

# NO reduction with CO in the presence and absence of H<sub>2</sub>O over Pd/γ-Al<sub>2</sub>O<sub>3</sub> and Pd-VO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts: The formation of HNCO, NH<sub>3</sub> and stable surface species

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## ABSTRACT

The reduction of NO by CO over Pd/γ-Al<sub>2</sub>O<sub>3</sub> and Pd-VO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts has been studied by combining activity and selectivity measurements with FTIR spectroscopy of gas phase products and adsorbed species under reaction conditions at 300 °C. Characterization of fresh, reduced samples, by H<sub>2</sub> chemisorption, TEM and FTIR spectroscopy of adsorbed CO and NO, indicated that the promoter is not covering the metal surface. Under dry conditions the rate of N<sub>2</sub> formation is lowered on the vanadia-modified alumina but the production of N<sub>2</sub>O was not altered. As a result the selectivity to N<sub>2</sub> decreased markedly on Pd-VO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. FTIR and XPS characterization of used catalysts demonstrated that the negative effect of VO<sub>x</sub> on N<sub>2</sub> formation is due to an oxidized state of Pd that develops under reaction conditions. FTIR analysis of the gas phase products showed that both catalysts produce small amounts of gas phase HNCO and NH<sub>3</sub> with the participation of surface –OH groups. FTIR spectra of the catalysts surface under reaction conditions demonstrate the presence of isocyanate (–NCO) and hydrogen containing compounds derived from HNCO. These stable species are not responsible for the production of N<sub>2</sub>O, but contribute to deactivation of the catalyst. They are rapidly eliminated upon water injection with a brief high production of NH<sub>3</sub>. Under steady state conditions water increases the CO conversion and the selectivity to N<sub>2</sub> and NH<sub>3</sub> on Pd/γ-Al<sub>2</sub>O<sub>3</sub>. The most notable effect is a marked reduction in N<sub>2</sub>O production. On Pd-VO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> water increases the conversion of both NO and CO, as well as the NH<sub>3</sub> formation. The selectivity to N<sub>2</sub> is not altered and it is lower than the ones of NH<sub>3</sub> and N<sub>2</sub>O. On both catalysts the NH<sub>3</sub> formation increases due to the rapid hydrolysis of –NCO and HNCO. The H<sub>2</sub> participation in the process of NH<sub>3</sub> formation is excluded due to the very low activity of Pd/γ-Al<sub>2</sub>O<sub>3</sub> and Pd-VO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> for the water–gas shift reaction.

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## 1. Introduction

Three-way catalysts (TWC) have provided a successful solution to limit the pollution caused by the exhaust gases of gasoline engines, since they can reduce the concentration of CO, NO<sub>x</sub> and hydrocarbons to very low values. The first generation of TWC catalysts were composed mainly of Pt and Rh as active metals but nowadays they have been replaced by Pd due mainly to economic considerations. Base metals and rare earth promoters are added to these new catalysts in order to increase the oxygen storage capacity, to maintain the thermal stability and to improve the general performance at the low temperatures of cold start operations. A high activity and a high selectivity to N<sub>2</sub> are desirable characteristics, taking into account that the NO + CO reaction produces N<sub>2</sub>O in significant amounts when catalysts are operated in the 200–400 °C temperature range. In the past several

metals or oxides like Cu [1], Cr [2], MoO<sub>x</sub> [3,4], La<sub>2</sub>O<sub>3</sub> [5,6] and mainly CeO<sub>x</sub> [6–9], have been tested as promoters of Pd/γ-Al<sub>2</sub>O<sub>3</sub> catalysts. The adsorption–desorption of NO and CO and the reactions of NO with CO (or CO + O<sub>2</sub>) have been used as a test procedure in order to understand the role of the promoters on the catalytic properties of palladium. There has been a general agreement about the enhancing dissociation of NO in the Pd-reducible oxides interface [6].

Not all reducible oxides are good promoters for the NO + CO reaction. In previous studies we have investigated the decomposition of NO and the reduction of NO by CO at 300 °C on Pd/α-Al<sub>2</sub>O<sub>3</sub>, Pd-VO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and WO<sub>x</sub>-Pd/γ-Al<sub>2</sub>O<sub>3</sub> [10–13] using stoichiometric mixtures of NO and CO at low concentrations. It was found that the Pd–V interaction allowed the reduction of VO<sub>x</sub> species (forming V<sup>4+</sup> sites) at low temperature. Consequently the catalytic activity for NO decomposition was higher than that measured on Pd/γ-Al<sub>2</sub>O<sub>3</sub>. Working at high conversion values (low space velocity) the binary catalyst showed a slightly higher selectivity to N<sub>2</sub> for the NO + CO reaction [11]. However, at lower conversions there was a negative effect of vanadium on both the

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catalytic activity and the selectivity to  $N_2$  [12] although a clear explanation for this behavior was not provided.

On  $WO_x$ -Pd/ $\gamma$ - $Al_2O_3$  [13] our work demonstrated that the Pd–W interaction facilitates the formation of reduced W species and weakens the adsorption of CO and NO on Pd. As a result here again the dissociation of NO was promoted but there was a detrimental effect on the NO + CO reaction. Furthermore, the FTIR characterization work showed that isocyanates and other surface species are formed on both Pd/ $\gamma$ - $Al_2O_3$  and  $WO_x$ -Pd/ $\gamma$ - $Al_2O_3$  without influencing the main reaction. Based on the above considerations we reexamined the effect of  $VO_x$  species in the NO + CO reaction performed over Pd/ $\gamma$ - $Al_2O_3$  catalysts. The formation and reactivity of adsorbed species and the oxidation state of Pd under reaction conditions were studied by *in situ* transmission FTIR and XPS spectroscopy. In addition, the effect of excess water on the stability of the adsorbed species, and the selectivity to nitrogen-containing products was investigated.

## 2. Experimental

### 2.1. Catalyst preparation

The support was  $\gamma$ - $Al_2O_3$  from Rhone-Poulenc (BET area 77 m<sup>2</sup>/g) grounded to 1.2 mm. A monometallic Pd/ $\gamma$ - $Al_2O_3$  catalyst was prepared by wet impregnation with a solution of Pd(AcAc)<sub>2</sub> in toluene ( $5 \times 10^{-3}$  g Pd(AcAc)<sub>2</sub>/cm<sup>3</sup>). Following the impregnation step the preparation was calcined in air at 500 °C for 2 h and reduced in H<sub>2</sub> at 300 °C to produce the Pd500 catalyst. In order to prepare the Pd- $VO_x$ / $\gamma$ - $Al_2O_3$  catalysts the alumina was first modified with the addition of vanadia using an aqueous solution of  $NH_4VO_3$  of appropriate concentration at a pH of 4 with a contact time of 24 h. The preparation was washed and then calcined at 400 °C for 4 h. The Pd- $VO_x$ / $\gamma$ - $Al_2O_3$  catalyst (Pd350V) was obtained by anchoring palladium to the  $VO_x$ / $\gamma$ - $Al_2O_3$  sample using the Pd(AcAc)<sub>2</sub>-toluene solution. After a contact time of 24 h, the catalyst was washed with toluene, calcined at 350 °C during 2 h and finally reduced in pure H<sub>2</sub> at 300 °C.

### 2.2. Catalyst characterization

The vanadium and palladium contents were determined by atomic absorption spectroscopy. The fraction of exposed palladium atoms was obtained from H<sub>2</sub> chemisorption measurements. These experiments were performed in a volumetric apparatus in the 50–500 Torr pressure range. Samples were previously reduced at 300 °C in flowing H<sub>2</sub> and evacuated overnight at the same temperature. The double isotherm method was used to determine the amount of irreversibly chemisorbed hydrogen (H/Pd)<sub>irr</sub>, at room temperature. The exposed palladium fraction, Pd<sub>sup</sub>/Pd<sub>tot</sub>, was calculated assuming that the surface stoichiometry is unity. Based on these measurements the Pd crystallite size was estimated using the equation  $d$  (nm) = 1.12/(H/Pd)<sub>irr</sub>. Using a similar adsorption procedure the (CO/Pd)<sub>irr</sub> ratio was determined.

Prereduced samples were analyzed by transmission electron microscopy (TEM) in order to obtain the palladium particle size distribution. Infrared spectra were recorded using a NICOLET 20 DXB instrument at 4 cm<sup>-1</sup> resolution. Catalyst samples of approximately 30–40 mg were pressed to form transparent disks of 13 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<sub>2</sub> windows, and coupled to a vacuum system for evacuation to 10<sup>-6</sup> Torr. It was possible to perform heat treatments up to 300 °C in air and H<sub>2</sub>, to dose small amounts of CO, NO<sub>2</sub>, CO<sub>2</sub>, NH<sub>3</sub> and NO through a leak valve and to maintain a steady flow of air, H<sub>2</sub>, He, or CO/He, NO/He and NO/CO/He mixtures over the

catalysts samples. A MKS Baratron (310-BH) pressure transducer allows pressure control in the 0.1–10 Torr range.

In experiments designed to observe adsorbed species formed under reaction conditions the samples were calcined in air, reduced in pure H<sub>2</sub> at 300 °C and purged with He. Subsequently a reference spectrum was taken and the gas flow was switched to a NO/CO/He mixture or the gas stream, containing reactants and products, coming from the test reactor. The growth in intensity of the IR bands was followed as a function of time. After a steady state condition was obtained the gas phase was flushed with He and the decay in intensity of the IR bands in the presence of NO, CO, He or H<sub>2</sub>O was observed.

For characterization purposes fresh (reduced) samples and those previously exposed to the NO/CO/He reaction mixture at 300 °C were evacuated, cooled to RT and exposed to 5 Torr of CO or NO for 2–5 min prior to spectra measurements. A FTIR spectra taken under vacuum conditions was used as a background.

### 2.3. Catalytic test

The NO + CO reaction was carried out in a pyrex glass flow reactor connected to a gas chromatograph, using a NO/CO/He gas mixture containing equal amounts of CO and NO (1100 ppm). The effect of V addition on the catalytic activity and the selectivity to N<sub>2</sub> of Pd/ $\gamma$ - $Al_2O_3$  was studied at 300 °C using 35 mg of catalyst diluted with an equal amount of pure alumina and a flow rate of 300 cm<sup>3</sup>/min (SV = 4.2 × 10<sup>5</sup> h<sup>-1</sup>) corresponding to an absolute reactor pressure of 1834 Torr. A few experiments were performed at a lower space velocity. Catalyst samples were prereduced in pure H<sub>2</sub> at the reaction temperature and purged with He. Measurements were performed on particles of decreasing size to verify the absence of internal mass transfer limitations. In order to investigate the reactivity of adsorbed species in the presence of water, a NO(1647 ppm)/CO(1590 ppm)/He mixture was first used and then, 1.5% water was added. Experiments were performed at 300 °C using 80 mg of catalyst diluted with an equal amount of pure alumina and a flow rate of 200 cm<sup>3</sup>/min (SV = 1.25 × 10<sup>5</sup> h<sup>-1</sup>). The catalytic activity for the water–gas shift reaction was also measured by using a CO(1470 ppm)/H<sub>2</sub>O(1.5%)/He mixture. A Sage syringe pump was employed for the water injection.

The reactor effluent was analyzed by on-line gas chromatography using a TCD detector and two Porapak Q columns. One was held at –11 °C to separate N<sub>2</sub>, CO, O<sub>2</sub> and NO, while the other, which operated at 80 °C, was used to identify N<sub>2</sub>O and CO<sub>2</sub>. The quantification of the reaction products was performed from the calculated areas of the chromatographic peaks, corrected with experimental response factors. In order to investigate the formation of NH<sub>3</sub> or HNCO the gas stream coming from the reactor was also analyzed by FTIR using a multiple-reflection infrared cell with a 2.4 m pathlength.

### 2.4. XPS characterization

XPS measurements on fresh and used samples were performed in a PHI 548 spectrometer equipped with a preparation chamber for heat treatment in O<sub>2</sub>, H<sub>2</sub> and the NO/CO/He mixture, using AlK $\alpha$  radiation of 1486.6 eV at 250 W, 20 mA, and a pass energy of 50 eV. Fresh samples were oxidized in chromatographic air at 300 °C for 1 h, evacuated to 2 × 10<sup>-7</sup> Torr, reduced in high purity H<sub>2</sub> at 573 K for 1 h, evacuated again to 2 × 10<sup>-7</sup> Torr and cooled to room temperature. Then the samples were transferred to the main chamber where the vacuum was lower than 5 × 10<sup>-10</sup> Torr. After analysis the samples were returned to the prechamber, exposed to the NO/CO/He mixture at 300 °C for 1 h, cooled to room temperature and evacuated up to 2 × 10<sup>-7</sup> Torr. The pretreated

samples were then reintroduced into the main chamber to perform a new XPS measurement.

In order to take into account the charging effects that shift the binding energy, the Al 2p binding energy was taken as a reference fixed at 74.0 eV. The spectra for O 1s, C 1s, Al 2p, and Pd 3d were obtained. For Pd, 100 scans were accumulated in order to increase the signal to noise ratio. Deconvolution of the spectra was made with the XPSPEAK Ver. 4.1 program, using Shirley's background subtraction and Gaussian-Lorentzian asymmetric functions for the peaks fit. The binding energies were determined with a precision of  $\pm 0.5$  eV. The atomic ratio estimations were obtained relating the peaks areas after the background subtraction and corrected by the corresponding atomic sensitivity factors to an approximated error of 20%.

### 3. Results

#### 3.1. Catalysts characterization

Table 1 reports the palladium and vanadium loadings, the irreversible hydrogen and carbon monoxide uptakes ( $H/Pd_{irr}$  and  $CO/Pd_{irr}$  respectively), and the TEM results.

The palladium loading of the samples was relatively low, in the 0.7–0.9 wt.% range. It is generally accepted that vanadia is very well dispersed by alumina and that the maximum capacity of this support to retain molecularly dispersed vanadium corresponds to 3.6–4.9  $VO_x$  units per  $nm^2$  [14,15]. From these values, the percentage of vanadia monolayer on sample Pd350V was estimated and corresponds approximately to a complete monolayer.

Results of  $H_2$  and CO chemisorption measurements for the catalysts are included in Table 1. The Pd500 catalyst, with a metal content of 0.68%, has a metal dispersion of 0.42. For the Pd350V sample the metal content is higher (0.87%) and the  $(H/Pd)_{irr}$  value is lower; 0.28. Two interpretations are possible to explain this result: (a) a decoration effect is the origin of the lower fraction of exposed Pd atoms, or (b) the palladium particles in Pd350V are larger than those in Pd500. The TEM results in Table 1 show that the average particle size of the Pd500 sample is 2.8 nm, while for catalyst Pd350V the average value is 4.06. Based on these results, the diminution of the fraction of exposed Pd atoms is assigned to large particles formed in the presence of  $VO_x$  species, despite the lower calcination temperature, as compared to Pd500. In fact a Pd(0.68%)/ $\gamma$ - $Al_2O_3$  catalyst calcined at 350 °C exhibited a  $H/Pd$  ratio of 0.47 corresponding to a particle size of 2.4 nm. It is important to observe that the average TEM particle size of Pd350V is in reasonably good agreement with the value estimated from chemisorption measurements.

Fig. 1 shows the infrared spectra of CO adsorption at room temperature on Pd500, and Pd350V. They present a band due to linear CO at 2080–2090  $cm^{-1}$  and another extending from 2000 to 1800  $cm^{-1}$  due to multiple coordinated species on the Pd surface. This broad band is partially resolved in one peak at  $\approx 1980$   $cm^{-1}$  and another at  $\approx 1930$   $cm^{-1}$  attributed to CO adsorbed on Pd(1 0 0) and Pd(1 1 1) surface planes respectively.

Several bands due to carbonate species on the alumina support were observed below 1700  $cm^{-1}$  except on the Pd350V sample

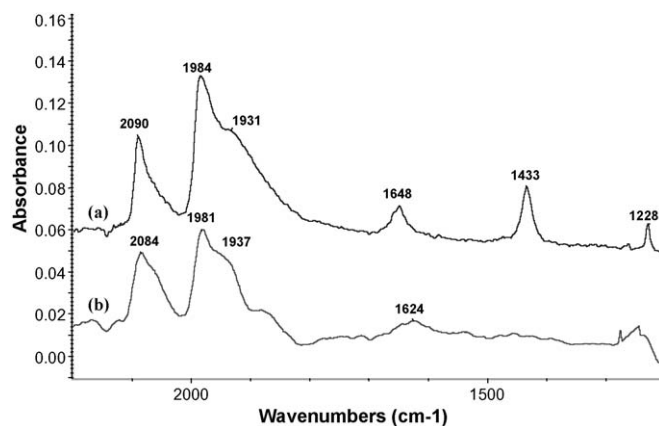


Fig. 1. FTIR spectra of reduced Pd500 (a) and Pd350V (b) catalysts at 25 °C, following exposure to 5 Torr of CO.

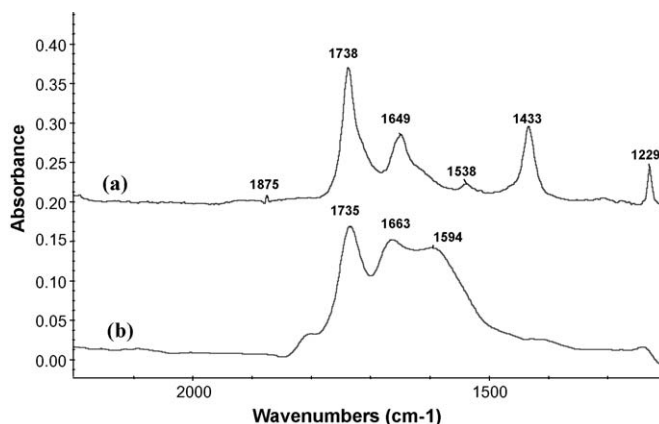


Fig. 2. FTIR spectra of reduced Pd500 (a) and Pd350V (b) catalysts at 25 °C, following exposure to 5 Torr of NO.

where the vanadium species are well dispersed. As mentioned before [13] an unequivocal identification of these adsorbed species is difficult due to the multiple surface structures that are possible under the influence of the Al–O bond. Based on previous studies the bands at  $\approx 1650$  and  $1228$   $cm^{-1}$  are attributed to the stretching vibration ( $\nu_{C=O}$ ) and the asymmetric stretching ( $\nu_{as}COO$ ) of bridged bidentate carbonate species. On the other hand the band at  $1435$   $cm^{-1}$  is associated with the presence of carbonates. It is important to state that these support bands were not observed in the absence of Pd, which seems to indicate that carbonates form on alumina sites generated during the catalyst pretreatment. Upon calcination at high temperatures these bands are attenuated.

The spectra of NO adsorption on Pd500 and Pd350V are shown in Fig. 2. The main band, located at 1735–1939  $cm^{-1}$ , is due to NO adsorption in the linear form on palladium atoms, in agreement with previous studies [13]. Peaks due to nitrates and nitrites species on the alumina surface are present at 1229, 1433, and 1649  $cm^{-1}$  on Pd500, similar to those observed upon CO adsorption. The weak band at 1538  $cm^{-1}$  observed on Pd500 is also attributed to NO interaction with the  $\gamma$ - $Al_2O_3$  surface.

On Pd350V the bands at 1229 and 1433  $cm^{-1}$  are absent due to the coverage of the alumina surface by  $VO_x$  species. However this catalyst presents two broad and overlapping bands at 1594 and 1663  $cm^{-1}$  which are attributed to NO adsorption on reduced V species. The partial reduction of V on the Pd- $VO_x/\gamma$ - $Al_2O_3$  catalyst has been demonstrated in a previous TPR study [11].

Table 1  
Main physicochemical properties of Pd/ $\gamma$ - $Al_2O_3$  and Pd- $VO_x/\gamma$ - $Al_2O_3$  catalysts.

Catalyst	V (wt.%)	Pd (wt.%)	$(H/Pd)_{irr}$	$(CO/Pd)_{irr}$	Particle size (nm) from	
					$(H/Pd)_{irr}$	TEM
Pd500	–	0.68	0.42	–	2.7	2.8
Pd350V	3.1	0.87	0.28	0.23	4.0	4.06

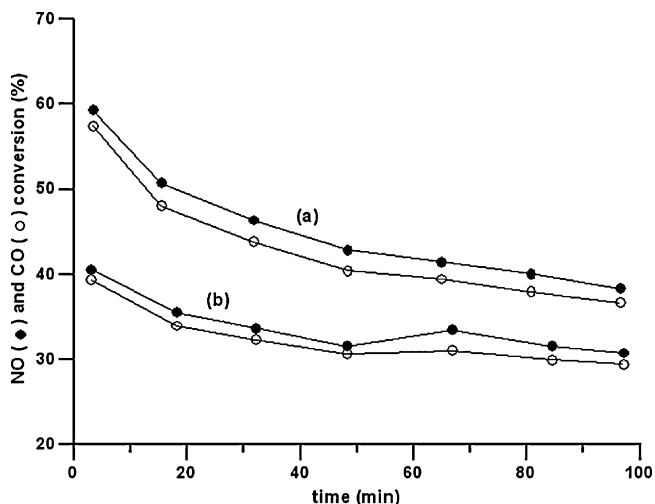


Fig. 3. NO reduction by CO at 300 °C. NO (●) and CO (○) conversion as a function of time for Pd500 (a) and Pd350V (b). Feed composition; [NO] = [CO] = 1100 ppm; absolute pressure = 1834 Torr; SV =  $4.2 \times 10^5 \text{ h}^{-1}$ .

### 3.2. Catalytic results

The conversion of NO and CO and the formation of  $\text{N}_2$  and  $\text{N}_2\text{O}$  as a function of time are shown in Figs. 3 and 4 for a space velocity of  $4.2 \times 10^5 \text{ h}^{-1}$ . A clear difference in activity and selectivity for the Pd500 and Pd350V samples was observed when they were tested at 300 °C. The catalysts presented a period of high deactivation, for both the NO and CO conversion, although steady state values were obtained after a reaction time of 1–2 h. The initial activity was fully recovered by an oxidation and reduction treatment. CO conversion values were always lower than those of NO, a behavior that is in accordance with previous studies [10,11,16].

The results in Fig. 3 clearly demonstrate the lower activity of Pd350V relative to that of Pd500 that was expected due to the lower metal dispersion ( $\text{H}/\text{Pd} = 0.28$ ). Regarding the selectivity of the catalysts for  $\text{N}_2$  and  $\text{N}_2\text{O}$  formation the results are shown in

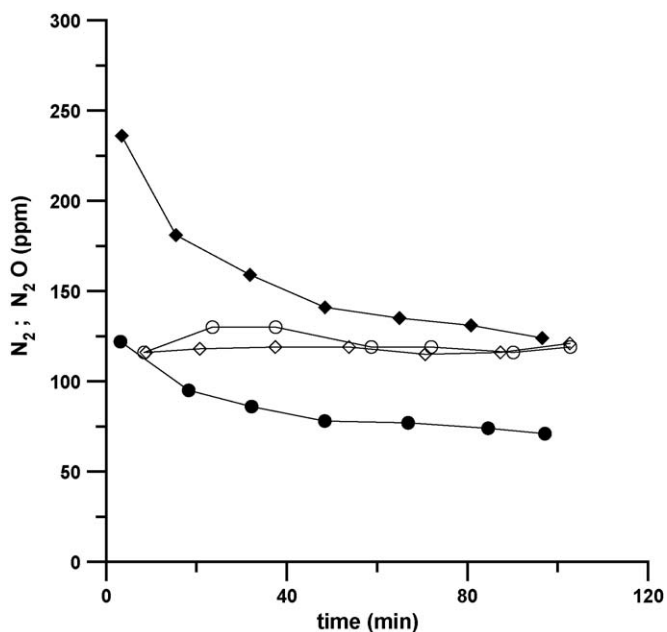


Fig. 4. NO reduction by CO at 300 °C. Product formation as a function of time for Pd500 (●  $\text{N}_2$ , ○  $\text{N}_2\text{O}$ ) and Pd350V (◆  $\text{N}_2$ , ◇  $\text{N}_2\text{O}$ ). Feed composition; [NO] = [CO] = 1100 ppm; absolute pressure = 1834 Torr; SV =  $4.2 \times 10^5 \text{ h}^{-1}$ .

Table 2

NO+CO reaction at 300 °C. NO and CO conversion and selectivity to  $\text{N}_2$  for Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  and Pd- $\text{VO}_x/\gamma$ - $\text{Al}_2\text{O}_3$  catalysts. SV =  $4.2 \times 10^5 \text{ h}^{-1}$ . Reaction time = 2 h.

Sample	$X_{\text{NO}}$ (%)	$X_{\text{CO}}$ (%)	$S_{\text{N}_2}$ (%) <sup>a</sup>
Pd500	38.3	36.7	50.6
Pd350V	30.7	29.4	37.0

<sup>a</sup> Selectivity to  $\text{N}_2$  ((amount of  $\text{N}_2$  formed)/(amount of  $\text{N}_2 + \text{N}_2\text{O}$  formed))  $\times 100$ .

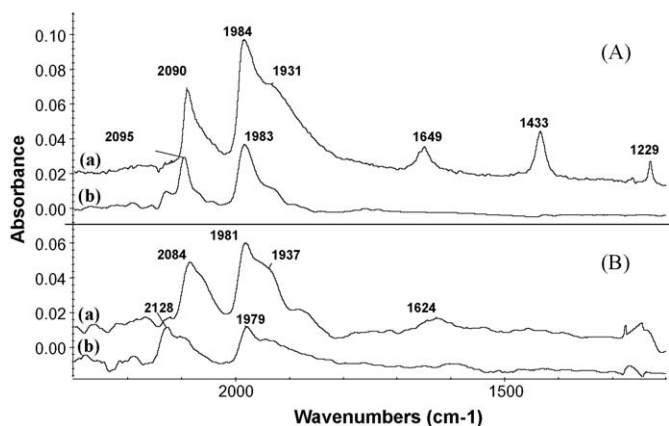
Fig. 4. The production of  $\text{N}_2$  was higher for Pd500 reflecting the level of NO conversion. In all cases the formation of  $\text{N}_2$  as a function of time followed the declining behavior exhibited by the conversion of NO and CO. In contrast the amount of  $\text{N}_2\text{O}$  formed was surprisingly similar for both catalysts and the values were not dependent on the reaction time. These results suggest that  $\text{N}_2$  and  $\text{N}_2\text{O}$  are formed by independent mechanisms. The catalytic activity for the NO + CO reaction and the selectivity to  $\text{N}_2$  for Pd500 and Pd350V at steady state conditions are summarized in Table 2. The selectivity of the Pd350V catalyst (37%) was much lower than that of Pd500 (50%). Based on these results it can be concluded that the presence of  $\text{VO}_x$  species is detrimental for the selectivity of the noble metal.

### 3.3. The oxidation state of Pd under reaction conditions

According to the results presented in Fig. 4, the main difference between the tested catalysts is in the production of  $\text{N}_2$ . The Pd surface on the Pd500 sample is more active for the  $\text{N}_2$  formation than that present on Pd350V, which in part may be attributed to the lower metal dispersion, and consequently to a diminished catalytic activity. However the production of  $\text{N}_2\text{O}$  is not altered. This behavior indicates that the Pd surface is somehow modified by the presence of  $\text{VO}_x$  species. In order to explore the oxidation state of the Pd surface under reaction conditions a catalyst pellet placed in the FTIR cell was exposed to the reaction mixture at 300 °C during 1 h in order to reach steady state conditions. Subsequently the cell was evacuated and cooled to room temperature and a background spectrum was taken prior to standard CO and NO adsorption studies. It is important to realize that only the CO and NO adsorption bands are detected. Those due to stable species formed under reaction conditions (discussed below) are not observed because they are present in the background and sample spectra. Fig. 5(A) and (B) compares the spectra of CO adsorption on the Pd500 and Pd350V samples before (a) and after (b) reaction. For the former catalyst all bands are attenuated due to the presence of adsorbed species, mainly that assigned to multiple coordinated species ( $1931 \text{ cm}^{-1}$ ). The position of the bands is slightly shifted, indicating that the Pd surface remains mainly in a metallic state. On the other hand the comparison of the CO spectrum corresponding to the Pd350V catalyst before and after reaction (Fig. 5(B)) clearly shows that the band due to linear CO was attenuated and in part shifted from 2084 to  $2128 \text{ cm}^{-1}$ , indicating the presence of oxidized Pd sites. The low frequency bands were also attenuated. These differences generated by the Pd–V interaction may be responsible for the relatively high formation of  $\text{N}_2\text{O}$  and low selectivity of the Pd350V catalyst.

The oxidation state of the Pd surface under reaction conditions was also probed by NO adsorption. Fig. 6(A) and (B) shows the spectra of NO adsorption on Pd500 and Pd350V. After reaction the linear NO band on Pd500 was slightly altered, indicating that the Pd surface remained in a metallic state. On the other hand the adsorption of NO on Pd350V clearly showed that the reaction produces a strong attenuation of the NO band, which is also shifted from 1735 to  $1748 \text{ cm}^{-1}$ . These results demonstrate that the presence of  $\text{VO}_x$  species and/or  $\text{V}_2\text{O}_5$  crystallites stabilize a Pd oxide surface under reaction conditions. Consequently, the catalytic





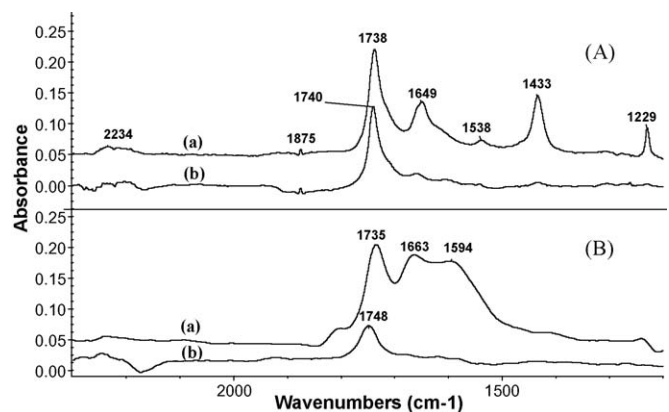
**Fig. 5.** FTIR spectra of fresh (a) and used (b) Pd500 (A) and Pd350V (B) catalysts at 25 °C following exposure to 5 Torr of CO. Used samples are those exposed to the NO + CO reaction mixture at 300 °C during 1 h.

activity for NO dissociation or N<sub>2</sub> formation is affected and N<sub>2</sub>O becomes the main reaction product.

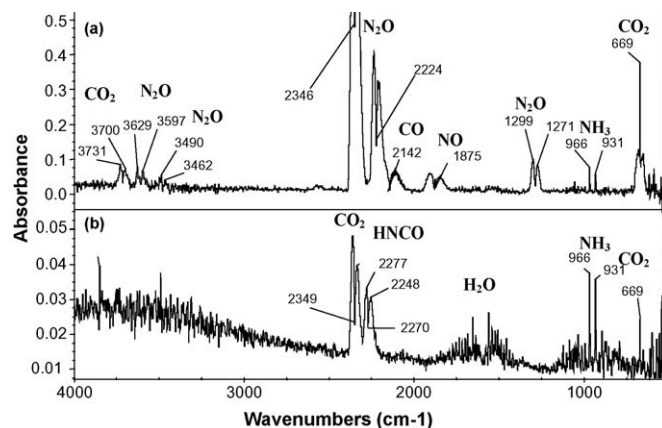
An independent confirmation of the oxidized state of Pd due to the presence of VO<sub>x</sub> species was obtained by analyzing the Pd XPS spectra on fresh and used samples. The results shown in Table 3 indicate that the intensity of the Pd 3d peak relative to that of Al 2p and the electron binding energy of the Pd3d<sub>5/2</sub> line for the Pd500 sample are not modified by the NO + CO reaction. The Pd3d<sub>5/2</sub> peak appears at 335.0–335.2 eV indicating a metallic state that is not modified by the reaction. On the other hand after reaction the Pd350V sample presents a lower Pd/Al ratio characterized by a binding energy value of 335.4 eV corresponding to metallic Pd, and a superimposed peak of similar intensity shifted to a higher binding energy; 336.7 eV. Therefore a fraction of the Pd surface is in an oxidized state under reaction conditions.

### 3.4. FTIR analysis of reaction products

The FTIR analysis of the product stream was carried out using a multiple-reflection cell. In order to increase the concentration of products a lower space velocity was used ( $1.4 \times 10^5 \text{ h}^{-1}$ ). The spectra of Fig. 7(a), corresponding to the NO + CO reaction at 300 °C on Pd350V, clearly shows bands due to unconverted CO and NO, centered at 2142 and 1875 cm<sup>-1</sup> respectively. In addition very intense bands showing the P and R branches of gaseous CO<sub>2</sub> and N<sub>2</sub>O are centered at 2346 and 2224 cm<sup>-1</sup>. Less intense bands due to these products are seen in the low and high frequency region of the



**Fig. 6.** FTIR spectra of fresh (a) and used (b) Pd500 (A) and Pd350V (B) catalysts at 25 °C following exposure to 5 Torr of NO. Used samples are those exposed to the NO + CO reaction mixture at 300 °C during 1 h.



**Fig. 7.** NO reduction by CO at 300 °C on Pd350V. (a) FTIR spectra of product gas at steady state conditions. Feed composition; [NO] = [CO] = 1100 ppm; absolute pressure = 1217 Torr; SV =  $1.4 \times 10^5 \text{ h}^{-1}$  (b) after flushing with He and heating the reactor-gas cell connection tubing.

spectrum. More significant is the presence of two infrared lines at 966 and 931 cm<sup>-1</sup> that are due to symmetric deformation vibrations of NH<sub>3</sub>. In this particular case the NH<sub>3</sub> concentration is about 60 ppm, corresponding to a selectivity of  $\approx 8\%$  ( $S_{\text{NH}_3} = (n_{\text{NH}_3}) / (2 \times n_{\text{N}_2} + 2 \times n_{\text{N}_2\text{O}} + n_{\text{NH}_3})$ ). This product could not be attributed to the reaction of adsorbed nitrogen atoms with hydrogen remaining on the metal surface after the reduction pretreatment, because an extensive helium purge at 300 °C was performed prior to the admission of the NO + CO mixture. In addition it was verified that H<sub>2</sub> is not produced by the reaction of residual water, which is present as an impurity (<5 ppm) with CO. More likely NH<sub>3</sub> was produced by hydrolysis of isocyanic acid (HNCO). This reaction product was formed during the NO + CO + H<sub>2</sub> reaction over Pt/SiO<sub>2</sub>, as demonstrated by DümpeImann et al. [17]. In the absence of hydrogen the formation of HNCO may be due to the interaction of isocyanate species (-NCO) with OH groups on the support surface. Although HNCO is a stable compound in the gas phase, its IR signal (at  $\approx 2270 \text{ cm}^{-1}$ ), is overlapped by the strong N<sub>2</sub>O bands. Consequently specific experiments were designed to investigate the presence of HNCO in the product stream. Following the detection of NH<sub>3</sub> by gas phase analysis the catalyst bed and the IR cell were purged with He until a flat spectrum was observed. Subsequently the 1/16 in. SS tube connecting the reactor with the gas cell was heated at a temperature  $\gg 100 \text{ °C}$  and a new FTIR spectrum was taken. Fig. 7(b) clearly shows the presence of low intensity bands due to NH<sub>3</sub>, H<sub>2</sub>O, CO<sub>2</sub>, and the P (2227 cm<sup>-1</sup>) and R (2248 cm<sup>-1</sup>) branch lines of HNCO centered at 2270 cm<sup>-1</sup> [18]. Similar experiments performed on the Pd500 catalyst also confirmed the formation of small amounts of NH<sub>3</sub> and HNCO, in addition to the main reaction products of the NO + CO reaction.

### 3.5. FTIR spectra of adsorbed species

As mentioned in Section 1, the formation of adsorbed species on the catalysts surface, under reaction conditions, was monitored by *in situ* FTIR spectroscopy. The gas mixture emerging from the reactor during the activity and selectivity measurements was diverted to the IR cell and flowed over a catalyst pellet maintained at 300 °C. In this way the examined catalyst is subject to the conditions prevailing at the reactor end. It is important to realize that the CO/NO ratio of the gas mixture entering the IR cell was higher than one, since the NO conversion was higher than the CO conversion. This was found to be a necessary condition for the formation of adsorbed species. Fig. 8 shows the development of the spectrum for Pd500 as a function of time (reactor S.V. =  $4.2 \times 10^5 \text{ h}^{-1}$ ; see Table 3 for NO and CO conversion values). Besides

**Table 3**  
Pd3d electron binding energy and Pd/Al atomic ratio from XPS measurements on fresh and used Pd500 and Pd350V catalysts.

Catalyst	Pretreatment at 300 °C	Pd3d/Al2p	Pd3d <sub>5/2</sub> (BE eV)	Pd*3d/Al2p	Pd*3d <sub>5/2</sub> BE (eV)
Pd500	Oxid. Red.	$1.3 \times 10^{-2}$	335.0	–	–
	NO+CO	$1.3 \times 10^{-2}$	335.2	–	–
Pd350V	Oxid. Red.	$1.2 \times 10^{-2}$	335.2	–	–
	NO+CO	$4.8 \times 10^{-3}$	335.4	$5.1 \times 10^{-3}$	336.7

the band due to gas phase CO<sub>2</sub> at 2360 cm<sup>-1</sup>, a very strong one due to surface isocyanate developed at 2258 cm<sup>-1</sup> and simultaneously other less intense bands appeared in the low frequency region (1400–1700 cm<sup>-1</sup>). The intensity of all bands grew slowly, attaining a constant value after a reaction time of about 100 min. This behavior correlates with the decay of the NO and CO conversion values shown in Fig. 3.

Under steady state conditions the examined catalysts developed a similar spectrum of adsorbed species although some differences in the intensity and the location of the bands were observed. Fig. 9 compares the spectra of Pd500 and Pd350V. The most intense band is that located at  $\approx 2260$  cm<sup>-1</sup> assigned to isocyanate. Bands in this region are well known and they have been preferentially assigned to the asymmetric stretching vibration of isocyanate (–NCO).

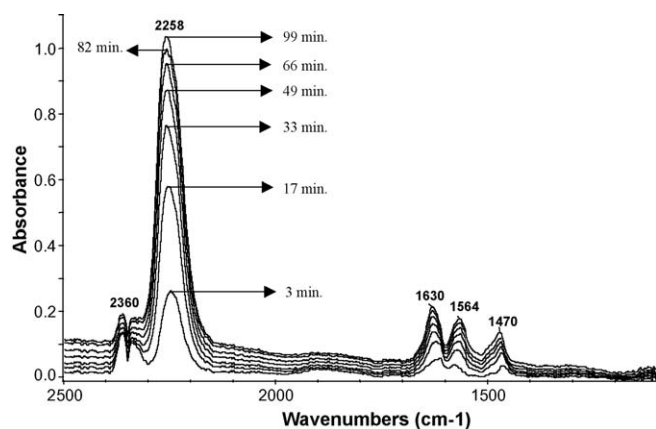
The spectrum of Pd500 in Fig. 8 and more clearly that of Pd350V in Fig. 9 indicate the contribution of two different isocyanate species. On Pd500 the main band is located at 2258–2260 cm<sup>-1</sup> with a shoulder at a lower frequency. On Pd350V the band at 2258–2260 cm<sup>-1</sup> appears with a lower intensity but an overlapping band at  $\approx 2217$  cm<sup>-1</sup> is also present. The presence of two isocyanate bands has been often attributed to species adsorbed on different support sites.

The bands in the isocyanate region and those at low frequencies were not modified when the IR cell was evacuated. By purging the IR cell with air or He at 300 °C they were slowly eliminated. The decrease in intensity as a function of time, in He flow, clearly demonstrated the presence of two superimposed isocyanate bands on all samples. The one located at a higher frequency ( $\approx 2260$  cm<sup>-1</sup>) decreased more rapidly, indicating that it belongs to a weaker adsorbed molecule.

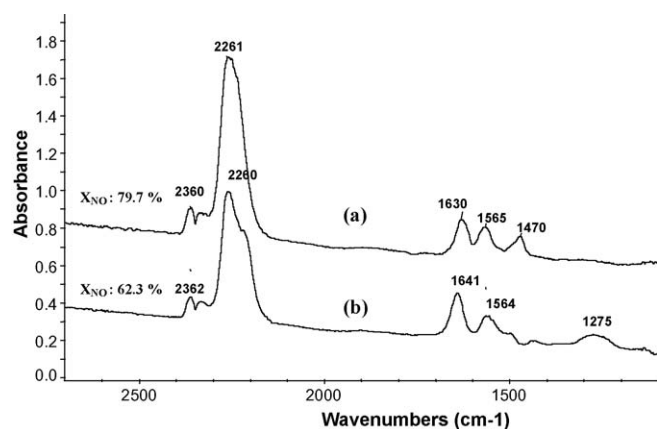
The less intense bands in the 1200–1650 cm<sup>-1</sup> region that are formed on Pd500 (1630, 1564 and 1470 cm<sup>-1</sup>) and Pd350V (1642, 1562 and 1273 cm<sup>-1</sup>), are more difficult to assign. As shown in Fig. 8, the growth of these bands is parallel to that of the isocyanate bands, an indication that they are somehow related. In several

studies of the CO + NO reaction on supported Pd catalysts these bands have been attributed to carbonate, nitrite and nitrate species adsorbed on the alumina support [4,19,20]. However by proper experimentation we have demonstrated that they are not formed when the catalysts are exposed to CO, CO<sub>2</sub>, NO, N<sub>2</sub>O, or NO<sub>2</sub> at 300 °C, that is the pure reactants and potential products of the CO + NO reaction. In the presence of NH<sub>3</sub> (5 Torr) all catalysts develop a broad band around 1260 cm<sup>-1</sup> attributed to surface coordinated ammonia that is more intense on the Pd350V sample. This band is similar to that observed under reaction conditions on Pd350V at 1273 cm<sup>-1</sup>. The simultaneous presence of CO and NO seems to be a necessary condition for the bands to appear. Recent published studies reported the formation of similar low frequency bands when catalysts and supports were exposed to isocyanic acid. They have been attributed to adsorbed NH<sub>2</sub> and NH<sub>3</sub> species [21], to the [N=C=O]<sup>-</sup> anion [22] and to cyanuric acid ((HNCO)<sub>3</sub>), s-triazine (C<sub>3</sub>N<sub>3</sub>H<sub>3</sub>) or melamine (C<sub>3</sub>N<sub>6</sub>H<sub>6</sub>) [23]. If the bands observed in the 1200–1650 cm<sup>-1</sup> region are due to IR absorption of species formed by reaction of –OH groups with surface isocyanate, the position of the bands should be shifted by deuterium substitution. To explore this possibility the reduction pretreatment of the catalyst samples prior to the NO + CO reaction was carried out with D<sub>2</sub>. In this way the isotopic replacement was accomplished. The spectrum shown in Fig. 10 for Pd500 demonstrate that the intensity and position of the band formed at 2260 cm<sup>-1</sup> is not altered. This is an expected result taking into account that it was assigned to Al–NCO or Pd–NCO species. On the other hand the low frequency region of the spectrum was clearly modified. A very broad band indicating the overlapping of different species appears between 1521 and 1572 cm<sup>-1</sup>. On Pd350V only a single band was observed at 1572 cm<sup>-1</sup> (not shown). These results demonstrate that the low frequency IR bands of adsorbed species formed during the NO + CO reaction on Pd catalysts, are in part due to hydrogen containing species.

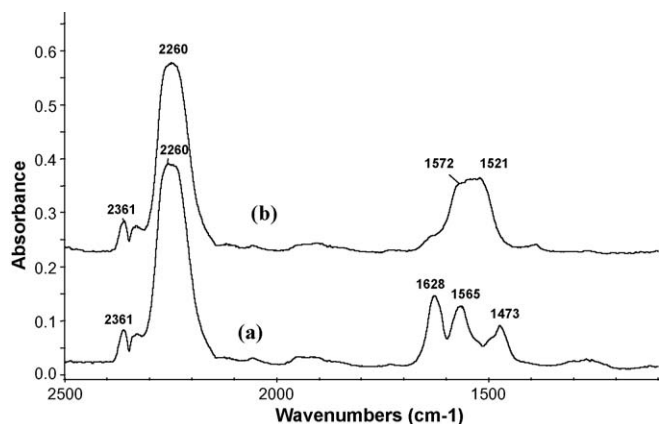
We have also investigated the reactivity of CO<sub>2</sub> + NH<sub>3</sub> and CO + NH<sub>3</sub> mixtures on our catalysts. Although several IR bands were



**Fig. 8.** NO reduction by CO at 300 °C on Pd500. FTIR spectra of adsorbed species as a function of time on stream. Feed composition; [NO] = [CO] = 1100 ppm; absolute pressure = 1834 Torr; SV =  $4.2 \times 10^5$  h<sup>-1</sup>.

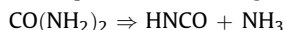


**Fig. 9.** NO reduction by CO at 300 °C. FTIR spectra of adsorbed species at steady state conditions on Pd500 (a) and Pd350V (b). Feed composition; [NO] = [CO] = 1100 ppm; absolute pressure = 1834 Torr; SV =  $4.2 \times 10^5$  h<sup>-1</sup>.



**Fig. 10.** NO reduction by CO at 300 °C on Pd500. Effect of H<sub>2</sub> (a) and D<sub>2</sub> (b) reduction on the FTIR spectra of adsorbed species.

generated they were different from those shown in Fig. 8 with the exception of the band at  $\approx 1260\text{ cm}^{-1}$  corresponding to adsorbed ammonia that was very intense on the Pd350V sample. A more interesting result was obtained when the catalysts were exposed to a mixture of HNCO and NH<sub>3</sub>. In order to do so a small amount of urea was added to the Pd500 and Pd350V samples during the preparation of the FTIR pellets. They were heated under vacuum at 350 °C to accomplish the following decomposition reaction [24];

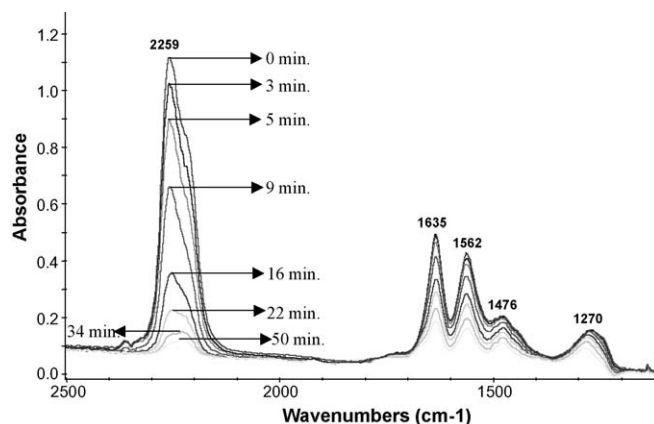


The room temperature spectra showed a strong isocyanate band at  $2260\text{ cm}^{-1}$  in addition to intense bands at 1623, 1570 and  $1468\text{ cm}^{-1}$  and 1632, 1563 and  $1272\text{ cm}^{-1}$  for Pd500 and Pd350V respectively. The band at  $1275\text{ cm}^{-1}$  on Pd350V, corresponds to NH<sub>3</sub> coordinated to the VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> support surface. The position of the remaining bands is very close to those formed during the NO + CO reaction, as observed in Fig. 9. Therefore the low frequency adsorbed species on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts are due to intermediates and/or products derived from a catalytic reaction involving HNCO (g) as discussed later.

### 3.6. Reactivity of adsorbed species

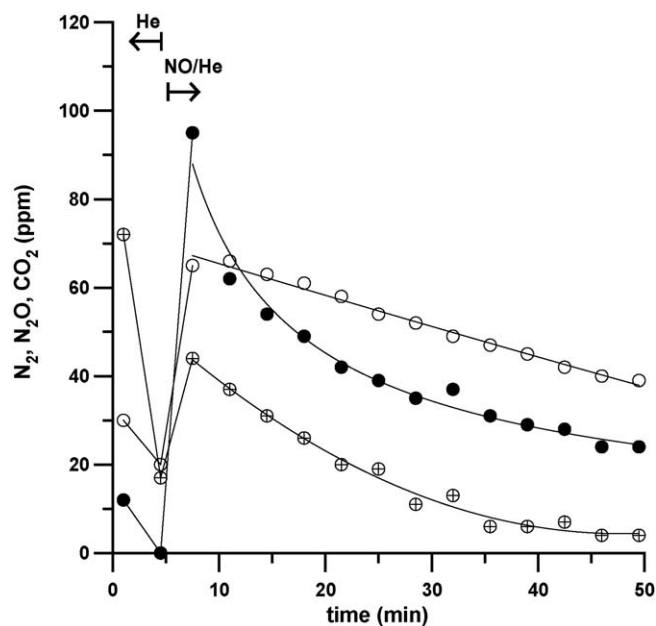
It has been suggested that the reactivity of surface isocyanates and other nitrogen containing species with NO may play a role in the process of N<sub>2</sub>O formation during the NO + CO reaction [13,21,25]. In order to explore the possibility that the -NCO + NO reaction provides an alternative route to produce N<sub>2</sub>O on our Pd catalysts, preformed isocyanate species were contacted with a NO/He mixture. Isocyanate formation was accomplished by flowing an NO/CO/He mixture (CO/NO > 1) during 1 h over a disk of the Pd350V catalyst placed in a small volume FTIR cell held at 300 °C. In one experiment the reaction mixture was replaced by a flow of He (80 cm<sup>3</sup>/min), the decrease in the concentration of adsorbed species was followed as a function of time and the cell output (N<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub>) was analyzed by an on-line GC. In a different experiment the cell was flushed with He during 4 min to remove the gas phase and weakly adsorbed species and subsequently the inert gas was replaced by a NO(3034 ppm)/He mixture.

Fig. 11 shows the change in the spectra of adsorbed species as a function of time for the Pd350V catalyst exposed to a flowing mixture of NO/He. All bands decreased continuously but the main variation occurs on the -NCO band at  $2260\text{ cm}^{-1}$ . After a reaction time of 50 min this band became smaller than those located at low frequency, an indication that they belong to different species. No change in frequency is observed with the exception of the NH<sub>3</sub> band located at  $1270\text{ cm}^{-1}$  which is shifted to a higher frequency as the



**Fig. 11.** Reactivity of adsorbed species formed on Pd350V to NO. Reaction conditions:  $T = 300\text{ °C}$ ; [NO] = 3034 ppm (in He); flow rate =  $70\text{ cm}^3/\text{min}$ .

surface concentration decreases. These features of the FTIR spectra are similar when the decomposition of adsorbed species is carried out in pure He. However the bands decreased faster in the presence of NO. Fig. 12 shows the dependence of products of isocyanate decomposition with time in the presence of NO. The initial values (1–4.5 min) of CO<sub>2</sub> (72 ppm), N<sub>2</sub> (30 ppm) and N<sub>2</sub>O (12 ppm), obtained in pure He, are mainly due to the previous NO + CO reaction. Upon switching to NO/He a large increase in concentration is observed. The formation of CO<sub>2</sub> is mainly due to the  $-\text{NCO} + \text{NO} \Rightarrow \text{N}_2 + \text{CO}_2$  reaction taking into account that the amount of adsorbed CO that could react with NO should be quite low. On the other hand the relatively high concentration of N<sub>2</sub> and N<sub>2</sub>O reflects the contributions of both, the  $-\text{NCO} + \text{NO}$  and the NO decomposition reactions. It is important to realize that the production of N<sub>2</sub> is higher than that of N<sub>2</sub>O (except for a short initial period) and consequently the selectivity to N<sub>2</sub> is always larger than that observed during the NO + CO reaction. Based on this result we may conclude that the reactivity of isocyanates and the other surface species with NO does not provide an alternative route for N<sub>2</sub>O formation on the Pd350V catalyst.



**Fig. 12.** Decomposition of adsorbed species in NO on Pd350V. Concentration of products as a function of time. (○) N<sub>2</sub>; (◻) CO<sub>2</sub>; (●) N<sub>2</sub>O. Reaction conditions:  $T = 300\text{ °C}$ ; NO = 3034 ppm (in He) at  $t > 4.5\text{ min}$ ; flow rate =  $80\text{ cm}^3/\text{min}$ .

**Table 4**

NO + CO reaction at 300 °C. The effect of water on the level of NO and CO conversion and the selectivity to nitrogen-containing products. SV =  $1.25 \times 10^5 \text{ h}^{-1}$ .

	Pd500		Pd350V	
	Dry feed	1.5% H <sub>2</sub> O	Dry feed	1.5% H <sub>2</sub> O
X <sub>NO</sub> (%)	48 (49) <sup>a</sup>	46 (50) <sup>a</sup>	40	48
X <sub>CO</sub> (%)	41 (41) <sup>a</sup>	46 (49) <sup>a</sup>	33	47
S <sub>N<sub>2</sub></sub> (%)	39 (45) <sup>a</sup>	47 (46) <sup>a</sup>	22	22
S <sub>N<sub>2</sub>O</sub> (%)	48 (53) <sup>a</sup>	29 (33) <sup>a</sup>	63	50
S <sub>NH<sub>3</sub></sub> (%)	13 (2) <sup>a</sup>	24 (21) <sup>a</sup>	15	28

<sup>a</sup> Sample pretreated in He at 400 °C prior to reaction.

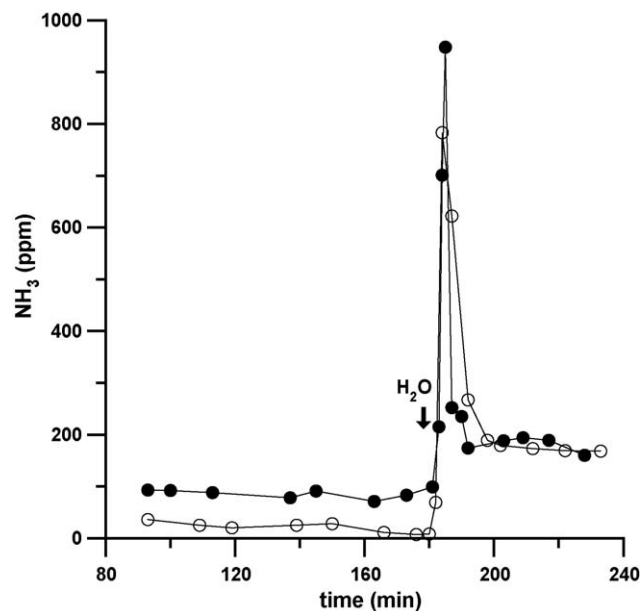
### 3.7. The effect of water in the NO + CO reaction

Experiments were performed using a wet feed mixture to observe the water effect on the catalytic activity, the gas phase products and the stability of the adsorbed species. The NO + CO reaction on Pd500 was first carried out under dry conditions (CO = 1590 ppm; NO = 1647 ppm; S.V. =  $1.25 \times 10^5 \text{ h}^{-1}$ ; T = 300 °C) until steady state conditions were obtained (X<sub>NO</sub> = 48%; X<sub>CO</sub> = 41%). The NH<sub>3</sub> concentration was  $100 \pm 10$  ppm, corresponding to a selectivity of  $\cong 13\%$ . According to GC analysis, CO conversion clearly increased (X<sub>CO</sub> = 46%), N<sub>2</sub> production augmented and the N<sub>2</sub>O yield decreased after water admission (1.5%). Both the activity and selectivity results are summarized in Table 4. There is a clear increase in the selectivity to N<sub>2</sub> and NH<sub>3</sub> and a marked decrease in the selectivity to N<sub>2</sub>O. The new steady-state conversion values (X<sub>NO</sub>  $\cong$  X<sub>CO</sub>  $\cong$  46%) were closer than those obtained under dry conditions. This behavior may be attributed to the participation of water–gas shift reaction enhancing CO consumption. However, by using a CO(1470 ppm)/H<sub>2</sub>O(1.5%)/He feed mixture, we found that the catalytic activity of the Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for the water–gas shift reaction was much lower than the one of the NO + CO reaction. At 300 °C (S.V. =  $2.5 \times 10^5 \text{ h}^{-1}$ ) the TOR<sub>CO</sub> for the former reaction was  $0.014 \text{ s}^{-1}$ . A higher value ( $0.040 \text{ s}^{-1}$ ) was measured for the NO + CO reaction at 250 °C. Consequently, only a minor influence of the water–gas shift reaction on the NO + CO + H<sub>2</sub>O reaction could be expected. It was found that the amount of oxygen associated with the reduction in N<sub>2</sub>O formation (77 ppm) was close to the quantity necessary to increase the conversion of CO to CO<sub>2</sub> (80 ppm).

Upon the water injection the gas-phase spectrum showed a sudden increase in NH<sub>3</sub> concentration, up to 950 ppm, that returned rapidly to a value higher than the one that corresponded to dry conditions;  $\cong 175$  ppm. This behavior can be observed in Fig. 13. The momentary increase in NH<sub>3</sub> production was due to the water reaction with the surface isocyanates and the other adsorbed species. In support of this interpretation, important alterations due to water presence were observed on the spectrum of adsorbed species. The intensity of the isocyanate band at  $2246 \text{ cm}^{-1}$  and those at  $1624$ ,  $1571$  and  $1470 \text{ cm}^{-1}$  decreased rapidly and was absent in a few minutes. Afterwards, the spectrum only displayed bands of adsorbed water [26]. Consequently, the main effect of water on Pd500 was the elimination of the stable surface species, the inhibition of N<sub>2</sub>O formation and an enhanced production of N<sub>2</sub> and NH<sub>3</sub>.

In order to observe the effect of surface water on the formation of NH<sub>3</sub>, the NO + CO reaction was also carried on a Pd500 sample pretreated to 400 °C in He prior to reaction. The results are presented in Fig. 13 and summarized in Table 4. Under dry conditions the NO and CO conversions were not altered but the NH<sub>3</sub> production was lower and the selectivity to N<sub>2</sub> and N<sub>2</sub>O increased. The conversion and selectivity values were not modified upon water injection.

When a similar study was performed over Pd350V the effect of water was different; an increase in both the NO and the CO conversion was observed (see Table 4). The increase in CO



**Fig. 13.** NO reduction by CO at 300 °C on Pd500. Effect of water addition on the production of gas phase NH<sub>3</sub>. Feed composition; [NO] = 1650; [CO] = 1590 ppm; SV =  $1.25 \times 10^5 \text{ h}^{-1}$ . Amount of water; 1.5%. X<sub>NO</sub> = 46%. (●) Sample reduced and purged in He at 300 °C. (○) Sample reduced at 300 °C and purged in He at 400 °C (40 min).

conversion was the largest, from 33 to 47%. Consequently, a clear increase in CO<sub>2</sub> production resulted. NH<sub>3</sub> production initially showed a behavior similar to the one observed on Pd500; i.e. a sudden increase and a decrease with a maximum of 470 ppm. Afterwards, NH<sub>3</sub> concentration reached a steady state value much higher than the one obtained under dry conditions. The selectivity to NH<sub>3</sub> increased from 15 to 28%. N<sub>2</sub> production was slightly higher and N<sub>2</sub>O yield was not altered. Due to the increase in NO conversion, the selectivity to N<sub>2</sub> remained constant at 22% and N<sub>2</sub>O selectivity decreased from 63 to 50%.

Consequently, the main effect of water on the NO + CO reaction over Pd350V was a higher conversion of CO and NO and a larger NH<sub>3</sub> production. Once again this behavior could not be attributed to the water–gas shift reaction because the TOR<sub>CO</sub> was low and similar to the one measured on Pd500.

## 4. Discussion

The central questions addressed in this paper are (a) why the presence of vanadia decreases the selectivity to N<sub>2</sub>, (b) what mechanistic picture is valid to explain the formation of nitrogen-containing products other than N<sub>2</sub> and N<sub>2</sub>O in addition to several unreactive surface species during the NO + CO reaction on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

According to the results in Table 1 the presence of a monolayer of VO<sub>x</sub> species on the alumina does not favor the dispersion of Pd. Large Pd crystals are formed on the VO<sub>x</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support and here again there was a good agreement in particle size from chemisorption and TEM measurements. Consequently there is no evidence for vanadia migration onto the palladium surface, such as has been reported for titania supported metals. Very few studies have been carried out on Pd-VO<sub>x</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. One relevant work is that of Macleod and Lambert [27] who prepared a highly dispersed VO<sub>x</sub>(10%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support that was subsequently loaded with 0.5% of palladium. The metal dispersion was 30%, lower than that obtained for the unpromoted Pd(0.5%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (47%).

The FTIR study of CO and NO adsorption on the reduced Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd-VO<sub>x</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts demonstrated that the

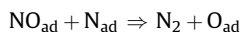


presence of  $\text{VO}_x$  species on the alumina support does not lead to changes in the oxidation state of palladium, as frequency shifts are not observed. The main alteration is a reduction in the amount of CO or NO adsorbed due essentially to a lower fraction of exposed palladium atoms emerging from the preparation procedure. However some morphological differences may exist between Pd particles supported on the alumina support and the vanadia-covered alumina. According to the FTIR spectra of adsorbed CO (Fig. 1) the Pd particles deposited on  $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$  exhibit a strong attenuation of the bands due to CO adsorbed on the Pd (1 0 0) and (1 1 1) planes although they maintain the relative intensity exhibited by the Pd500 catalyst. The band of linear CO is not reduced but it becomes broader indicating the important contribution of Pd atoms with low coordination. This behavior may be explained if small Pd particles remain attached to a fraction of the alumina surface not covered by  $\text{VO}_x$  species and large Pd particles are located on the  $\text{VO}_x$  monolayer.

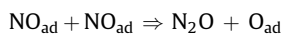
The catalytic activity results presented here demonstrate that the rate of  $\text{N}_2$  production is affected when the palladium particles are supported on vanadia-modified alumina. The reduction of a vanadia monolayer in the presence of Pd was clearly demonstrated by TPR [11,12]. The promoter forms reduced species at relatively low temperature that may play a role in the adsorption and dissociation of NO, a condition that enhances the decomposition of NO. However oxygen retained by  $\text{VO}_x$  species cannot be removed by reaction with CO, and consequently the redox behavior of vanadium oxide is not sustained.

The role of the promoter became more complex observing the activity and selectivity results presented in Figs. 3 and 4 respectively. One common feature for Pd/ $\gamma\text{-Al}_2\text{O}_3$  and Pd- $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$  was the decrease in NO and CO conversion and  $\text{N}_2$  production as a function of time on run. This behavior will be discussed later in connection with the formation and identification of stable adsorbed species on the catalyst's surface. The relative levels of CO and NO conversion and  $\text{N}_2$  production are qualitatively in accordance with the lower of the fraction of exposed Pd atoms on the vanadia-modified alumina (the lower fraction of exposed Pd atoms is partially compensated by the larger metal content). The most interesting result was the similar and quite stable production of  $\text{N}_2\text{O}$  shown in Fig. 4 for the tested catalysts.

At this point it is convenient to recall the mechanisms proposed for the NO + CO reaction and the  $\text{N}_2$  and  $\text{N}_2\text{O}$  formation on metal surfaces. The conventional view is that NO is adsorbed and dissociated on reduced metals, followed by a recombination of adsorbed N atoms to form  $\text{N}_2$ , while the reaction of adsorbed NO with N atoms leads to  $\text{N}_2\text{O}$ . On the other hand, adsorbed O atoms are removed by reaction with CO adsorbed on the metal surface. However, the following alternative reaction step for  $\text{N}_2$  formation has been proposed [28];



Keeping these facts in view, and by using isotopic label experiments, Burch et al. [29] have concluded that  $\text{N}_2$  is derived from a pseudo-adsorbed form of  $\text{N}_2\text{O}$ . On the other hand, they have postulated that  $\text{N}_2\text{O}$  was formed from identical surface species that were identified as  $\text{NO}_{\text{ad}}$ .



Based on this model,  $\text{N}_2\text{O}$  production would mainly depend on the surface characteristics that influence NO adsorption, while  $\text{N}_2$  formation would reflect the effect of the surface sites on NO dissociation. After the reduction pretreatment at 300 °C, metallic Pd predominates on Pd500 (as demonstrated by both the present FTIR and XPS results and the previous  $\text{H}_2$ -TPR experiments [11]). As shown in Figs. 5(a) and 6(a) and in Table 3, this condition is

maintained after reaction, thus favoring NO dissociation and  $\text{N}_2$  formation.

Turning the attention to the Pd350V sample the lower activity of the NO + CO reaction towards  $\text{N}_2$  formation in part reflects the effect of a diminished fraction of exposed Pd atoms compared to Pd500. However this condition does not influence the production of  $\text{N}_2\text{O}$  as it remains surprisingly similar and very stable. After the reduction pretreatment at 300 °C metallic Pd and partially reduced vanadium species coexist on the alumina surface, as was demonstrated by the present FTIR results and previous  $\text{H}_2$ -TPR and  $\text{CH}_4$ -TPR experiments [10,30]. According to our model [30], sintering of partially reduced  $\text{VO}_x$  species diminished the coverage of the support and the effect of the Pd–V interaction. Under reaction conditions the oxygen produced from NO dissociation reverts the effect of the reduction process, the  $\text{VO}_x$  species spread on the support and a Pd–V interaction characterized by an oxidized state of Pd develops. As clearly shown by the FTIR and XPS results in Figs. 5(b) and 6(b) and Table 3 respectively the presence of  $\text{VO}_x$  species on the alumina surface stabilizes a partially oxidized Pd phase. This behavior is certainly induced by the promoter because it is absent on the Pd500 catalyst. If the partially oxidized Pd state in Pd350V reduces the activity for NO dissociation the presence of nitrogen atoms and the subsequent formation of  $\text{N}_2$  will be affected. On the other hand the amount of NO that can adsorb on the oxidized surface is maintained and consequently the reaction leading to  $\text{N}_2\text{O}$  is not altered. The promoter only affects the reaction leading to  $\text{N}_2$ , suggesting that the formation of  $\text{N}_2$  and  $\text{N}_2\text{O}$  occurs by independent reaction pathways. A similar proposition was made by Muraki et al. [31] who studied the NO + CO reaction on a Pd/ $\alpha\text{-Al}_2\text{O}_3$  catalyst.

The oxidation state of Pd has been recently related to the acid-base and electrophilic–electrophobic properties of oxide supports [32,33]. According to Okurama et al. [32] an electron deficient state of Pd, which is oxidized more easily, is created by an acidic support with electrophilic properties. It is known [34] that vanadium markedly reduces the concentration of Lewis acid sites on the alumina support while Brønsted sites are created when a high vanadium content is used. In our Pd350V catalyst the absence of carbonate, nitrite and nitrate bands on the FTIR spectra of CO and NO adsorption (see Figs. 1 and 2) suggests a reduced concentration of Lewis sites. However, new electrophilic sites could be created by the presence of  $\text{VO}_x$  species. These sites, which are responsible for the oxidized state of Pd, are evidenced by the FTIR spectra of coordinated  $\text{NH}_3$  that takes place during the NO + CO reaction. The correspondent band assignment will be discussed later.

It is important to recall that in a previous study [11] we found a beneficial effect of V on the selectivity to  $\text{N}_2$ . However in that work the catalyst was tested at very high conversion, that is at very low NO and CO concentration. Under this condition  $\text{N}_2$  was also produced by  $\text{N}_2\text{O}$  decomposition and the  $\text{N}_2\text{O}$  + CO reaction, leading to a higher  $\text{N}_2$  selectivity.

The FTIR analysis of gas phase products clearly demonstrated the presence of small amounts of HNCO and  $\text{NH}_3$ , in addition to  $\text{N}_2$ ,  $\text{N}_2\text{O}$  and  $\text{CO}_2$ , for all the catalysts tested. The formation of HNCO during the reaction of NO + CO +  $\text{H}_2$  mixtures at 230 °C on Pt/ $\text{SiO}_2$  and Pd/ $\text{SiO}_2$  catalysts is well documented in previous studies [17,35]. This compound is apparently formed by the reaction of –NCO groups located on the metal surface with adsorbed H atoms [35]. It is also known that NO reduction by CO in water presence on Pd/ $\text{SiO}_2$  forms HNCO and  $\text{NH}_3$  [36], but the concentrations are lower. In our case HNCO and  $\text{NH}_3$  were detected in the absence of  $\text{H}_2$  and with a low water content (according to the gas supplier, water in the feed should be below 5 ppm). The spectra of Fig. 7(a) demonstrate the absence of water in the product stream. Only when the gas lines were heated well above 100 °C the presence of water was revealed. As mentioned before, the presence of residual

hydrogen from reduction pretreatments can be excluded due to prolonged helium purging. Therefore the formation of HNCO (g) is attributed to the reaction of –NCO groups located on the Pd particles and/or on the support with –OH groups present on the alumina surface. HNCO is then transported through the gas phase and deposited on the lines connecting the reactor with the gas cell. In fact the formation of HNCO (g) has been invoked to explain the process of isocyanate transport from the metal to the support [37,38]. Surface –OH groups are also responsible for the continuous hydrolysis of HNCO leading to NH<sub>3</sub>. The number of –OH groups on the alumina surface, following the oxidation and reduction pretreatment at 300 °C may be assumed to be  $8 \times 10^{14}/\text{cm}^2$  [39]. In addition the presence of some physically adsorbed water was revealed on the background spectrum of the catalysts surface prior to reaction. The bands due to –OH groups appear at 3730 and 3680 cm<sup>-1</sup> and a weak but broad band due to molecular water was observed at 3560 cm<sup>-1</sup>. When the sample was reduced with deuterium these bands were shifted to 2745, 2710 and 2650 cm<sup>-1</sup>. In this case the FTIR analysis of the reaction products showed the presence of ND<sub>3</sub> (at 745 cm<sup>-1</sup>) and NHD<sub>2</sub> (808 and 817 cm<sup>-1</sup>). The NH<sub>3</sub> band was absent. These results indicate that surface –OH groups and water adsorbed on the alumina surface are responsible for the formation of isocyanic acid and ammonia.

The reactor was loaded with 80 mg of catalysts and a similar amount of alumina in order to obtain the results presented in Fig. 13. Under dry conditions 0.16 mmol of NH<sub>3</sub> were produced in 180 min (assuming an average NH<sub>3</sub> concentration of  $\cong 100$  ppm). Taking into account the BET surface area of the alumina support the total number of –OH groups was equivalent to an NH<sub>3</sub> production of  $\cong 0.05$  mmol. Additional hydrogen, which was provided by physically adsorbed water on the alumina surface and also on cold areas of the gas cell, facilitates the HNCO hydrolysis and increases the NH<sub>3</sub> amount to 0.16 mmol. In order to support this interpretation the NH<sub>3</sub> formation was also measured on a sample pretreated in He at 400 °C after the standard reduction at 300 °C. In this way the amount of surface water available for NH<sub>3</sub> formation could be reduced. The results in Fig. 13 show that the initial NH<sub>3</sub> concentration was lower, around 35 ppm, and decreased steadily to a value of  $\cong 10$  ppm in 180 min. Assuming an average value of 20 ppm the total production of NH<sub>3</sub> was close to 0.032 mmol. Taking into account that the surface concentration of –OH groups on an alumina dehydroxylated at 400 °C is  $\cong 6 \times 10^{14}/\text{cm}^2$  [39], the expected amount of NH<sub>3</sub> is 0.04 mmol. In this case a better hydrogen mass balance was obtained.

In accordance with our interpretation Dämpelmann et al. [17,38] demonstrated that a rapid hydrolysis of HNCO leading to NH<sub>3</sub> occurs on the alumina surface. They showed that HNCO produced on a Pt/SiO<sub>2</sub> catalyst by the H<sub>2</sub> + CO + NO reaction was completely converted to NH<sub>3</sub> and CO<sub>2</sub> on a bed of pure alumina held at 210 °C.

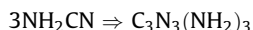
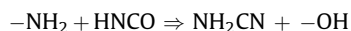
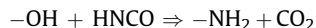
According to the preceding interpretation, the formation of HNCO (g) depends on the presence of isocyanate species on the catalyst surface. It is well known that isocyanate groups form on Rh, Pt and Pd particles by the CO<sub>ad</sub> + N<sub>ad</sub> reaction [40] and it is generally accepted that they are transferred to the support surface. However the presence of isocyanate species on the metal surface remains a controversial subject [41]. On Pd/Al<sub>2</sub>O<sub>3</sub> catalysts an isocyanate band generated by CO–NO interaction found at 2254 cm<sup>-1</sup> by Keiski et al. [19] was assigned to Pd–NCO. On the other hand, a band located at 2241 cm<sup>-1</sup> observed by Almusaiter and Chuang [20] on a similar catalyst has been assigned to Al–NCO. In a previous work we observed two close bands located at 2249 and 2233 cm<sup>-1</sup> that were tentatively assigned to isocyanate species on different alumina sites [13]. Similar isocyanate bands were obtained by Bamwenda et al. [42] using a Pd(1%)/Al<sub>2</sub>O<sub>3</sub> for the selective reduction of NO with C<sub>3</sub>H<sub>6</sub> in the presence of oxygen.

Recently the formation of an isocyanate band on Pd (1 1 1), in the presence of a CO + NO mixture (CO/NO = 1.5), has been demonstrated. Using infrared reflection absorption spectroscopy Hess et al. [43] found a strong and stable isocyanate band located at 2240–2250 cm<sup>-1</sup>. Consequently stable isocyanate species may exist on both the Pd and the alumina surface. In our study the isocyanate band develops slowly reaching a steady state value in about 100 min as shown in Fig. 8, following closely the decline in NO and CO conversion and N<sub>2</sub> production observed in Figs. 3 and 4. The main band appears at  $\cong 2260$  cm<sup>-1</sup> on all catalysts with a shoulder at a lower frequency. On the Pd350V sample this feature seems to indicate the effect of the promoter on the adsorption of –NCO groups on the alumina surface. In addition Fig. 9 shows that the band at 2260 cm<sup>-1</sup> is more intense on the Pd500, reflecting higher isocyanate coverage on the unpromoted alumina surface and/or the effect of a higher Pd dispersion. However, both the similar deactivation behavior of all catalysts and the strong correlation with growth of the isocyanate bands indicate that accumulation of –NCO groups also affects the catalytic activity of the metal. The transport of isocyanate from the Pd surface to the support is rapid at short reaction times due to higher availability of potential adsorption sites on the alumina surface, but it will slow down as –OH groups are consumed. Consequently the concentration of isocyanate on the metal will build up until steady state equilibrium between –NCO groups on the Pd particles and the alumina support arises. According to this interpretation, and mainly based on the results of Hess et al. [43] for Pd (1 1 1), we are inclined to believe that in our catalysts isocyanate species are bound to the metal and the support surface. Therefore they play an important role in catalyst deactivation.

As shown in Fig. 8 the growth of the isocyanate bands with time is accompanied by the appearance of several bands in the low frequency region. The broad band at 1270–1275 cm<sup>-1</sup> formed on Pd350V under reaction conditions (see Fig. 11), is assigned to the symmetric deformation vibration of NH<sub>3</sub> coordinated to V<sup>5+</sup>. According to Davydov and Budneva [44] NH<sub>3</sub> adsorption on oxidized V<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> produces a band at 1270 and 1250 cm<sup>-1</sup> respectively. In our case the main surface species on the alumina support are vanadium dimers [11,45]. On the fresh reduced Pd350V sample the addition of NH<sub>3</sub> at 300 °C results in the appearance of a band at a lower frequency ( $\cong 1260$  cm<sup>-1</sup>) suggesting the presence of vanadium in a lower oxidation state (V<sup>4+</sup>). A band at 1420–1450 cm<sup>-1</sup> due to NH<sub>4</sub><sup>+</sup> adsorption on Bronsted acid sites was not observed. In Fig. 11 the band at 1270 cm<sup>-1</sup> shifts to a higher frequency as the surface concentration decreases, indicating the adsorption on sites of different strengths.

Regarding the more symmetric bands in the 1400–1650 cm<sup>-1</sup> region, it has been verified that they are not due to the direct interaction of CO and NO with the alumina support, that is to the formation of carbonate, nitrate or nitrite species, or to the exposure of the catalysts to N<sub>2</sub>O or CO<sub>2</sub>. It has already been demonstrated by Unlund [46] many years ago that bands located in the 1400–1650 cm<sup>-1</sup> region on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst are due to species containing C and N atoms. Hauck et al. [22] assigned bands at 1648, 1563 and 1497 cm<sup>-1</sup> to the adsorption of the [N=C=O]<sup>-</sup> anion during the hydrolysis of isocyanic acid in the presence of NO at 150 °C on TiO<sub>2</sub>. Adsorbed NH<sub>3</sub> was found to be another reaction product. In our study the direct adsorption of HNCO on the alumina support is unlikely due to the higher reaction temperature that facilitates the formation of NH<sub>3</sub>. Quite recently Piazzesi et al. [23] observed several IR bands at approximately 1619, 1544 and 1480 cm<sup>-1</sup> upon adsorption of HNCO on TiO<sub>2</sub> at 150 °C. The authors suggested that they may be due to formation of cyanuric acid, s-triazine or melamine on the support surface. It is known that melamine could be obtained directly from HNCO using an

oxide catalyst at  $\geq 300^\circ\text{C}$  [47]. In addition, a recent study [48] demonstrated that HNCO and  $\text{NH}_3$ , which are the products of urea decomposition on an oxide catalyst, form a melamine complex that accumulates on the surface. In our case the reaction may proceed according to the following sequence:



Consequently melamine, cyanamide ( $\text{NH}_2\text{CN}$ ) and  $-\text{NH}_2$  groups formed on the catalyst surface may be responsible for some of the bands observed in the  $1400\text{--}1650\text{ cm}^{-1}$  region. The bands located at  $1630$  and  $1642\text{ cm}^{-1}$  on Pd500 and Pd350V (see Fig. 9) may be tentatively assigned to the deformation mode of  $-\text{NH}_2$  groups while the band at  $1562\text{--}1564\text{ cm}^{-1}$  is likely due to the NCN bending and ring deformation mode of the melamine molecule [49]. Another potential reaction product is ammonium isocyanate ( $(\text{NH}_4)^+\text{NCO}^-$ ), formed by reaction of HNCO with  $\text{NH}_3$ . Therefore the band located at  $1470\text{ cm}^{-1}$  on Pd500 (weaker on Pd350V) may be attributed to the asymmetric bending vibration of the ammonium ion. The position of the bands due to  $\text{NH}_3$ ,  $-\text{NH}_2$  and  $\text{NH}_4^+$  should be modified by deuteration, as observed in Fig. 10, and this behavior supports the proposed assignments. To our knowledge this study provides the first attempt to identify the species responsible for the IR bands observed in the  $1400\text{--}1600\text{ cm}^{-1}$  region.

The reaction products mentioned above and the corresponding band assignments are tentative and must be confirmed by more detailed studies. However it is evident from the present results that the NO + CO reaction on Pd/ $\gamma\text{-Al}_2\text{O}_3$  catalysts at low temperatures is very complex due to the participation of secondary reactions leading to several gaseous and stable adsorbed products in addition to  $\text{N}_2$ ,  $\text{N}_2\text{O}$  and  $\text{CO}_2$ .

The adsorbed species identified in this study are not relevant for the production of the main nitrogen-containing products of the NO + CO reaction:  $\text{N}_2\text{O}$  and  $\text{N}_2$ . However the accumulation of surface deposits lead to catalyst deactivation. In addition the surface isocyanates are responsible for the formation of isocyanic acid and ammonia, which are undesirable gas contaminants.

It has been demonstrated that the water addition to a dry NO + CO feed rapidly eliminates the surface deposits leading to a brief high production of  $\text{NH}_3$  on both Pd/ $\gamma\text{-Al}_2\text{O}_3$  and Pd- $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ . This behavior suggests that water reacts with  $-\text{NCO}$  and HNCO, forming  $\text{NH}_3$  and  $\text{CO}_2$ . The low activity of Pd/ $\gamma\text{-Al}_2\text{O}_3$  and Pd- $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$  for the water–gas shift reaction predicts a minor influence on the production of  $\text{H}_2$ , and then on the one of  $\text{NH}_3$ .

Under steady state conditions the presence of water at a high concentration relative to that of NO and CO does not inhibit the rate of NCO formation, but it accelerates the hydrolysis process by enhancing  $\text{NH}_3$  emission.

Despite the enhanced production of  $\text{NH}_3$ , there is a beneficial effect of water addition on the catalytic activity of Pd/ $\gamma\text{-Al}_2\text{O}_3$ . The selectivity to  $\text{N}_2\text{O}$  decreased from 48 to 29%, while maintaining the level of NO conversion. Oxygen removal is facilitated by the higher CO conversion. In addition, a higher selectivity to  $\text{N}_2$  was observed.

It is important to realize that the rapid elimination of surface deposits upon water injection did not recover the high initial activity of fresh catalyst. It was necessary to suppress water injection in order to observe an increase in NO conversion and  $\text{N}_2$  production.

Despite the increase in  $\text{NH}_3$  concentration in water presence,  $\text{N}_2$  remains as the main product on Pd/ $\gamma\text{-Al}_2\text{O}_3$ . This behavior is different from the performance observed on Pt catalysts. Cant et al. [36] showed that a Pt/ $\text{Al}_2\text{O}_3$  catalyst at  $\approx 280^\circ\text{C}$  gave a yield of  $\text{NH}_3$  of  $\approx 75\%$  ( $X_{\text{NO}} = 100\%$ ) in the presence of  $\approx 2800$  ppm of water.

Therefore, the production of  $\text{N}_2$  and  $\text{N}_2\text{O}$  was low, being the latter the main product. Based on this comparison, Pd/ $\gamma\text{-Al}_2\text{O}_3$  is the preferred catalyst metal for the NO + CO reaction in both the presence and the absence of water.

The present results demonstrate that the activity of the Pd- $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$  catalyst improved in water presence. An increase in NO and CO conversion is observed due probably to the elimination of surface deposits. In fact, the levels of conversion became comparable to those of Pd/ $\gamma\text{-Al}_2\text{O}_3$ . However, the selectivity to  $\text{N}_2$  was not modified, the one of  $\text{N}_2\text{O}$  decreased slightly and the selectivity to  $\text{NH}_3$  increased. Consequently, the Pd/ $\gamma\text{-Al}_2\text{O}_3$  catalyst exhibits a better selectivity to  $\text{N}_2$  for the NO + CO reaction in water presence.

## 5. Conclusions

This paper focuses the attention on the influence of  $\text{VO}_x$  species on the activity and selectivity of  $\gamma\text{-Al}_2\text{O}_3$  supported Pd in the NO + CO reaction at  $300^\circ\text{C}$ . The characterization work suggests that the promoter is not deposited on the metal surface.  $\text{VO}_x$  species dispersed on the alumina support have a negative effect on  $\text{N}_2$  formation due to a Pd–V interaction that stabilizes Pd in an oxidized form affecting the dissociation of NO. On the other hand the formation of  $\text{N}_2\text{O}$  seems to occur by a mechanism dependent mainly on the reaction of adsorbed NO. The formation of  $\text{N}_2\text{O}$  is not altered by vanadium. Consequently the selectivity to  $\text{N}_2$  at similar reaction conditions is about 50% for Pd/ $\gamma\text{-Al}_2\text{O}_3$  and 35%, for Pd- $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ . FTIR analysis of the gas phase products demonstrated that the both catalysts produce small amounts of HNCO and  $\text{NH}_3$  under dry conditions. The former product arises from the reaction of  $-\text{NCO}$  species with  $-\text{OH}$  groups while ammonia is generated by hydrolysis of HNCO. The adsorption of coordinated  $\text{NH}_3$  to  $\text{V}^{5+}$  under reaction conditions has been observed on the Pd- $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$  catalyst. Isocyanate species are formed on both catalysts on the metal and the support surface. In addition stable compounds resulting from the subsequent reaction of HNCO, like  $\text{C}_3\text{H}_3(\text{NH}_2)_3$ , slowly build up on the catalyst surface and gave IR bands in the  $1400\text{--}1650\text{ cm}^{-1}$  region. The formation of these adsorbed species explains the observed decrease in NO and CO conversion and  $\text{N}_2$  production with time. It was found that the reactivity of the surface species toward NO is low and the main reaction products are  $\text{N}_2$  and  $\text{CO}_2$ . Consequently they do not provide an alternative route for the formation of  $\text{N}_2\text{O}$  during the NO + CO reaction. In the presence of water surface isocyanates and derived species are not observed because they are hydrolyzed to form a higher amount of  $\text{NH}_3$ . On Pd/ $\gamma\text{-Al}_2\text{O}_3$  the main beneficial effect of water is a lower selectivity to  $\text{N}_2\text{O}$  formation and a higher selectivity to  $\text{N}_2$  and  $\text{NH}_3$ . On Pd- $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$  water clearly increases the conversion of NO and CO and the selectivity to  $\text{NH}_3$ . The selectivity to  $\text{N}_2$  is not modified and that of  $\text{N}_2\text{O}$  decreases slightly.

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