Catalysis Today 85 (2003) 23–29

www.elsevier.com/locate/cattod

NO reduction by ethanol on Pd and Mo catalysts supported on HZSM-5

Ana Luiza S.M. Salgado [a], Fabio Barboza Passos [b], Martin Schmal [c,*]

[a] NUCAT/PEQ/COPPE, Universidade Federal do Rio de Janeiro, Caixa Postal 68502, CEP 21945-970, Rio de Janeiro, Brazil
[b] Departamento de Engenharia Química, Universidade Federal Fluminense, Rua Passos da Pátria, 156, CEP 24210-240, Niterói, Brazil
[c] NUCAT/PEQ/COPPE, e EQ, Universidade Federal do Rio de Janeiro, Caixa Postal 68502, CEP 21945-970, Rio de Janeiro, Brazil

Abstract

The reduction of NO with ethanol reaction was studied. The results showed that the Pd-Mo/HZSM5 was more active at high temperatures than Pd/HZSM-5, due to a molybdenum promotion effect. However, the selectivity to N_2 practically was not altered. Mo/HZSM-5, although less active, presented a high selectivity to N_2. Concerning the carbon species formation, both catalysts showed a high selectivity to ethylene. Some formation of acetaldehyde was observed only in the Mo containing catalysts. The catalytic results showed also that Pd-Mo/HZSM-5 is very selective to CO_2 at high temperatures.

Keywords: Pd; Mo; HZSM-5; NO reduction with ethanol

1. Introduction

Automobiles and industries are the major responsible for pollutant gases emission. NO_x is an important pollutant that contributes to acid rain and photochemical smog formation [1]. The addition of oxygenates to the gasoline is being used by several countries. In particular, ethanol is a clean fuel that reduces SO_2, aromatic compounds and soot emission. Some catalysts were investigated for the ethanol oxidation [2–6], but little attention has been paid to the reaction between the use of ethanol as a NO reductant. Mello et al. [7] investigated the NO reduction in the presence of ethanol on Pd and Pd-Mo/Al_2O_3 catalysts. The addition of Mo was not beneficial to the conversion of NO, but there was a considerably increase in the selectivity for N_2. Serban et al. [8] reported HZSM-5 was active for NO reduction with ethanol in oxidant conditions.

In this work, we have investigated the use of Pd and Mo catalysts supported on HZM-5 to the NO reduction in the presence of ethanol. Additionally, we have probed the interaction of NO and ethanol with the catalysts using temperature programmed desorption of adsorbed NO (NO TPD) and temperature programmed desorption of adsorbed ethanol (ethanol TPD) experiments.

2. Experimental

Pd/HZSM-5 was prepared by ion-exchange of a HZSM-5 (Degussa, SAR = 17.2), using a $Pd(NH_3)_2(NO_3)_2$ (Aldrich) aqueous solution. The zeolite was initially calcined at 600 °C, during 4 h. The ion exchange was performed at 80 °C during 24 h, under constant stirring. Then the samples was filtered

---

* Corresponding author. Fax: +55-21-290-6626.
E-mail addresses: fbpassos@engenharia.uff.br (F.B. Passos), schmal@peq.coppe.ufrj.br (M. Schmal).

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00190-1

Table 1
Composition of the catalysts and desorption product distribution on Pd-Mo/HZSM-5 catalysts

Catalyst	Pd (%)	Mo (%)	Products distribution (%)		
			NO	N_2	N_2O
HZSM-5	–	–	74	9	17
Pd/HZSM-5	0.95	–	81	11	8
Mo/HZSM-5	–	2.4	75	18	7
Pd-Mo/HZSM-5	0.67	2.5	47	42	11

and washed with distilled and deionized water. Mo/HZSM-5 was prepared by impregnation of 5 g of HZSM-5 with 30 cm^3 of a $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ aqueous solution. The slurry was stirred for 24 h at room temperature. The excess of water was removed under vacuum at 90 °C.

The composition of the catalysts is presented on Table 1.

Pd-Mo/HZSM-5 was prepared by impregnating the calcined Pd/HZSM-5 with the $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as described for the Mo/HZSM-5 catalyst.

The prepared solids were dried at 110 °C during 18 h and calcined under air flow (300 cm^3/min) with a heating rate of 0.5 °C/min and kept at a final temperature of 500 °C for 2 h.

NO TPD analysis was carried out in a micro-reactor coupled to a quadrupole mass spectrometer (Balzers, PRISMA). All the samples were pretreated under He flow (50 cm^3/min) at 550 °C for 1 h. After cooling to room temperature, the samples were reduced in H_2 flow (30 m^3/min) at 500 °C for 1 h, followed by He purging for 30 min at 500 °C and cooling under He flow to room temperature. NO was adsorbed on the catalyst by flowing (50 cm^3/min) a 1% NO/He gaseous stream through the sample for 30 min. After the adsorption, the samples were purged with He (50 cm^3/min) to remove NO weakly adsorbed. In the case of ethanol TPD, the gas mixture was obtained by flowing He through a saturator containing ethanol at room temperature. The mass of the samples were 200 and 100 mg for the NO TPD and ethanol TPD, respectively.

NO reduction with ethanol was performed in a continuous micro-reactor at room temperature coupled to a quadrupole mass spectrometer and to a gas chromatograph equipped with a Chromosorb 102 column. The samples were submitted to the same pretreatment described for the TPD experiments. The NO reduction of ethanol was studied using a feed containing 0.3% ethanol, 0.3% NO and balance He. The space velocity was 82,500 h^{-1}. The temperature of reaction was varied between 280 and 350 °C. The ethanol/He mixture was obtained by flowing He through a saturator containing ethanol at 5 °C.

3. Results and discussion

The NO TPD profile for HZSM-5 is presented on Fig. 1. The amount of NO desorbed was small, with a major desorption peak being observed at 122 °C and a small peak observed at 315 °C. Products of the decomposition of NO were also observed, with the desorption of N_2 observed at 120 °C and the N_2O desorption peaks at 315 and 495 °C. There was not any desorption of NO_2 species.

The palladium addition to the zeolite caused some changes on the TPD after NO adsorption (Fig. 2). A major desorption of NO was observed at 110 °C as observed for HZSM-5 but in a larger amount. The second peak of NO desorption was observed at a higher temperature as compared to HZSM-5, around 380 °C. This

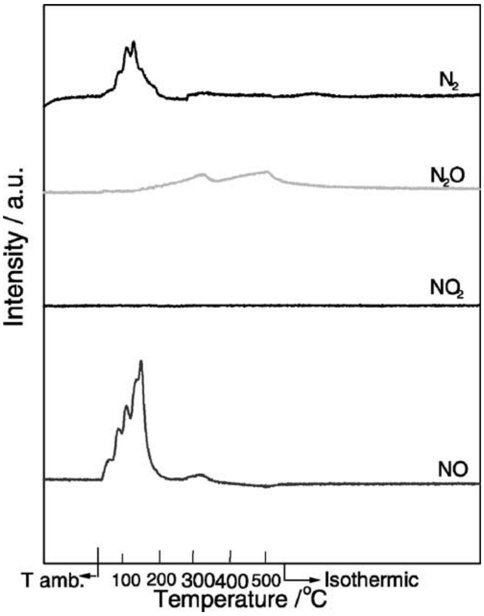

Fig. 1. TPD of adsorbed NO on HZSM-5.

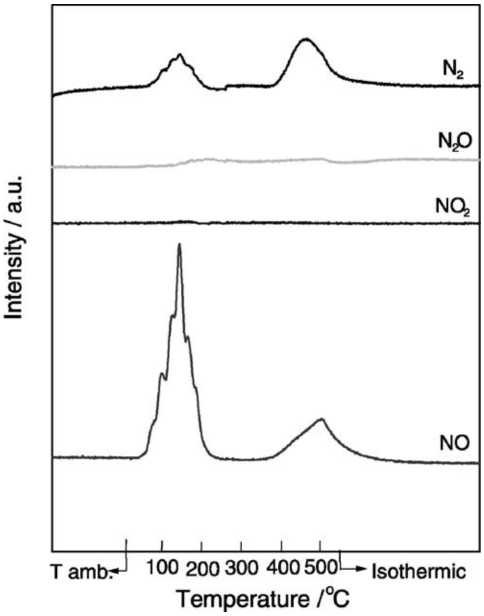

Fig. 2. TPD of adsorbed NO on Pd/HZSM-5.

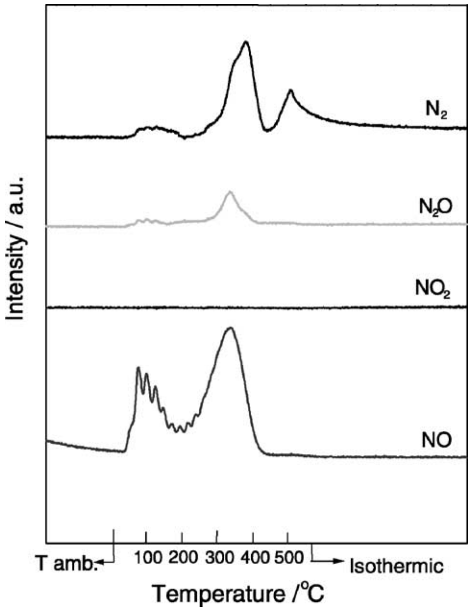

Fig. 3. TPD of adsorbed NO on Mo/HZSM-5.

desorption is related to NO adsorbed on palladium sites. The NO decomposition occurred with N_2 formation at 120 and 380 °C. The first peak may be related to the HZSM-5 desorption profiles, and the second one is due to NO decomposition on Pd sites. The N_2O formation was quite small, and NO_2 was not observed. A different NO TPD for unreduced Pd/HZSM-5 was observed [9] with the formation of peaks at 92 and 242 °C and a tail evidenced between 402 and 600 °C. Besides a NO_2 desorption peak was detected at 262 °C. In other work [10], only NO desorption was observed.

Table 1 shows the distribution of desorbed species on NO TPD for the several investigated catalysts. For Pd/HZSM-5 catalysts most of NO (80%) desorbed in a reversible way. This behavior shows palladium catalyst does not present a great capacity to dissociate NO.

The NO TPD for Mo/HZSM-5 is shown on Fig. 3. Low temperature (110 °C) NO desorption was parallel to a small decomposition to N_2 and N_2O. At higher temperatures (300 °C) a major NO desorption peak was detected with decomposition to N_2 and N_2O. The desorption of N_2 was also observed at 500 °C. The higher formation of N_2 for Mo/HZSM-5 (Table 1) may be explained by a mechanism, where adsorbed NO reacts with oxygen from molybdenum oxide, forming NO_2. NO_2 however is very unstable and decomposes to N_2 and O_2. The oxygen formed in the decomposition would be able to regenerate the molybdenum oxide. The oxidation of partially reduced molybdenum oxide may also form N_2 and N_2O [11,12].

Fig. 4 presents the TPD profile after adsorption of NO on Pd-Mo/HZSM-5. The NO desorption at high temperature was not detected, indicating all strongly adsorbed NO was decomposed. The low temperature desorbed NO may be ascribed to adsorption on acid sites of HZSM-5. A large formation of N_2 was detected at 344 °C, and another at 485 °C. N_2O desorption at 100 °C is related to decomposition of NO adsorbed on acid sites catalyzed by the presence of molybdenum oxide, whereas the N_2O desorption at 315 °C is similar to the desorption observed for HZSM-5. Again, NO_2 was not detected.

Table 1 shows the higher formation of N_2 for Pd-Mo/HZSM-5. This result points out to a synergetic effect for Pd and Mo, as previously observed for Pd-Mo/Al_2O_3 catalysts [11,13].

Ethanol TPD profiles for HZSM-5 are presented on Fig. 5. Weakly adsorbed ethanol desorbed at 150 °C, accompanied by the decomposition to H_2, CH_4 and a CO in a lesser extent.

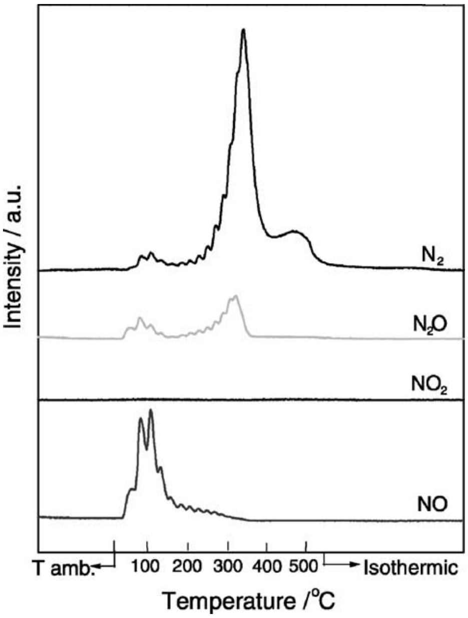

Fig. 4. TPD of adsorbed NO on Pd-Mo/HZSM-5.

At higher temperatures, there was the desorption of ethylene formed by ethanol dehydration on acid sites of HZSM-5. Acetaldehyde desorbed at 100 °C and more pronouncedly at 260 °C.

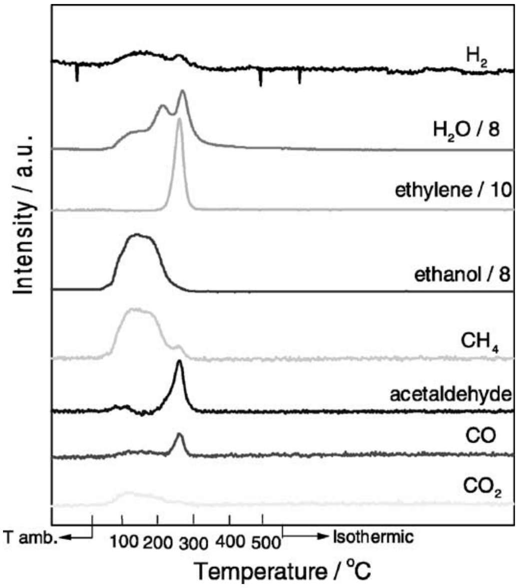

Fig. 5. TPD of adsorbed ethanol on HZSM-5.

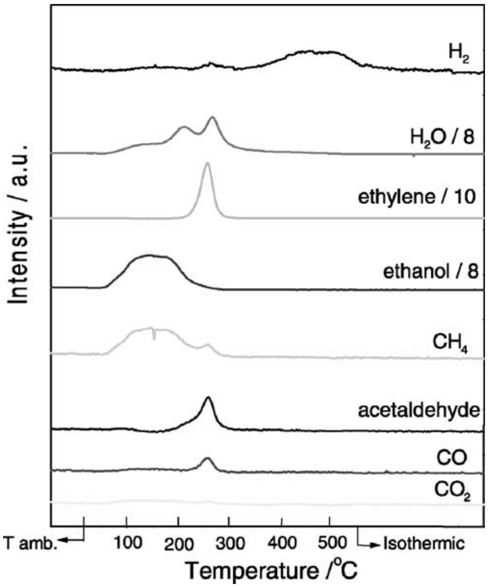

Fig. 6. TPD of adsorbed ethanol on Pd/HZSM-5.

Fig. 6 shows the TPD of adsorbed ethanol on Pd/HZSM-5. The formation of ethylene in this case is smaller than in the case of HZSM-5. Acetaldehyde desorption was evidenced with the formation of CO, CH_4 and H_2. At low temperatures, only methane and hydrogen were noticed. Besides, a broad peak at 475 °C was observed for hydrogen.

The TPD of adsorbed ethanol on Mo/HZSM-5 and on Pd-Mo/HZSM-5 are presented on Figs. 7 and 8, respectively. Mo/HZM-5 presented a profile similar to the observed for Pd/HZSM-5, except for a higher decrease on the ethylene formation. The desorption of ethanol occurred at 150 °C and there was the formation of acetaldehyde, CO, CH_4 and H_2 at 260 °C. The H_2 desorption at high temperature was also observed. In the case of Mo/Al_2O_3 the presence of acetaldehyde at low temperatures was explained by the dehydrogenation activity of MoO_x.

Pd-Mo/HZM-5 catalyst profile showed a high formation of acetaldehyde. Desorption peaks of acetaldehyde were detected at 100 and 260 °C with a tail at 300 °C. The formation of H_2 was considerably high with peaks at 180 and 470 °C.

All the samples showed a high formation of ethylene due to acidity of the support. The presence of molybdenum caused an increase in the capacity of

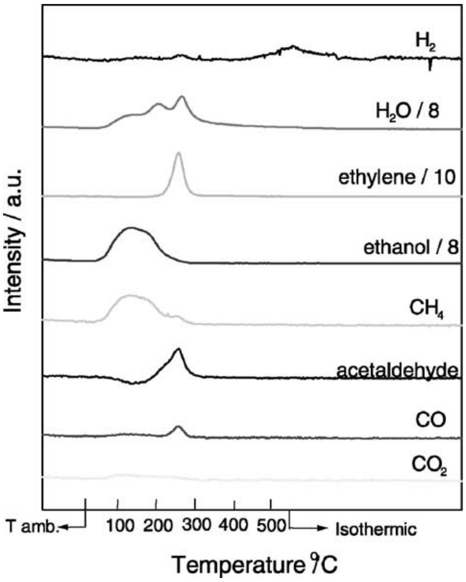

Fig. 7. TPD of adsorbed ethanol on Mo/HZSM-5.

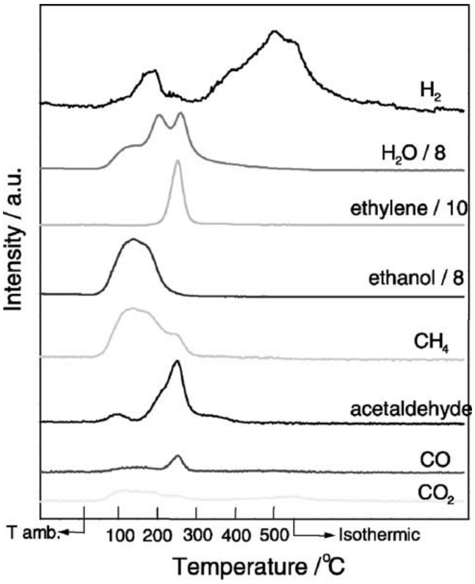

Fig. 8. TPD of adsorbed ethanol on Pd-Mo/HZSM-5.

acetaldehyde formation mainly in the Pd-Mo/HZSM-5 catalyst.

The results for the reduction of NO with ethanol are presented on Table 2. HZSM-5 was not active for this reaction but there was ethylene formation from ethanol dehydration, and some CO_2 formation. Thus, oxygen is essential so HZSM-5 is active for NO reduction of ethanol, as Serban et al. [8] found HZSM-5 active in oxidant conditions.

Mo/HZSM-5 showed the highest selectivity for N_2, but there was a small decrease on conversion with the increase of the temperature showing some deactivation of this catalyst.

Pd/HZM-5 and Pd-Mo/HZSM-5 catalysts showed similar activities until the temperature of 300 °C, but

Table 2
NO reduction with ethanol on Pd-Mo/HZSM-5 catalysts

Catalyst	T (°C)	No conversion (%)	N species distribution (%)		Ethanol conversion (%)	C species distribution (%)			
			N_2	N_2O		CO	CO_2	Acet.[a]	Ethyl.[a]
HZSM-5	280	0	0	0	100	0	45	0	55
	300	0	0	0	100	0	23	0	77
	350	0	0	0	100	0	23	0	77
Pd/HZM-5	280	12	64	36	100	0	30	0	70
	300	24	78	22	100	3	28	0	69
	350	47	72	28	100	16	34	0	50
Mo/HZSM-5	280	10	100	0	100	0	0	1	99
	300	7	100	0	93	0	8	14	78
	350	6	100	0	100	0	30	6	64
Pd-Mo/HZSM-5	280	6	62	38	100	0	12	6	82
	300	21	67	33	100	8	15	7	69
	350	78	71	29	100	15	55	0	30

[a] Acet.: acetaldehyde; Ethyl.: ethylene.

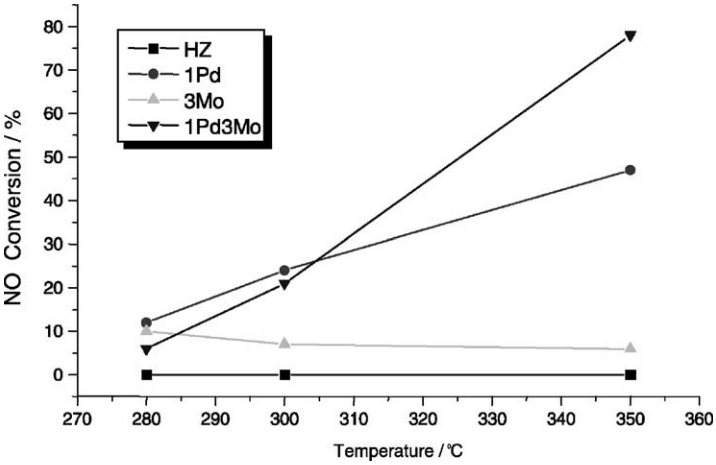

Fig. 9. Reduction of NO with ethanol in function of the temperature.

at 350 °C Pd-Mo/HZSM-5 showed a higher conversion. This trend was also observed for Al_2O_3 supported Pd and Mo catalysts in the reaction of NO with CO and for the reduction of NO with ethanol [7]. Besides, the selectivity for N_2 was not altered by the presence of Mo, differing from NO TPD results where the presence of Mo increased NO decomposition.

The conversion of ethanol includes the reduction of ethanol, the total oxidation to CO_2, the dehydration to ethylene and the dehydrogenation to acetaldehyde. The selectivity to ethylene was high due to the acidity of the zeolite. The selectivity to products of partial oxidation was not relevant. The high selectivity to ethylene was also observed for Al_2O_3 supported catalysts [7].

The higher conversion at higher temperatures obtained for Pd-Mo/HZSM-5 (Fig. 9) may be explained by a change in the activation energy of the rate limiting step of the reaction, favoring the reaction between adsorbed NO and adsorbed ethoxy species. The conversion of NO for Pd-Mo/HZSM-5 was superior to the sum of the conversions of Pd/HZSM-5 and Mo/HZSM-5, proving the synergy between Pd and

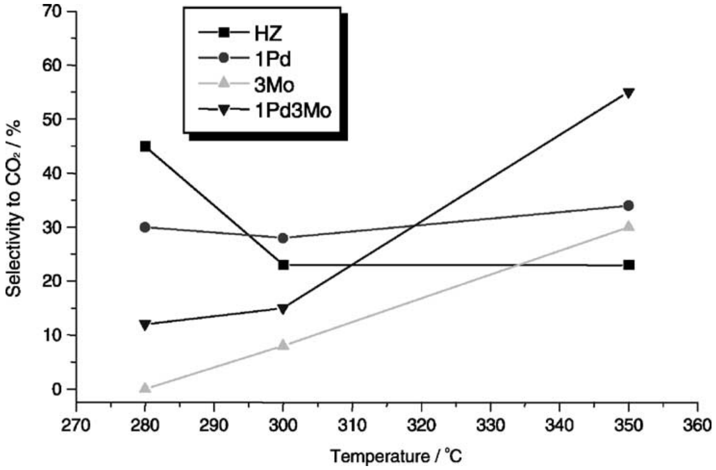

Fig. 10. Selectivity to CO_2 formation for the reduction of NO with ethanol.

Mo. This synergy was also observed in previous characterization studies in our laboratory.

Acetaldehyde formation was verified only for molybdenum containing catalysts. This result is consistent to IR spectroscopy of adsorbed ethanol on the catalysts where we have observed the formation of adsorbed acetaldehyde.

The selectivity for CO_2 was greatly improved for Pd-Mo/HZSM-5 at higher temperatures (Fig. 10). This result shows that Pd-Mo/HZSM-5 are better catalysts for both NO reduction and to complete oxidation of ethanol.

4. Conclusions

NO TPD showed the introduction of Mo favored the decomposition of NO to N_2. Partially reduced molybdenum oxide is the species that promote the formation of N_2. The presence of Mo also promoted the formation of acetaldehyde from adsorbed ethanol. Ethanol is dehydrated to ethylene on the investigated catalysts due to the acidity of HZSM-5. In the reduction of NO with ethanol, Pd-Mo/HZM-5 catalysts were more active at higher temperatures than Pd/HZSM-5, however, the selectivity for N_2 was not altered. Mo/HZSM-5 though less active, was more selective to N_2. Concerning the carbon species formed, all the catalysts formed ethylene. A small amount of acetaldehyde was formed for Mo containing catalysts. Pd-Mo/ZSM-5 was very selective for CO_2 at higher temperatures.

References

[1] J.N. Armor, Appl. Catal. B: Environ. 1 (1992) 221.
[2] R.W. McCabe, P.J. Mitchell, Ind. Eng. Chem. Res. Dev. 23 (1984) 196.
[3] Y.Y. Yao, Ind. Eng. Chem. Res. Dev. 23 (1984) 60.
[4] H. Rajesh, U.S. Ozkan, Ind. Eng. Chem. Res. Dev. 32 (1993) 1622.
[5] M. Nagai, R.D. Gonzalez, Ind. Eng. Chem. Res. Dev. 24 (1985) 525.
[6] P. Larsson, A. Andersson, Appl. Catal. B: Environ. 24 (2000) 175.
[7] L.F. Mello, M.A.S. Baldanza, F.B. Noronha, M. Schmal, Stud. Surf. Sci. Cat. 130 (2000) 647.
[8] M. Serban, I. Halasz, R. Datta, Catal. Lett. 63 (1999) 217.
[9] L.J. Lobree, A.W. Aylor, J.A. Reimer, A.T. Bell, J. Catal. 181 (1999) 189.
[10] M. Ogura, M. Hayashi, S. Kage, M. Matsukata, E. Kikuchi, E. Appl. Catal. B: Environ. 23 (1999) 247.
[11] I. Halasz, A. Brenner, M. Shelef, Appl. Catal. B: Environ. 2 (1993) 131.
[12] T. Iizuka, M. Itoh, H. Hattori, K. Tanabe, J. Chem. Soc., Faraday Trans. 1 (78) (1982) 501.
[13] M.A.S. Baldanza, L.F. Mello, M.A. Vannice, F.B. Noronha, M. Schmal, J. Catal. 192 (2000) 64.