Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 133–135 (2008) 475–479
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Direct decomposition of nitric oxide on bimetallic catalysts: Effect of metals bonding

Julia María Díaz Cónsul [a], Carlos Alexandre Peralta [a], Juan A.C. Ruiz [b], Heloise O. Pastore [b], Ione Maluf Baibich [a,*]

[a] *Instituto de Química, Universidade Federal do Rio Grande do Sul, CP 15003, 91501-970, Porto Alegre, RS, Brazil*
[b] *Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13083-970, Campinas, SP, Brazil*

Available online 4 January 2008

Abstract

Pd-Mo and Mo-Pd bimetallic catalysts supported on Al_2O_3-thin-layer-modified SiO_2 and Si-MCM-41 were investigated for the direct decomposition of nitric oxide. The catalysts were prepared from [$Pd(acac)_2$] and [$Mo(CO)_6$]. The Al_2O_3/SiO_2 and Al_2O_3/Si-MCM-41 supported catalyst surface areas did not change significantly upon metal impregnation. Temperature programmed reduction profiles suggest the presence of large particles that are easily reduced. Consequently, low palladium dispersions were found. All the catalysts studied were active in the NO decomposition reaction, Mo-Pd catalysts being the most selective.

Keywords: NO_x; MCM-41; Pd-Mo catalyst; NO decomposition

1. Introduction

The emission of pollutant gases from combustion in engines and industrial ovens has become an important issue when pollution is the subject [1]. Several types of catalysts have been developed to convert NO_x [2–10] to less aggressive compounds. Several studies show the role of the support on the catalyst activities [11]. Mesoporous silicas as MCM-41 have been shown to be interesting materials due mainly to properties such as uniform pore size distributions, high superficial areas and thermal stabilities [12,13]. Additionally, with the incorporation of alumina, it is possible to combine desired properties and to obtain a special support with even higher thermal stabilities and better acidic properties [14,15].

Among the metals, palladium is an attractive catalyst since has the capability of being active either for CO and hydrocarbon oxidations and/or NO reduction [16–19]. However, the high retention of oxygen leads to partial NO decomposition to N_2 and N_2O [20–22]. To enhance the selectivity of the decomposition reaction of NO to N_2 and O_2, a second metal is incorporated onto the support promoting a bimetallic interaction [23,24]. Our research group has recently compared several catalysts prepared with Pd in Al_2O_3-thin-layer-modified SiO_2 and Si-MCM-41 supports [19]. Additionally, we have developed a technique to incorporate molybdenum and tungsten that uses photochemical activation of metalcarbonyls to produce metallic species in low oxidation state [25,26].

In the present work, bimetallic Pd-Mo catalysts were prepared from [$Pd(acac)_2$] and [$Mo(CO)_6$] precursors activated photochemically and deposited on Al_2O_3-thin-layer-modified SiO_2 and Si-MCM-41. The catalysts were characterized by BET surface areas, hydrogen chemisorption, TPR, X-ray diffraction, ICP-OES and tested in the direct NO decomposition reaction.

2. Experimental

2.1. Synthesis of Si-MCM-41 [27]

Reaction mixtures were prepared by dissolving the required amount of sodium silicate (Nuclear, $Na_2SiO_3{\cdot}5H_2O$), in distilled water to give a 1.5 mol L^{-1} solution. To this clear solution, an aqueous suspension of cetyltrimethylammonium bromide

* Corresponding author. Tel.: +55 51 33086304; fax: +55 51 33087304.
E-mail address: ione@iq.ufrgs.br (I.M. Baibich).

0920-5861/$ – see front matter
doi:10.1016/j.cattod.2007.11.035

(CTABr) (10.11 g of CTABr in 20.5 mL of water) was added and aged for 24 h at room temperature. The mixture was stirred and the pH was slowly lowered from 13.40–13.60 to 10.80 by the addition of concentrated acetic acid. The suspension was then stirred for 4 h at 347–349 K. The final gel composition was: SiO_2:Na_2O:0.25$(CTA)_2O$:0.5HBr:100H_2O. The reaction mixture was transferred to a Teflon-lined stainless steel autoclave and placed in a pre-heated oven at 423 K, for a period of 66 h. After the hydrothermal treatment, the samples were filtered and thoroughly washed with distilled water. The solids were air dried and sieved to 0.106 mm. To eliminate the organic part of these materials, a solvent extraction was performed in a Soxhlet system with 0.30 mol L^{-1} HCl solution in 50/50 ethanol/heptane, at 363 K, over a period of 40 h. Thereafter, the samples were activated by heating from room temperature to 773 K at a rate of 5 K min^{-1}, under dry argon and then maintaining at that temperature for 20 h under dry oxygen.

2.2. Modification of the support surfaces by grafting reaction of a Al_2O_3 thin layer [19]

Aluminum oxide was immobilized either on the support by immersing 10 g of silica gel (Merck) or Si-MCM-41 (synthesized as explained above), previously heated under vacuum at 423 K for 8 h, in 50 mL of a 0.14 mol L^{-1} solution of aluminum isopropoxide in dry toluene. The mixture was heated at reflux temperature under an argon atmosphere for 24 h with mechanical stirring. The resulting solid was filtered under an inert atmosphere in a Schlenk apparatus and washed with warm toluene, ethanol and diethyl ether. The remaining solvent was removed under vacuum at 383 K. In order to promote the Al–O–R bond hydrolysis, the modified supports were immersed in deionized water for 4 h, at room temperature. The mixture was filtered, washed with water and finally dried under vacuum at 393 K. The grafting reaction was repeated twice to obtain an Al_2O_3 layer (5% of Al) on the silica gel and on the Si-MCM-41 surfaces [15]. These samples were referred to as Al_2O_3/SiO_2 and Al_2O_3/Si-MCM-41 respectively.

2.3. Pd incorporation [19]

The palladium catalysts were prepared by impregnation of the support (SiO_2, Al_2O_3/SiO_2 or Al_2O_3/Si-MCM-41) with a toluene solution of palladium acetylacetonate (8×10^{-3} g Pd mL^{-1}). The support was previously dried and activated at 723 K in air for 3 h followed by another hour at the same temperature under vacuum. The solid (2 g) and the solution (7.5 mL) were left in contact for 24 h at room temperature. The liquid was removed; the solid was dried under vacuum, activated in air at 473 K for 2 h and finally reduced with hydrogen under the same conditions. The palladium metal loading was adjusted to 1 wt.%.

For the preparation of Si-MCM-41 supported catalysts, palladium(II) acetate (98%) dissolved in acetone was transferred to an acetone suspension of the molecular sieves and the mixture was stirred for 6 h and evacuated until the excess of acetone was eliminated. After drying at 383 K, the sample was heated at 773 K at a rate of 5 K min^{-1} for 4 h, under a flow of oxygen.

2.4. Molybdenum incorporation

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

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

2.5. Catalysts characterization

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

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

2.6. Catalytic activity

Catalytic experiments with NO were carried out in a fixed-bed quartz reactor. Prior to reaction, the catalysts were reduced *in situ* at 573 K for 4 h. The NO decomposition reaction was studied as a function of time at 723 K, using a feed mixture containing 500 ppm of NO in an argon background. The flow rate was adjusted to 120 cm^3 min^{-1} and the space velocity was 30,000 h^{-1}. The effluent gases were analyzed by a FTIR MB100-BOMEM Spectrometer equipped with a multiple reflection gas cell (7.0 m path length and 2.1 L volume). The NO, NO_2 and N_2O stretching bands at 1955–1790, 1658–1565 and 2266–2159 cm^{-1} respectively, were monitored. In order to calculate the NO conversions from the IR data, a method using the measured absorbance values [28] was used to determine the NO concentration at the entrance of the gas IR cell (reactor exit).

Table 1
BET surface areas, pore volume and pore diameter results

Catalysts	BET specific surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore diameter (nm)
Al_2O_3/SiO_2	233	0.38	–
$Pd/Al_2O_3/SiO_2$[a]	245	0.48	–
$Mo/Al_2O_3/SiO_2$	236	0.50	–
$Pd\text{-}Mo/Al_2O_3/SiO_2$	238	0.18	–
$Mo\text{-}Pd/Al_2O_3/SiO_2$	254	0.85	–
Al_2O_3/Si-MCM-41	562	0.52	2.81
Pd/Al_2O_3/Si-MCM-41[a]	531	0.55	3.23
Mo/Al_2O_3/Si-MCM-41	567	–	–
$Pd\text{-}Mo/Al_2O_3$/Si-MCM-41	548	0.55	3.16
$Mo\text{-}Pd/Al_2O_3$/Si-MCM-41	540	0.51	3.27

[a] From reference [13].

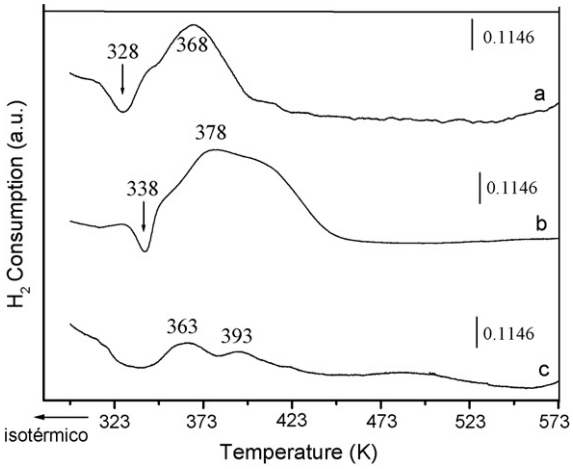

Fig. 1. TPR profiles of palladium catalysts: (a) $Pd/Al_2O_3/SiO_2$, (b) Pd/SiO_2 and (c) Pd/Al_2O_3/Si-MCM-41.

3. Results and discussion

The catalysts prepared on Al_2O_3/SiO_2 as support presented surface area around 245 $m^2\ g^{-1}$ even after Pd and/or Mo impregnation (Table 1). The surface areas of the catalysts prepared from Al_2O_3/Si-MCM-41 were approximately 550 $m^2\ g^{-1}$ with a slight tendency to decrease with metal incorporation.

In Table 2 it can be seen that palladium loadings on Al_2O_3/SiO_2 were higher than on Al_2O_3/Si-MCM-41 probably due to the fact that SiO_2 has larger pore diameters (8 nm) than Si-MCM-41 (3 nm), which makes it easier for the $[Pd(acac)_2]$ molecule to reach the anchoring sites. On the other hand, for Mo the loadings on Al_2O_3/Si-MCM-41 were in general much higher than on Al_2O_3/SiO_2 reflecting the interaction that is known to occur between this type of compound and the support: the compound interacts with Lewis acid sites through the oxygen of the carbonyl [25]. As in Si-MCM-41, the aluminum Lewis acid sites should be more accessible because of the higher surface area, consequently this support retains more molybdenum than SiO_2.

Temperature programmed reduction profiles (Fig. 1) are analogous for all Pd catalysts. In general, we can observe a hydrogen peak at room temperature due to PdO reduction (Table 2), a negative peak due to palladium hydride decomposition (328–338 K) and a large band that appears either as a shoulder or two peaks in the 363–393 K temperature range, possibly due to PdO particles strongly bound to the support.

Furthermore, high degrees of reduction were obtained (Table 2) suggesting the presence of easily reduced large particles. The presence of the hydride peak is also evidence for large particles [20].

The TPR profiles for the bimetallic catalysts (Fig. 2) present the same peaks due to palladium in the ranges from 328 to 338 K and from 363 to 393 K. Additionally, there are peaks at 513 and 593 K, that are not present in Fig. 1 and that are not usual for Pd catalysts that might be attributed to Pd-Mo interaction. These species would interact more strongly with the support [20]. Konopny et al. [29] reported the occurrence of bimetallic interaction between Pd and Mo in $PdMo/Al_2O_3$ catalysts. Noronha et al. [30] found that the palladium addition promoted mainly the reduction of Mo^{6+} to Mo^{4+}, which suggests the existence of a strong interaction between Pd^0 and a Mo oxide.

The catalyst $Mo/Al_2O_3/SiO_2$ presented a reduction peak at 863 K due to MoO_3 reduction. Hydrogen chemisorption showed low dispersion values (Table 2) for the bimetallic catalysts in comparison with the monometallic ones. This result suggests that molybdenum atom inhibits the reaction of the exposed palladium atoms even when it is firstly deposited on the support. In this case, Mo probably migrates to the palladium

Table 2
TPR, H_2 chemisorption and chemical analysis results

Catalysts	Hydrogen consume (μmol/g cat.)		Pd reducibility (%)	Pd dispersion (%)	Pd (wt.%)	Mo (wt.%)
	Room temperature	During temperature heating				
$Pd/Al_2O_3/SiO_2$[a]	69	20	96	40	0.98	–
$Mo/Al_2O_3/SiO_2$	4	15	80	–	–	0.23
$Pd\text{-}Mo/Al_2O_3/SiO_2$	85	4	98	6	0.98	0.17
$Mo\text{-}Pd/Al_2O_3/SiO_2$	84	4	100	7	0.91	0.21
Pd/Al_2O_3/Si-MCM-41[a]	45	5	55	70	0.75	–
Mo/Al_2O_3/Si-MCM-41	-	–	–	–	–	0.67
$Pd\text{-}Mo/Al_2O_3$/Si-MCM-41	45	12	81	12	0.75	0.36
$Mo\text{-}Pd/Al_2O_3$/Si-MCM-41	52	20	95	19	0.80	1.56

[a] From reference [13].

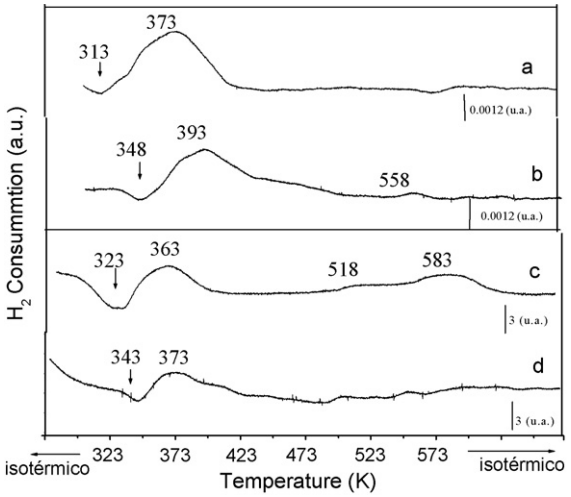

Fig. 2. TPR profiles of bimetallic catalysts: (a) Pd-Mo/Al_2O_3/Si-MCM-41, (b) Mo-Pd/Al_2O_3/Si-MCM-41, (c) Pd-Mo/Al_2O_3/SiO_2 and (d) Mo-Pd/Al_2O_3/SiO_2.

exposed sites with the temperature treatment. Tonetto et al. [20] and Konopny et al. [29] reported similar results for PdMo-alumina catalysts. These authors observed a decrease in the hydrogen chemisorption capacity of palladium due to molybdenum addition.

The catalytic tests for NO decomposition showed that all the catalysts prepared in this work show activity for the NO reaction (Figs. 3 and 4). As usual for Pd catalysts, the activity was maintained at 100% conversion over a period of time and after it decomposes concomitantly to N_2O formation, that occurs because of oxygen retention by Pd [20]. The catalyst Pd-Mo/Al_2O_3/SiO_2 remains for a longer time at 100% conversion, but the catalysts Mo-Pd/Al_2O_3/SiO_2 had the highest activity above 200 min, remaining active after all catalysts had deactivated. Furthermore, the catalysts Mo-Pd (Mo was deposited initially) were the most selective, signifying that there was a lower degree of N_2O formation compared with catalysts where Pd was deposited initially (Pd-Mo). Even having low dispersion values, meaning inhibition of the palladium exposed sites, these bimetallic catalysts presented high activity, which is not due to the loss of dispersion as

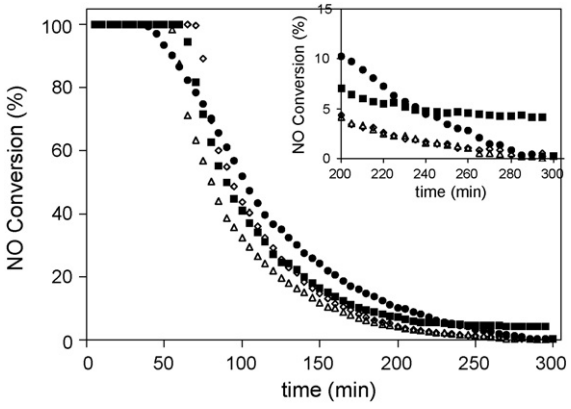

Fig. 3. NO conversion as a function of reaction time at 723 K. (◇) Pd-Mo/Al_2O_3/SiO_2, (■) Mo-Pd/Al_2O_3/SiO_2, (△) Pd-Mo/Al_2O_3/Si-MCM-41, (●) Mo-Pd/Al_2O_3/Si-MCM-41 (500 ppm NO/Ar, 100,000 h^{-1}).

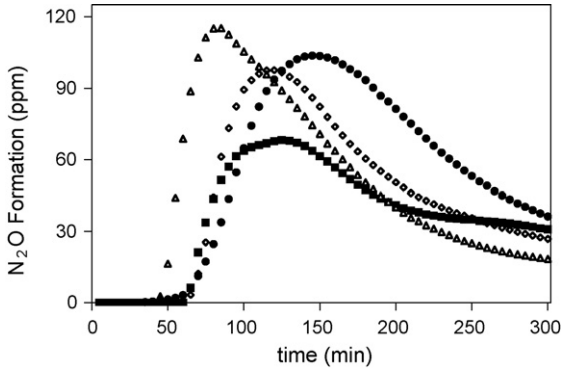

Fig. 4. N_2O formation as a function of reaction time at 723 K. (◇) Pd-Mo/Al_2O_3/SiO_2, (■) Mo-Pd/Al_2O_3/SiO_2, (△) Pd-Mo/Al_2O_3/Si-MCM-41, (●) Mo-Pd/Al_2O_3/Si-MCM-41 (500 ppm NO/Ar, 100,000 h^{-1}).

compared to what is observed with the monometallic catalysts. The interaction of the Pd and Mo atoms is probably successful in maintaining these bimetallic catalysts active for a longer period of time, even if the fractions of exposed atoms decreases, in comparison with the monometallic ones. This result is in accord with the work of Damiani and coworkers [24] who found that the addition of molybdenum results in an increase of residual activity in the bimetallic catalysts with regard to Pd/Al_2O_3 one. The interaction between Pd and Mo appears to be responsible for the observed modification in NO activity.

4. Conclusions

The surface areas of SiO_2 and Si-MCM-41 supported catalysts did not change upon metal incorporation and thermal treatments.

TPR profiles suggested the presence of large easily reduced Pd particles. Hydrogen chemisorption showed low Pd dispersion when Mo was present. The bimetallic catalysts showed additional peaks probably due to interaction between the two metals.

All the catalysts were active for NO decomposition. The Mo-Pd catalysts were the most selective in comparison with the catalysts where Pd was first deposited (Pd-Mo).

Acknowledgements

The authors acknowledge the financial support provided by CNPq, FAPERGS, FAPESP and COPESUL. We also would like to thanks Dr. John Spencer of Greenwich University, GB, for proofreading this article.

References

[1] B.J. Alloway, D.C. Ayres, Chemical Principles of Environmental Pollution, Blackie Academic & Professional, London, 1994.
[2] X. Wang, J.J. Spivey, H.H. Lamb, Appl. Catal. B: Environ. 56 (2005) 261.
[3] D. Nazimek, W. Ćwikta-Bundyra, Catal. Today 90 (2004) 39.
[4] G.D. Mariadassou, F. Fajardie, J.F. Tempère, J.M. Manoli, O. Touret, G. Blanchard, J. Mol. Catal. A: Chem. 161 (2000) 179.
[5] J. Wang, S. Ji, J. Yang, Q. Zhu, S. Li, Catal. Commun. 6 (2005) 389.

[6] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B: Environ. 39 (2002) 283.
[7] V.I. Parvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233.
[8] Y. Traa, B. Burger, J. Weitkamp, Micropor. Mesopor. Mater. 30 (1999) 3.
[9] A. Fritz, V. Pitchon, Appl. Catal. B: Environ. 13 (1997) 1.
[10] Z. Liu, S.I. Woo, Catal. Rev. Sci. Eng. 48 (2006) 43.
[11] A.M. Sica, I.M. Baibich, C.E. Gigola, J. Mol. Catal. A: Chem. 195 (2003) 225.
[12] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 357 (1992) 710.
[13] K. Wan, Q. Liu, C. Zhang, Mater. Lett. 57 (2003) 3839.
[14] P. Iengo, M.D. Serio, A. Sorrentino, V. Solinas, E. Santacesaria, Appl. Catal. A: Gen. 167 (1998) 85.
[15] J.M.D. Cónsul, I.M. Baibich, E.V. Benvenutti, D. Thiele, Quím. Nova 28 (2005) 393.
[16] M. Li, K. Seshan, L. Lefferts, Appl. Catal. B: Environ. 50 (2004) 143.
[17] S. Naito, M. Iwahashi, I. Kawakani, T. Miyao, Catal. Today 73 (2002) 355.
[18] G.D. Mariadassou, Catal. Today 90 (2004) 27.
[19] J.M.D. Cónsul, C.A. Peralta, E.V. Benvenutti, J.A.C. Ruiz, H.O. Pastore, I.M. Baibich, J. Mol. Catal. A: Chem. 246 (2006) 33.
[20] G.M. Tonetto, M.L. Ferreira, D.E. Damiani, J. Mol. Catal A: Chem. 193 (2003) 121.
[21] M. Konsolakis, I. Yentekakis, J. Catal. 198 (2001) 142.
[22] J.N. Armor, Appl. Catal. B: Environ. 01 (1992) L31.
[23] A.M. Sica, C.E. Gigola, Appl. Catal. A: Gen. 239 (2003) 121.
[24] A.M. Eberhardt, E.V. Benvenutti, C.C. Moro, G.M. Tonetto, D.E. Damiani, J. Mol. Catal. A: Chem. 201 (2003) 247.
[25] R.M.J. de Almeida, S.B.C. Pergher, C.E. Gigola, I.M. Baibich, Can. J. Anal. Sci. Spectrosc. 48 (2003) 21.
[26] I.M. Baibich, J.H.Z. dos Santos, V.C. da Silveira, C. Gigola, A.M. Sica, Can. J. Anal. Sci. Spectrosc. 43 (1998) 26.
[27] H.O. Pastore, M. Munsignatti, D.R.S. Bittencourt, M. Rippel, Micropor. Mesopor. Mater. 32 (1999) 211.
[28] R.M. Dallago, J. Schifino, I.M. Baibich, R.C. Veses, Can. J. Anal. Sci. Spectros. 49 (2004) 78.
[29] L. Konopny, A. Juan, D. Damiani, Appl. Catal. B: Environ. 15 (1998) 115.
[30] F.B. Noronha, M.A.S. Baldanza, M. Schmal, J. Catal. 188 (1999) 270.