Catalysis Communications 10 (2008) 74–78

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Characterization of Co/sulfated zirconia catalysts for selective reduction of NO by methane

Claudia Quincoces [a], Aldo Rubert [a], Paulo Araya [b], Delia Gazzoli [c], M. Gloria González [a,*]

[a] CINDECA, Facultad de Ciencias Exactas, UNLP-CONICET, 47 N° 257, 1900 La Plata, Argentina
[b] Departamento de Ingeniería Química, Universidad de Chile, Facultad de Ciencias físicas y matemáticas, Casilla 2777, Santiago, Chile
[c] Dipartimento di Chimica, Università di Roma 'La Sapienza', Roma, Italy

ARTICLE INFO

Article history:
Received 5 May 2008
Received in revised form 30 July 2008
Accepted 31 July 2008
Available online 7 August 2008

ABSTRACT

In this study, Co based catalysts (0.5–5 wt% Co) supported on sulfated zirconia were prepared for NO selective reduction by methane. The effect of Co loading on the catalyst structure, the catalytic activity and stability, as well as the deactivation rate by 6 vol% water in the feed are reported. The best results were obtained with catalysts up to 2 wt% Co loading. XPS and DRS analyses indicated the existence of the Co^{+2} in fresh samples. The higher activity was shown by a catalyst containing octahedral Co^{+2} species supported on sulfated zirconia having tetragonal–monoclinic structure.

1. Introduction

The interest in developing active catalysts for the selective catalytic reduction (SCR) of nitrogen oxides by hydrocarbon in oxygen excess has increased in last years. Zeolitic catalysts exchanged with Co such as Co-ZSM5, Co/FER, Co-MOR showed to be active but not stable under real operation conditions (water vapor, high-temperatures, *S* presence) for the NO selective reduction by light hydrocarbons in fixed and mobile sources. One major disadvantage of these catalysts is the water vapor deactivation, inevitably existent in combustion exhaust conditions, diminishing their durability and making them inadequate from a practical point of view. Therefore, the development of catalysts on non zeolitic supports is required to achieve high activity and stability for commercial applications. It is well known that activity and selectivity for this reaction are dependent on support acidity, consequently, sulfated zirconia (SZ) was selected to explore its possibilities in the NO*x* selective reduction by hydrocarbons. Pietrogiacomi et al. [1] showed that under lean conditions, catalysts as CoO*x*/SZ are able to promote the selectivity of NO reduction by propene. The selectivity enhancement was ascribed to the presence of sulfates that makes Co(II) less reducible and prevent Co_3O_4 formation.

Li et al. [2] found that Co/SZ presented high activity and stability in SCR with methane for GHSV = 3600 h^{-1} which is far from conditions for technological application. Support structure and Co species present on the catalyst surface were not studied in the previously mentioned work.

The aim of this work is to study the behavior of Co catalysts on sulfated zirconia under severe operation conditions (high GHSV, water vapor presence) for NO selective reduction by methane in oxygen excess. Particularly, the attention was focused on the effect of 6% water on the catalytic performance and structural changes of Co/SZ catalyst.

2. Experimental

2.1. Catalyst preparation

Samples denominated Co/ZS were prepared on sulfated zirconia. The support (sulfated zirconia, S_g = 140 m^2 g^{-1}, V_p = 0.17 cm^3 g^{-1}, r_p = 3.3 nm) was obtained by the known method of two stages [3,4] and calcined in air for 3 h at 550 °C. Catalysts were prepared by incipient wetness impregnation at room temperature with an aqueous solution of Co $(C_2H_3O_2)_2 \cdot 4H_2O$, containing the adequate amount of organic salt to achieve a load between 0.5 and 5 wt% Co on the support. Impregnated samples were dried at 100 °C and calcined in oxygen at 500 °C for 1 h. Prior to reaction, catalysts were treated in reaction medium at 700 °C. The catalyst were named Co(*x*)/SZ, where *x* correspond to the wt% Co load.

2.2. Catalyst characterization

Fresh and used samples were characterized by thermal analysis (DT-TGA), X-ray diffraction (XRD), diffuse reflectance spectroscopy (UV–Vis DRS) and X-ray photoelectron spectroscopy (XPS).

XRD patterns were performed on a Philips PW 1732/10 equipment by using Cu Kα radiation (λ = 1.5404 Å). The UV–Vis DRS spectra was recorded between 200 and 800 nm on Varian spectrometer. XPS spectra were recorded on a Leybold-Heraeus LHS10 spectrometer in FAT mode (50 eV) using Al Kα radiation (148.6 eV, 12 kV, 20 mA). The binding energy (BE) was referenced

* Corresponding author. Tel.: +54 221 4211353; fax: +54 221 425 4277.
E-mail address: mgg@quimica.unlp.edu.ar (M.G. González).

1566-7367/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2008.07.037

to the Zr 3d5/2 peak at 182.5 eV. Thermal analysis (DT-TG) was carried out in a Shimadzu non simultaneous analyzer over 0.015 g sample heated at a rate of 10 °C min^{-1} in 20 cm^3 min^{-1} air stream.

Catalytic measurements were carried out in a fixed bed reactor constructed in quartz (i.d. = 0.8 cm) between 200 and 700 °C. The feed mixture to the reactor was constituted by 1500–2000 ppm of methane, 500 ppm of NO, 2–10 vol% of O_2 and He as balance. The catalyst weight was 0.277 g., the space velocity (GHSV) was between 15.000 and 30.000 h^{-1} based on apparent support bulk density of 2 g cm^{-3}. The feed and the effluent of the reactor were analyzed in an 'on line' chromatograph Shimadzu GC-8A with detector of thermal conductivity by using a CTR1 column (Alltech) at 40 °C. This system permits identification of N_2, O_2, N_2O, CO_2 and CH_4 signal.

NO and methane conversions were calculated in terms of N_2 and CO_2 formed, respectively.

3. Results

3.1. Catalytic performance

Fig. 1 shows the effect of temperature on the activity of Co(1)/SZ for NO reduction by methane, on calcined and pretreated samples. Volcano-type NO conversion versus temperature curves was observed in both catalysts. Fig. 1 shows that pretreated sample presents a higher NO conversion, lower temperature of maximum conversion and an increase of the temperature-conversion window than in the calcined sample at 500 °C. In the pretreated Co(1 wt%) sample the NO to N_2 conversion increased in a monotonous way with the temperature up to 560 °C. Above this temperature, the catalyst lost selectivity to N_2 and the methane combustion was the predominant reaction.

3.1.1. Effect of Co loading

A series of catalysts with a Co load between 0.5 and 5 wt% was evaluated in conditions above described. Fig. 2A and B show NO and CH_4 conversions as a function of temperature over Co/SZ catalysts, respectively. The maximum NO to N_2 conversion decreased in the following order: Co(0.5%) ≅ Co(1%) ≅ Co(2%) ≫ Co(5 wt%).

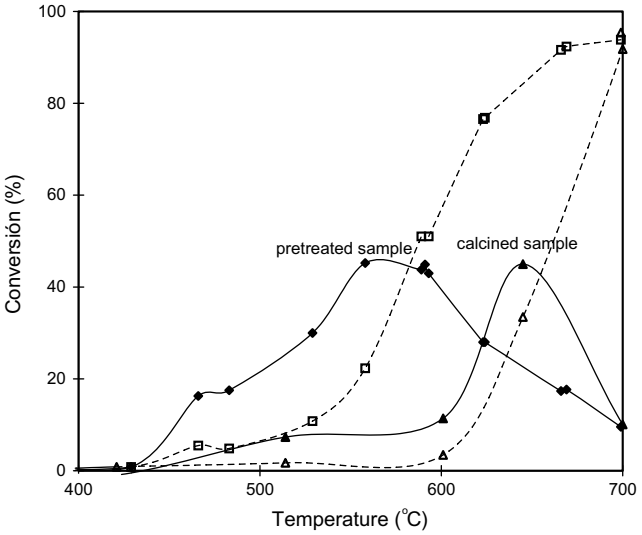

Fig. 1. Effect of catalysts pretreatment on NO conversion (full lines) and methane oxidation (dotted lines) in reaction media at 700 °C. Pretreated (■) and calcined (▲) Co(1)/ZrS sample. Reaction conditions: NO = 500 ppm, CH_4 = 1500 ppm,O_2 = 2%, GHSV = 15000 h^{-1}.

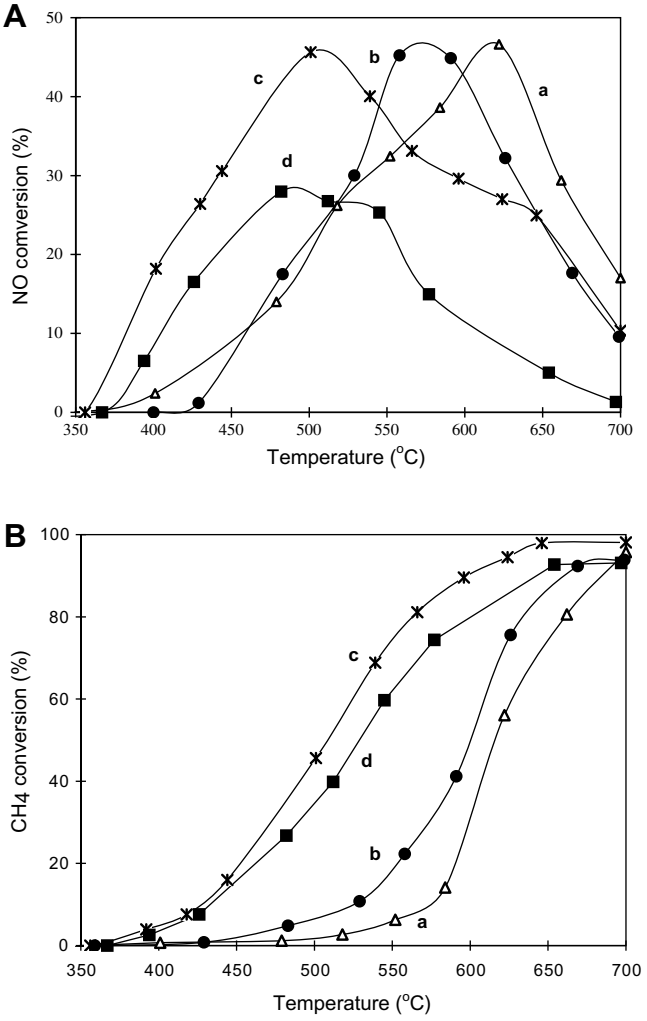

Fig. 2. (A) NO conversion versus temperature as a function of Co loading: (a) 0.5 wt% Co, (b) 1 wt% Co, (c) 2 wt% Co and (d) 5 wt% Co. Reaction conditions: NO = 500 ppm, CH_4 = 1500 ppm, O_2 = 2%, GHSV = 15000 h^{-1}. (B) Methane conversion versus temperature as a function of Co loading. (a) 0.5 wt% Co, (b) 1 wt% Co, (c) 2 wt% Co and (d) 5 wt% Co. Reaction conditions: NO = 500 ppm, CH_4 = 1500 ppm, O_2 = 2%, GHSV = 15000 h^{-1}.

The maximum conversion shifted towards lower temperatures (about 120 °C) in the Co(2 wt%) catalyst respect to the sample with 0.5 and 1 wt% of Co. Fig. 2B shows that methane oxidation increases with Co content. After certain critical metal loading (2%), the methane conversion decreases with further increase of metal content.

Selectivities to N_2 at 500 °C were 0.62 for Co(2 wt%) and 0.40 for Co(5 wt%), this indicates an important decrease (50%) for the catalyst with higher Co loading, at maximum NO conversion temperature.

3.1.2. Effect of water vapor

Fig. 3 shows NO and methane conversions vs. temperature either in presence or absence of 6% water in the feed, for Co(2)/SZ catalyst. The water presence produced a decrease in NO and methane conversions. At 520 °C, conversions decreased approximately 30%, for both reactions, and the maximum NO conversion temperature was shifted around 50 °C for a ratio CH_4/NO = 4, 10 vol% of O_2 and GHSV = 30000 h^{-1} (Fig. 3, curve b). Comparing the activity of catalysts without (Fig. 3, curve a), and after removal of water (Fig. 3, curve c), 85% of NO initial conversion was

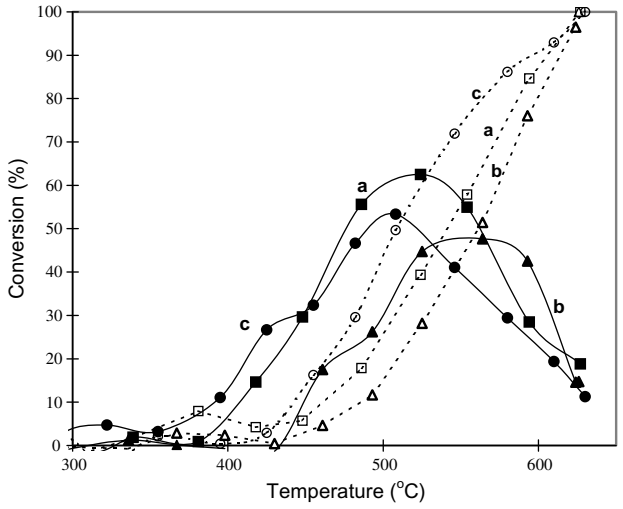

Fig. 3. Effect of 6% water vapor on NO conversion (full lines) and CH_4 oxidation (dotted lines) over Co(2)/SZr catalyst. Reference: (a) feed without water (1st cycle), (b) feed with 6% water vapor and (c) feed without water (2nd cycle). Reaction conditions: NO = 500 ppm, CH_4 = 2000 ppm, O_2 = 2%, GHSV = 30000 h^{-1}.

recovered and the methane conversion was increased. Therefore, water presence decreases NO reduction and enhances methane combustion, modifying the selectivity to N_2 production. This is attributed to modifications and water adsorption on active phase.

From a practical point of view, catalyst stability is an important aspect to take into account since it affects its useful life and the corresponding process economy. Stability of catalysts was measured for 38 h on stream at 500 °C with water. The catalysts present an initial deactivation up to reaching a quasi-stationary conversion for the NO reduction while methane oxidation increases with reaction time. This behavior indicates a convenient NO activity level in reaction conditions used (500 °C, GHSV: 30000 h^{-1}).

3.2. Catalyst characterizations

3.2.1. X-ray diffraction

Spectra of sulfated zirconia, calcined and pretreated catalysts and a catalyst sample extracted from the reactor, are shown in Fig. 4. In spectra of sulfated zirconia and calcined catalyst, the tetragonal zirconia ($2\theta = 30.24$) is the only phase observed. Pretreated catalyst and the sample extracted from the reactor show crystallinity increase and peaks corresponding to tetragonal ($2\theta = 30.24$) and monoclinic ($2\theta = 28.15$ and 31.40) phases. The crystallographic partial transformation in monoclinic phase is correlated with the high temperature (700 °C) used during pretreatment and reaction stages. Chen et al. [5] found that the sulfated zirconia crystalline phase corresponds to the tetragonal form (metastable tetragonal phase) up to 600 °C. At higher temperatures, formation of the monoclinic phase can be observed.

3.2.2. UV–Vis diffuse reflectance spectroscopy

Fig. 5 shows DRS data obtained with different Co(2)/SZ samples (pretreated and used in reaction with and without water). In order to analyze Co content effect on formation of superficial species, a sample containing 5% Co is included in Fig. 5.

The absorption spectra of pretreated Co(2)/SZ sample (spectrum a) shows a band with a maximum at 530 nm, attributed to octahedrally coordinated Co^{+2} [6].

DRS spectra of Co(2)/SZ samples used with dry feed at 500 °C are shown in spectra (b). Two signals at 530 and 750 nm are present. The first one is typical of Co^{+2} species, whereas the second one can be attributed to Co^{+3} species associated to segregated Co_3O_4 species [6]. This last species has also been observed in Co(2)/SZ sample treated in wet reaction (spectrum c) and in the Co(5)/SZ (spectrum d), which showed a lower activity for the SCR–CH_4 than the Co(2)/SZ sample pretreated at 700 °C (spectrum a). Spinel Co_3O_4 phase presence is attributed to formation of Co superficial clusters at higher Co content [7].

3.2.3. X-ray photoelectron spectra

XPS analysis was performed on Co/SZ samples to determine the state and the surface composition of the active phase. Table 1 shows XPS data of samples containing 2 and 5 wt% Co. In Co(2)/SZ, after calcination, cobalt is present mainly as Co^{+2}, as was indicated by the presence of satellite peaks at 5.5 eV from the main lines with $I_{sat}/I_{main} = 0.82$ Spectra of Co(2)/SZ samples, pre-treated and after reaction, showed coexistence of Co^{+2} and traces of Co^{+3} species.

The Co(5)/SZ samples, calcined and after reaction, show similar features. The values of the I_{sat}/I_{main} ratio (0.50, 0.56) indicated that cobalt species are present as Co^{+2} and Co^{+3}. The interaction between supported species and support developed during thermal treatment or under reaction condition can modify the surface

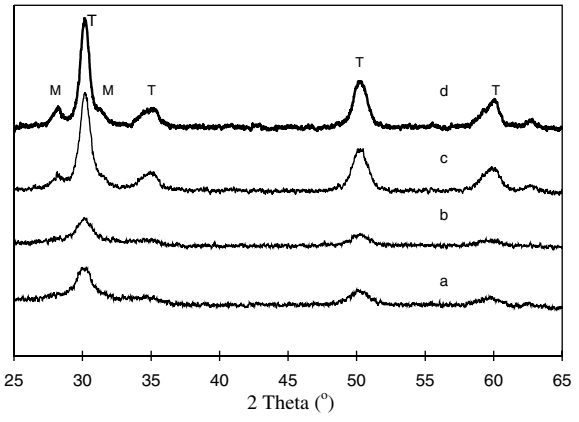

Fig. 4. XRD patterns of Co(2)/SZ catalysts: (a) sulfated zirconia, (b) catalyst calcined at 500 °C, (c) catalyst pretreated in reaction media at 700 °C and (d) Co(2)/SZ samples after SCR–NO reaction with water.

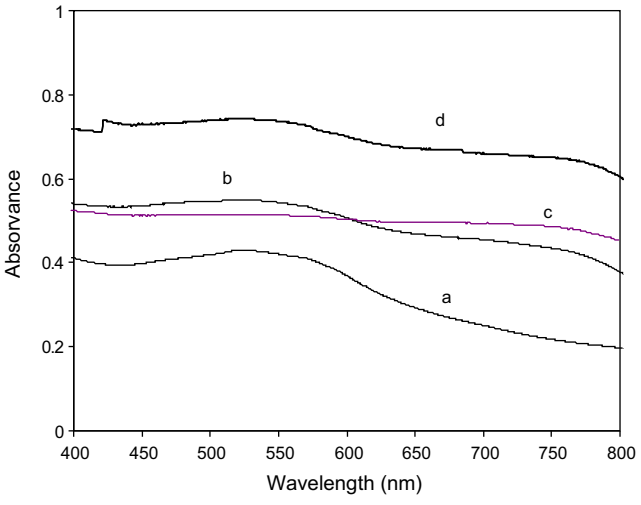

Fig. 5. UV–Vis diffuse reflectance spectra of Co(2)/SZr samples. (a) Pretreated in reaction media at 700 °C, (b) after dry reaction, (c) used in reaction 38 h with water and (d) Co(5)/SZ sample after dry reaction.

Table 1
XPS parameters of Co/SZ samples

Catalysts	$Co2p_{3/2}$ eV)	I_{sat}/I_{main}	(nCo/nZ)[a]s	(IS_{2p} /IZr_{3d})	Co species
Co(2%)/SZ, calcined	781.8	0.82	0.15	0.014	Co(II)
Co(2%)/SZ, pretreated	782.6	0.58	0.12	0.014	Co(II), Co(III)traces
Co(2%)/SZ after reaction	782.2	0.54	0.18	0.011	Co(II), Co(III)traces
Co(5%)/SZ, calcined	782.1	0.50	0.12	–	Co(II), Co(III)
Co(5%)/SZ after reaction	782.2	0.56	0.23	0.011	Co(II), Co(III)

[a] Surface atomic ratio.

composition influencing the catalytic performances. As for Co(2)/SZ catalysts, the little variation in the atomic surface composition for calcined and pretreated samples (0.15 and 0.12, respectively) can be attributed to some agglomeration of the cobalt species with ensuing exposure of a higher fraction of bare support. The increase in the nCo/nZr atomic ratio, measured after reaction, can indicates that during reaction agglomeration of the cobalt species yields larger particles that tend to attenuate the signal coming from the underlying support. The larger change in the nCo/nZr atomic ratio for calcined and after reaction Co(5)/SZ samples, Table 1, further support the hypothesis that during reaction cobalt species form aggregates, as Co_3O_4-like species, as also evidenced by DRS results.

3.2.4. Thermogravimetric analysis

The thermal behavior of Co/ZS catalysts was investigated by TGA in an oxidizing stream. The support and calcined sample present a peak at 700 °C and a shoulder around 770 °C which are assigned to the decomposition of SO_4^{2-}. The presence of a shoulder suggests the existence of two types of sulfur, one more labile and other bound strongly to the support and probably responsible for the NO reduction activity [8]. A weight loss observed around 630 °C could be attributed to a multilayer of sulfates, which can be related with Brönsted acid sites and the weight loss at higher temperature could be assigned to surface sulfates related to Lewis super acid sites. During pretreatment at 700 °C, it was observed by TG analysis, that the principal remaining species were surface sulfates. This suggests that the catalyst acidity was modified during the pretreatment step.

The catalyst exposed firstly to feed without water, then in reaction with 6 vol% water and finally in dry reaction, all cycles up to 700 °C, is the one with higher weight loss (17.1 wt/wt%) respect to the fresh catalyst weight. These results suggest that in the calcined sample there exists excess of labile sulfates lost during pretreatment [9–11], but the residual sulfate concentration remaining on the catalyst is enough to sustain NO reduction activity. Catalysts continue losing sulfates and this loss is more evident when operating up to 700 °C in water presence.

4. Discussion

XRD, DRS, TGA and XPS results can explain the differences in the behavior of catalysts for the SCR–NO with methane. In fact, both, the sulfated zirconia structural type and the Co environment in the host lattice could be modified by the pretreatment at 700 °C and reaction conditions (high temperature, water presence in the feed).

The highest activity was observed in the Co(2)/SZ sample pretreated at 700 °C. The UV–Vis spectra and the XRD patterns for this catalyst showed the presence of Co^{+2} species in octahedral positions on zirconia with predominantly tetragonal structure. Thus, the fact that this configuration favors the catalytic NO reduction must be assumed as a hypothesis.

The Co(2)/SZ catalyst treated in reaction with water and the catalyst with the highest Co load (5 wt%) showed the presence of Co^{+3} associated to segregated Co_3O_4. The formation of spinel phase is favored by the oxidation of Co^{+3} expose in an oxidant media and to formation of Co superficial clusters as the cobalt load increases [6]. The existence of Co_3O_4 decreases selectivity to N_2 while favoring the catalytic oxidation of CH_4.

Reaction deactivation can be associated to the presence of segregated Co_3O_4 and to inhibition of active sites by water adsorption which inhibits adsorption of reactants, essential step in mechanisms of catalytic reactions. The partial recovery of the reducing activity after water vapor removal suggests that water obstructs sites reversibly, while the Co_3O_4 phase formed in reaction with water increases the hydrocarbon oxidation reaction decreasing methane amount for NO reduction (Fig. 3).

Other aspect to take into account in deactivation is the loss of sulfate species by water and temperature effect, due to its relation with catalyst acidity. According to the relation reported by different authors [12–15] between zirconia structure and the type of acid sites, we are able to attribute the behavior of catalysts to changes observed during pretreatment and reaction steps in the crystalline structure of sulfated zirconia.

5. Conclusions

Impregnation of sulfated zirconia with cobalt followed by pretreatment at 700 °C in reaction media led to a series of catalysts whose activities in the SCR–NO by methane varied as a function of Co load and reaction conditions. In pretreated catalysts, it was possible to observe a partial structural change of zirconia and modifications of Co environment in the host lattice of catalysts.

The best catalyst for NO reduction was pretreated Co(2)/SZ, which presents Co^{+2} in octahedral coordination on tetragonal-monoclinic zirconia. This result accompanies the hypothesis that sulfate and cobalt cooperate for the determination of selectivity and catalytic activities for the SCR-NO with methane over Co/SZ catalysts.

Acknowledgements

Authors thank to ANPCyT, CONICET and UNLP for their financial support to the present work.

References

[1] D. Pietrogiacomi, S. Tuti, M.C. Campa, V. Indovina, Appl. Catal. B 28 (2000) 43.
[2] N. Li, A. Wang, J. Tang, X. Wang, D. Liang, T. Zhang, Appl. Catal. B 43 (2003) 195.
[3] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, G. Strukul, J. Catal. 149 (1994) 181.
[4] M.A. Risch, E.E. Wolf, Appl. Catal. A 172 (1998) L1–L5.
[5] F.R. Chen, G. Goudurier, J.F. Joly, J.C. Verdine, Am. Chem. Soc. Div. Petrol. Chem. Prepr. 36 (1991) 878.
[6] I.D. Lick, A. Carrascull, M. Ponzi, E. Ponzi, I.L. Botto, Mater. Chem. Phys. 92 (2005) 327.
[7] D. Pietrogiacomi, M.C. Campa, S. Tuti, V. Indovina, Appl. Catal. B 41 (2003) 301.
[8] A. Clearfield, G.P.D. Serrettem, A.H. Khazi-Syed, Catal. Today 20 (1994) 295.
[9] T. Yang, T. Chang, C. Yeh, J. Mol. Catal. A 115 (1997) 339–346.
[10] E.C. Sikabwe, M.A. Coelho, D.E. Resasco, R.L. White, Catal. Lett. 34 (1995) 23.
[11] W.E. Alvarez, H. Liu, E.A. Garcia, E.H. Rueda, A.J. Rouco, D.E. Resasco, Stud. Surf. Sci. Catal. 101 (1996) 553.

[12] J.T. Miller, E. Glusker, R. Peddi, T. Zheng, J.R. Regalbuto, Catal. Lett. 51 (1998) 15.
[13] M. Misono, Y. Nishizaka, M. Kawamoto, H. Kato, Stud. Surf. Sci. Catal. 105 (1997) 1501.
[14] Y. Zhao, W. Li, M. Zhang, K. Tao, Catal. Commun. 3 (2002) 239.
[15] B. Xu, W.M.H. Sachtler, J. Catal. 167 (1997) 224.