Characterization of Pd-mordenite Catalysts for NO Decomposition

Andréa Marins de Oliveira · Ignacio Costilla ·
Carlos Gigola · Ione Maluf Baibich ·
Victor Teixeira da Silva · Sibele B. Castellã Pergher

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Abstract The aim of this study was to characterize Pd catalysts supported on three different mordenite zeolites (a commercial sample and two laboratory preparations) previously tested for the NO decomposition reaction. H₂ chemisorption, TPR, FTIR spectroscopy of adsorbed CO and NO, DRS UV–vis and TPD of NO were used to characterize the catalysts. After reduction at 573 K a large fraction of Pd⁰ particles and some Pd²⁺ ions were found in the commercial sample and one laboratory preparation. In contrast a sample prepared with a mordenite synthesized using a natural clay was found to exhibit mainly ionic Pd. The amount of Pd⁰ (PdO) relative to Pd²⁺ depends on the oxidation temperature and the metal loading. The catalysts exhibited similar levels of activity for the NO decomposition reaction at 673 K but a different selectivity to N₂O. This behavior was related to differences in metal dispersion and other surface conditions that influence the formation of PdO particles.

Keywords Pd · Mordenite · CO and NO adsorption · TPR · TPD of NO

1 Introduction

The use of transition metals supported on zeolite for the decomposition of NO is the most suitable solution for nitrogen oxide reduction in pollution emission control because this process does not require the addition of reagents such as hydrocarbons, ammonia, CO or hydrogen [1–4]. The zeolite system CuZSM-5 has been intensively studied due to its high NO decomposition activity [5].

The activities of zeolite catalysts containing transition metals are related to the type of metal and the properties of the zeolite, including pore dimensions and active site accessibility [6]. Palladium supported on zeolites leads to the formation of catalysts with high NO_x reduction activity. The importance of zeolite acid sites in stabilizing molecularly dispersed PdO (or Pd²⁺) species is well known, and they can be the active center for the reaction. However, the structures of Pd active species during the reaction and the interactions of Pd species with molecules present in the reaction media still remain ambiguous [7].

In a previous study with Pd/zeolite catalysts, the NO decomposition reaction using mordenite prepared in two different forms was evaluated and compared with a catalyst supported on commercial mordenite [8]. Although the samples exhibited similar levels of activity the selectivity was different. The samples prepared with mordenite synthesized from clay led to lower N₂O formation than mordenite synthesized from standard reagents. The selectivity to N₂O was lower when the commercial support was used. Therefore, the present study was aimed to characterize the Pd species present in these catalysts that are

A. M. de Oliveira · I. M. Baibich
Instituto de Química, Universidade Federal do Rio Grande do Sul, CP 15003, Porto Alegre, RS 91501-970, Brazil

I. Costilla · C. Gigola
PLAPIQUI, km 7 Camino “La Carrindanga”, C.C. 717-8000
Bahia Blanca, Argentina

V. T. da Silva
Programa de Engenharia Química/NUCAT/COPPE—UFRJ-Ilha do Fundão—Centro de Tecnologia, Sala G-116, Rio de Janeiro, RJ, Brazil

S. B. Castellã Pergher (✉)
Departamento de Química, Universidade Regional Integrada do Alto Uruguai e das Missões—campus Erechim, Av. Sete de Setembro, 1621, Erechim, RS 99700-000, Brazil
e-mail: pergher@uricer.edu.br

responsible for the observed activity and selectivity. Different techniques, such as hydrogen chemisorption, temperature-programmed reduction, infrared spectroscopy of CO and NO molecules adsorbed onto the catalysts, diffused reflectance spectroscopy in the UV–Vis region and temperature-programmed desorption of NO were used.

2 Experimental

2.1 Catalyst Preparation

The mordenite zeolite support used in this study was synthesized by the Environmental Chemistry Laboratory (LAQAM) of URI—Campus de Erechim, along with a commercial mordenite (CBV 10A) provided by ITQ-Valence—Spain, MOR-COM. The synthesized mordenite was prepared by standard IZA methods [9] using two distinct procedures: (a) using sodium aluminate as the source of aluminum and Aerosil silica (Degussa) as the source of silicon (MOR-IZA) and (b) using a natural clay (MINA) as an alternative Al and Si source [8] (MOR-ARG).

The supports were pretreated at 673 K for 5 h with a heating rate of 5 K min^{−1}. Intermediate 1 h steps at 423 and 573 K were used before the final desired temperature was reached. Palladium was incorporated into the supports through ionic exchange with a 0.8 mmol L^{−1} solution of Pd(NO₃)₂ with a solid/solution concentration of 30 g L^{−1} at 323 K for 36 h. The material was filtered, washed with deionized water, dried at 373 K for 24 h and calcinated at 673 K under a synthetic air flow for 5 h. This method was adapted from Aylor et al. [10].

2.2 Catalysts Characterization

The chemical composition of the solids was determined by optical emission spectrometry with an inductively coupled plasma (ICP-OES) source. The equipment was manufactured by Perkin-Elmer (model Optima 2000 DV) and used for the analysis of Na, Pd and Al. The samples were dissolved in a solution of HCl:HNO₃ (6:2) at 383 K. Experiments involving the temperature-programmed desorption of NO (TPD) were performed in a quadrupole mass spectrometer (Balzers-Prisma) coupled with an analytical Quadstar system. The samples were pretreated at 573 K for 3 h with hydrogen, purged with helium for 30 min and cooled to room temperature. The adsorption was carried out with a flow rate of 50 mL min^{−1} with 500 ppm of NO in helium until the signal on the detector stabilized. After stabilization, the catalyst sample was heated at 20 K min^{−1} to 773 K in helium flow (50 mL min^{−1}), holding the final temperature for 1 h.

For FTIR characterization, catalyst samples of approximately 40 mg were pressed to form transparent disks 13 mm in diameter that were mounted in the beam path of an IR cell sealed with CaF₂ windows. The samples were calcinated in air at 573 K and then reduced with hydrogen at the same temperature. Subsequently, the samples were cooled to room temperature under vacuum and dosed with 5 Torr of either CO or NO. After a few minutes, the IR spectra were obtained. The cell was evacuated and a new spectrum was obtained to observe the stability of the bands. After the adsorption of CO, the oxidation and reduction treatments were repeated prior to the adsorption of NO. An FTIR spectrum taken under vacuum conditions was used as the background. Infrared spectra were recorded using a NICOLET 20 DXB instrument with a 4 cm^{−1} resolution.

The fraction of exposed palladium atoms (H/Pd) was obtained from H₂ chemisorption measurements. The experiments were performed in a volumetric apparatus in the 10–100 torr pressure range. Samples of 250 mg were previously reduced at 573 K in flowing H₂ and evacuated overnight at the same temperature. The double isotherm method was used to determine the amount of irreversibly chemisorbed hydrogen, (H/Pd)_{irr}, at room temperature. The first isotherm measured the amount of absorbed and chemisorbed hydrogen. Subsequently the amount of absorbed hydrogen and that weakly chemisorbed was measured after evacuation at room temperature for 30 min. The amount of irreversible chemisorbed hydrogen was determined by subtracting the second isotherm from the first.

Diffuse Reflectance Spectroscopy analysis in the UV–vis region (DRS UV–vis) was carried out with a Cary 500 Spectrophotometer using BaSO₄ as a reference. The references for these experiments were the catalyst supports. The samples were previously calcinated in air at 673 K.

Temperature programmed reduction measurements were performed in a conventional equipment using a H₂ (5%)/Ar mixture with a flow rate of 30 mL/min^{−1} up to 773 K. Samples were previously treated at 573 or 673 K in air, purged in Ar and cooled to 243 K.

3 Results and Discussion

The results obtained for the chemical compositions of the samples are summarized in Table 1. The different zeolites have a BET area in the range 315–360 m²/g, a similar Na content but different SiO₂/Al₂O₃ ratios. The PdMOR-COM and PdMOR-IZA catalysts showed metal contents of approximately 0.7–0.8% by weight. The metal loading on PdMOR-ARG was lower.

Table 1 Main catalysts properties

Sample	Pd (wt%)	Al (wt%)	Pd/Al	SiO ₂ /Al ₂ O ₃	Na (wt%)	(H/Pd) _{irr} * (%)
PdMOR-COM	0.77	4.14	0.05	12	2.85	15.0 (0.47)
PdMOR-IZA	0.72	2.70	0.07	18	3.31	9.5 (0.55)
PdMOR-ARG	0.42	2.44	0.04	20	3.29	6 (0.44)

* (H/Pd)_{abs} values in parenthesis

As described above the catalysts samples used in the present study were calcined in air at 673 K after the addition of Pd. For the hydrogen chemisorption measurements they were reduced in flowing H₂ at 573 K. The results presented in Table 1 indicate a low uptake of H₂ for all samples, which suggests the presence of large Pd particles.

The sample with the higher metal dispersion after reduction at 573 K was PdMOR-COM. The H/Pd ratio of 0.15 corresponds to a particle size of 7.5 nm ($d(\text{nm}) = 1.12/(\text{H/Pd})$). In this case the average Pd particle size was also checked by TEM and was found to be 5 nm in close agreement with the chemisorption measurement. The behavior of the PdMOR-IZA sample was similar but the metal dispersion was lower; 9.5%. For the PdMOR-ARG sample the low H/Pd ratio, 6%, was surprising taking into account the lower metal loading.

Suspecting an effect of the pretreatment conditions on the Pd dispersion the chemisorption measurement for the PdMOR-ARG sample was repeated after calcination in air at 523 and 673 K followed by reduction at 573 and 673 K. No change in dispersion was observed.

Using the back-sorption isotherms and taking into account the (H/Pd)_{irr} values the amount of absorbed H₂ forming the β -hydride was estimated. As observed in Table 1 the (H/Pd)_{abs} values at 40 Torr and 297–298 K were in the 0.44–0.55 range which are close to that reported for bulk Pd (0.65) [11]. Consequently Pd particles are formed on all samples after H₂ reduction at 573 K.

In order to obtain information on the oxidation–reduction behavior of the catalysts samples comparative TPR experiments were carried out. Before the experimental results emerging from the TPR study are presented it is important to recall that the chemical state and the particle size of the Pd phase on Pd/zeolite catalysts depends strongly on the pretreatment conditions; the atmosphere and the temperature. It has been shown by Homeyer and Sachtler [12] that oxidation of Pd/NaY catalysts above 573 K lead to the formation of PdO that reacts with surface protons leading to well dispersed Pd²⁺ species. The reduction of these species was characterized by a TPR profile where the H₂ consumption peak appeared at 450 K.

On the other hand they found that an oxidizing pretreatment below 573 K leads to the formation of PdO. In this case the reduction process takes place at lower temperature forming Pd metal particles.

The reduction profiles for the PdMOR-COM and PdMOR-ARG samples oxidized at 673 K are presented in Fig. 1a–b. The broad peak at low temperature (≈ 250 –260 K) is due to Ar desorption from the zeolite support. The reduction of Pd took place at ≈ 304 K, and the presence of a hydride decomposition negative peak was clearly observed at 347 K. Both the H₂ consumption and the hydride decomposition peaks were larger on PdMOR-COM in view of the higher Pd loading. The amount of H₂

Fig. 1 TPR of PdMOR-COM (a) and PdMOR-ARG (b) catalysts after calcination at 823 K

consumed during the reduction process on PdMOR-COM and PdMOR-ARG corresponds to the reduction of 90–95% of the Pd present.

When the oxidation pretreatment was performed at 573 K the reduction occurred at ≈ 273 K and the hydrogen consumption peak overlapped with that of Ar desorption. In this case the amount of H_2 consumed was equivalent to reduction of $\approx 80\%$ of the metal. This result indicates that the formation of PdO or Pd^{2+} is not complete at 573 K.

The effect of the oxidation temperature on the subsequent reduction process is similar to that observed by Homeyer and Sachtler [12] mentioned above. Oxidation at >573 K generates mainly Pd^{2+} species that are reduced at 304 K. On the other hand when the oxidation pretreatment is carried out at ≤ 573 K PdO particles are formed and the reduction temperature is shifted to a lower temperature.

Figure 2 presents the CO adsorption spectra of the reduced PdMOR catalysts. The spectra showed that bands corresponding to CO adsorbed on the metallic palladium in the linear (at approximately 2100 cm^{-1}) and bridge forms (below 2000 cm^{-1}) are well defined in the PdMOR-COM and PdMOR-IZA catalysts. These results confirm that Pd could be obtained in a reduced form after the hydrogen treatment at 573 K. In the PdMOR-COM catalyst, the band corresponding to the bridge form of adsorbed CO is asymmetric and appears at a lower frequency, thereby indicating a stronger adsorption in several crystal planes [13]. According to the IR spectrum in Fig. 2c, the intensity of the band due to linear CO is lower than that due to multiple coordinated species which is in accordance with the small metal dispersion of PdMOR-IZA as compared to PdMOR-COM.

The spectrum of the PdMOR-ARG catalyst is quite distinct. In Fig. 2b the noise level is high due to the relatively low transmittance of this sample (observed in the background spectrum) and the low Pd content. The bands due to adsorbed CO are weak and wide, and those corresponding to CO adsorbed in the linear form appear in a broad frequency range suggesting the simultaneous presence of Pd^0 , Pd^+ or Pd^{2+} species after reduction. Due to the quality of the spectrum specific band assignments cannot be given. The linear bands disappear completely under vacuum, which suggests a weak interaction.

The spectrum of CO adsorption at room temperature on PdMOR-COM was also obtained after oxidation at 673 K. In this case a sharp and intense band was observed at 2147 cm^{-1} which is assigned to CO located on Pd^{2+} . A similar band was detected when CO adsorption at room temperature was performed on a sample used for NO decomposition at 673 K, indicating the redispersion of Pd into Pd^{2+} ions.

The results of the FTIR study of NO adsorption are shown in Fig. 3. The PdMOR-COM and PdMOR-IZA

Fig. 2 Infrared Spectra of Adsorbed CO after reduction at 573 K. **a** PdMOR-COM, **(b)** PdMOR-ARG and **(c)** PdMOR-IZA catalysts

catalysts reveal a band at 1744 cm^{-1} corresponding to linear NO adsorbed onto Pd^0 . The intensity of this band is greater for the catalyst prepared with the commercial mordenite (MOR-COM) followed by MOR-IZA. This is in accordance with the CO adsorption and hydrogen chemisorption measurements that demonstrated the higher metal dispersion of PdMOR-COM. All samples showed a band at 1876 cm^{-1} that has been previously observed on Pd/H-MOR and Pd/H-ZSM5 catalysts calcined in oxygen [14, 15] that is assigned to NO molecules adsorbed onto oxidized Pd (Pd^{2+}). Consequently in our samples a fraction of Pd remains in an oxidized form after the hydrogen treatment.

On the PdMOR-ARG sample (Fig. 3b) the bands are weak and the spectrum is more complex. The NO-Pd^0 band appears at a slightly higher frequency, 1754 cm^{-1} and it has an intensity comparable to that of Pd^{2+}NO located at

Fig. 3 Infrared Spectra of Adsorbed NO after reduction at 573 K. **a** PdMOR-COM, **(b)** PdMOR-ARG catalyst and **(c)** PdMOR-IZA catalysts

1875 cm^{-1} . Consequently the fraction of oxidized Pd is higher on PdMOR-ARG as compared to PdMOR-COM or PdMOR-IZA. In addition a strong band appears at 1819 cm^{-1} that is absent in the other samples. This band can be attributed to Pd^+ species, thereby reinforcing the premise that this catalyst in the reduced state contains Pd in oxidizing form. Studies conducted by Aylor et al. [10] on PdZSM-5 attributed the appearance of a band at 1815 cm^{-1} to cationic Pd species.

The spectra in Fig. 3 shows that adsorption of NO on the reduced samples forms a band at 2260 cm^{-1} that diminishes and almost completely disappears when exposed to vacuum. A band at $\approx 2230\text{ cm}^{-1}$ has been observed on previous studies carried out on H-MOR and PdH-MOR after an oxidizing pretreatments [14] and it has been tentatively assigned to NO_2 adsorption on the zeolite.

The spectra of Figs. 2 and 3 also show a very intense band between 2358 and 2360 cm^{-1} after exposure to 5 Torr of CO or NO. The frequency is very similar to that of CO_2 gas, although it belongs to an adsorbed molecule. A similar band was obtained upon exposing a reduced sample to CO_2 . It is observed that the intensity of the band was higher than that of CO and NO indicating that corresponds to a molecule located on the support surface. In all of the studied catalysts, the band was slowly eliminated under vacuum. The formation of CO_2 during CO adsorption may arise from the reaction of CO with oxidized Pd species. CO disproportionation is unlikely to occur at room temperature. More intriguing is the appearing of CO_2 upon NO adsorption. One possibility is the formation of CO_2 by reaction of surface carbonates with NO or NO_2 . Supporting this explanation we found that calcinations of the samples in air at 673 K prior to reduction practically eliminates the CO_2 band at 2360 cm^{-1} .

The DRS UV-vis spectra of the mordenite-supported Pd catalysts are shown in Fig. 4. Characterization of the samples by DRS UV-vis after calcination in air provides information on a surface condition that resemble the state of the catalysts after the NO decomposition reaction at 673 K . A previous UV-Vis study of PdMOR catalysts was performed by Shimizu et al. [7] on samples calcined at 823 K . Based on this work the band around 200 nm , observed in all three catalysts, has been assigned to charge transfer between oxygen of the support and Pd^{+2} (LMCT). The bands extending from around 300 nm to 450 nm , are due to d-d transitions of Pd^{2+} ions affected by different oxygen environments and/or the presence of water (PdO ; $\text{Pd}(\text{H}_2\text{O})_4^{2+}$; $\text{Pd}(\text{O}_z)_n^{2+}$). On samples calcined at high temperature (well dehydrated) the d-d band has been observed at $460\text{--}480\text{ nm}$ [7]. In our case the lower calcination

Fig. 4 Diffuse Reflectance Spectra in the visible region of PdMOR-IZA **(a)**, PdMOR-COM **(b)** and PdMOR-ARG **(c)** catalysts after calcinations in air at 673 K

Table 2 TPD of NO and catalytic results

Catalysts	NO ($\mu\text{mol g}^{-1}$ cat)	N ₂ ($\mu\text{mol g}^{-1}$ cat)	N ₂ O ($\mu\text{mol g}^{-1}$ cat)	N ₂ O* (ppm) [8]
PdMOR-COM	6.74	9.02	57.2	4
PdMOR-IZA	5.02	3.95	37.15	18
PdMOR-ARG	2.42	3.85	29.66	8

* N₂O formed after 200 min of reaction at low conversion (below 20%). $T = 673$ K

temperature (673 K) and the exposure of the samples to room air lead to a UV–vis spectrum showing that different oxidized forms of Pd are present in the PdMOR catalysts. For example a band at 300 nm is well defined on PdMOR-IZA, also present but less intense on PdMOR-ARG and nearly absent on PdMOR-COM.

Analyses of TPD of NO (Table 2) showed that there is a concomitant reaction during the thermal desorption that, with heating, produces N₂ and N₂O. A nitrogen mass balance shows that the amount of nitrogen containing products desorbing is higher for PdMOR-COM followed by PdMOR-IZA. Taking into account that these catalysts have almost the same metallic content, the behavior is attributed to the difference in metal dispersion. On the other hand the lower amount of NO, N₂ and N₂O desorbing from PdMOR-ARG mainly reflects the effect of the low metal loading. The selectivity to N₂O ($\text{N}_2\text{O}/(\text{N}_2\text{O} + \text{N}_2)$) follows the order PdMOR-IZA (0.90) > PdMOR-ARG (0.88) > PdMOR-COM (0.86) in accordance with the results of the NO decomposition reaction [see Table 2]. It has been demonstrated by Xu and Goodman [16] that the formation of N₂O depends strongly on the Pd particle size; large particles favor the production of N₂O. Based on the chemisorption and FTIR results Pd particles are present on PdMOR-COM and PdMOR-IZA after reduction at 673 K and they are responsible for the high initial catalytic activity for NO decomposition [8]. The only observable difference between these samples is the metal dispersion. NO dissociation produces nitrogen and oxygen atoms. Oxygen, that remains on the metal surface, inhibits the adsorption of NO and lead to oxidation of the metal (PdO), causing deactivation and N₂O formation. This behavior is similar to that found on Al₂O₃ supported Pd [17]. On Pd/zeolites if the reaction is carried out at >573 K the acidic support allows the redispersion of PdO leading to Pd²⁺ formation. The amounts of PdO and Pd²⁺ produced will depend on the reaction temperature and the metal loading. The support material may also play a role. On PdMOR-IZA the low metal dispersion relative to that of PdMOR-COM and the formation of different oxidized species in the presence of oxygen as revealed by the DRS UV–vis study may lead to a larger fraction of PdO particles where the formation of N₂O is favored. Again this interpretation one may argue that the production of N₂O on PdMOR-ARG is lower with a metal dispersion of 6%. However the FTIR spectra of adsorbed NO has demonstrated that a large fraction of Pd remains in an oxidized

form after the hydrogen treatment at 573 K. If this fraction is unable to chemisorb hydrogen. The actual Pd dispersion is higher than 6%.

Despite the mentioned differences in selectivity, the three PdMOR catalysts exhibit a comparable activity for NO decomposition [8]. They showed a conversion of 100% for a running time of about 100 min followed by a steady deactivation. In view of the similar metal loading this behavior is understandable for the PdMOR-COM and PdMOR-IZA samples. On the other hand the high catalytic activity of PdMOR-ARG with a much lower loading is surprising. The FTIR results indicate that Pd²⁺ ions are still present in this sample after reduction at 573 K. Moreover under reaction conditions the low metal loading (0.42%) facilitates the process of oxidative redispersion increasing the concentration of Pd²⁺ sites that became active for NO adsorption under reaction conditions [7]. We suspect that these Pd²⁺–NO entities enhance the dissociation of NO. However the extent of oxidative redispersion under reaction conditions will be limited by the availability of surface protons created during the hydrogen treatment. Consequently the formation of stable PdO particles eventually leads to catalyst deactivation.

4 Conclusion

The characterization of PdMOR catalysts under reducing and oxidizing conditions has been performed in order to explain the activity and selectivity for the NO decomposition reaction. A sample prepared with commercial mordenite (PdMOR-COM) and two preparations (PdMOR-IZA; PdMOR-ARG) obtained by a standard IZA method using different sources of Si and Al were compared. After reduction at 573 K Pd⁰ particles are formed on PdMOR-COM and PdMOR-IZA the metal dispersion being higher for the former sample. The FTIR results demonstrate that a fraction of Pd in an oxidized form (Pd²⁺; Pd⁺) remains in all samples after reduction and this situation predominate on PdMOR-ARG mainly due to the lower Pd content. These Pd species are formed by oxidative redispersion during air calcination at >573 K. The TPR results demonstrate that the reduction of ionic Pd is more difficult than that of PdO. The TPD of adsorbed NO have shown that the amount of desorbing products depends mainly on the fraction of exposed Pd atoms and the selectivity to N₂O is

in reasonable agreement with the results obtained for the NO decomposition reaction at 673 K. The lower metal dispersion of the reduced PdMOR-IZA sample and the distinct oxygen environment of the zeolite support revealed by the DRS UV–vis study may favor the formation of PdO and the production of N₂O. The lower metal loading of PdMOR-ARG and the higher concentration of oxidized species lead to a catalyst with an activity and selectivity comparable to that of PdMOR-COM.

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References

1. Mosqueda-Jiménez BI, Jentys A, Seshan K, Lercher JA (2003) *Appl Catal B* 43:105
2. Cordatos H, Gorte RJ (1996) *J Catal* 159:112
3. Ramachandran B, Herman RG, Choi S, Stenger HG, Lyman CE, Sayle JS (2000) *Catal Today* 55:281
4. Pieterse JAZ, Booneveld S (2007) *Appl Catal B* 73:327
5. Iwamoto M, Yahiro H, Mine Y, Kagawa S (1989) *Chem Lett* 18:213
6. Chen H-Y, Wang X, Sachtler WHM (2000) *Appl Catal A* 194–195:159
7. Shimizu K-C, Okada F, Nakamura Y, Satsuma A, Hattori T (2000) *J Catal* 195:151
8. de Oliveira AM, Baibich IM, Machado NRCF, Mignoni ML, Pergher SBC (2008) *Catal Today* 133–135:560
9. International Zeolite Association. <http://www.iza-online.org>
10. Aylor AW, Lobree LJ, Reimer JA, Bell AT (1997) *J Catal* 172:453
11. Frazier GA, Glosser R (1980) *J Less Common Met* 74:89
12. Homeyer T, Sachtler WMH (1989) *Appl Catal* 54:189
13. Bradshaw AW, Hoffmann FM (1978) *Surf Sci* 72:513
14. Descorme C, Gélin P, Lécuyer C, Primet M (1998) *J Catal* 177:352
15. Pommier B, Gélin P (2001) *Phys Chem Chem Phys* 3:1138
16. Xu X, Goodman DW (1994) *Catal Lett* 24:33
17. Pisanu AM, Gigola CE (1999) *Appl Catal B* 20:179