Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Catalysis A: Chemical 201 (2003) 247–261

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

NO decomposition on PdMo/γ-Al_2O_3 catalysts

A.M. Eberhardt [a], E.V. Benvenutti [b], C.C. Moro [b], G.M. Tonetto [a,*], D.E. Damiani [a,1]

[a] *PLAPIQUI (UNS-CONICET), Camino La Carrindanga km 7, CC 717, 8000 Bahía Blanca, Argentina*

[b] *Instituto de Química, Universidad Federal de Rio Grande do Sul—UFRGS, CP 15003, 91501-970 Porto Alegre, RS, Brazil*

Received 1 October 2002; received in revised form 11 February 2003; accepted 16 February 2003

Abstract

Studies of the NO decomposition reaction on Pd/γ-Al_2O_3, Mo/γ-Al_2O_3 and PdMo/γ-Al_2O_3 catalysts were made. The catalytic tests revealed that the binary catalyst has different behavior for the NO decomposition, being the principal differences a longer steady state activity and an increase of oxygen evolution at elevated temperatures. Characterization by TPR, hydrogen chemisorption and FT–IR of CO indicated that palladium physicochemical properties are altered by an effective interaction with molybdenum. The results would suggest a decoration effect of Mo over Pd particle. This interaction appears to be responsible for the observed modification in NO activity and selectivity.
© 2003 Elsevier Science B.V. All rights reserved.

Keywords: NO decomposition; Pd catalyst; Molybdenum

1. Introduction

At present, one of the significant problems in air pollution is the removal of nitrogen oxides. Nitrogen oxides contribute to smog, can affect human health, and are harmful to plants and animals. They contribute to acidic deposition. Furthermore, NO_x reacts with certain volatile organic compounds (VOCs) in the presence of sunlight to form photochemical oxidants, including ozone.

The term "NO_x" can refer to all of the oxides of nitrogen, but in air pollution working NO_x generally refers only to NO and NO_2. There are two sources of nitrogen oxides in the combustion of typical fuels. The first is the oxidation of atmospheric N_2 at the high temperatures of combustion. The other one is the oxidation of nitrogen-containing compounds in the fuel.

The reduction of NO in the presence of CO and/or H_2 on supported noble metal catalysts is intensively investigated. There are many publications about supported Pd catalysts associated with the removal of NO in automotive exhausts [1,2]. Ghandi et al. [3] were among the first in the use of molybdenum in automotive three-way catalysts. They found that improved net NO_x activity, with minimum NH_3 formation, is accomplished by the incorporation of molybdenum oxide in Pt and Pt-Rh catalysts. Halasz et al. studied the catalytic reduction of nitric oxide by CO, H_2 and CO + H_2 on PdMo/Al_2O_3 [4–6]. They reported that at higher temperatures molybdenum can improve the performance of the catalyst, especially at slightly oxidizing conditions. Schmal et al. [7] confirmed the high selectivity for N_2 in the CO + NO reaction on

* Corresponding author. Present address: University of Western Ontario, Faculty of Engineering, 1151 Richmond Street, London, Ont., Canada N6A 5B9. Tel.: +1-519-661211; fax: +1-519-6613498.
E-mail addresses: tonetto@surf.ssw.uwo.ca (G.M. Tonetto), ddamiani@plapiqui.edu.ar (D.E. Damiani).
[1] Co-corresponding author. Tel.: +54-291-4861700; fax: +54-291-4861600.

1381-1169/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1381-1169(03)00122-5

$PdMo/Al_2O_3$. Based on TPD analysis of NO and CO adsorption, a redox mechanism for NO reduction to N_2 involving partially reduced molybdenum oxide was proposed. The same group [8] studied the effect of MoO_3 on Pd/Al_2O_3 catalysts for the reduction of NO by methane and demonstrated that the selectivity towards N_2 was enhanced due to the promoting effect of NO decomposition on the MoO_x surface.

In view of that, the objective of this work is to examine the effects of molybdenum on the activity of Pd catalysts for NO decomposition. Experimental results about NO decomposition reaction are presented and discussed.

2. Experimental

2.1. Catalysts preparation

Pd/Al_2O_3 sample was prepared by wet impregnation of the support with a solution of $Pd(C_5H_7O_2)_2$ (Alfa) in toluene (Merck). The support material was γ-Al_2O_3 (Condea, Puralox, 148 $m^2\,g^{-1}$). After impregnation, the catalyst was dried in Ar at 150 °C for 2 h and then calcined in air (chromatographic grade) at 500 °C during 2 h. Mo/Al_2O_3 catalyst was prepared in similar way using a solution of $MoO_2(C_5H_7O_2)_2$ (Alfa) in toluene.

The bimetallic samples were prepared by wet impregnation utilizing the same precursors. The metals were co-impregnated or impregnated in sequence. After impregnation the sample was dried and calcined similarly to the monometallic catalysts. Table 1 summarizes catalyst preparation data.

In all cases, prior to impregnation the support was dried under N_2 at 150 °C for 2 h. The palladium and molybdenum contents were determined by atomic absorption spectroscopy.

2.2. H_2 chemisorption

Hydrogen chemisorption experiments were conducted in a conventional glass volumetric apparatus at 25 °C. Catalysts were reduced in flowing H_2 at 500 °C for 1 h. The samples were then outgassed overnight before cooling to 25 °C and measuring the first isotherm between 10 and 500 Torr. This consumption is related to the total uptake of hydrogen. A second isotherm was then obtained after pumping for 30 min, in order to measure the amount of absorbed and weakly held hydrogen. The corresponding uptake values were determined by extrapolating the linear portion of the isotherms to zero pressure. The amount of irreversibly adsorbed gas was obtained by subtracting these values.

The fraction of exposed palladium was calculated assuming that one hydrogen atom is adsorbed per surface palladium atom.

2.3. O_2 sorption experiments

Oxygen sorption experiments were carried out at 400 °C in the same volumetric apparatus used for H_2 chemisorption measurements. Previously, the samples were pre-reduced in H_2 flow at 500 °C for 2 h and evacuated at this temperature overnight. An ultimate vacuum near 10^{-5} Torr was obtained. The O/Me ratio (Me: Pd, Mo or Pd + Mo) ratios were determined by

Table 1
Characterization of the catalysts

Catalyst	Metal loading (wt.%)		Preparation	Pd_{exp}[a] (%)
	Pd	Mo		
Pd/Al_2O_3	0.82	–	w.i.[b]	55
Mo/Al_2O_3	–	0.71	w.i.	–
$PdMo(c)/Al_2O_3$	0.45	0.74	w.i.–co-impregnation	36
$PdMo/Al_2O_3$	1.00	0.87	w.i.–sequence[c]	45
$MoPd/Al_2O_3$	0.95	0.76	w.i.–sequence[d]	39

Metallic content and hydrogen uptakes as exposed metal percentage.
[a] Fraction of exposed palladium.
[b] w.i.: Wet impregnation.
[c] Pd impregnated on Mo/Al_2O_3.
[d] Mo impregnated on Pd/Al_2O_3.

extrapolating the sorption isotherm to zero pressure to correct for physisorption on the support. In order to test whether the oxygen taken up forms a stable oxide, a second isotherm was recorded after an evacuation of 30 min at 500 °C. High purity oxygen was used (99.99% from AGA).

2.4. TPR experiments

TPR experiments were carried out in an apparatus similar to that described by Robertson et al. [9] to which some changes were introduced [10]. Standard methods of gas purification were used. The reference and the sample were held in an oven that could be heated at linear rate of 10 °C min^{-1} between 0 and 500 °C. The temperature of the catalyst bed was measured with a 1/16 in. od stainless steel sheathed Chromel–Alumel thermocouple placed in contact with the top of the catalyst bed. The flow rate of reducing gas (a 5%H_2–95%Ar mixture) was 20 cm^3 min^{-1}.

Fresh samples of catalysts (40 mg) were oxidized in flowing air chromatographic grade at 500 °C for 1 h, purged and cooled in Ar to −50 °C, followed by TPR.

2.5. IR studies

Five square centimeter disks of catalysts, weighting 50 mg, were made by pressing the catalyst powder. They were heated to 300 °C in vacuum (10^{-5} Torr) during 1 h. Then they were exposed to 200 Torr of oxygen at 200 °C during 1 h. The oxygen was pumped off to a final pressure of 10^{-5} Torr during 1 h at 300 °C. Following this, the material was exposed to 300 Torr of hydrogen at 200 °C for 1 h, and finally evacuated for an additional hour at 300 °C. The treatments were carried out using a quartz IR cell [11]. The infrared spectra were recorded on a FT–IR 8300 Shimadzu spectrometer with 4 cm^{-1} resolution and 100 scans. The spectra were recorded at room temperature. The CO pressure in the analysis camera was 25 Torr.

2.6. Catalytic activity measurements

The catalysts were tested in a glass-made packed bed reactor (6 mm od) placed in an electrically heated oven. A temperature controller was used to control the reaction temperature (Omega CN3800), which was measured by means of a shielded J-type Omega thermocouple placed in the furnace close the catalyst bed. The reaction mixture contained 1100 ppm of NO in He. The reaction products were analyzed in a Varian 3700 gas chromatograph operating in the TCD mode. Two Porapak Q columns operated isothermally at 40 and −20 °C with He as carrier gas were used for separation. Chromatographic peaks were integrated by means of a Hewlett-Packard 3390 A integrator.

The catalytic activity measurements were done on catalyst samples that were previously reduced at 300 °C in the presence of a 5% H_2 in Ar mixture. The tests were done in two ways. (1) The catalyst sample was heated to 400 °C in He flow. Once the final temperature was reached the catalyst was contacted with the reaction mixture during 2 h. Samples of reaction products were taken regularly. (2) The catalyst sample was heated in the reaction mixture from 20 to 500 °C. Samples of the reaction products were taken at different reaction temperatures. Catalyst weight was adjusted in order to keep constant the weight of palladium in the different experiments. The reaction mixture flow rate was maintained at 35 cm^3 min^{-1}.

3. Results and discussion

3.1. Catalysts preparation and H_2 chemisorption

Table 1 presents palladium and molybdenum contents and summarizes the hydrogen chemisorption measurement results. Exception made of the PdMo(c)/Al_2O_3 the remaining samples resulted with about the same Pd and Mo loading. The table shows a decrease in the H_2 chemisorption capacity of palladium due to molybdenum addition. Similar results were reported by Konopny et al. [12] for PdMo-alumina catalysts prepared using different Pd precursors. Also, it has been observed in our laboratory for RuMo samples [13,14] and by others in RhMo catalysts [15]. High temperature oxidation favors the formation of MoO_3 that after exposure to pure H_2 at 300 °C reduces to suboxides that could migrate onto the palladium surface impeding its contact with H_2. It is well known that low molybdenum loading on alumina lead to quite stable molybdenum species. However, it has been reported evidences of MoO_3 formation on bimetallic RuMo catalysts

despite of their low molybdenum content [14]. Surface octahedral molybdate and tetrahedral species have been detected, even with molybdate loading down to 0.1 wt.% on γ-alumina. Xiong et al. [16] reported that the octahedral molybdate is formed on γ-alumina at all molybdate loading.

Noronha et al. [17] found that molybdenum addition induces modifications in the Pd metallic phase. In Pd-MoO_3/Al_2O_3 catalyst they observed: (i) a decrease in the amount of adsorbed hydrogen; (ii) an increase in the CO_{lineal}/CO_{bridge} ratio; and (iii) the disappearance of the NO adsorption band on palladium. These results suggest the blockage of palladium surface by the molybdenum oxide species.

The precursor and the impregnation sequence also influence the exposed metallic fraction. When molybdenum was incorporated by impregnation on the Pd/Al_2O_3 catalyst, the exposed palladium fraction was smaller than on catalysts prepared using an inverse order of impregnation. That is to say, when a Mo/Al_2O_3 sample was impregnated with a $Pd(Acac)_2$ solution. The lowest value in the exposed metallic fraction was presented in the $PdMo(c)/Al_2O_3$ catalyst, in which the metallic precursors were co-impregnated on the support.

3.2. O_2 sorption

The oxygen consumption is reported related to the moles of Pd present in the sample. Previous experiments carried on alumina showed that physisorption onto the support is negligible. Therefore, the observed oxygen uptake is due to the metals. Data is given in Table 2.

The O/Pd ratio obtained for the monometallic palladium sample is higher than expected. Leon y Leon and Vannice [18] also found O/Pd ratios higher than unity that was attributed to the presence of small quantities of PdO_2. This explanation can not account for the high O/Pd ratio obtained for the monometallic Pd sample since PdO_2 can not be formed under the experimental conditions prevailing during the experiments reported in Table 2. The formation of Pd_2O_3 is also discarded since it decomposes at 0 °C.

Table 2
Characterization of the catalysts

Catalyst	O–Pd[a] ($T_{reduction}$ = 500 °C)	N_{Mo}[b]
Pd/Al_2O_3	1.47	–
Mo/Al_2O_3	0.23	5.5
$PdMo(c)/Al_2O_3$	2.42	5.0
$PdMo/Al_2O_3$	2.75	3.3

O_2 chemisorption.
[a] O_2 chemisorption on catalysts pre-reduced at 500 °C.
[b] Mo oxidation state (in samples reduced at 500 °C).

Hoost and Otto [19] showed evidence of oxygen uptake higher than unity for PdO during temperature programmed oxidation (TPO) of $Pd/\gamma Al_2O_3$ catalysts having low Pd loading. The authors suggested a higher oxidation state of Pd or the presence of highly dispersed oxygen-rich species following similar results by Lesage-Rosemberg et al. [20].

The amount of oxygen consumed in the oxidation of Mo is obtained as the difference between the total oxygen uptake by the sample and the amount of oxygen adsorbed on Pd [21]. The following balances apply:

H_2 balance

$$PdO + H_2 \rightarrow Pd^0 + H_2O \quad (1)$$

$$Pd^0 + \tfrac{1}{2}H_2 \rightarrow Pd\text{-}H \quad (2)$$

$$H/Pd\ (\text{titration with } H_2) - Pd_{(s)}/Pd\ (= H/Pd) = [H_2 \text{ used to reduce PdO}]\cdot \quad (3)$$

O_2 balance

$$Pd^0 + \tfrac{1}{2}O_2 \rightarrow PdO \quad (4)$$

$$MoO_{x-1} + \tfrac{1}{2}O_2 \rightarrow MoO_x \quad (5)$$

According to Eq. (1), there are two hydrogen atoms per oxygen atom, therefore, to obtain the amount of oxygen used to oxidize Pd, Eq. (3) must be divided by 2. Therefore,

$$O/Pd^{\oplus} = \frac{[H/Pd\ (\text{titration with } H_2) - H/Pd]}{2}\cdot \quad (6)$$

Considering Pd and Mo loading and their molecular weight the oxygen uptake by Mo is:

$$O/Mo = \frac{Pd(\%)\ PM_{Mo}[O/Pd\ (\text{from Table 2}) - O/Pd^{\oplus}]}{Mo(\%)\ PM_{Pd}}\cdot \quad (7)$$

Then the oxidation state of Mo is:

$$N_{Mo} = 6 - 2\,(O/Mo)\cdot \quad (8)$$

According to the data shown in Table 2 the presence of Pd increases Mo reducibility. De Vries et al. [22] reported that the reduction of MoO_3-PtO_2/γ-Al_2O_3 with H_2 leads to a mixture of Mo(VI), Mo(V) and Mo(IV) species. They found a relationship between the extent of Mo(VI) reduction and the amount of PtO_2 in the sample. Similar results were given for the Pd-Mo system [17,23].

3.3. TPR experiments

TPR profiles of catalysts are given in Fig. 1, where the hydrogen consumption is plotted against temperature. The positive peaks between 10 and 40 °C in the TPR profiles are assigned to the reduction of palladium oxide. On the other hand, the TPR profile of Mo/Al_2O_3 catalyst evidences very low hydrogen consumption just before 500 °C. It is important to note that no change in the sample color was observed (Mo/Al_2O_3 is white after calcination and this color remains after the TPR experiment).

A characteristic negative peak attributed to palladium hydride decomposition is usually observed in the TPR profile of Pd catalysts. This peak correlates well with the average Pd particle size since the hydride formation is a bulk phenomenon. In the present case, the negative peak is hardly visible. The relative high dispersion of the monometallic sample may inhibit the formation of the hydride. The presence of broad hydrogen consumption peak in the 80–200 °C temperature range could prevent the observation of the negative peak in the bimetallics. This broad peak would be related to highly dispersed palladium oxide, which is reduced at temperatures higher than 100 °C [24] or palladium–molybdenum species more strongly linked

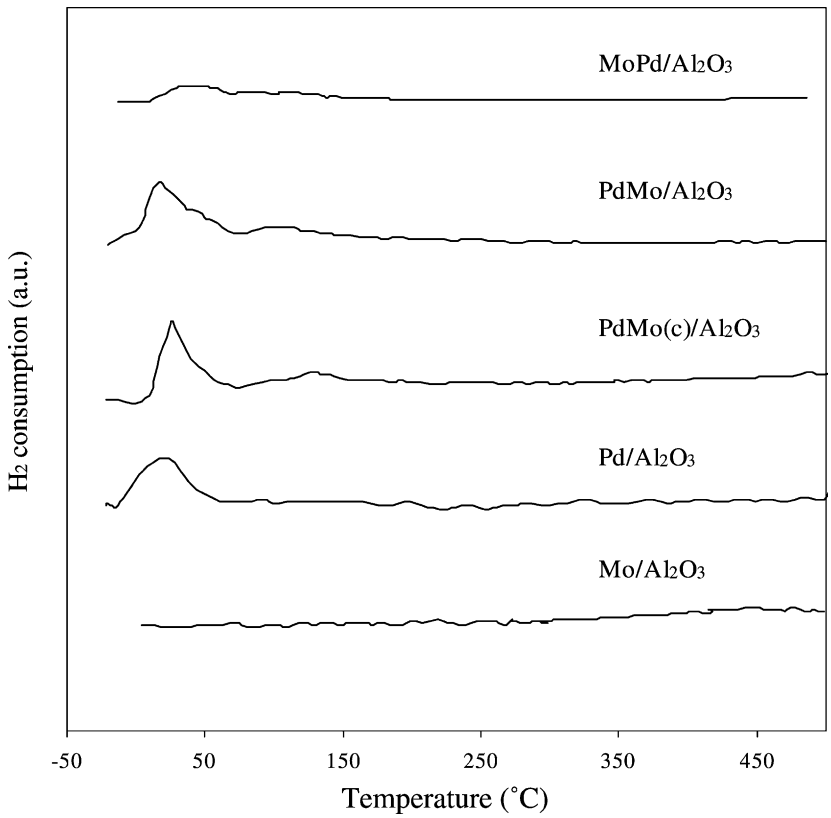


Fig. 1. TPR profiles. Oxidation temperature = 500 °C.

to the support than the PdO species, which would explain the reduction at higher temperature. Another possible explanation would be the bronze formation, due to the hydrogen spillover from the noble metal toward molybdenum trioxide. The process can be represented as follows:

$$H_2 + MoO_3 \rightarrow H_xMoO_3$$

where the stable stoichiometry of bronze is $H_{1.6}MoO_3$ [25]. This H_2 consumption, which is not present in the Pd/Al_2O_3 sample, demonstrates the interaction between palladium and molybdenum.

3.4. IR studies

As it is presented in Fig. 2, the IR spectrum of CO adsorbed on Pd/Al_2O_3 catalyst showed two main bands of absorption at 2094 and 1975 cm^{-1}, a shoulder weakly insinuated at 1940 cm^{-1} and a small band at 2150 cm^{-1}. The first two bands are similar to those reported by numerous authors for CO adsorption on supported palladium catalysts [26–28]. They are assigned to lineal and multiply connected CO, respectively. The bands of low frequency are generally attributed to adsorbed species in bridge form on the (1 0 0) and (1 1 1) planes of palladium [27,28]. The shoulder present at low frequency has been attributed to multiply coordinated species [29].

According to Tessier et al. [26], the absorption band at 2150 cm^{-1} can be assigned to Pd^{2+}–C≡O. They found ionic palladium in catalysts prepared using acetilacetonate precursors, after reduction at 300 °C. These authors consider that the high exposed metallic fraction (65%) favors a transfer of electrons from palladium to the support. This type of species was not detected at higher reduction temperatures.

Evacuation of the phase gas during 30 min at room temperature induces a strong decrease in the intensity of the band corresponding to lineal CO. This phenomenon was also observed by Pitchon et al. [29] and it was pointed out as an indication that lineal species are adsorbed on low coordination sites without any interaction with bridged species. The intensity of the assigned signal to CO multiply connected remains practically unaffected, although a shift to smaller wave numbers was observed. This result is coincident with previous works. Eischens and Pliskin [30] observed that the frequencies of the bands move toward higher wave numbers upon increasing the surface coverage with CO. This was assigned to the stronger competition among adsorbed CO molecules for electrons of superficial metallic atoms.

Fig. 3 shows the FT–IR spectrum of CO adsorbed on $PdMo/Al_2O_3$ sample. The same absorption bands as in Pd/Al_2O_3 catalyst were found. The most

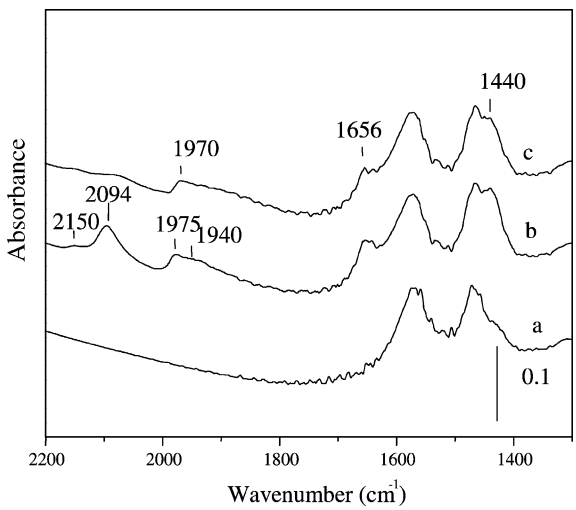


Fig. 2. FT–IR spectra of CO absorbed on Pd/Al_2O_3 sample (treatment = 300 Torr H_2 at 200 °C for 1 h). References: (a) catalyst; (b) 25 Torr of CO; (c) 30 min vacuum.

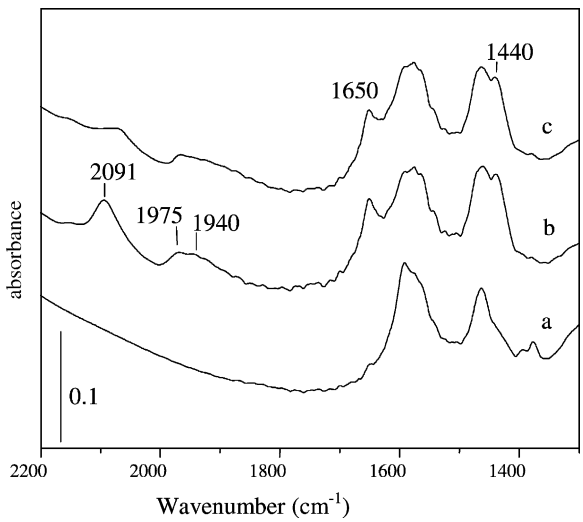


Fig. 3. FT–IR spectra of CO absorbed on $PdMo/Al_2O_3$ sample (treatment = 300 Torr H_2 at 200 °C for 1 h). References: (a) catalyst; (b) 25 Torr of CO; (c) 30 min vacuum.

evident difference among spectra is the change in the $CO_{lineal}/CO_{bridged}$ relationship.

Determining the concentration of palladium species by integration of signals intensities is not possible because the absorption coefficients "ε" are not known. However, for samples containing the same species (showing bands at identical positions) it is reasonable to admit that ε-values do not vary significantly from one sample to the other. In this way, the relationship of relative abundance between lineal and multiply connected CO could be estimated integrating the intensities of signals at 2094, 1975 and 1940 cm^{-1} expressed in the following way:

$$\tau = \frac{I_{2094\,cm^{-1}}}{(I_{1975\,cm^{-1}} + I_{1940\,cm^{-1}})}.$$

For Pd/Al_2O_3 and $PdMo/Al_2O_3$ samples, τ was 0.5 and 0.7, respectively. These results suggest that molybdenum addition generates a decrease of multiply connected species on palladium. This observation could be explained assuming that Pd is partially covered by molybdenum species, and this result is in agreement with those of H_2 chemisorption. Thus, when the exposed Pd surface decreases, the adsorption of linearly adsorbed CO is also favored.

Molybdenum addition also originates that the assigned signal for lineal CO on palladium moves toward lower wave numbers. Balakrishnan et al. [31] reported the same effect in $PtAu/SiO_2$ catalyst versus the one for the monometallic sample. They attributed this to a decrease of dipole–dipole interactions. Volpe reported a comparable shift on the IR spectra of CO adsorbed on Pd-Pb/alumina [32]. This author postulates that although a larger number of molecules linearly adsorbed is found in the bimetallic system, these molecules are not placed in adjacent positions and the interaction between dipoles is expected to be smaller due to dilution that originates the Pb addition. However, it is also pointed out that Pb addition, forming a superficial alloy, could produce an electronic change in palladium. If the electronic density is increased in this metal, it could diminish the strength of C=O bond because of a larger backbonding of electrons from Pd to C. The latter would be the cause of the signal shift to smaller frequencies in bimetallic catalyst. This argument has been used in many occasions to postulate electronic effects in bimetallic systems.

According to Peri [33], characteristic absorption bands for CO on molybdenum are seen around 2025 and 2045 cm^{-1} for Mo^0 and at 2100 cm^{-1} for $Mo^{\delta+}$. We did not find any signal for CO adsorbed on Mo neither on Mo/Al_2O_3 nor on $PdMo/Al_2O_3$ (see Fig. 3). This would be due to the absence of partially reduced species. It has not been observed CO adsorption on calcined Mo/alumina catalysts [33].

For Pd/Al_2O_3 and $PdMo/Al_2O_3$ spectra, the increase in intensity of bands at 1440 and around 1650 cm^{-1} is assigned to carboxylate formation over alumina [34].

3.5. Catalytic activity measurements

Fig. 4 shows the NO conversion as a function of time at 400 °C after reduction treatments at 300 °C. Since the same palladium mass was used in reaction, relative performances can be discussed. The Pd containing samples presented a similar qualitative behavior: the initial NO decomposition at 400 °C on the reduced surface was almost complete and then it diminished gradually. The only observed products were N_2 and N_2O. It would indicate that the decrease of the activity in the time was originated by the oxygen retention on the metallic surface. In all the cases, the nitrogen balance allowed to discard the possible formation of NO_2.

Fig. 5 presents the activity corresponding to Mo/Al_2O_3 sample. The Mo catalyst reduced at low temperature was weakly active for the NO decomposition. The activity fluctuated among 2–5% during the reaction time. The total content of molybdenum in the catalyst was similar to the amount of molybdenum in the $PdMo/Al_2O_3$ sample used in the catalytic tests. According to TPR results (Fig. 1), molybdenum is present as MoO_3 over the support after reduction at 300 °C.

It has been reported that alumina shows some activity for NO decomposition [35]. Fig. 5 superimposes NO conversion obtained on alumina (after being exposed to hydrogen at 300 °C) with the results obtained on the Mo/Al_2O_3 sample. This result indicates that the catalytic activity showed by Mo/Al_2O_3 reduced at 300 °C could de due to the contribution of the support. Therefore, this would indicate that the promotion effect that molybdenum exerts on the NO decomposition reaction is due to its interaction with palladium.

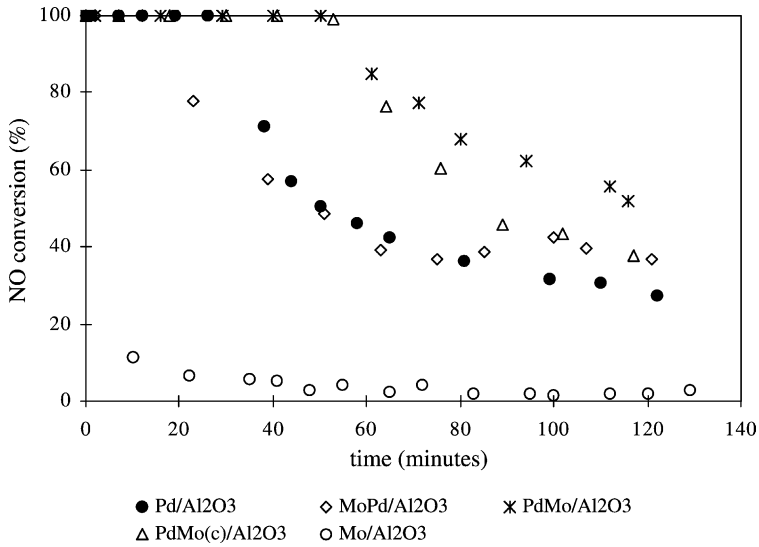


Fig. 4. NO conversion as a function of reaction time at 400 °C. SV = 4×10^4 mol feed/(h mol Pd).

The same figure reveals an increase in the activity of Mo/Al_2O_3 sample when both, the reduction temperature and reduction time increase (500 °C for 2 h). A severe reduction treatment would originate a higher number of oxygen vacancies. These are postulated in [36,37] as the possible active site for NO decomposition on metallic oxides. These oxygen vacancies would be originated during a reduction treatment not achievable in the TPR study.

In general, the bimetallic catalysts presented a better behavior that the palladium sample. The data presented in Fig. 4 can be analyzed in terms of the activity presented by the catalysts after a reaction time of 2 h, named from now as "residual conversion" ($X_{residual}$).

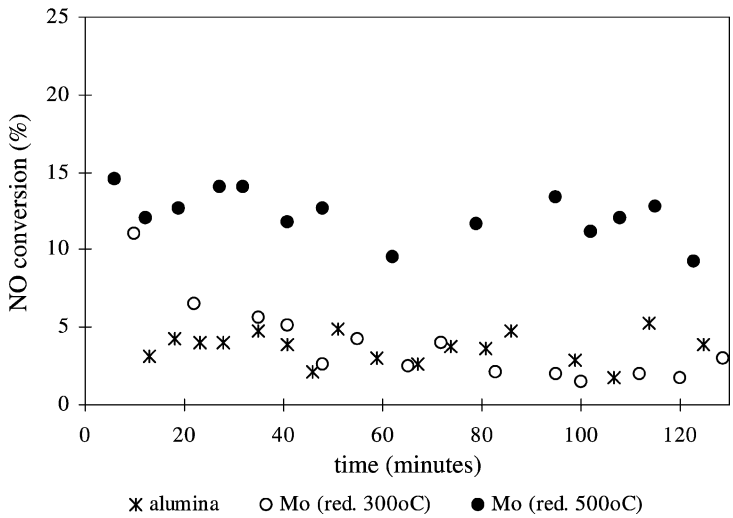


Fig. 5. NO conversion over alumina and Mo/Al_2O_3 sample (after different reduction treatments) at 400 °C. SV = 4×10^4 mol feed/(h mol Pd).

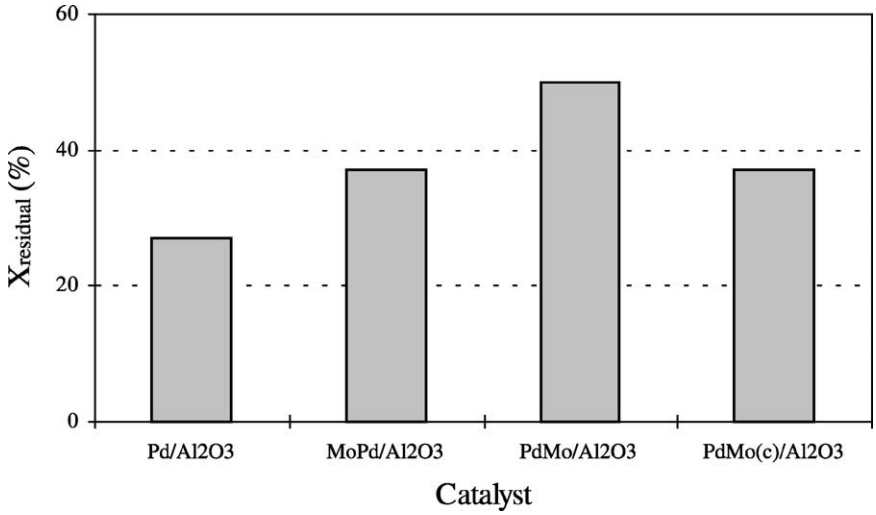


Fig. 6. Residual conversion after 2 h in reaction at 400 °C. SV = 4×10^4 mol feed/(h mol Pd).

Fig. 6 presents the residual conversion of all the studied samples. The addition of molybdenum originates an increase of $X_{residual}$ in bimetallic catalysts with regard to Pd/Al_2O_3 catalyst.

Comparing the activity of Pd/Al_2O_3, Mo/Al_2O_3 and different Pd-Mo systems in terms of conversion, it is found that those corresponding to the bimetallics are not the sum of the activities of the monometallics. It should be considered that in the bimetallic catalysts there are different potential active sites for the studied reaction. We speculate that those sites could be: Pd, MoO_3, Al_2O_3, MoO_x and the Pd–MoO_x interface. The catalytic activity of Pd, MoO_3 and Al_2O_3 is known. It was shown in Figs. 4 and 5. In the bimetallic catalysts, the interaction between the metals is important. The reducibility of Mo increases in these catalytic systems, therefore, there will be more MoO_x species in Pd-Mo samples than in Mo/Al_2O_3 catalyst.

To further elucidate the relationship between the activity and a Pd–Mo interaction, the reaction was carried out over $PdMo/Al_2O_3$ catalyst, using fresh samples reduced at different temperatures: 300, 400, and 500 °C. During the studies, a mass of catalyst smaller than the one employed during the first reaction test, was used. The results are presented in Fig. 7. It can be observed that the time during which the catalyst exhibited very high conversion (from now on named $t_{x\ =\ 100\%}$) diminished with the increase of reduction temperature while the residual activity remained the same for the three catalysts. Increasing the reduction temperature results in a more severe Pd coverage by Mo species. This was observed also for RuMo catalysts [13,14]. The Mo suboxides migrate towards palladium particles during the reduction treatment, diminishing the Pd exposed area. This decoration effect originates a decrease in $t_{x\ =\ 100\%}$ value, since molybdenum is much less active than Pd for the decomposition of NO. For this reason, $t_{x\ =\ 100\%}$ diminishes when the reduction temperature increases.

It is more difficult to understand why $X_{residual}$ value remains constant in spite of the different reduction treatment since the higher the reduction temperature, the higher the number of co-ordinative unsaturated sites (CUS) presents on MoO_x species. The fact that equal $X_{residual}$ values are obtained leads to conclude that this parameter, although depending on Mo, it is not a direct function of the CUS number in MoO_x.

Fig. 7 can be interpreted taking into account the ideas represented in Scheme 1(A). Upon increasing the reduction temperature, the number of MoO_x species increases. The Pd decoration process modifies the extension of the Pd–MoO_x interface. The more severe the decoration process, the shorter the Pd–MoO_x interface. Therefore, the number of active sites in the interface drops during the process of Pd masking. At the same time, those in the MoO_x region increase. In this

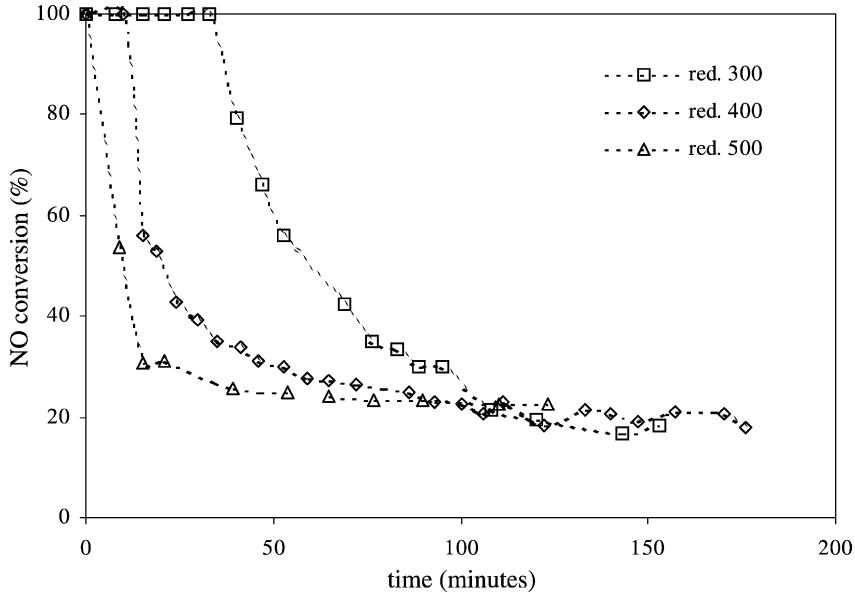
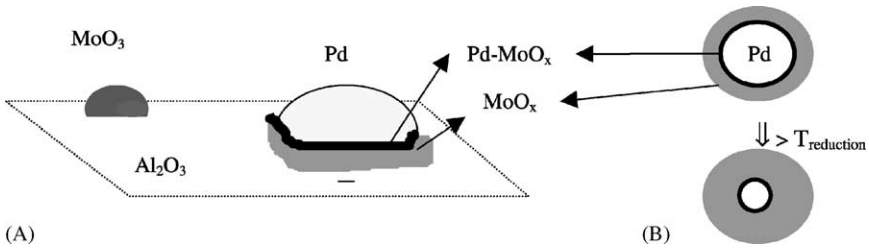


Fig. 7. NO conversion over $PdMo/Al_2O_3$ catalyst (after different reduction treatments over fresh samples) at 400 °C. SV = 4×10^4 mol feed/(h mol Pd).

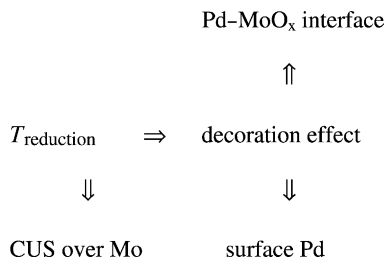


Scheme 1. Possible sites on bimetallic catalyst.

way, the different variables under consideration could be compensated and it would explain experimental results. In Scheme 2, the relationship between different parameters is visualized: residual activity depends on Pd, MoO_x and Pd–MoO_x. The total number of sites is approximately constant, since the increase of active sites on MoO_x is compensated by the loss of sites on the Pd surface and the Pd–MoO_x interface.

The following reduction–reaction sequence was carried out on a given sample in order to study a possible reactivation of the catalysts by means of a reduction.

- Reduction at 300 °C in Ar/H_2: 95/5 mixture during 30 min, purge in He.



Scheme 2. Relationship between residual activity with Pd, MoO_x and Pd–MoO_x sites.

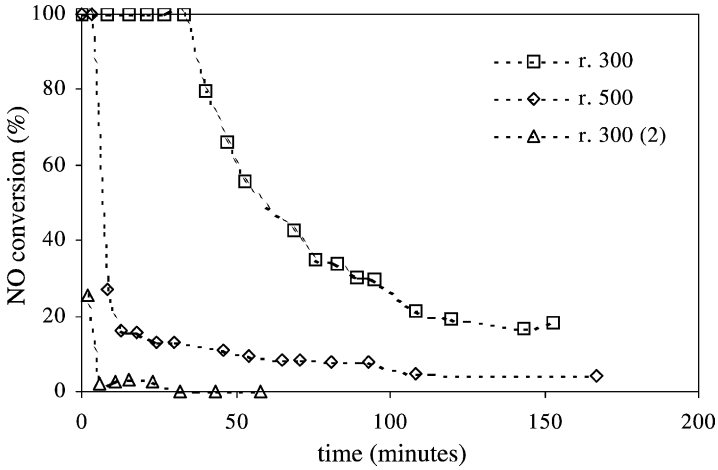


Fig. 8. NO conversion over $PdMo/Al_2O_3$ catalyst (after different reduction treatments over the same sample) at 400 °C. SV = 4×10^4 mol feed/(h mol Pd).

- Reaction at 400 °C during 120 min, purge in He.
- Reduction at 500 °C in Ar/H_2: 95/5 mixture during 30 min, purge in He.
- Reaction at 400 °C during 120 min, purge in He.
- Oxidation at 500 °C in air during 90 min, purge in He.
- Reduction at 300 °C in Ar/H_2: 95/5 mixture during 30 min, purge in He.
- Reaction at 400 °C during 120 min.

Fig. 8 shows the NO conversion on the $PdMo/Al_2O_3$ catalyst. A gradual deactivation of the catalyst is observed after the sequence of different treatments. It is found that the residual activity diminishes with the progressive cycles of reduction–reaction. It is also notorious that initial activity in each cycle is similar to the final activity of the previous cycle.

Therefore, the reduction of an aged catalyst does not allow reactivating the catalyst. An oxidation at 500 °C followed by a mild reduction does not turn to the original. This treatment is expected to produce the formation of MoO_3 leading to a Mo free Pd surface almost identical to the original one.

Similar results, not shown here, were obtained for Pd/Al_2O_3. In the case of the Mo/Al_2O_3 sample, its activity increased when the reduction treatment temperature was increased (Fig. 5). As already mentioned, this would be a consequence of an increase of the number of CUS on the molybdenum surface.

The experimental results point out a degradation of the active sites during the reaction. The initial activity in each cycle is similar to the final activity for the previous cycle, indicating a "memory" of the catalyst that is not possible to modify with severe reduction or oxidation treatments.

The information obtained from the monometallic catalysts suggests that this behavior could be related essentially to palladium. On the other hand, the residual activity of $PdMo/Al_2O_3$ catalysts after the second reduction at 300 °C is smaller than the one of Mo/Al_2O_3. This would indicate a Pd–Mo interaction. Therefore, the aging or deterioration of the active site would also include Mo species.

Recently, it was reported [38] that palladium is re-dispersed in the presence of NO_x. The formation of (PdO)NO volatile species is suspected. To analyze this last hypothesis, X-ray fluorescence analysis of the fresh and aged samples were done. The equipment used was a X-ray fluorescence spectrometer, PHILIPS PW 1400 with chromium anode, operated at 60 kV and 40 mA. The results indicated that some loss of molybdenum (9.8%) took place after 6 h in reaction. This loss is associated to the relative high partial pressure of molybdenum oxides. There was not any palladium loss.

Using transmission electron microscopy (JEOL 100CX), the statistical distribution of particle size was obtained for the same sample. As it is observed

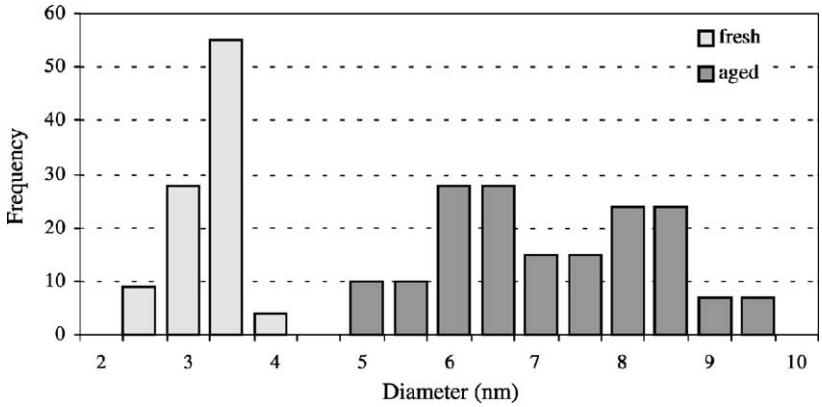


Fig. 9. Particle size histograms obtained from TEM micrographs of fresh and aged $PdMo/Al_2O_3$ catalyst exposed to NO decomposition.

in the histograms presented in Fig. 9, the average particle diameters were 3 and 6.7 nm for fresh and aged $PdMo/Al_2O_3$ catalyst, respectively. Also, after reaction, the particles lost their rounded shape.

Conrad et al. [39] found that the interaction of NO with Pd(1 1 1) at 727 °C causes the formation of PdO by means of the $NO \rightarrow N_2 + PdO$ reaction. They consider that the oxidation of the surface originates the formation of PdO microcrystals whose (1 0 0) planes are parallel to the Pd(1 1 1) surface. The oxide phase persists even after vacuum treatments at high temperatures. This is not expected for PdO bulk according to its thermodynamic properties. After elimination of the upper layers, the LEED pattern turns to be identical to the one of Pd(1 1 1). But the photoemission spectrum showed evidences of existence of considerable quantities of oxygen inside the metal.

Figs. 10 and 11 show the product distribution as a function of the reaction temperature. For both the catalysts, the maximum formation of N_2O occurs at 350 °C and it concludes at 400 °C, but there is a higher formation of N_2O in the monometallic sample. Our results also show a much higher selectivity to N_2 in the presence of molybdenum. This agrees with data

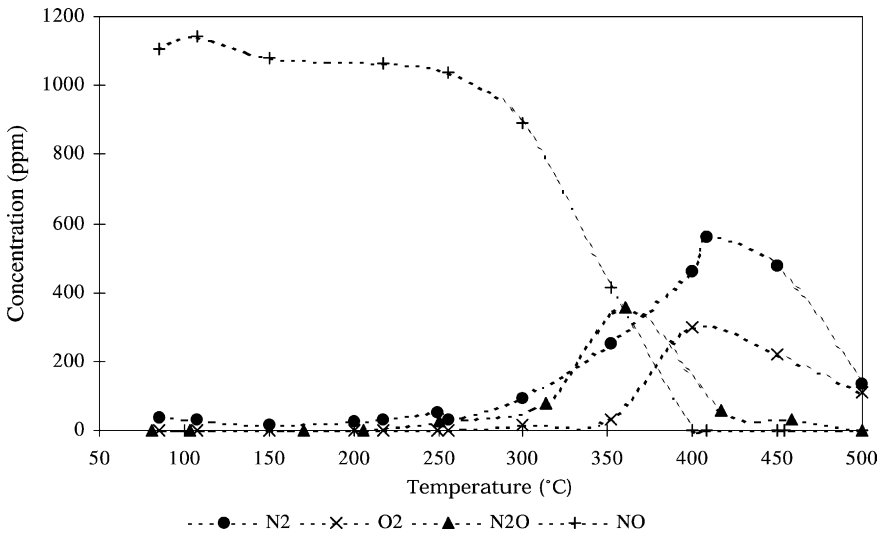


Fig. 10. Temperature dependence of decomposition of NO over Pd/Al_2O_3 catalyst. SV = 4×10^4 mol feed/(h mol Pd).

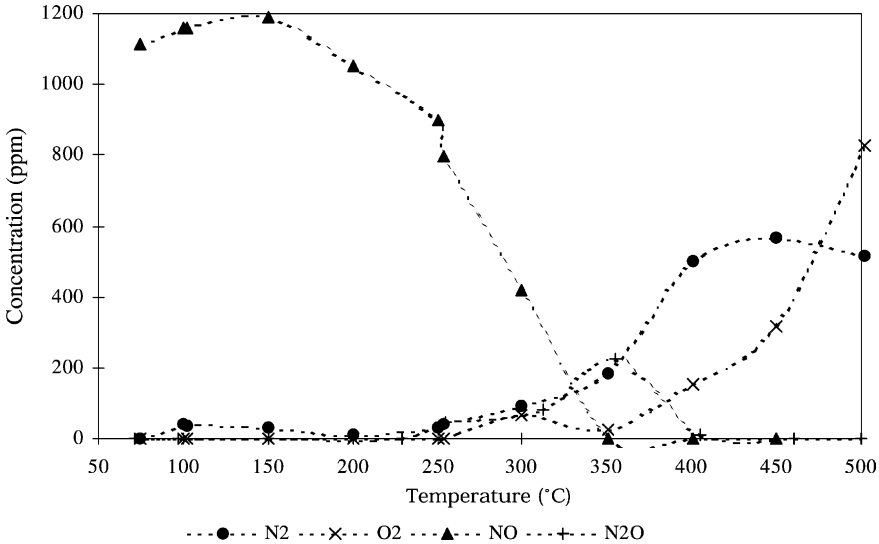


Fig. 11. Temperature dependence of decomposition of NO over $PdMo/Al_2O_3$ catalyst. SV = 4×10^4 mol feed/(h mol Pd).

reported by da Silva and Machado [40]. They published the selectivity values calculated from temperature programmed desorption (TPD) profiles of NO on Pt-*y*Mo/γ-Al_2O_3 catalysts that show that N_2 selectivity increases with molybdenum content in the catalyst.

The oxygen evolution is different in the studied samples. Over Pd/Al_2O_3, oxygen production begins at 350 °C, it shows a maximum value at 400 °C. On the other hand, over $PdMo/Al_2O_3$ sample, the oxygen formation starts when the reaction temperature reaches 300 °C and it continues increasing with the temperature. This result could indicate that molybdenum addition to the palladium catalyst favors the release of oxygen from the surface. N_2 formation at 500 °C on Pd/Al_2O_3 sample is not enough to close the nitrogen balance. Iwamoto et al. [41] consider that the loss of nitrogen and oxygen in the balance can be attributed to the formation of NO_2.

On metal oxide compounds, it is generally accepted that active sites are adjacent anion vacancies [36]. IR studies show [40] that NO adsorbed preferentially on MoO_x species in Pt-*y*Mo/γ-Al_2O_3 catalyst. Schmal et al. [7] suggested that in CO + NO reaction on PdMo/γ-Al_2O_3 catalysts, NO adsorption and dissociation occur on species Mo^{4+}. It has also been reported that a promoter can reduce oxygen inhibition. Hamada et al. [42] have shown that by adding Ag to cobalt oxide, both the activity and resistance to oxygen poisoning are increased. The active species seems to be a complex of cobalt and silver oxides. The enhancement observed with silver may be due to its low affinity for oxygen. El Hamadaoui et al. [2] indicated that chromium promotes the dissociation of NO compared to pure palladium. Under static conditions, the behavior of this catalyst is similar to that of Rh. It was suggested that this behavior was due to the influence of this element on the electronic properties of palladium.

Another explanation for the nature of the interactions between Pd and Mo could be considered. The activity of the catalytic system could be related to the formation of oxygen vacancies lying on the thin oxide overlayer that covers the metal. The mechanism of formation is associated to a junction effect between the metal and the oxide as proposed by Frost [43] using a detailed analysis of the electronic properties of the surface.

We have been working with M-Mo systems for several years in different catalytic systems. It is clear to us that Mo tends to cover nearby metallic particles of most of Group VIII metals. There is an important difference in the heat of vaporization of Mo and Group VIII metals (for example: the heat of vaporization is 33 kcal/(g mol) and 148 kcal/(g mol) for MoO_3 and Ru, respectively). Besides the vapor pressure of MoO_3 at temperatures close to 400 °C is 1 mmHg approximately, while for bulk Pd a similar vapor pressure

is reached at substantially higher temperatures. There are also very important differences in free surface energy, being considerably lower the free surface energy of MoO_3 that is mobile at the temperatures used in the pre-treatments of our paper.

In all the M-Mo systems that we studied in the last 12 years we always found a decrease in hydrogen or CO chemisorption on the metal M, with M being Pd, Ru or Rh, when Mo was added to the catalyst regardless the procedure used in the preparation. This (together with other experiments) indicated some sort of surface coverage by Mo of the M surface. We never found, however, that the presence of the overlayer increased the activity in the case of the syngas reaction to produce oxygenates. We found a severe loss of activity, although accompanied by an increase of the selectivity to methanol and ethanol [13,14] that theoretical studies suggested was associated to changes in the adsorption modes of CO induced by the presence of MoO_x moieties on the surface of Ru [44]. However, using PdMo catalysts we found that the bimetallic sample was more active than monometallic Pd for the combustion of methane [12]. Although in this case, the increase of activity (or its absence) for methane combustion depended on the Pd precursors used in the catalyst preparation.

Therefore, it seems that the same combination of metal and oxides do not result in similar effect in all cases. It is evident that the explanation proposed by Frost fits better in those cases, where vacancies are postulated to be part of the reaction mechanism. In the case of the paper under discussion, it is clear that MoO_3 reduced at higher temperatures is more active. It is also clear that PdMo is more active than Pd and MoO_3 reduced at low temperature and that the activity of PdMo is not the sum of those of Pd and MoO_3 reduced at low temperature. However, the PdMo could indeed be the sum of the activities of Pd and MoO_3 on top of Pd behaving like MoO_3 reduced at high temperature as a consequence of the presence of vacancies generated by a process like Frost's. It is not clear why the TPR or the IR experiments do not detect the formation of reduced Mo oxides in PdMo. Although we found that totally covered Pd by MoO_x moieties allowed the formation of Pd hydride indicating that the blockage of the surface was not complete and that reduction was possible [45].

In sum, we considered exhaustively the activity of the studied catalytic system in terms of the formation of oxygen vacancies. Although it looks plausible, based on our previous experience on Mo-modified metals used in a family of reactions and in the IR and TPR experiments of the present paper we believe that our proposal of active sites formed in the Pd–MoO_x interface offers a reasonable explanation of the observed phenomena.

Although the catalytic decomposition of NO to O_2 and N_2 over noble metals or oxide catalysts is too slow to be considered on a practical scale, this reaction is significant for its activity in other important pollution control reactions [46].

4. Conclusions

The catalytic tests revealed that the binary catalysts has different behavior for the NO decomposition reaction, being the principal differences a better performance in the reaction time and an increase of oxygen evolution an elevated temperatures for PdMo/alumina catalyst when comparing with its molybdenum free counterpart. Characterization by TPR, hydrogen chemisorption and FT–IR of CO indicated that palladium physicochemical properties are altered by an effective interaction with molybdenum. The results would suggest a decoration effect of Mo over Pd particle. This interaction appears to be responsible for the observed modification in NO activity.

Acknowledgements

We thank the Universidad Nacional del Sur (UNS) and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for their financial support.

References

[1] M. Valden, J. Aaltonen, E. Kausisto, M. Perra, C. Barnes, Surf. Sci. 307 (1994) 193.
[2] A. El Hamadaoui, G. Bergeret, J. Massardier, M. Primet, A. Renouprez, J. Catal. 148 (1994) 47.
[3] H. Gandhi, H. Yao, H. Stepien, Catalysis Under Transient Conditions, in: A. Bell, L. Hedegies (Eds.), ACS Symp. Ser.

No. 178, Am. Chem. Soc., Washington, DC, 1982, p. 143.
[4] I. Halaz, A. Bremmer, M. Shelef, Appl. Catal. B 2 (1993) 131.
[5] I. Halaz, A. Bremmer, M. Shelef, Catal. Lett. 16 (1992) 311.
[6] I. Halaz, A. Bremmer, M. Shelef, Catal. Lett. 18 (1993) 289.
[7] M. Schmal, M. Baldanza, M. Vannice, J. Catal. 185 (1999) 138.
[8] L. de Mello, M. Baldanza, F. Noronha, M. Schmal, Studies in Surface Science and Catalysis, vol. 130, in: A. Corma, F. Melo, S. Mendioroz, J. Fierro (Eds.), Elsevier, Amsterdam, 2000, pp. 647.
[9] S. Robertson, B. Mc Nicol, J. de Baas, S. Kloet, J. Jenkins, J. Catal. 37 (1975) 424.
[10] D. Damiani, E. Pérz Millán, A. Rouco, J. Catal. 101 (1986) 162.
[11] J. Foschiera, T. Pizzolato, E. Benvenutti, J. Braz. Chem. Soc. 12 (2001) 159.
[12] L. Konopny, A. Juan, D. Damiani, Appl. Catal. B 15 (1998) 115.
[13] A. Juan, D. Damiani, J. Catal. 137 (1992) 77.
[14] A. Juan, D. Damiani, Catal. Today 15 (1992) 169.
[15] B. Kip, E. Hermans, J. van Wolput, N. Hermans, J. van Grondelle, R. Prins, Appl. Catal. 35 (1987) 109.
[16] G. Xiong, C. Li, Z. Feng, P. Ying, Q. Xin, J. Liu, J. Catal. 186 (1999) 234.
[17] F. Noronha, M. Baldanza, M. Schmal, J. Catal. 188 (1999) 270.
[18] C. Leon y Leon, M. Vannice, Appl. Catal. 69 (1991) 569.
[19] T. Hoost, K. Otto, Appl. Catal. A 92 (1992) 39.
[20] E. Lesage-Rosemberg, G. Vlaic, H. Dexpert, P. Legarde, E. Freund, Appl. Catal. 22 (1986) 211.
[21] S. Kawi, O. Alexeev, M. Shelef, B. Gates, J. Phys. Chem. 99 (1995) 6926.
[22] J. De Vries, H. Yao, R. Baird, H. Gandhi, J. Catal. 84 (1983) 8.
[23] S. Kawi, O. Alexeev, M. Shelef, B. Gates, J. Phys. Chem. 99 (1995) 6926.
[24] H. Lieske, J. Volter, J. Phys. Chem. 89 (10) (1985) 1842.
[25] P. Sermon, G. Bond, J. Chem. Soc., Faraday Trans. 1 (72) (1976) 730.
[26] D. Tessier, A. Rakai, F. Bozon-Verduraz, J. Chem. Soc., Faraday Trans. 88 (5) (1992) 741.
[27] F. Hoffmann, Surf. Sci. Rep. 3 (1983) 107.
[28] A. Ortega, F. Hoffmann, A. Bradsshaw, Surf. Sci. 119 (1982) 79.
[29] V. Pitchon, M. Primet, H. Praliaud, Appl. Catal. 62 (1990) 317.
[30] R. Eischens, W. Pliskin, Adv. Catal. 10 (1958) 1.
[31] K. Balakrishnan, A. Sachev, J. Schwank, J. Catal. 121 (1990) 441.
[32] M. Volpe, Thesis, UNS, 1991.
[33] J. Peri, J. Phys. Chem. 86 (9) (1982) 1615.
[34] M. Pereira da Silva, R. Mello Viera, M. Schmal, Appl. Catal. 190 (2000) 177.
[35] A. Amirnazmi, J. Benson, M. Boudart, J. Catal. 30 (1973) 55.
[36] E. Winter, J. Catal. 22 (1971) 158.
[37] T. Yamashita, A. Vannice, J. Catal. 163 (1996) 158.
[38] B. Adelman, W. Sachtler, Appl. Catal. B 14 (1997) 1.
[39] H. Conrad, G. Ertl, J. Küppers, E. Latta, Surf. Sci. 65 (1977) 245.
[40] M. da Silva, B. Machado, in: Proceedings of the Acta Symp. Iberoam. Catal., Brazil, 2000, p. 641.
[41] M. Iwamoto, H. Yahiro, Y. Mine, S. Kagawa, Chem. Lett. (1989) 213.
[42] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, Chem. Lett. (1990) 1069.
[43] C. Frost, Nature 334 (1988) 577.
[44] A. Juan, D.E. Damiani, N.J. Castellani, Catal. Lett. 19 (1993) 43.
[45] A. Juan, C.C. Moro, D.E. Damiani, Colloids Surf. Part A: Physicochem. Eng. Aspects 122 (1997) 257.
[46] R. Burch, P. Millington, A. Walker, Appl. Catal. B 4 (1994) 65.