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Performance of Pd-Mo/γ-Al$_2$O$_3$ catalysts for the selective reduction of NO by methane

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Abstract

Pd-Mo/γ-Al$_2$O$_3$ catalysts were prepared by wet impregnation using organometallic precursors. The performance of these catalysts in the selective catalytic reduction of NO by methane (denoted NO–CH$_4$) was compared with corresponding palladium- and molybdenum-supported catalysts prepared by the same method.

Characterization by TPR, hydrogen chemisorption and FTIR of CO and NO showed evidence of palladium–molybdenum interaction. The experimental results indicated an encapsulation effect of partially reduced Mo species over Pd particle.

The catalytic tests revealed that the binary catalysts have different behaviors for the studied reaction. The activity for NO–CH$_4$ reaction is higher for the binary samples in the temperature range 200–500 °C. On the other hand, a decrease in the activity (at 500 °C) was observed over the Pd-Mo/Al$_2$O$_3$ samples after 2 h under reaction conditions, being similar to the activity displayed by Pd/Al$_2$O$_3$. This is thought to be associated with a poisoning of MoO$_x$ sites by the oxygen formed during the dissociation of NO. The oxygen taken up by the MoO$_x$ species does not seem to be removed by methane. Higher initial activity on bimetallic catalysts is attributed to the greater number of active sites and a synergetic effect between Pd and Mo.
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1. Introduction

The negative impact of man-made NO$_x$ emissions on the environment is well known: nitrogen oxides are extremely harmful pollutants. Much effort has therefore been put into the control of this contaminant. The selective catalytic reduction by hydrocarbons (HC-SCR) is an attractive technique for NO$_x$ reduction to N$_2$ in exhaust gas streams. Methane is one of the hydrocarbons of interest. It is the primary component of natural gas (over 85%), it is relatively inexpensive and it presents attractive properties as a reducing agent.

Cobalt- and copper-exchanged ZSM-5 catalysts have been reported to be effective for the CH$_4$-SCR of NO at reasonable temperatures (400 °C) [1]. The poor thermal and hydrothermal stability of zeolite-based catalysts, however, makes them impossible to be used under practical conditions [2]. Alumina-based catalysts, which present high hydrothermal stability, are potential candidates for the abatement of NO. It is well known that supported noble metal catalysts (e.g. Pt, Pd) are active for the reaction of NO with H$_2$, CO

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or NH_3 [3–5]. It has been also reported that they show a high level of activity for NO–CH_4 reaction, but that they give relatively high selectivity to N_2O, NH_3 and CO [6]. Finally, the addition of molybdenum to Pd-supported catalyst has been reported to improve the catalytic properties for NO reduction [7–10]. Based on these results, and taking into consideration the fact that molybdenum oxide volatilization is possible at high temperatures, and that molybdenum stability can be improved by using low Mo loading [8], we prepared Pd-Mo catalysts by wet impregnation. We used acetyl acetonate precursors and low metallic loading (Mo weight loading was chosen to be as close at 0.9 wt.% always).

We have observed the effect of Mo over Pd/Al_2O_3 catalyst on NO decomposition [11]. The catalytic tests revealed that the binary catalyst has a different behavior for the NO decomposition, the main differences being a longer steady-state activity and an increase in oxygen evolution at high temperatures. Characterization results indicated that Pd–Mo interaction appears to be responsible for the observed modification in NO activity and selectivity.

In another study [12], adsorption and dissociation of NO on $Pd(1\,1\,1)$, MoO_x-$Pd(1\,1\,1)$ and MoO_x-γAl_2O_3 model surfaces have been investigated using a molecular orbital approach of the extended Hückel type (EHMO), including repulsion terms. Our results of EHMO showed that the NO adsorption energy on MoO_x-$Pd(1\,1\,1)$ model is lower than the one for $Pd(1\,1\,1)$ or MoO_x-γAl_2O_3. In addition, the interaction of N_2 and O_2 with the surface is also notoriously modified in the bimetallic model. These results would indicate the existence of an interface

Pd-Mo with different catalytic properties to the metals individually.

As a continuation of those studies, this paper will report the preparation, characterization and evaluation in NO–CH_4 reaction of Pd-Mo catalysts supported on alumina.

2. Experimental

2.1. Preparation of catalysts

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, $148\,m^2/g$). Prior to impregnation the support was dried under N_2 at $150\,^\circ C$ for 2 h. Mo/Al_2O_3 catalyst was prepared in a similar manner using a solution of $MoO_2(C_5H_7O_2)_2$ (Alfa) in toluene. After impregnation the catalysts were dried in Ar at $150\,^\circ C$ for 2 h and then calcined in air (chromatographic grade) at $500\,^\circ C$ during 2 h.

The bimetallic samples were prepared utilizing the same precursors. The metals were co-impregnated or impregnated in sequence. The catalyst Pd-Mo/Al_2O_3 was prepared by wet impregnation of the Mo/Al_2O_3 with a solution of $Pd(C_5H_7O_2)_2$. On the other hand, Pd-$Mo(c)/Al_2O_3$ catalyst was made by impregnation of alumina with a solution of both precursors in toluene. After impregnation, the sample was dried and calcined similarly to the monometallic catalysts. Table 1 summarizes catalyst preparation data. The Pd and Mo contents were determined by atomic absorption spectroscopy (AAS).

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 ± 5
Mo/Al_2O_3	–	0.71	w.i.	–
Pd-$Mo(c)/Al_2O_3$	0.45	0.74	w.i.–co-impregnation	36 ± 5
Pd-Mo/Al_2O_3	1.00	0.87	w.i.–sequence[c]	45 ± 5

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.

2.2. Characterization of catalysts

2.2.1. H_2 chemisorption

The chemisorption uptakes were measured in a conventional glass apparatus [13]. Before the reduction, the catalysts were oxidized in air at 500 °C during 1 h. The samples were then purged in He and reduced at 500 °C in flowing H_2 during 1 h. Following reduction, the samples were evacuated for 20 h at reduction temperature and cooled to adsorption temperature (25 °C) under vacuum. Irreversible uptakes were determined from dual isotherms measured for hydrogen using the method of Benson et al. [14]. The fraction of exposed palladium was calculated assuming that one hydrogen atom is adsorbed per surface palladium atom.

2.2.2. TPR experiments

TPR experiments were performed in a conventional apparatus, as previously described [15]. Before reduction, the catalysts were oxidized in flowing chromatographic air at 500 °C for 1 h and purged and cooled in Ar. Then, a mixture of 5% hydrogen in argon was passed through the sample and the temperature was raised from −50 to 500 °C at a heating rate of 10 °C/min.

2.2.3. IR studies

The samples were pressed into a 10 mg/cm^2 self-supporting wafers. Prior to each experiment, the catalysts were evacuated (10^{-5} Torr, 1 Torr = 1.333224 Pa) at 300 °C for 1 h. Then they were exposed to 200 Torr of O_2 at 200 °C during 1 h. The O_2 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 additional 1 h at 300 °C. After that, the catalysts were exposed to 25 Torr of CO. After adsorption, the samples were out-gassed and the spectra were recorded at room temperature. For NO studies, the pre-treatment of the sample was similar. Following NO adsorption, the catalysts were out-gassed at 100, 200 and 300 °C.

The treatments were carried out using a quartz IR cell [16]. The infrared spectra were recorded on a FTIR 8300 Shimadzu spectrometer with 4 cm^{-1} resolution and 100 scans.

2.2.4. Catalytic activity measurements

The catalytic activity of the sample was tested for the reduction of NO with CH_4. The catalyst (∼50 mg) was tested in flow system using a glass reactor (6 mm o.d.) operating at atmospheric pressure. The reactor was mounted horizontally in an electrically heated oven. The reaction products were analyzed by on line gas chromatograph operating in TCD mode. Two Porapak Q columns operated isothermally at 40 and −20 °C with He as carrier gas were used for separation. The reaction mixture composition was 735.4 ppm of NO and 183.9 ppm of CH_4 in He balance (stoichiometric mixture, for practical purpose 1 ppm = 4.1 × 10^{-11} g mol cm^{-3}). Prior to each activity measurement, the catalysts were pre-treated (in situ) under flow of 5% H_2 in Ar, at 300 °C for 30 min.

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 with a space velocity of 3.99 × 10^4 feed mol/h mol Pd. Conversion data was measured in a temperature range 150–500 °C.

3. Results and discussion

### 3.1. Preparation of catalysts and H_2 chemisorption

The choice of the catalysts preparation method reported here derives from preliminary work carried out by our laboratory. Different parameters such as the metal precursors, the metal loading and preparation technique were analyzed [4,17,18].

Some of the results concerning the characterization by TPR and hydrogen chemisorption were reported in our previous work [12] and are here reproduced to facilitate comparisons.

Table 1 lists all the prepared catalysts and their metal content determined by atomic absorption spectroscopy. According to the results of Yao [19], the concentration of saturation of MoO_3 on γ-Al_2O_3 is 4 μmol Mo/m^2 (BET). Considering this value, 13.2% of the surface of the Mo/Al_2O_3 catalyst surface is covered by molybdenum.

When Pd loadings are compared, palladium concentrations are higher for Pd/Al_2O_3 and Pd-Mo/Al_2O_3 than in Pd-Mo(c)/Al_2O_3 samples. Molybdenum loadings, however, remain practically constant. This result is consistent with the type of interactions between the metal precursors and the support. Several reports indicate that the fixation of the metal acetyl

acetonates on alumina occurs by a ligand-exchange mechanism. A covalented bond is originated and Ha-cac ($C_5H_8O_2$) is generated, which remains adsorbed on the surface of alumina. This mechanism was found valid for Pd(acac)$_2$ [17,20,21] and MoO$_2$(acac)$_2$ [22] and can be represented by the following scheme of general reaction:

$$S–OH + M(acac)_x \rightarrow S–OM(acac)_{x-1} + Hacac(ad)$$
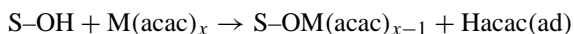
When the catalyst precursor is calcined, the remaining acac ligand combusts and PdO and MoO$_3$ particles are formed.

Boitiaux et al. [20] reported that acetylacetone (Hacac) generated during fixation of Pd(acac)$_2$ and adsorbed on the support, affects the impregnation mechanism of palladium. They found that: (a) a support capable of retaining 0.3 wt.% of palladium, only retains 0.07 wt.% when acetylacetone is pre-adsorbed; and (b) when a support, that has retained 0.3 wt.% of Pd, is submerged in a solution containing an excess of acetylacetone, 80% of palladium in the support is lost into the solution. In view of this, the minimum palladium loading in the sample Pd-Mo(c)/Al$_2$O$_3$ may be understood as a competition for sites between the complex of palladium and acetylacetone generated during the co-impregnating of the precursors Pd(acac)$_2$ and MoO$_2$(acac)$_2$. The molybdenum complex is not affected.

Another bimetallic sample was prepared. Mo-Pd/Al$_2$O$_3$ catalyst was synthesized by wet impregnation of Pd/Al$_2$O$_3$ sample with a solution of MoO$_2$(acac)$_2$. The metal loadings determined by AAS were 0.95 wt.% of Pd and 0.76 wt.% of Mo. The similarities in metallic contents between Mo-Pd/Al$_2$O$_3$ and Pd-Mo/Al$_2$O$_3$ indicates that Pd and Mo do not compete for the same sites on alumina.

The hydrogen chemisorption measurement results (expressed as Pd exposed fraction) are also summarized in Table 1. Assuming hemispherical particle and superficial density of 1.27×10^{19} Pd$_s$ atoms/m^2, metal particle size in Pd/Al$_2$O$_3$ catalyst is 2 nm ($d_p = 1.12/Pd_{exp}$) [23]. In relation to Pd monometallic catalyst, bimetallic samples show a decrease in the H$_2$ chemisorption capacity of Pd when Mo is also present. During the preparation procedure, high oxidation temperature favors the formation of MoO$_3$, which after exposure to H$_2$ at high temperature reduces to a suboxide that tends to migrate onto the Pd

surface preventing its contact with H$_2$ [18]. Similar results were reported for Ru-Mo samples [24] and Rh-Mo catalysts [25].

The TPR results for the four samples are showed in Fig. 1. Mo/Al$_2$O$_3$ presents a very low hydrogen consumption just before 500 °C, due to partial reduction of MoO$_3$. The hydrogen consumption peak is small as a result of the low Mo loading. In this condition, the interaction between Mo and alumina is strong and the reduction of MoO$_3$ requires higher temperatures [26–28].

On the other hand, the TPR profiles for Pd/Al$_2$O$_3$ sample presents a low temperature peak, around 25 °C. This signal is attributed to the reduction of palladium oxide. In bimetallic samples, we find the signal assigned to the reduction of palladium oxide.

The negative peak around 60 °C is attributed to palladium hydride decomposition. Its small size shows a connection with the average particle size presented by the samples, since the hydride formation is a bulk phenomenon. The hydrogen consumption at high temperature corresponds to the partial reduction of MoO$_3$.

The reduction profiles for the binary samples present an additional hydrogen consumption peak in the 80–200 °C temperature range. This broad peak would be related to highly dispersed palladium oxide, which is reduced at temperatures higher than 100 °C [29] or it could be to assigned to a partial reduction of MoO$_x$ species caused by close contact with the noble metal, according to similar results reported for Pd-V/Al$_2$O$_3$ catalyst [30]. Another possible explanation would be the bronze formation, due to the hydrogen spillover from the noble metal towards MoO$_3$ [31]. This H$_2$ consumption is not present in Pd/Al$_2$O$_3$ sample, which demonstrates the interaction between Pd and Mo.

Fig. 2 shows the FTIR spectrum of Pd/Al$_2$O$_3$ after exposure to CO. The absorption band at 2094 cm^{-1} is assigned to linear CO and the signal at 1975 cm^{-1} is attributed to multiple connected CO [32,33]. The shoulder present at low frequency (1940 cm^{-1}) has been attributed to multiple coordinated species [34]. According to Tessier et al. [35], the absorption band at 2150 cm^{-1} can be assigned to Pd^{2+}–C≡O. They found ionic palladium in catalysts prepared using acetyl acetonate precursors, after reduction at 300 °C. They consider that the high exposed metallic fraction (65%) favors a transfer of electrons from the palladium to the support. The increase in intensity of
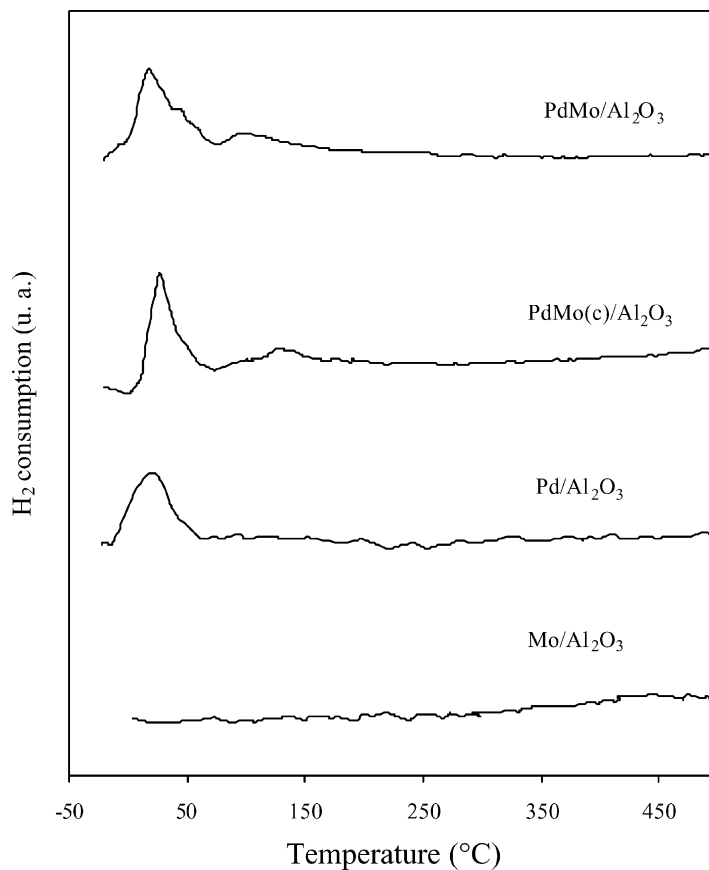
Fig. 1. TPR profiles. Oxidation temperature: 500 °C.

bands at 1440 and around $1650 \, cm^{-1}$ is assigned to carboxilate formation over alumina [36].

Fig. 3 shows the FTIR spectrum of CO adsorbed on Pd-Mo/Al$_2$O$_3$ sample. the same absorption bands as in Pd/Al$_2$O$_3$ catalyst were found. Upon Mo addition, changes were observed in the intensity of linear and bridged bands. For samples containing the same species (showing bands at identical positions), it seems reasonable to admit that the absorption coefficient values do not vary significantly from one sample to the other. Therefore, the relationship of relative abundance between lineal and multiple connected CO could be estimated integrating the intensities of signals at 2094, 1975 and $1940 \, cm^{-1}$ expressed as follows:

$$\tau = \frac{I_{2094}}{I_{1975} + I_{1940}}$$

In the case under discussion, the observed τ for Pd/Al$_2$O$_3$ and Pd-Mo/Al$_2$O$_3$ samples was 0.5 and 0.7, respectively. These results suggest that molybdenum addition generates a decrease of multiple connected species on palladium. This observation could be explained assuming a Pd particle encapsulation by molybdenum species, and this result is in agreement with the results of H$_2$ chemisorption. Thus, when the fraction of exposed Pd decreases, the adsorption of linear CO is also favored.

According to Peri [37], characteristic absorption bands for CO on molybdenum appear 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 for Mo/Al$_2$O$_3$ sample. As shown in Fig. 3, no band corresponding to molybdenum for Pd-Mo/Al$_2$O$_3$ catalyst was found either. This would be due to the absence
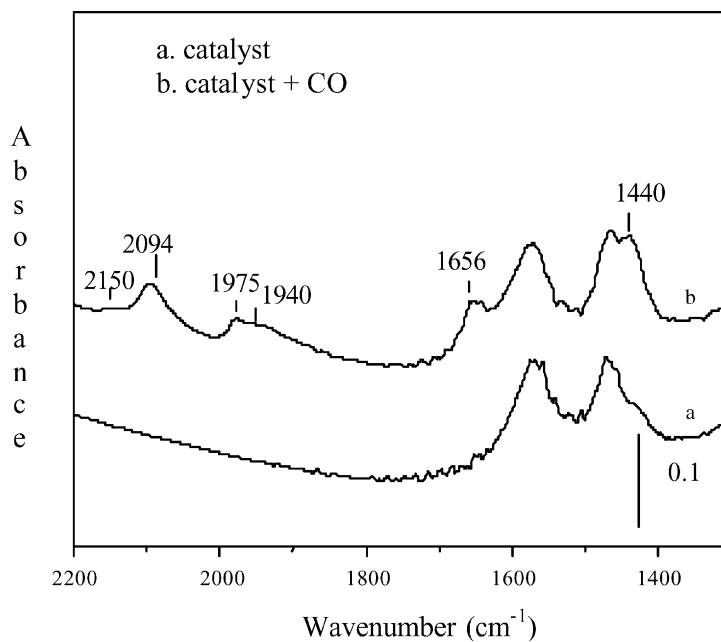
Fig. 2. FTIR spectra of CO absorbed on Pd/Al$_2$O$_3$ sample. References: (a) catalyst; (b) 25 Torr of CO.
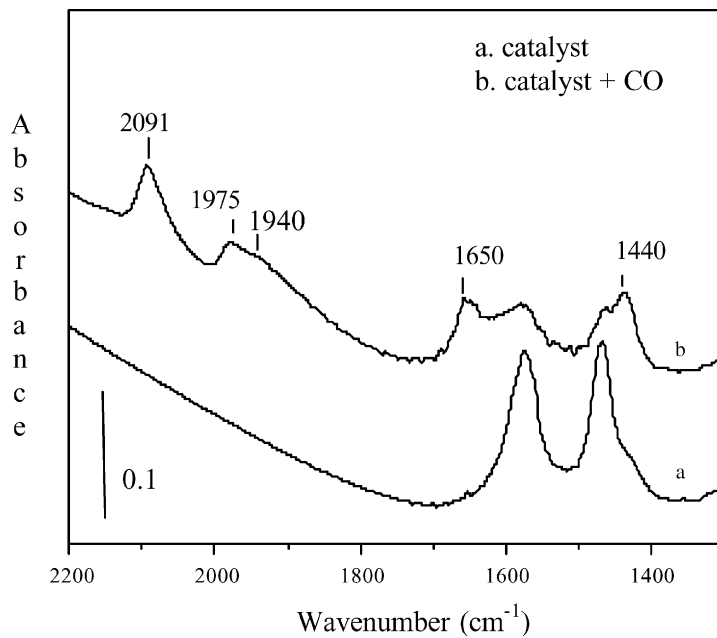

Fig. 3. FTIR spectra of CO absorbed on Pd-Mo/Al$_2$O$_3$ sample. References: (a) catalyst; (b) 25 Torr of CO.

of partially reduced species. No CO adsorption was observed on calcined Mo/alumina catalysts [37].

Fig. 4 shows the FTIR spectrum of Pd/Al$_2$O$_3$ after exposure to NO at room temperature, followed by evacuation at different temperatures. The bands at 1465, 1314 and 1228 cm^{-1} have been reported for NO adsorption on alumina due to nitrate and nitrite complexes [38]. The broad band observed around 1760 cm^{-1} was assigned to linear NO adsorbed on a-top site over Pd in the Pd/Al$_2$O$_3$ catalysts [39,40]. The intensity of this band increased with temperature. An intensity increase of the signal is observed at 1573 cm^{-1}, which can be attributed to NO threefold bridged [38]. This band diminishes with the temperature and presents its maximum value at 200 °C.

The FTIR spectra of Mo/Al$_2$O$_3$ after exposure to NO (not presented here) do not show any characteristic signal for NO adsorbed on Mo species, at 1723 or 1819 cm^{-1} [37,40,41]. It is possible to presume that reduction temperature was too smooth, since Mo^{+6} does not adsorb NO [41]. The Mo content in Mo/Al$_2$O$_3$ catalyst is low (0.71%), originating a stronger interaction

with the support and making difficult its reducibility [26–28].

The infrared spectra of NO adsorption on Pd-Mo/Al$_2$O$_3$ catalyst are presented in Fig. 5. The IR spectra basically show the same bands present on Pd/Al$_2$O$_3$. The band at 1742 cm^{-1} corresponding to NO linear presents its maximum intensity at 100 °C, and diminishes with temperature. But the Mo addition led to the suppression of the bands attributed to the adsorption of NO threefold bridged on Pd. This result may be of consequence to the smaller space for the adsorption due to the decoration of palladium particles by molybdenum species.

Hoost et al. [42] found a decreasing NO adsorption on La-promoted Pd/Al$_2$O$_3$ catalyst, which was attributed to either the coverage of Pd particles with LaO$_x$ patches or to an increase in the NO dissociation. Noronha et al. [9] did not observe any bands attributed to the adsorption of NO on Pd in Pd/MoO$_3$/Al$_2$O$_3$ catalyst with 11.6 wt.% of Mo and 1 wt.% of Pd.

Summing up, on the Pd-Mo/Al$_2$O$_3$ catalyst, the decrease of H$_2$ adsorption, the suppression of the adsorption of threefold bridged NO–Pd and the increase
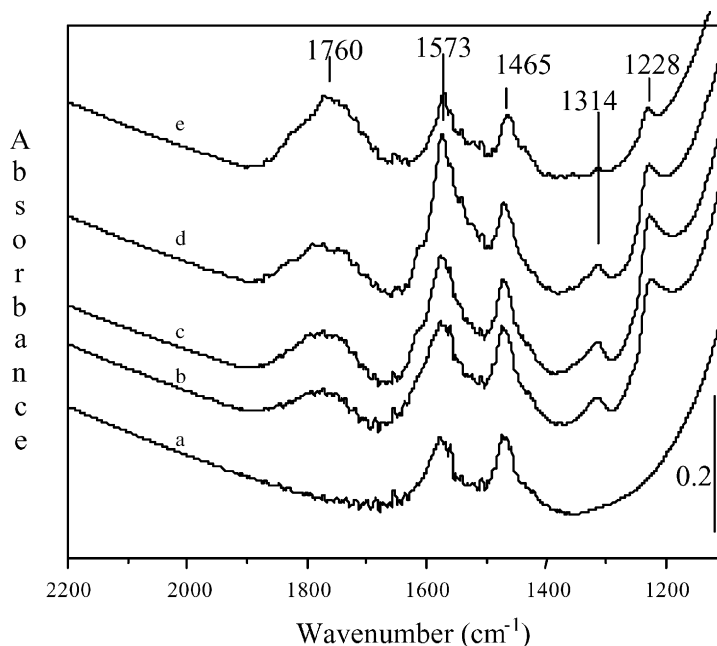

Fig. 4. FTIR spectra of NO absorbed on Pd/Al$_2$O$_3$ sample. References: (a) catalyst; (b) 25 Torr of NO at 25 °C; (c) 100 °C; (d) 200 °C; (e) 300 °C.
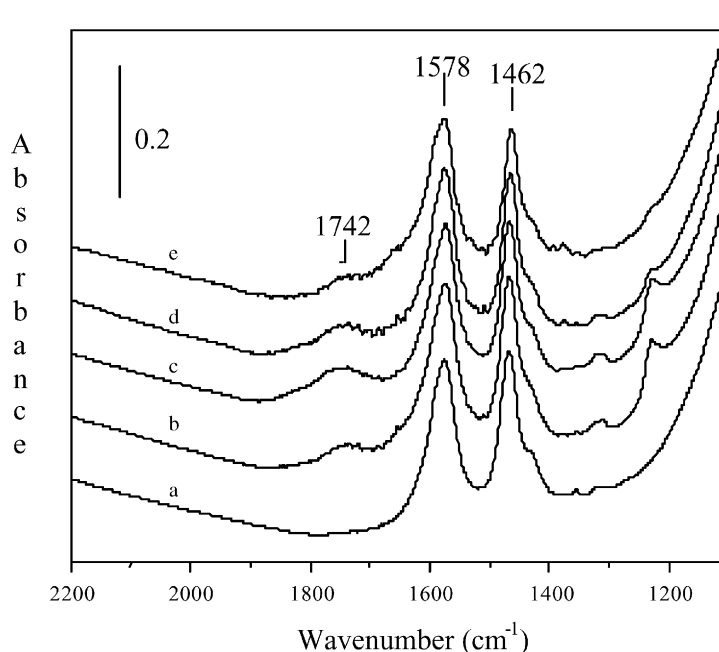
Fig. 5. FTIR spectra of NO absorbed on Pd-Mo/Al$_2$O$_3$ sample. References: (a) catalyst; (b) 25 Torr of NO at 25 °C; (c) 100 °C; (d) 200 °C; (e) 300 °C.

of the linear/bridged CO ratio are consistent with the decoration of Pd surface by Mo species.

3.2. Catalytic activity measurements

Fig. 6 shows the NO conversion as a function of reaction temperature. Pure γ-alumina was initially tested as catalyst for NO reduction in the presence of methane. The experimental data show that un-promoted alumina exhibits very low activity for the reduction of NO.

The deposition of an active metal on alumina enhances the activity. Over Pd/Al$_2$O$_3$ catalyst, the conversion of NO increases from 300 °C and it reaches 87% at 500 °C. The Mo/Al$_2$O$_3$ catalyst showed low activity, it was 20% at 500 °C. The bimetallic samples have better catalytic performance for the reduction of NO than that of monometallic palladium sample, and complete conversion of NO was observed over Pd-Mo catalysts at 450 °C.

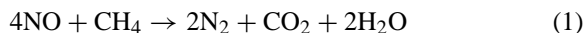Fig. 7 shows the methane conversion as a function of reaction temperature. The Mo/Al$_2$O$_3$ catalyst did

not present activity for methane, and the same was observed for pure γ-alumina. The total conversion of NO was achieved at 450 °C over bimetallic catalysts and at 500 °C for Pd/Al$_2$O$_3$ sample.

The catalyst's weight was adjusted in order to keep the weight of palladium in the different experiments constant. When Mo was added on Pd/Al$_2$O$_3$ catalyst, CH$_4$ conversion activity was only slightly better.

The activities of the bimetallic catalysts do not depend on the manner of impregnation.

Figs. 8 and 9 show the distribution of products and reactants as a function of reaction temperature when the reaction is carried out on Pd/Al$_2$O$_3$ and Pd-Mo/Al$_2$O$_3$ samples.

The main products for the NO–CH$_4$ reaction were N$_2$, N$_2$O and CO$_2$. For the purpose of discussing the product distribution of the CO–CH$_4$ reaction system, it is sufficient to consider the two following stoichiometry equations:

$$4NO + CH_4 \rightarrow 2N_2 + CO_2 + 2H_2O \tag{1}$$

$$8NO + CH_4 \rightarrow 4N_2O + CO_2 + 2H_2O \tag{2}$$
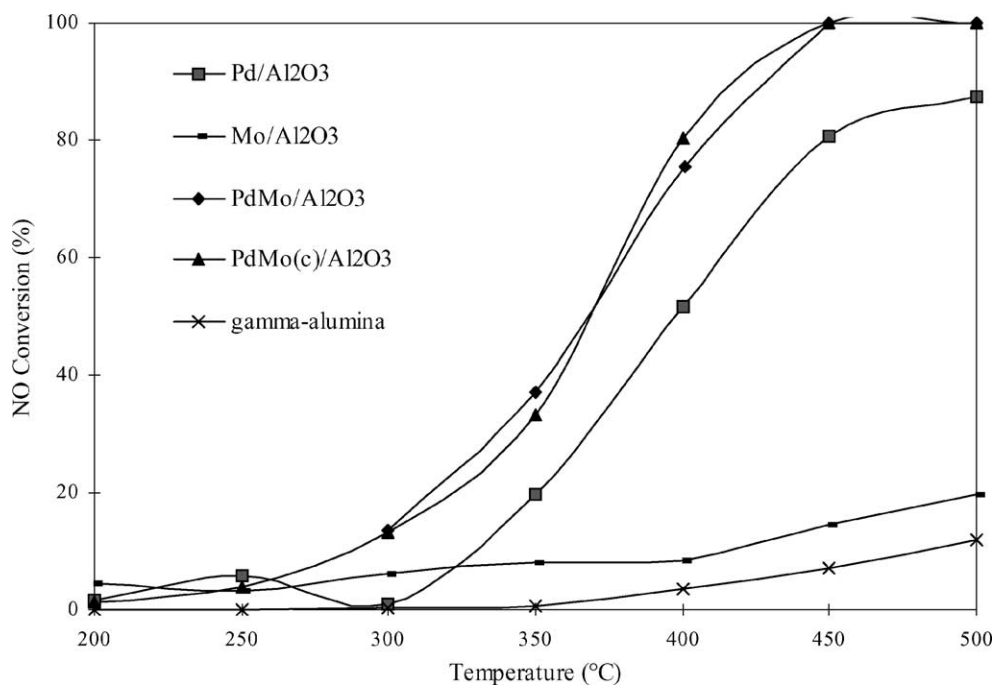
Fig. 6. NO conversion as a function of reaction temperature. $SV = 4 \times 10^4$ feed mol/h mol Pd.
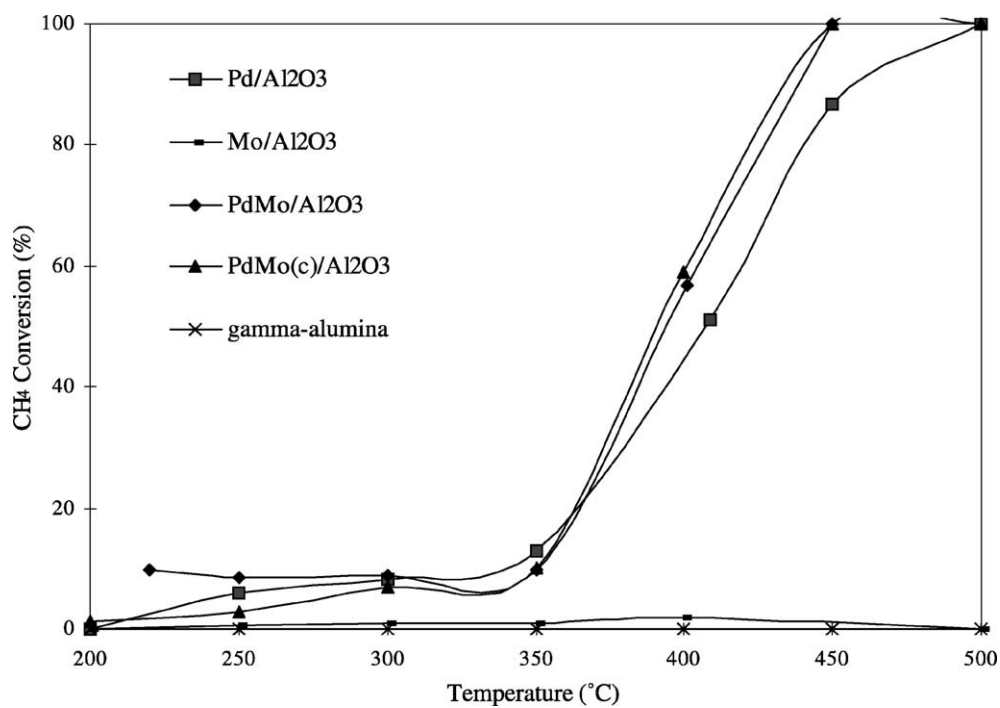

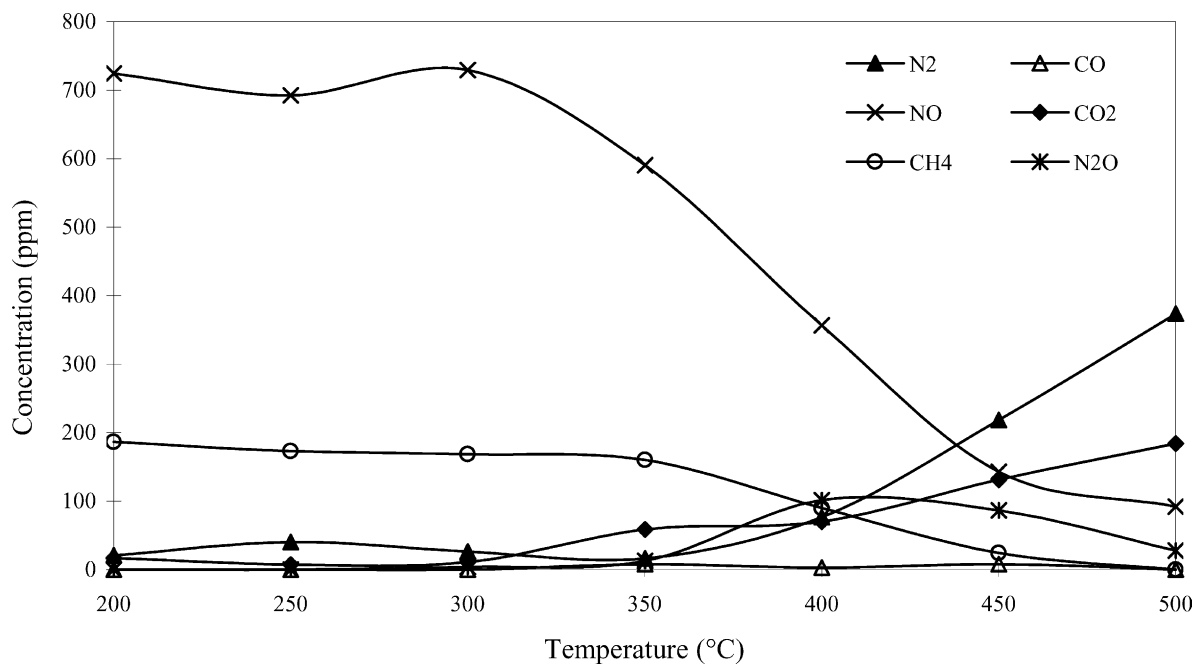Fig. 7. Methane conversion as a function of reaction temperature. $SV = 4 \times 10^4$ feed mol/h mol Pd.

Fig. 8. Products and reactants distribution as a function of reaction temperature for Pd/Al$_2$O$_3$ catalyst. SV $= 4 \times 10^4$ feed mol/h mol Pd.
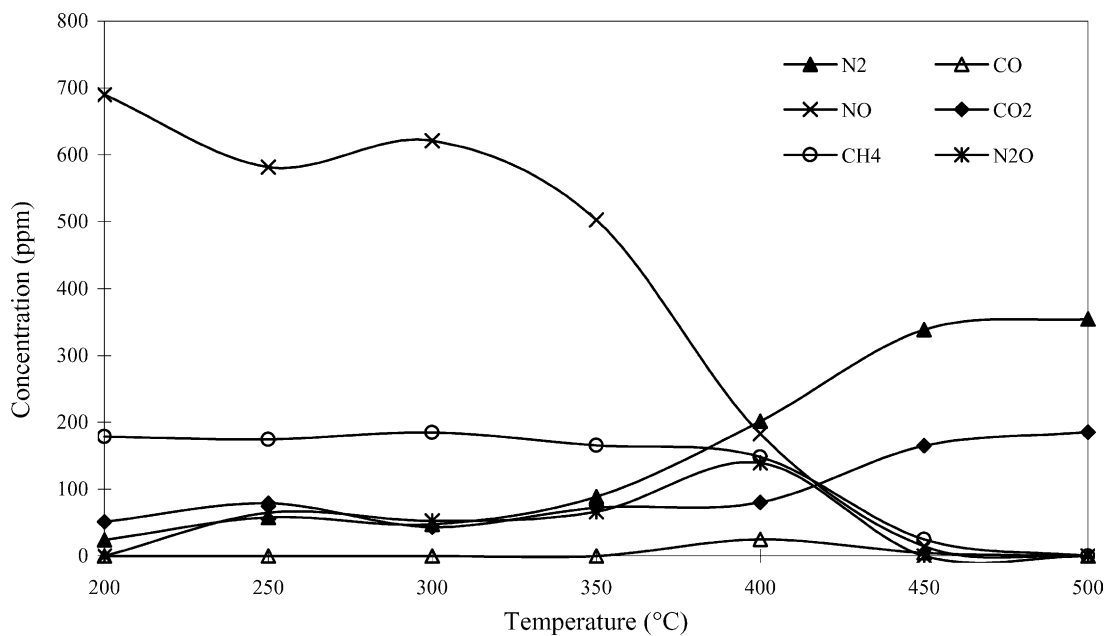

Fig. 9. Products and reactants distribution as a function of reaction temperature for Pd-Mo/Al$_2$O$_3$ catalyst. SV $= 4 \times 10^4$ feed mol/h mol Pd.

Over Mo/Al$_2$O$_3$ sample, according Figs. 5 and 6, the reaction would be:

$$2NO \rightarrow N_2 + O_2 \tag{3}$$

$$2NO \rightarrow N_2O + \tfrac{1}{2}O_2 \tag{4}$$

In all the cases, the nitrogen balance closed at 7% on the basis of assuming that species present were N$_2$ and N$_2$O (but it does not allow to discard the possible formation of NO$_2$ or NH$_3$).

When the reaction was carried out on Pd/Al$_2$O$_3$ sample, the maximum formation of N$_2$O occurred in the temperature range of 400–450 °C. Nitrogen production started when the reaction temperature reached 350 °C and it continued increasing until 400–500 °C. The formation of N$_2$O was a little greater than N$_2$ production, closely at 400 °C.

The catalytic activity of the Pd-Mo/Al$_2$O$_3$ for the reduction of NO with methane as a function of temperature is presented in Fig. 9. The concentration of N$_2$O went through a maximum at 400 °C. Unlike N$_2$O, the amount of N$_2$ increased constantly along with tem-

perature. The total selectivity to N$_2$ was observed at 450 °C.

The formation of CO only was detected at 400 °C for Pd-Mo/Al$_2$O$_3$ (~25 ppm) whereas for the Pd/Al$_2$O$_3$ sample CO was formed between 350 and 450 °C (~8 ppm).

Comparing the catalysts, in the bimetallic sample, three conclusions emerge:

1. NO production begins at lower temperatures, but from 450 °C its formation is not significant.
2. The formation of N$_2$ always is greater than N$_2$O production.
3. Total conversion of NO is reached at 450 °C with total selectivity to N$_2$.

In order to study the effect of the temperature pre-treatment on the NO–CH$_4$ reaction, new samples were reduced at 300 °C (during 30 min), at 500 °C (for 2 h) under flow of 5% H$_2$ in Ar, or oxidized at 500 °C (for 2 h). The catalysts were then purged under He flow. The studied samples were further exposed
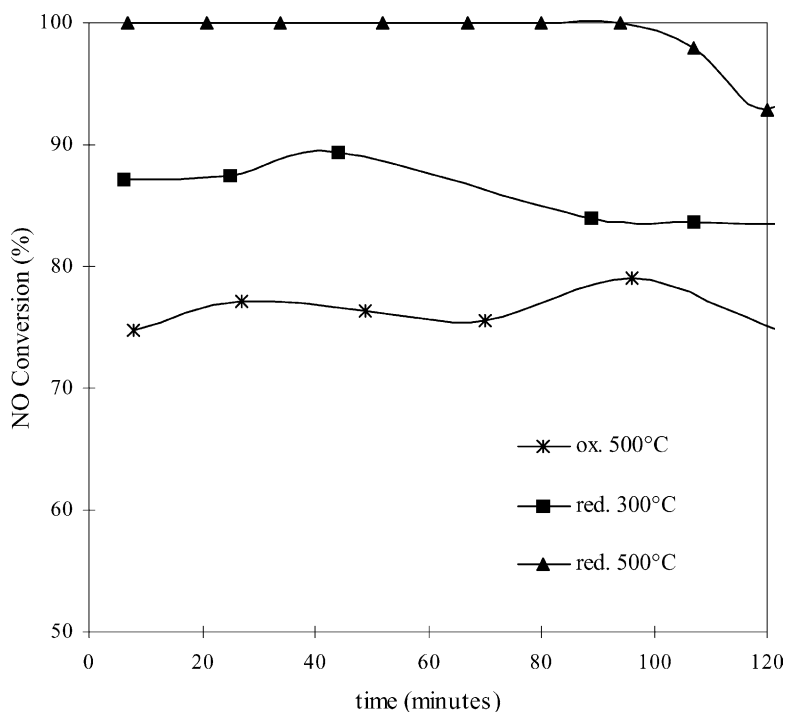

Fig. 10. NO conversion over Pd/Al$_2$O$_3$ catalyst (after different pre-treatments) at 500 °C. SV $= 4 \times 10^4$ feed mol/h mol Pd.
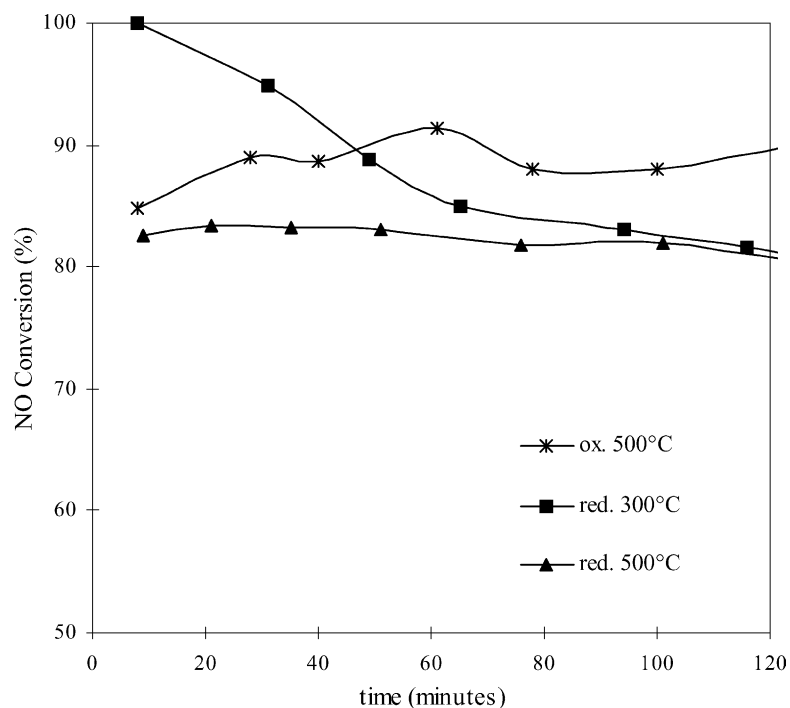
Fig. 11. NO conversion over Pd-Mo/Al$_2$O$_3$ catalyst (after different pre-treatments) at 500 °C. SV $= 4 \times 10^4$ feed mol/h mol Pd.

to the reaction mixture at 500 °C for 2 h. Samples of reaction products were taken regularly.

Figs. 10 and 11 present NO conversion as a function of the reaction time. Again, since the same palladium mass was used in the reaction, relative performances will be discussed.

Both catalysts present total methane conversion after the pre-treatments, except when the reaction was carried out over Pd-Mo/Al$_2$O$_3$ catalyst pre-reduced at 500 °C (methane conversion was 95%). Methane conversion is stoichiometric only on the surface of Pd/Al$_2$O$_3$ catalyst pre-reduced at 500 °C, according to the reactions mentioned above ((1) and (2)).

When the samples were pre-reduced at 300 °C, Pd-Mo/Al$_2$O$_3$ catalyst exhibited at first total NO conversion, which then diminished gradually. After 120 min, the activity was similar to the one displayed by the monometallic sample. For Pd/Al$_2$O$_3$ catalyst, the conversion of NO fluctuated near 86%. After reduction at 500 °C, Pd/Al$_2$O$_3$ catalyst presented total conversion during 90 min, and then it decreased to

96% for another 120 min. In bimetallic sample, the NO conversion was lower, close at 85%.

When samples were oxidized, NO conversion over Pd/Al$_2$O$_3$ catalyst was ∼77% and for Pd-Mo/Al$_2$O$_3$ it was initially 83% and then increased slightly (∼90%).

The most significant differences are the following:

- When the samples are reduced at 500 °C, the molybdenum addition diminishes the activity.
- When the samples are reduced at 300 °C, the bimetallic catalyst initially presents greater conversion than the monometallic sample, but after 2 h of reaction, both catalysts exhibited equal activity.

4. Discussion and conclusions

Characterization by TPR, hydrogen chemisorption and FTIR of CO and NO adsorbed indicate that palladium physicochemical properties are altered by an effective interaction with molybdenum. The results suggest a decoration effect of Mo species over Pd parti-

cle. This interaction appears to be responsible for the observed modification in NO activity.

After a reducing treatment at 500 °C, methane and NO conversions over Pd/Al_2O_3 sample were total. The only detected products were N_2 and CO_2. These observations suggest that the NO–CH_4 reaction on Pd catalysts takes place via NO adsorption and dissociation on metallic Pd sites forming N_2, whereas the generated oxygen is retained in the catalyst surface and is removed by reaction with CH_4, regenerating the active sites. These results are consistent with previous works of Burch and Scire [43].

After an oxidizing pre-treatment, NO conversion immediately reaches a 77% steady-state value, while methane conversion is complete. On the oxidized surface, the reaction begins with the oxidation of methane. The removal of oxygen through reaction by methane is fast at this temperature, thus leading to an increased availability of sites for the adsorption and dissociation of NO [44]. The value of conversion for NO in stationary state is smaller than the one obtained after reduction at 300 and 500 °C. This suggests that a different number of palladium atoms participate in the reaction. The methane conversion is more than necessary to consume all the oxygen generated by the decomposition of NO. It could be thought that the catalyst accumulates oxygen during the oxidizing treatment. It is known that O_2 is an oxidant more powerful than NO and it could be cause of the non-stoichiometric methane consumption. Therefore, as the reaction advances and the available oxygen reacts, the activity would have to achieve a level of stoichiometric stationary state. Methane and NO conversions, however, are not modified in 120 min. The water steam produced during the methane oxidation constitutes an oxygen source at 500 °C. Consequently, it can be considered that the reactions of reformed with steam (reactions (5) and (6)) are simultaneous with the reduction of NO with methane (reactions (1) and (2)).

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \tag{5}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{6}$$
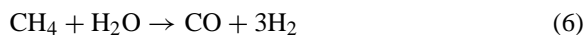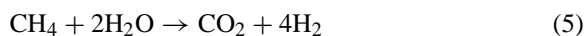
According to reaction (1), when the NO conversion is 77%, it is generated an amount of water sufficient to eliminate the excess of methane by reaction (5).

Reaction (6) is not considered because no appreciable formation of CO was observed.

These results are in agreement with those reported by Mouaddib et al. [45]. They observed that Pd/alumina catalysts could be active in the reformed reaction of methane with steam at as low temperature as 400 °C, in deficient oxygen atmospheres. Pisanu [44] studied the reduction of NO by C_2H_6 at 400 °C over Pd/α-Al_2O_3 catalyst. She found that the reactions of reformed with steam are promoted on the surface of pre-oxidized catalyst, as a result of a dispersion or reconstruction of oxide of palladium associated to the reaction of oxidation of C_2H_6.

When Pd/Al_2O_3 catalyst is pre-reduced at 300 °C, the steady-state conversion of NO is 86%. This value was smaller than that one presented by the same catalyst pre-reduced at 500 °C. This could be indicating that the oxidation degree of Pd, and therefore the number of active sites for NO adsorption, depends on the reducing temperature of the pre-treatment. Although TPR study indicated that palladium is in metallic state at temperatures greater than 100 °C, FTIR spectrum of adsorbed CO indicated the existence of Pd^{2+}–$C\equiv O$ for same sample reduced at 200 °C. It also has to be considered that different activities (Fig. 10) could be the consequence of differences in the conformation of the surface of the catalyst due to the reduction treatments. The adsorption and dissociation of NO seem to be sensitive to the presence of edges and steps on the surface [46–48]. When the catalyst was pre-reduced under smooth conditions (300 °C for 30 min), the reaction of reformed by steam would also be present, although in a lesser extent.

Results of characterization performed at different temperatures suggest the blockage of the Pd surface by the molybdenum oxide species. When the bimetallic catalyst is reduced at 500 °C, this effect is severe, and it originates a diminution in the catalytic activity of the sample.

The fractions of palladium exposed for Pd/Al_2O_3 and Pd-Mo/Al_2O_3 samples are 0.55 and 0.45, respectively. These values of dispersion were obtained with the catalysts previously reduced at 500 °C. Since the same palladium mass was used in reaction, Pd-Mo/Al_2O_3 sample exposes a metallic surface 18.2% lower than Pd/Al_2O_3, and its conversion is smaller in 17%.

Molybdenum, on the other hand, is the cause of the greater initial activity for NO observed on the catalyst

pre-reduced at $300\,^{\circ}$C. During the reduction treatment of Pd-Mo samples, MoO_x species are formed. These sites are proposed in [10] as preferred for the adsorption and dissociation of NO, this being the first step of the mechanism postulated for the NO–CH$_4$ reaction.

But, during the course of the reaction, the bimetallic sample is deactivated. The MoO_x sites would be poisoned with the O formed during the dissociation of NO. The oxygen taken up by the MoO_x species does not seem to be removed by methane.

When Pd-Mo sample was pre-reduced at $300\,^{\circ}$C, the activity for NO conversion after 2 h in reaction was similar to the displayed by Pd/Al$_2$O$_3$ catalyst. According to CO and NO FTIR results (performed at $200\,^{\circ}$C), Pd particles are partially covered by Mo species. Nevertheless, Pd seems to be as active in this case (Pd-Mo sample) as it is on monometallic Pd where the dispersion is higher. The modifications in the catalytic performance should not be attributed to the simple fact that more active sites are available on the binary sample than in sample Pd/alumina. A synergetic effect between palladium and Mo should be invoked.

Acknowledgements

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