ELSEVIER

Catalysis Today 42 (1998) 45–50

CATALYSIS TODAY

A study on the roles of cobalt species in NO_x reduction by propane on Co-Beta

Hirofumi Ohtsuka[a,*], Takeshi Tabata[a], Osamu Okada[a],
Luigina M.F. Sabatino[b], Giuseppe Bellussi[b]

[a] *Research and Development Department, Osaka Gas Co., Ltd., Torishima 6-19-9, Konohana-ku, Osaka 554, Japan*
[b] *Eniricerche SpA., 20097, S. Donato Milanese, Italy*

Abstract

The states of cobalt loaded on Beta zeolite and their roles in selective catalytic reduction of nitrogen oxide (NO_x) by propane were studied. Raman spectroscopy clearly indicated that Co_3O_4 was formed on highly loaded samples. Spectroscopic characterization combined with catalytic activity tests showed that highly dispersed cobalt is essential for NO_x reduction. Co_3O_4 promotes NO_x reduction at low temperatures, but decreases the selectivity to NO_x reduction especially at high temperatures through promotion of propane oxidation by oxygen. At ca. 100% loading, a broad band which cannot be assigned to zeolite framework nor Co_3O_4 was observed at around $600\,cm^{-1}$. The intensity of this band showed a strong dependency on SiO_2/Al_2O_3 ratio, and we suggest it is related to Co–O–Co species. This cobalt species was suggested to have high activity towards NO_x reduction. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: NO_x; Propane; Co-Beta; Raman spectroscopy

1. Introduction

Recently, with increasing global concerns over air pollution caused by nitrogen oxides, improved NO_x emission control methods have been sought. At present, selective catalytic reduction by ammonia (ammonia-SCR) is the only established method available for lean NO_x reduction. However, because it uses ammonia as a reductant, it must be operated with a complicated control system to avoid ammonia leakage. Therefore, its use is limited to large scale facilities such as power plants, and application to smaller facilities such as cogeneration plants and automotive emission controls is considered to be impractical. Selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) may be an option, since it may provide a convenient and inexpensive process for lean NO_x reduction if the fuel or unburned hydrocarbons can be used as reductants. However, considering the case of natural gas-fueled appliances, light alkanes such as methane and propane are the only available reductants. Besides, the importance of the selectivity to NO_x reduction as defined by (reduced NO_x)/(consumed hydrocarbon) must be stressed, since low selectivity to NO_x reduction requires a higher concentration of reductants.

The present authors have previously reported that cobalt ion exchanged Beta zeolite (Co-Beta) shows

---

*Corresponding author. Tel.: +81-6-462-3231; fax: 81-6-464-1805; e-mail: ohtsuka@osakagas.co.jp

PII S0920-5861(98)00075-3

high activity and selectivity in selective catalytic reduction of NO_x by propane (C_3H_8-SCR) under the condition of actual gas engine exhaust [1]. Some studies have been performed [2] to shed light on the loaded states of cobalt and their roles in NO_x reduction, but further study is required to understand the states and the roles of loaded cobalt. In this paper, Co-Beta catalysts with various ion exchange levels and SiO_2/Al_2O_3 ratios will be investigated by means of Raman spectroscopy. The states of loaded cobalt and their roles in propane-SCR will be discussed by combining spectroscopic data with catalytic activity test results.

2. Experimental

2.1. Catalyst preparation

Beta zeolites having various SiO_2/Al_2O_3 ratios were prepared according to patent literature [3]. Cobalt was loaded on Na or H form Beta by ion exchange at 60°C using a cobalt acetate solution, and the exchange procedure was repeated several times to obtain the required cobalt loading. The resultant cobalt ion-exchanged Beta was washed and dried at 110°C, followed by calcination in air at 500–550°C. Cobalt content was determined by inductively-coupled plasma atomic emission spectrometry, and ion exchange levels were calculated, assuming that one divalent cobalt ion is exchanged for two monovalent cations such as Na^+ or H^+. Hereafter, abbreviations such as Co-Beta (22.3, 80%) will be used, where the two parameters 22.3 and 80% denote the SiO_2/Al_2O_3 ratio of the zeolite and the ion exchange level, respectively. Co-Beta (22.3, 104%) and Co-Beta (22.3, 132%) were prepared by impregnation of cobalt acetate to Co-Beta (22.3, 80%). XRD analysis of the impregnated sample showed no peaks for Co_3O_4 spinel.

2.2. Catalytic activity measurement

Catalytic activity was measured in a fixed-bed flow reactor made of stainless steel (14 mm (i.d.)×600 mm). The reactor was heated by three electric furnaces with individual PID control arranged in the flow direction. Typically a 4 ml sample which had been pressed into pellets and crushed to 1–2 mm particles was used. Test gases were generated by mixing helium-balanced standard gases using mass flow controllers. Water was added by a micro-feeder pump (Furue Science, Tokyo) through a vaporizer which was kept at 300°C. The gas composition at the inlet and the outlet of the reactor was analyzed by a gas chromatograph and a chemiluminescence NO_x analyzer equipped with an NO_2 converter.

2.3. Raman measurement

Raman spectra were measured in air by using 514.5 nm radiation from an argon ion laser (Coherent Innova 300) and a triple polychromator (Spex 1877) equipped with a liquid N_2 cooled CCD detector (Princeton Instruments 1752PB or 1100PF). Back-scattering configuration was used. The samples were pretreated by calcination in air at 500°C for 9 h.

3. Results and discussion

3.1. Raman spectra

Raman spectra of Co-Beta samples having the same SiO_2/Al_2O_3 ratio of 22.3 and various ion exchange levels are shown in Fig. 1. These spectra were measured on as-prepared samples, but no significant change was observed in the spectra after reaction experiments up to 500°C. The spectrum of Co-Beta (22.3, 80%) closely resembles that of H-Beta (22.3), suggesting that loaded cobalt is well-dispersed. On the other hand, in the spectrum of Co-Beta (22.3, 132%), in addition to the bands of the zeolite framework, sharp bands are observed at 689 and 521 cm^{-1}. These bands are assigned to Co_3O_4 spinel [2]. This indicates that on Co-Beta (22.3, 132%), loaded cobalt is agglomerated to form cobalt oxide spinel, though it is too small or too little to be observed by XRD. The 689 cm^{-1} band of Co-Beta (22.3, 104%) is slightly stronger than that observed in Co-Beta (22.3, 80%) or H-Beta (22.3), which suggests the formation of a trace amount of Co_3O_4. In the spectrum of Co-Beta (22.3, 97%), a characteristic broad and strong band is observed at around 600 cm^{-1}. As this band cannot be attributed to zeolite framework nor Co_3O_4, it is considered to relate to a state of loaded cobalt other

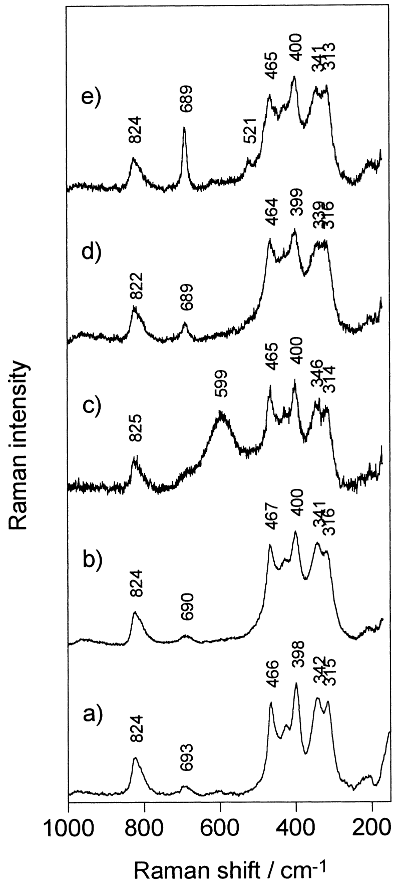

Fig. 1. Raman spectra of Co-Beta: (a) H-Beta (22.3), (b) Co-Beta (22.3, 80%), (c) Co-Beta (22.3, 97%), (d) Co-Beta (22.3, 104%), and (e) Co-Beta (22.3, 132%).

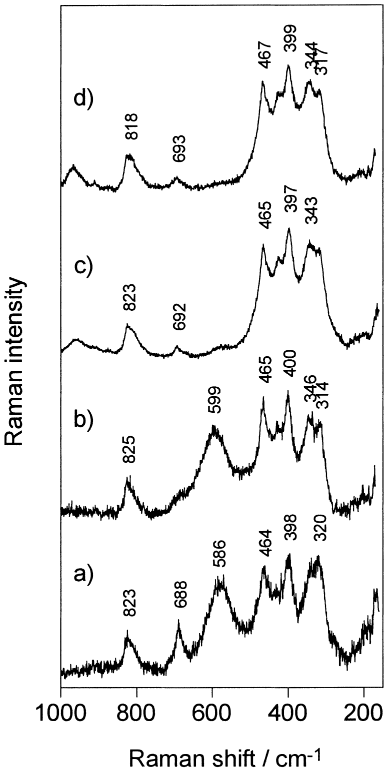

Fig. 2. Raman spectra of Co-Beta: (a) Co-Beta (17.5, 102%), (b) Co-Beta (22.3, 97%), (c) Co-Beta (44.1, 110%), and (d) Co-Beta (73, 106%).

than Co_3O_4. To obtain further information on this band, Raman measurement was performed on samples with different SiO_2/Al_2O_3 ratios and similar ion exchange levels around 100%. Fig. 2 shows the results. A similar band is observed in the spectra of Co-Beta (17.5, 102%) and (44, 110%), but the band is very weak in the latter sample, and almost disappears from the spectra of Co-Beta (73, 106%). Cobalt content is in proportion to Al/(Si+Al) if the ion exchange level is the same. Therefore, it would be natural if the intensity is in inverse proportion to SiO_2/Al_2O_3 ratio. However, the band intensity shows a much higher order dependency. Cobalt clusters linked to two nearby aluminum sites may explain such dependency, since the increase of such Al site pairs with increasing Al/(Si+Al) should show an order dependency higher than unity. Moreover, the fact that the band appears only in the case of around 100% or higher cobalt loading supports the formation of such cobalt clusters. The presence of oxygen bridged metal dimer in zeolite has been discussed on Cu-ZSM-5 [4,5] with respect to its high activity for direct decomposition of NO observed in over-exchanged conditions. Feng and Hall [6] have recently investigated the probability of Fe–O–Fe bridge formation on Fe-ZSM-5 by means of computational methods and concluded that such bridge formation occurs when SiO_2/Al_2O_3 ratio is less than 50, while it will be extremely rare when SiO_2/Al_2O_3 ratio is 78 or higher. If the species is a μ-oxo-bridged cobalt dimer, i.e. Co–O–Co, like the Cu–O–Cu [4,5] or Fe–O–Fe [6], the band can be assigned to Co–O symmetric stretch mode, since oxo-bridged Fe or Cr complexes show a symmetric stretch band around 500 cm^{-1} [7,8]. It may be also possible that

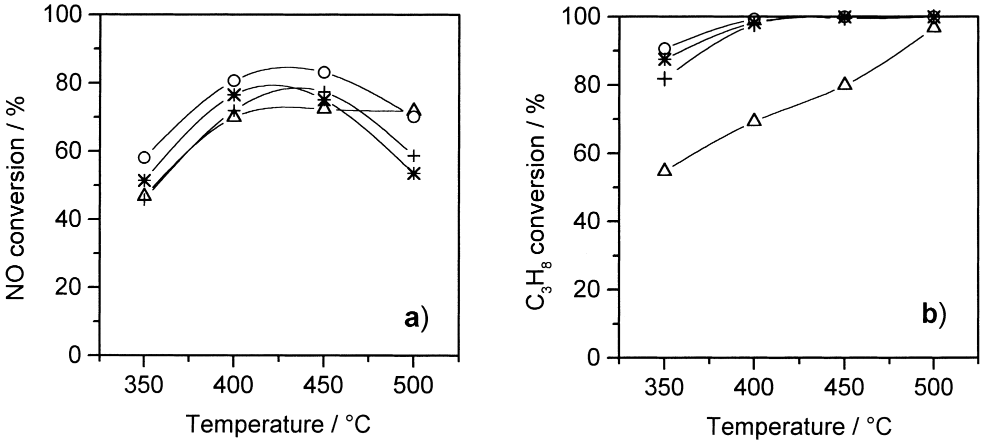

Fig. 3. NO_x (a) and C_3H_8 (b) conversions in C_3H_8-SCR on Co-Beta: (△) (22.3, 80%), (○) (22.3, 97%), (+) (22.3, 104%) and (*) (22.3, 132%). Reaction conditions: NO 150 ppm, C_3H_8 500 ppm, CO 1000 ppm, H_2 660 ppm, O_2 10%, CO_2 6%, H_2O 9%, and GHSV 15 000 h^{-1}.

the species is clusters of more than three cobalt atoms as proposed on Fe-ZSM-5 [9] and over-exchanged Cu-ZSM-5 [10].

3.2. C_3H_8-SCR activity

The C_3H_8-SCR activity of Co-Beta samples of the same SiO_2/Al_2O_3 ratio of 22.3 is shown in Fig. 3. The reaction conditions containing 10% oxygen and 9% water vapor simulate the exhaust from a lean-burning gas engine operated at an excess air ratio (λ) of 2 except for NO_x and C_3H_8 concentrations. In the case of Co-Beta (22.3, 80%), C_3H_8 conversion does not reach 100% even at 500°C, and high NO_x conversion is maintained up to this temperature. This indicates that highly dispersed cobalt is responsible for the highly selective NO_x reduction. On the other hand, Co-Beta (22.3, 132%) shows high NO_x and C_3H_8 conversion at lower temperatures, but shows a sharp decrease in NO_x conversion at high temperatures. At 500°C, C_3H_8 conversion exceeds 95% on all the samples shown in Fig. 3. Therefore, at this temperature, NO_x conversion is considered to be mainly determined by selectivity to NO_x reduction. Whereas Co-Beta (22.3, 80%) and (22.3, 97%) shows NO_x conversion about 70%, that on Co-Beta (22.3, 132%) is 54%. This suggests that on Co-Beta (22.3, 132%), a species, probably Co_3O_4, exists, which causes a decrease in selectivity to NO_x reduction. It is well known that Co_3O_4 has high activity for hydrocarbon oxidation. The sharp decrease in selectivity to NO_x reduction at high temperatures is explained by C_3H_8 oxidation by oxygen competing with SCR reaction. It is noticed that Co-Beta (22.3, 97%) shows the highest NO_x conversion among the four samples at all temperatures between 350°C and 500°C except that Co-Beta (22.3, 80%) shows similar NO_x conversion at 500°C. The activity, i.e. both NO_x and C_3H_8 conversion of Co-Beta (22.3, 104%) is mostly between that of Co-Beta (22.3, 80%) and (22.3, 132%). The decrease in NO_x reduction selectivity at high temperatures occurs like Co-Beta (22.3, 132%) although the effect is a little small and NO_x conversion at 500°C is 59%. This clearly shows that even if the amount of impregnation is decreased, similar activity with Co-Beta (22.3, 97%) is not obtained.

Since NO_x conversions are mainly determined by the selectivity to NO_x reduction under the condition in Fig. 3, activity tests were carried out at higher space velocity. Fig. 4 shows the results. Since C_3H_8 conversion does not reach 100% even at 500°C, the reaction rate also affects the NO_x conversions. Under this condition, Co-Beta (22.3, 97%) also shows the highest NO_x conversion among the four samples at all temperatures between 350°C and 500°C. The cobalt-impregnated samples show a significant decrease in NO_x conversions at 500°C, but show higher NO_x conversions than Co-Beta (22.3, 80%) at lower temperatures below 450°C. This indicates that the presence of Co_3O_4 may be favorable for C_3H_8-SCR at

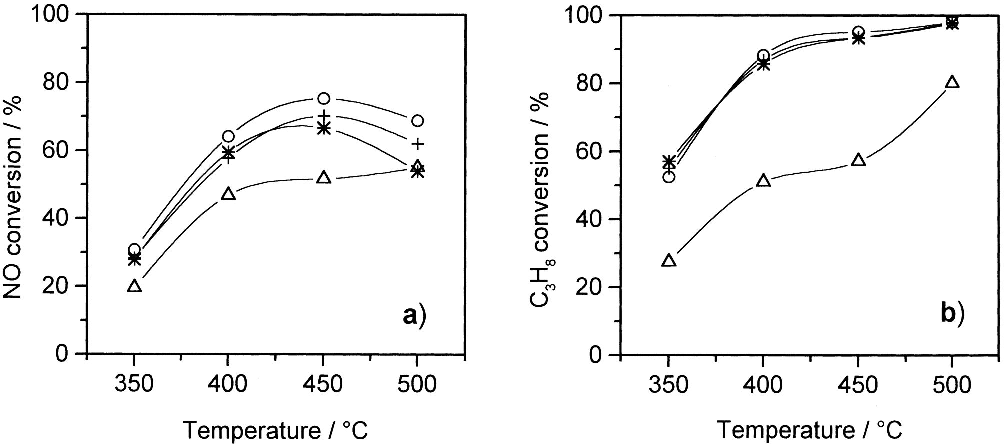

Fig. 4. NO_x (a) and C_3H_8 (b) conversions in C_3H_8-SCR on Co-Beta: (△) (22.3, 80%), (○) (22.3, 97%), (+) (22.3, 104%) and (*) (22.3, 132%). Reaction conditions: NO 150 ppm, C_3H_8 500 ppm, CO 1000 ppm, H_2 660 ppm, O_2 10%, CO_2 6%, H_2O 9%, and GHSV 45 000 h^{-1}.

least under a condition in which the reaction rate affects the NO_x conversion.

Thus, Co-Beta (22.3, 97%) shows both high activity and selectivity for C_3H_8-SCR reaction, and the relation of such activity with the Co species characterized by the band at 600 cm^{-1} is assumed. Fig. 5 shows the C_3H_8-SCR activity of Co-Beta samples of different SiO_2/Al_2O_3 ratios and similar ion exchange levels. Co-Beta (17.5, 102%), which similarly shows the band at 600 cm^{-1} shows similar C_3H_8-SCR activity and keeps around 80% NO_x conversion between 400°C and 500°C. On the other hand, Co-Beta (44.1, 110%) whose 600 cm^{-1} band is very weak, shows considerably low activity. It shows quite low NO_x and C_3H_8 conversions below 400°C, but shows comparable NO_x conversion with Co-Beta (22.3, 97%) at 500°C. It is noticed that the activity, i.e. both NO_x and C_3H_8 conversion of Co-Beta (44.1, 110%) resembles that of Co-Beta (22.3, 80%) rather than (22.3, 97%). This result assures that highly dispersed cobalt is responsible for the highly selective NO_x reduction, and that the Co species characterized by the band at 600 cm^{-1} has both high activity and selectivity for NO_x reduction.

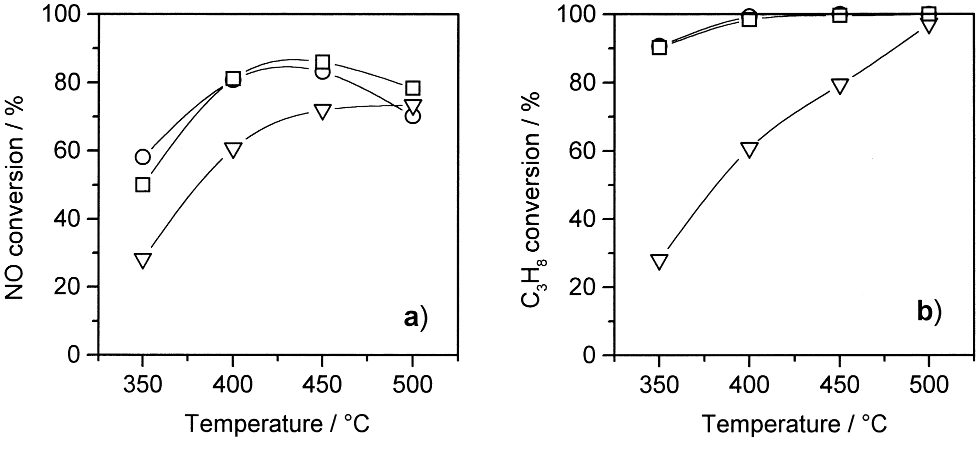

Fig. 5. NO_x (a) and C_3H_8 (b) conversions in C_3H_8-SCR on Co-Beta: (□) (17.5, 102%), (○) (22.3, 97%), and (▽) (44.1, 110%). Reaction conditions: same as in Fig. 3.

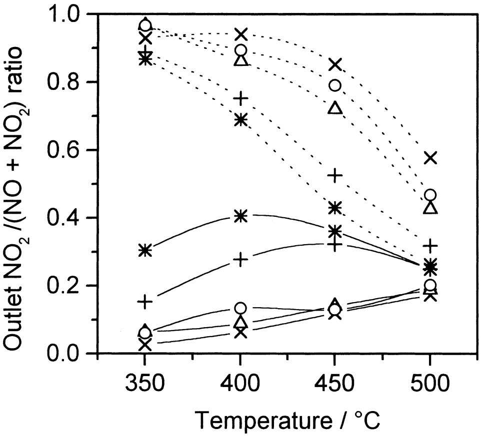

Fig. 6. NO/NO_2 equilibration on Co-Beta: (△) (22.3, 80%), (○) (22.3, 97%), (+) (22.3, 104%), (*) (22.3, 132%) and (×) blank (empty reactor). Reaction conditions: NO (solid curve) or NO_2 (dotted curve) 150 ppm, O_2 10%, H_2O 9%, and GHSV 15 000 h^{-1}.

3.3. NO *oxidation activity*

To shed light on the difference in activity, NO oxidation activity was measured. The results are shown in Fig. 6. In this experiment, CO and H_2 were removed from the feed since they may reduce NO_2 to NO. CO_2 was also removed for simplicity. NO oxidation activity of Co-Beta (22.3, 80%) is very low. On the other hand, Co-Beta (22.3, 104%) and (22.3,132%) shows high activity and in the case of the latter, the equilibrium level is almost attained above 450°C. It has been reported that NO oxidation to NO_2 is the initial step of NO reduction on H- [11], Cu- [12] and Co- [13] zeolites. Stakheev et al. [14] have reported the promotion of C_3H_8-SCR on Co-ZSM-5 by the presence of Co_3O_4 and ascribed to the promotion of NO oxidation to NO_2. The results of Co-Beta (22.3, 104%) and (22.3, 132%) are consistent with their results. It should be noted, however, that the NO oxidation activity of Co-Beta (22.3, 97%) is low and is comparable with Co-Beta (22.3, 80%). This means that its high activity for C_3H_8-SCR does not originate from the NO oxidation activity. This suggests that the species characterized by the band at 600 cm^{-1} has specific reactivity which differs from highly dispersed cobalt and Co_3O_4.

4. Conclusions

In the HC-SCR reaction on Co-Beta using propane as a reductant, highly dispersed cobalt is essential for the high activity and selectivity for NO_x reduction. At high ($\gg$100%) cobalt loading, cobalt oxide (Co_3O_4) is formed. Cobalt oxide promotes hydrocarbon oxidation by oxygen, and decreases the selectivity to NO_x reduction at high temperatures (>450°C), although it increases NO_x conversion at low temperatures (<450°C) through promotion of NO oxidation to NO_2. At cobalt loading around 100%, a characteristic band which shows a strong dependency on SiO_2/Al_2O_3 ratio is observed in Raman spectra, which suggests the presence of μ-oxo cobalt species. Those samples showed both high activity and selectivity for NO_x reduction, which suggests that the species has specific reactivity which differs from highly dispersed cobalt and Co_3O_4.

References

[1] T. Tabata, M. Kokitsu, H. Ohtsuka, O. Okada, L.M.F. Sabatino, G. Bellussi, Catal. Today 27 (1996) 91.
[2] H. Ohtsuka, T. Tabata, O. Okada, L.M.F. Sabatino, G. Bellussi, Catal. Lett. 44 (1997) 265.
[3] R.L. Wedlinger, G.T. Kerr, E.J. Rosinski, US Patent 3 308 069 (1967).
[4] M. Iwamoto, H. Yahiro, N. Mizuno, W.-X. Zhang, Y. Mine, H. Furukawa, S. Kagawa, J. Phys. Chem. 96 (1992) 9360.
[5] J. Valyon, W.K. Hall, J. Phys. Chem. 97 (1993) 7054.
[6] X. Feng, W.K. Hall, Catal. Lett. 46 (1997) 11.
[7] J. Sanders-Loehr, W.D. Wheeler, A.K. Shiemke, B.A. Averill, T.M. Loehr, J. Am. Chem. Soc. 111 (1989) 8084.
[8] D.J. Hewkin, W.P. Griffith, J. Chem. Soc. A (1966) 472.
[9] R.W. Joyner, M. Stockenhuber, Catal. Lett. 45 (1997) 15.
[10] R. Pirone, E. Garufi, P. Ciambelli, G. Moretti, G. Russo, Catal. Lett. 43 (1997) 255.
[11] M. Sasaki, H. Hamada, Y. Kintaichi, I. Ito, Catal. Lett. 15 (1992) 297.
[12] J.O. Petunchi, W.K. Hall, Appl. Catal. B 2 (1993) L17.
[13] Y. Li, T.L. Slager, J.N. Armor, J. Catal. 150 (1994) 388.
[14] A.Yu. Stakheev, C.W. Lee, S.J. Park, P.J. Chong, Catal. Lett. 38 (1996) 271.