Mo) γ-Al_2O_3 supported catalysts. For the bimetallic catalysts it was observed a monolayer of Mo oxide covering the alumina surface and the Pd particles dispersed on them. With increasing Mo content, MoO_3 crystals are formed. The results indicate that Mo^{+6} is reduced to Mo^{+4} at lower temperatures in the presence of palladium particles, and this favors the formation of a bimetallic phase. In the same study, TPD results indicate that the presence of the Mo monolayer favors the formation of N_2 and reduces N_2O production. For the Pd-Mo bimetallic catalysts a band near 2230 cm^{-1} corresponding to adsorbed isocyanate was observed under reaction conditions. This band did not disappear after purging with Ar and was found to be very stable. However, other nitrogen containing products, besides N_2 and N_2O, were not detected.

The objective of the present work was to extend the study of palladium and palladium-molibdenum catalysts supported on Al_2O_3-modified SiO_2 and Si-MCM-41, that proved active in the direct NO decomposition reaction [8,9], to the reduction of NO with CO. Furthermore, additional characterization of the catalysts was carried out by FTIR spectroscopy of adsorbed CO, NO and other surface species present under reaction conditions.

2. Experimental

2.1. Molybdenum incorporation

The Mo incorporation was carried out first through a photochemical activation of the organometallic compound $[Mo(CO)_6]$ (Aldrich) dissolved in hexane in the presence of the supports; Al_2O_3/SiO_2 or Al_2O_3/Si-MCM-41. The preparation of the supports was described in previous studies [8] and elsewhere [14]. The quantities used were calculated to give 2 wt.% of Mo on the support (1.5 g of support; 0.083 g of $[Mo(CO)_6]$; 50 mL of hexane).

The photochemical reactions were performed at room temperature under an Ar atmosphere using a Philips HPL-N (125 W) UV lamp fitted into a Pyrex cold finger. In order to observe the reaction progress, small liquid samples were withdrawn for analysis by FTIR where the decrease in the ν(CO) band was monitored. After the irradiation, the solid was filtered and washed with hexane. Finally, the generated subcarbonyl species were decomposed by thermal treatment under vacuum at 723 K.

2.2. Pd incorporation

The palladium catalysts were prepared by impregnation of the supports (Al_2O_3/SiO_2 or Al_2O_3/Si-MCM-41) or the corresponding Mo catalysts with a toluene solution of palladium acetylacetonate (8.10^{-3} g Pd mL^{-1}). The support was previously dried and activated at 723 K in air for 3 h followed by another hour at the same temperature under vacuum. The solid (2 g) and the solution (7.5 mL) were left in contact for 24 h at room temperature. The liquid was removed and the solid was dried under vacuum, calcined in air at 473 K for 2 h and finally reduced in hydrogen under the same conditions. The palladium metal loading was adjusted in the synthesis to be 1 wt%.

2.3. Catalysts characterization

The specific surface area of the solid previously degassed at 473 K, under vacuum, was determined by BET (Brunauer, Emmett and Teller) multipoint technique on a ASAP 2010, Micromeritics apparatus, using nitrogen as probe. The mesopore size distribution was obtained using BJH (Barret, Joyner and Halenda) method.

TPR experiments were carried out on catalysts samples of 0.25 g calcined in air at 723 K for 4 h and purged at 423 K in Ar flow during 0.5 h. The samples were then cooled to room temperature and the reduction performed with a heating rate of 10 K min^{-1} using a H_2(1.5%)-Ar mixture. For the Pd catalysts the highest reduction temperature was 573 K while Pd-Mo catalysts were studied up to 873 K.

The palladium dispersion was determined by a hydrogen chemisorption method. The samples were pre-heated at 423 K (10 K min^{-1}) in flowing Ar (30 mL min^{-1}) for 0.5 h. They were then reduced at 573 K (10 K min^{-1}) under a flow of 1.74% H_2/Ar (30 mL min^{-1}). Following reduction, the samples were purged with Ar for 1 h at 573 K and cooled to 343 K (adsorption temperature) for hydrogen chemisorption using the dynamic method.

FTIR spectra of CO and NO adsorption were obtained in a NICOLET 20 DXB instrument at 4 cm^{-1} resolution. Catalysts samples of approximately 28 mg were pressed to form transparent disks of 10 mm in diameter that were mounted in a metal holder. The holder was placed in the beam path of a stainless steel cell, sealed with CaF_2 windows, and coupled to a vacuum system for evacuation to 10^{-6} Torr. Samples were calcined at 573 K, reduced at the same temperature in flowing hydrogen, purged with helium and cooled to room temperature. Following evacuation of the cell, an FTIR spectrum was obtained and used as a background. Adsorbates were dosed at a pressure of 5 Torr and the sample was exposed to the gas phase for 6 min. Subsequently, the cell was evacuated and a new spectrum was obtained. In an experiment designed to observe adsorbed species formed under reaction conditions catalyst samples were calcined in air, reduced in pure hydrogen at 573 K and purged with helium. The temperature was then lowered to 548 K, a reference spectrum was taken and the gas flow was switched to the NO/CO/He mixture coming from the flow reactor. Spectra of adsorbed species were obtained after a reaction time of ≅80 min.

2.4. Catalytic activity

Catalytic experiments were carried out in a fix-bed Pyrex glass micro reactor (i.d. 0.42 cm) mounted axially in an electrical furnace. The catalyst temperature was measured with a thermocouple placed upstream of the bed. In the tests 50 mg samples of the catalysts *in situ* reduced in flowing H_2 at 573 K for 20 min were used, except for the Pd/Al_2O_3/SiO_2 where 44 mg were loaded.

For the NO + CO reaction a feed mixture containing 1560 ppm NO and 1450 ppm CO in He was used. The total flow rate was 100 mL min^{-1}. The NO + CO reaction was studied at three temperatures (523, 548 and 573 K). The reactor effluent was analyzed by on line chromatography using a thermal conductivity detector and two Porapak Q columns. One held at 263 K (1/8″ × 6 m) allowed the separation of N_2, O_2, CO and NO. A shorter Porapak Q column (1/8×″ × 2.5 m) operated at 353 K was used to identify N_2O and CO_2. The flow rate was about 16 mL min^{-1} for both columns. Additionally, the reaction products were analyzed by FTIR using a multiple reflection infrared cell with a 2.4 m pathlength.

The N_2 and N_2O selectivities were calculated using the following equations:

$$SN_2(\%) = 2[N_2] \times 100/(X_{NO} \times [NO]_o)$$

$$SN_2O(\%) = 2[N_2O] \times 100/(X_{NO} \times [NO]_o)$$

Where $[N_2]$ and $[N_2O]$ are the concentrations (ppm) of the main nitrogen containing products, $[NO]_o$ is the concentration in the feed mixture and X_{NO} is the conversion of NO.

3. Results and discussion

3.1. Catalysts characterization

Table 1 summarizes the main catalysts properties; surface area, metal contents, Pd metal dispersion and the fraction of Pd reduced during the TPR experiments. The results corresponding to the monometallic Pd samples were presented and discussed in detail in a previous study [8]. It was observed that the deposition of alumina decreased markedly the BET surface area of the Si-MCM-41 support and reduced the subsequent loading of Pd. However, the metal dispersion was quite high; 70%. A large fraction of the metal content was not reduced during the transient TPR measurements, suggesting that small particles remained as oxidized species on the silica support. When Pd was deposited on the Mo modified Al_2O_3/Si-MCM-41 support it was easily reduced but the metal dispersion was much lower. This result could be ascribed to the formation of large Pd particles but may also be due to the migration of Mo over the metal surface. The presence of a small amount of Mo also altered the metal dispersion of the Pd/Al_2O_3/SiO_2 catalyst; it decreased from 40 to 7%. Here again it is difficult to distinguish between particle growth and Mo migration to explain the drop in the fraction of exposed Pd atoms.

3.2. FTIR spectra of CO and NO adsorption

CO adsorption on the Pd and Pd-Mo catalysts showed typical bands due to linear (~2095 cm^{-1}) and multiple coordinated species (≅1800–2000 cm^{-1}) on metallic Pd, as shown in Figs. 1–2. Under the present experimental conditions no bands attributed to Mo-CO are expected. The position of the linear CO band indicates the presence of Pd in a reduced state on all catalysts. It is important to recall that the catalysts pellets were reduced in pure H_2 at 573 K prior to the FTIR experiments. Under this condition the degree of reduction was higher than that found during the TPR measurements.

Fig. 1 shows the spectra of the Pd/Al_2O_3/SiO_2 and Mo-Pd/Al_2O_3/SiO_2 catalysts. The location of the CO adsorption bands is similar, but the intensity is higher on the monometallic sample in accordance with a higher fraction of exposed Pd atoms. In the presence of Mo (0.21%) the bands due to linear and multiple coordinated CO species are attenuated. The ratio of integrated intensity of linear and multiple coordinated species remains unchanged, 0.39 vs. 0.41 (see Table 1), despite the large decrease of the fraction of exposed Pd atoms; from 40 to 7%. This result suggests that the change in dispersion is not due to a larger Pd particle size. In agreement with previous chemisorption and TPR studies Mo atoms that migrate over the Pd particles are responsible for the large drop in the fraction of exposed Pd atoms [15].

In a previous study we have found that Mo deposited on the Pd particles modified both the intensity and the frequency of the linear and bridge CO bands [16], reflecting a weaker adsorption. This behavior was assigned to changes in the electronic properties of Pd induced by a strong interaction that develops when $Mo(CO)_6$ adsorbs and decompose on large Pd particles deposited first on the alumina support.

The spectrum of CO adsorption on Pd/Al_2O_3/Si-MCM-41, shown in Fig. 2(a) clearly indicates that the metal dispersion on this support is higher, in agreement with the chemisorption value. In this case, the ratio of linear to multiple coordinated species is ≅0.32. Upon addition of Mo (1.56%) it increases to 0.46, suggesting again that the decrease in exposed metal atoms fraction, from 70 to 19%, must be attributed to the migration of Mo on the Pd surface.

According to Figs. 1 and 2, the linear and bridge CO adsorption bands are slightly shifted to lower wavenumbers

Table 1
Catalysts characterization results

Catalysts	BET surface area ($m^2\ g^{-1}$)	Pd loading (wt.%)	Mo loading (wt.%)	H/Pd (%)	Pd reducibility (%)	FTIR *L*/*B*[a]
$Pd/Al_2O_3/SiO_2$	245	0.98	–	40	96	0.39
$Mo\text{-}Pd/Al_2O_3/SiO_2$	254	0.91	0.21	7	100	0.41
Pd/Al_2O_3/Si-MCM-41	531	0.75	–	70	55	0.32
Mo-Pd/Al_2O_3/Si-MCM-41	540	0.80	1.56	19	95	0.46

[a] Ratio of integrated intensities of linear (*L*) and bridge (*B*) CO adsorption bands.

upon Mo addition. This effect is mainly due to a dilution of the surface Pd atoms caused by the presence of Mo on the Pd particles. In other words, the interaction between the adsorbed CO molecules is reduced, consequently increasing the Pd-CO interaction and leading to lower frequencies of ν(CO) stretching mode.

The NO adsorption study on the $Pd/Al_2O_3/SiO_2$, Mo-$Pd/Al_2O_3/SiO_2$, Pd/Al_2O_3/Si-MCM-41 and Mo-Pd/Al_2O_3/Si-MCM-41 catalysts is shown in Figs. 3 and 4. In the 1739–1745 cm^{-1} region a band characteristic of linear adsorption of NO on Pd was observed. In addition a broad and weaker band appears at 1650–1660 cm^{-1}, which has been assigned to bridge [17] NO species or bent NO [18]. The small band at 1875 cm^{-1} corresponds to gas phase NO. The two monometallic catalysts presented similar spectra (Figs. 3(a) and 4(a)) in agreement with the results for CO adsorption. The terminal band was the most affected when the cell was evacuated (spectra not shown in the figures), with a higher decrease in intensity when the support was Al_2O_3/Si-MCM-41 reflecting a weaker adsorption. An interesting observation was a significant increase of the 1650–1660 cm^{-1} band for all catalysts when the cell was evacuated. This behavior, that was first reported by Moriki et al. [19], suggests a conversion of linear NO species to bridge species as coverage decreases.

The NO adsorption on the bimetallic catalysts is presented in Figs. 3(b) and 4(b). The spectra show, as it was observed for CO adsorption, a marked decrease in the bands intensity, mainly for the linear NO band on Mo-Pd/Al_2O_3/Si-MCM-41. In this case a new band appears at 1805 cm^{-1} that may be due to NO adsorbed on partially reduced Mo. A similar band assignment

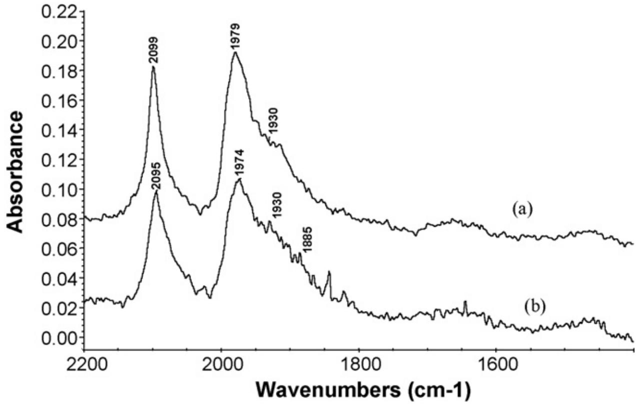

Fig. 1. FTIR spectra of $Pd/Al_2O_3/SiO_2$ (a) and Mo-$Pd/Al_2O_3/SiO_2$ (b) catalysts at 298 K exposed to 5 Torr of CO.

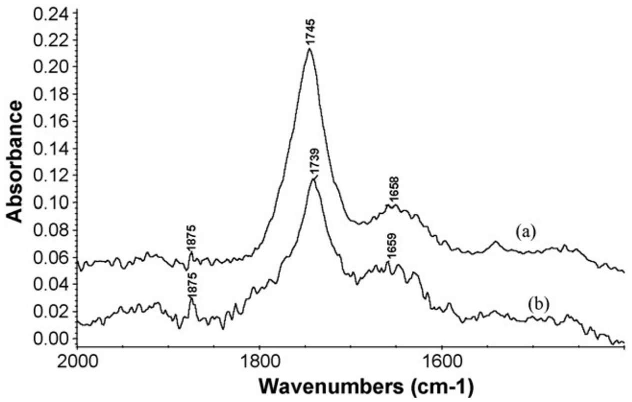

Fig. 3. FTIR spectra of $Pd/Al_2O_3/SiO_2$ (a) and Mo-$Pd/Al_2O_3/SiO_2$ (b) catalysts at 298 K exposed to 5 Torr of NO.

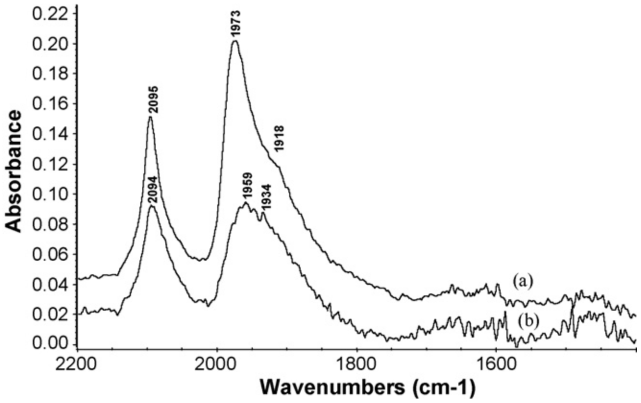

Fig. 2. FTIR spectra of Pd/Al_2O_3/Si-MCM-41 (a) and Mo-Pd/Al_2O_3/Si-MCM-41 (b) catalysts at 298 K exposed to 5 Torr of CO.

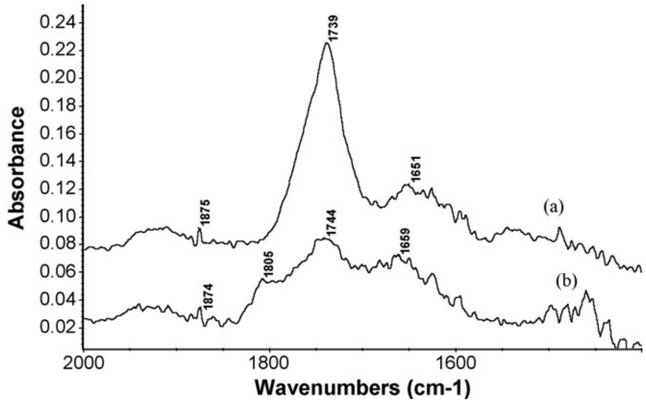

Fig. 4. FTIR spectra of Pd/Al_2O_3/Si-MCM-41 (a) and Mo-Pd/Al_2O_3/Si-MCM-41 (b) catalysts at 298 K exposed to 5 Torr of NO.

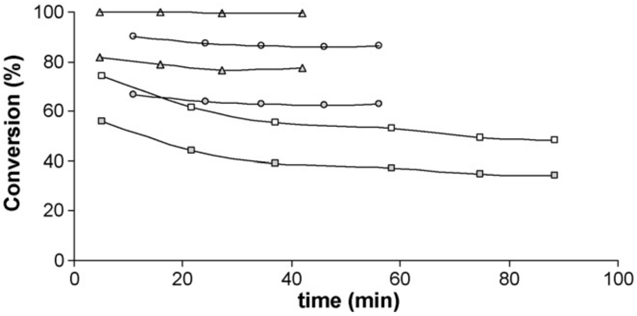

Fig. 5. NO reduction by CO on $Pd/Al_2O_3/SiO_2$. NO (open symbols) and CO (close symbols) conversion as a function of reaction time: (□,■) 523 K, (○,●) 548 K, (△, ▲) 573 K (1450 ppm CO/He + 1560 ppm NO/He, $p = 1340$ Torr, S.V. = $5 \times 10^4\ h^{-1}$).

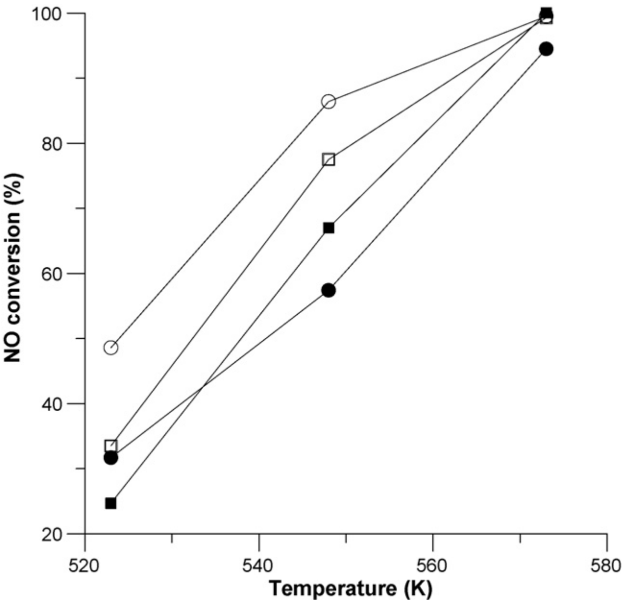

Fig. 6. NO reduction by CO. Dependence of NO conversion on temperature. $Pd/Al_2O_3/SiO_2$ (○); Mo-$Pd/Al_2O_3/SiO_2$ (●); Pd/Al_2O_3/Si-MCM-41 (□); Mo-Pd/Al_2O_3/Si-MCM-41 (■) (1450 ppm CO/He + 1560 ppm NO/He; $p = 1340$ Torr, S.V. = $5 \times 10^4\ h^{-1}$).

was made by Baldanza et al. [20]. The catalyst supported on Al_2O_3/SiO_2 had a smaller decrease in bands intensities, due to the low Mo loading (seven times less than the catalyst supported on Al_2O_3/Si-MCM-41).

These CO and NO adsorption results showed that despite the fact that molybdenum was impregnated first, it migrate to the Pd surface during the thermal treatment carried out to decompose the Pd precursor, affecting mainly the fraction of exposed Pd atoms.

3.3. Catalytic tests for the NO + CO reaction

The $Pd/Al_2O_3/SiO_2$, Mo-$Pd/Al_2O_3/SiO_2$, Pd/Al_2O_3/Si-MCM-41 and Mo-Pd/Al_2O_3/Si-MCM-41 catalysts were tested for the reduction of NO using CO as a reducing agent. The main reaction products were N_2, N_2O and CO_2. Fig. 5 shows the variation of the NO and CO conversion with time for the $Pd/Al_2O_3/SiO_2$ catalyst at 523, 548 and 573 K. At the lowest temperature, 523 K, there was an initial decline in activity but a steady state value was observed after a reaction of ≅90 min. This deactivation process, that was absent on the other catalysts, was not investigated. The NO conversion was always higher than that of CO, which is a typical behavior for the NO + CO reaction on Pd catalysts [21] and is in accordance with the formation of N_2O as a reaction product. The dependence of NO conversion on temperature is shown in Fig. 6 for all catalysts tested. Clearly, the $Pd/Al_2O_3/SiO_2$ catalyst was the most active, due to the higher metal content and good metal dispersion. The Pd dispersion on Pd/Al_2O_3/Si-MCM-41 was higher but the metal content was lower. There was a rapid increase in conversion with temperature for all the samples tested and nearly complete elimination of NO was observed at 573 K. In the presence of Mo the conversion was lower and this effect was more noticeable on the $Pd/Al_2O_3/SiO_2$ catalyst due to the marked decrease in metal dispersion. Using the steady state NO conversion values at 523 K (see Fig. 6) and the hydrogen chemisorption values reported in Table 1 the turn over rate (TOR_{NO}) was estimated. We recognize that this procedure only allows a rough comparison of the rates because the conversion values were not similar (except for the Mo-$Pd/Al_2O_3/SiO_2$ and Pd/Al_2O_3/Si-MCM-41 catalysts) and the reactor was not operated under true differential conditions. However, taking into account that the reaction orders are +1 for NO and −1 for CO [22] and that similar NO and CO partial pressures were used, large differences are not expected at moderate conversion values. The results presented in Table 2 shows that the specific activity of the $Pd/Al_2O_3/SiO_2$ catalyst ($0.029\ s^{-1}$) was close to that of a Pd/Al_2O_3 with similar metal loading and dispersion ($0.043\ s^{-1}$), tested under true differential conditions. Consequently, there seems to be a negligible influence of the support material on the catalytic activity of Pd catalysts. On the other hand, the addition of Mo increases the specific activity of both the $Pd/Al_2O_3/SiO_2$ and the Pd/Al_2O_3/Si-MCM-41 by a factor of three. This promotional effect of Mo is in accordance with the results reported by Schmal et al. [13] who compared the activity and selectivity of Pd/Al_2O_3 and Pd-MoO_3/Al_2O_3 catalysts. The authors found that both catalysts gave the same NO conversion at 533 K (17.4%), although the fraction of exposed metal atoms decreased by a factor of 2.4 in the presence of 7.5% Mo. This high loading of Mo also increased the selectivity to N_2. The action of the promoter was attributed to the adsorption and dissociation of NO on partially

Table 2
NO + CO reaction rate data at 523 K

Catalysts	TOR_{NO} (seg.$^{-1}$)[b]
Pd(0.68%)/Al_2O_3[a]	0.043 (9.3%)
$Pd/Al_2O_3/SiO_2$	0.029 (48.6%)
Mo-$Pd/Al_2O_3/SiO_2$	0.118 (31.7%)
Pd/Al_2O_3/Si-MCM-41	0.015 (33.5%)
Mo-Pd/Al_2O_3/Si-MCM-41	0.043 (24.7%)

Total pressure = 1340 Torr; p_{NO} = 1560 ppm; p_{CO} = 1450 ppm; S.V. = $5 \times 10^4\ h^{-1}$.

[a] Unpublished study. H/Pd = 0.42; spacial velocity = $6.5 \times 10^5\ h^{-1}$.

[b] Values in parentheses are the NO conversions used to calculate the rates.

reduced Mo species and the CO role to recover the reduced state of the promoter.

3.4. Effect of Mo and the support material on the reaction selectivity

Before discussing the influence of the support material and Mo on the selectivity of our catalysts, it is important to comment on the gas phase analysis of reactions products by FTIR. Using a long path gas cell the feed mixture and the stream of reaction products at 523, 548 and 573 K were analyzed. The spectrum of the feed mixture in Fig. 7(a) only shows bands of similar intensity due to CO and NO. At a reactor temperature of 523 K there is a clear decrease in the intensity of the NO and CO bands due to the NO + CO reaction on Pd/Al_2O_3/SiO_2. The strong CO_2 and N_2O bands in the FTIR spectrum (Fig. 7(b) correspond to an NO conversion of 48.6%. More interesting is the presence of two small bands at 966 and 927 cm^{-1} due to the symmetric bending of NH_3 molecule in gas phase [23]. At higher temperatures the intensity of the NH_3 bands increases, as shown in Fig. 6(b) and (c), indicating a dependence on the NO conversion. Consequently NH_3 is a secondary product of the NO + CO reaction on Pd catalysts.

In the literature, ammonia formation is associated with the hydrolysis of adsorbed isocyanate species (-NCO) or gas phase isocyanic acid (HNCO) that are formed during the NO + CO + H_2O reaction [10] or the NO + CO + H_2 reaction [11], when Pd or Pt catalysts are used. Very recently we have observed the formation of HNCO (g), -NCO_{ad} and gas phase NH_3 when the NO + CO reaction was carried out on Pd/Al_2O_3 [12] in the absence of H_2 and H_2O. We have also tested a Pd/SiO_2 catalyst with similar results. In the present study the formation of -NCO_{ad}, that exhibits a strong band at 2256 cm^{-1} [24], was not detected as shown in Fig. 8. However, the formation of HNCO (g) and then of NH_3 may be due to the rapid interaction of -NCO formed on the metal surface with OH groups from the support surface. It is important to state that the presence of residual hydrogen from the reduction pretreatment can be excluded due to the prolonged helium purging. The HNCO (g) formed on the catalysts surface may be transported through the gas phase and deposited on the cool lines connecting the reactor with the gas cell where it is converted to NH_3 by presence of water at a ppm level. If HNCO (g) reaches the gas cell, it will not be detected due to the overlap of its IR signal (at $\cong$2270 cm^{-1}) by the strong N_2O band.

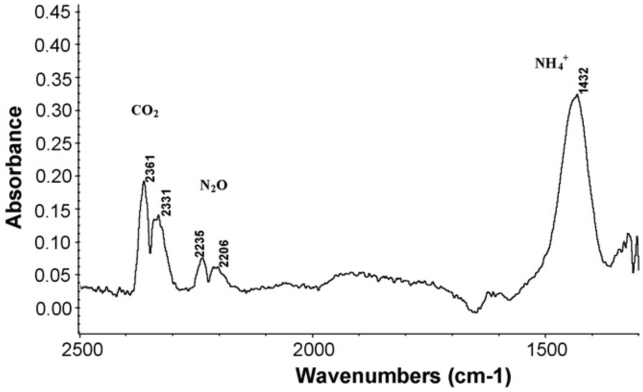

Fig. 8. NO reduction by CO on Pd/Al_2O_3/SiO_2 at 548 K. FTIR spectra of adsorbed species after a reaction time of 77 min.

Fig. 8 shows the spectrum of the Pd/Al_2O_3/SiO_2 catalyst at 548 K, exposed to the reaction mixture coming from the test reactor. Bands due to gas phase CO_2 and N_2O (the main reaction products) and a very strong band at 1432 cm^{-1}, corresponding to the asymmetric bending mode of NH_4^+ bounded to the support surface, were observed. Similar spectra (not shown here) were found for the Mo-Pd/Al_2O_3/SiO_2, Pd/Al_2O_3/Si-MCM-41 and Mo-Pd/Al_2O_3/Si-MCM-41 catalysts. Ammonium ions are formed by the interaction of gas phase NH_3 with Brønsted acid sites that are present on the Al_2O_3/SiO_2 and the Al_2O_3/Si-MCM-41 support. To confirm the reactivity of gas phase NH_3 with the catalysts surface we have examined the FTIR spectra of Al_2O_3/SiO_2 and SiO_2 samples exposed to 5 Torr of NH_3 at 548 K. Prior to NH_3 adsorption the samples were calcined in air at 723 K and reduced in H_2 at 573 K to reproduce the preparation procedure of the Pd catalysts. The spectrum in Fig. 9 shows a strong and stable NH_4^+ band at 1432 cm^{-1} that only appears on the Al_2O_3/SiO_2 support. These results confirmed the acidic character of the Al_2O_3-modified support materials used in the present study.

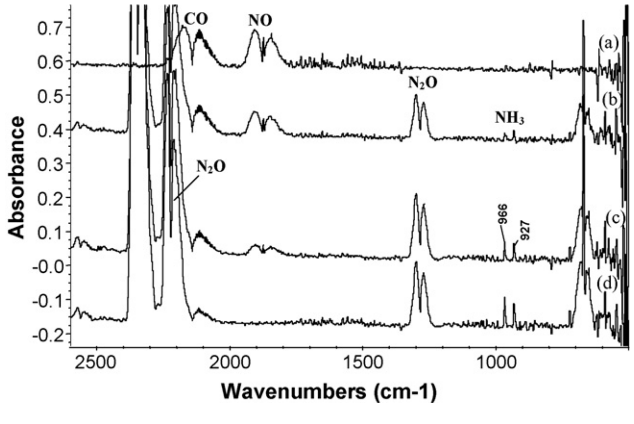

Fig. 7. NO reduction by CO on Pd/Al_2O_3/SiO_2. FTIR spectra of gas phase compounds: (a) feed stream, (b) at 523 K, (c) at 548 K and (d) at 573 K.

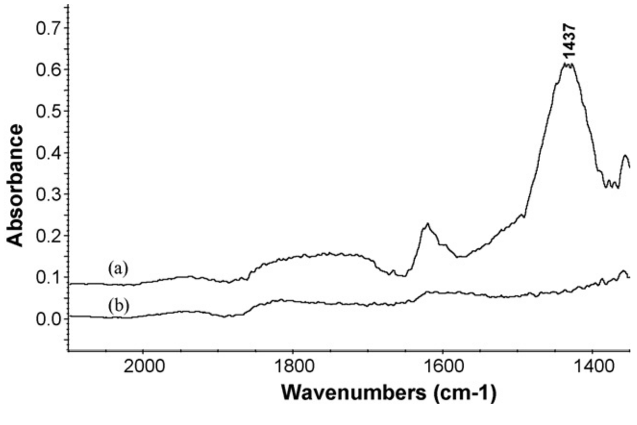

Fig. 9. FTIR spectra of Al_2O_3/SiO_2 (a) and SiO_2 (b) at 548 K exposed to 5 Torr of ammonia.

Although NH_3 is a minor product of the NO + CO reaction it may participate in the NO reduction process. According to Cant et al. [25] the addition of NH_3 to the NO + CO mixture increases the rate of NO removal approaching the rate of the faster NO + NH_3 reaction.

The main nitrogen containing products of the NO + CO reaction on the Pd/Al_2O_3/SiO_2, Mo-Pd/Al_2O_3/SiO_2, Pd/Al_2O_3/Si-MCM-41 and Mo-Pd/Al_2O_3/Si-MCM-41 catalysts were N_2O and N_2. The corresponding selectivity values, S N_2O (%) and S N_2 (%), at different conversion levels are presented in Table 3. It is observed that the formation of N_2O always exceeded that of N_2 and the values decreased with an increase in conversion (increasing the temperature). On the other hand, the selectivity to N_2 exhibited a smaller increase with increasing conversion. As pointed out by a reviewer the data reflect the combined effect of conversion and temperature on the selectivity. However, the effect of temperature became more important at >573 K due to the N_2O + CO reaction. The main decrease in S N_2O and increase in S N_2 was found for the Mo-Pd/Al_2O_3/SiO_2 catalysts. The selectivity to N_2O at high conversion was 48%, the lowest value in this study. However, the production of N_2 and the corresponding selectivity was higher on the other catalysts. This result was due to an increasing formation of NH_3 with temperature for the mentioned sample. The last column in Table 3 shows that the nitrogen balance at low conversion (T = 523 K) was close to 100% for all catalysts, with an experimental error of about 3–4%. Under this condition the small amount of NH_3 formed did not affect the nitrogen balance. The situation was different at the high NO conversion obtained at 573 K. In this case the nitrogen balance showed a clear deficit, which was quite large on the Mo-Pd/Al_2O_3/SiO_2 catalyst. In other words, the presence of Mo suppressed the formation of N_2O but promoted the production of NH_3. Assuming that the large deficit in the nitrogen balance at 573 K is due to the formation of NH_3, the concentration was ≅300 ppm for Mo-Pd/Al_2O_3/SiO_2 and ≅100 ppm for the other catalysts. Although the amount of NH_3 expected from the reaction of isocyanate species with OH groups, or H_2O present as an impurity in the feed mixture is small, it may be amplified due to the subsequent reaction with NO and CO, as demonstrated by Cant et al. [26].

Table 3
Effect of NO conversion at steady state on the selectivity to N_2O and N_2O

Catalysts	X_{NO}[a] (%)	S N_2O (%)	S N_2 (%)	S (N_2 + N_2O) (%)
Pd/Al_2O_3/SiO_2	48.6	68.7	32.2	100.9
	86.4	58.3	35.5	93.8
	99.5	55.5	37.3	92.8
Mo-Pd/Al_2O_3/SiO_2	31.7	79.4	20.8	100.2
	57.4	66.2	27.8	94.0
	94.5	48.0	31.4	79.4
Pd/Al_2O_3/Si-MCM-41	33.5	71.6	30.7	102.3
	77.5	66.2	30.3	96.5
	99.3	60.9	32.7	93.6
Mo-Pd/Al_2O_3/Si-MCM-41	24.7	68.8	34.5	103.3
	67.0	66.8	36.1	102.9
	100.0	58.5	36.5	95.0

S.V. = 5×10^4 h^{-1}.

[a] Conversion values from Fig. 6.

When the selectivities of Pd/Al_2O_3/SiO_2 and Mo-Pd/Al_2O_3/SiO_2 are compared at similar NO conversion levels, 99.5 and 94.5% respectively, it is observed that Mo decreases the selectivity to N_2O but promotes the formation of N_2 and NH_3.

This effect of Mo on the reaction selectivity was not clearly observable on Mo-Pd/Al_2O_3/Si-MCM-41 despite the fact that the Mo loading was much higher. A likely explanation is that in this case the Pd-Mo interaction was limited, as reflected by the smaller change in the fraction of exposed Pd atoms.

In general our results are in agreement with those of Schmal et al. [13] for Pd-Mo/Al_2O_3 in the sense that Mo addition to Pd catalysts promotes the activity for the NO + CO reaction and reduces the formation of N_2O. However, the Pd-Mo interaction that develops on the modified silica supports enhances the production of NH_3, which is another undesirable gas contaminant. Schmal et al.[13] did not mention the formation of NH_3 or HNCO which may be due to the high loading of Mo that diminished the concentration of surface OH groups.

4. Conclusions

The characterization of Pd and Mo-Pd catalysts supported on alumina-modified supports, Al_2O_3/SiO_2 and Al_2O_3/Si-MCM-41, demonstrated that Mo in low loadings migrates on top of the Pd crystallites reducing the fraction of exposed Pd atoms. The change in hydrogen chemisorption values and the linear to bridge intensity ratio of the FTIR spectra of adsorbed CO supports this conclusion. The Pd-Mo interaction enhanced the specific activity of Pd for the NO + CO reaction in the 523–573 K temperature range. The FTIR analysis of the reaction products demonstrated that NH_3 is produced in addition to CO_2 and N_2O. The absence of H_2 and H_2O suggests that NH_3 is formed by reaction of isocyanate species formed on the Pd surface with surface OH groups. The presence of NH_3 was confirmed by the FTIR spectra of adsorbed NH_4^+ ions under reaction conditions, reflecting the Brønsted surface acidity of the supports. The typical IR isocyanate bands often identified on Pd/Al_2O_3 catalysts were not observed. The Pd and the Mo-Pd catalysts exhibited a high selectivity to N_2O (>50%) that decreased at increasing NO conversion. On the other hand, the production of N_2 and NH_3 shows an increase with conversion. At constant temperature, with similar NO conversion, the presence of Mo favors the formation of NH_3.

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