Catalysis Letters 61 (1999) 65–69

Effect of SO_2 on selective catalytic reduction of NO by CH_3OCH_3 over γ-alumina in excess oxygen

S.G. Masters and D. Chadwick *

Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, UK

Received 11 March 1999; accepted 8 June 1999

The DME-SCR activity was suppressed upon exposure of a γ-alumina catalyst to SO_2, in contrast to methanol-SCR, which remains active at the same surface sulphate coverage. This difference in behaviour is attributed to the limited availability of surface methoxy, which may be regarded as a prerequisite for NO_x reduction over γ-alumina under lean conditions, in the case of dimethyl ether in the presence of SO_2.

Keywords: SO_2, NO reduction, dimethyl ether, γ-alumina

1. Introduction

We have recently reported [1] on the effect of SO_2 on catalytic activity of γ-alumina for NO reduction to N_2 by methanol in excess oxygen, where it was demonstrated that the activity increased initially upon exposure under SCR conditions of a γ-alumina catalyst to SO_2. This effect was attributed to formation of Brønsted acid sites by adsorbed SO_2, whereby methanol activation into surface methoxy was promoted. Longer exposure to SO_2 led to a decline in catalytic activity, yet as a consequence of this capability for methanol activation, the catalytic system remained active for NO reduction despite sulphation of the γ-alumina. Since methanol (MeOH) and dimethyl ether (DME) display similar performances for selective reduction of NO over γ-Al_2O_3 and promoted aluminas [2], it is of interest to establish if the SCR activity using dimethyl ether was also enhanced initially upon SO_2 addition as observed for methanol, and whether SCR using oxygenates over γ-Al_2O_3 is generally sulphur tolerant.

We demonstrate here that the catalytic activity for NO reduction by dimethyl ether is suppressed upon exposure of γ-alumina to SO_2, with no evidence for a transient initial increase, in contrast to methanol at the same surface sulphate concentration.

2. Experimental

The surface areas, pore volumes and average pore diameters of the fresh and sulphated γ-Al_2O_3 catalysts are given in [1]. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a VG ESCALAB MK II spectrometer using Al Kα radiation (1486.6 eV). The quoted binding energies were referenced to the C 1s peak at 284.8 eV from adventitious carbon. The experimental XPS atomic ratios (S 2p/Al 2p) were obtained by correcting the intensity ratios with sensitivity factors derived from Briggs and Seah [3].

The catalytic activity was measured in a fixed-bed microflow reactor mounted vertically in an electrically heated furnace [4]. The catalyst sample (particle size 106–250 μm) was positioned between pre and post packing of SiC (particle size 106–250 μm) to ensure plug-flow conditions. Intra- and extraparticle diffusion limitation was experimentally confirmed to be absent. The feed gas mixture was obtained by blending helium-balanced standard gases, each controlled independently by mass flow controllers. All gases, certified quality, were used without further purification. The catalytic activity was calculated based on NO conversion measured by a chemiluminescence NO_x analyser. N_2O formation was not detected during SCR of NO. Other compounds (O_2, CO, CO_2, SO_2, H_2O, CH_3OH, CH_3OCH_3) in the effluent stream were analysed on-line with a Shimadzu 14B gas chromatograph with a TCD detector and a Porapak-Q column. The carbon material balance was retained throughout the experiments. The SCR feed gas mixture consisted of 1700 ppm NO, 1700 ppm CH_3OCH_3 and 3% O_2 containing either 0, 17 or 102 ppm SO_2, respectively. The flow rate was maintained at 120 $cm^3\ min^{-1}$ and the quoted GHSV values are based on the measured bulk density of γ-Al_2O_3 used (0.49 g/cm^3).

3. Results and discussion

3.1. Effect of SO_2 on SCR activity

The effect of SO_2 addition to the feed gas mixture on SCR activity over γ-alumina (surface area: 256 m^2/g and NH_3-TPD: 1.28×10^{-3} mmol NH_3/m^2; γ-alumina (A) of [1]) was monitored as a function of time-on-stream at

---

[*] To whom correspondence should be addressed.

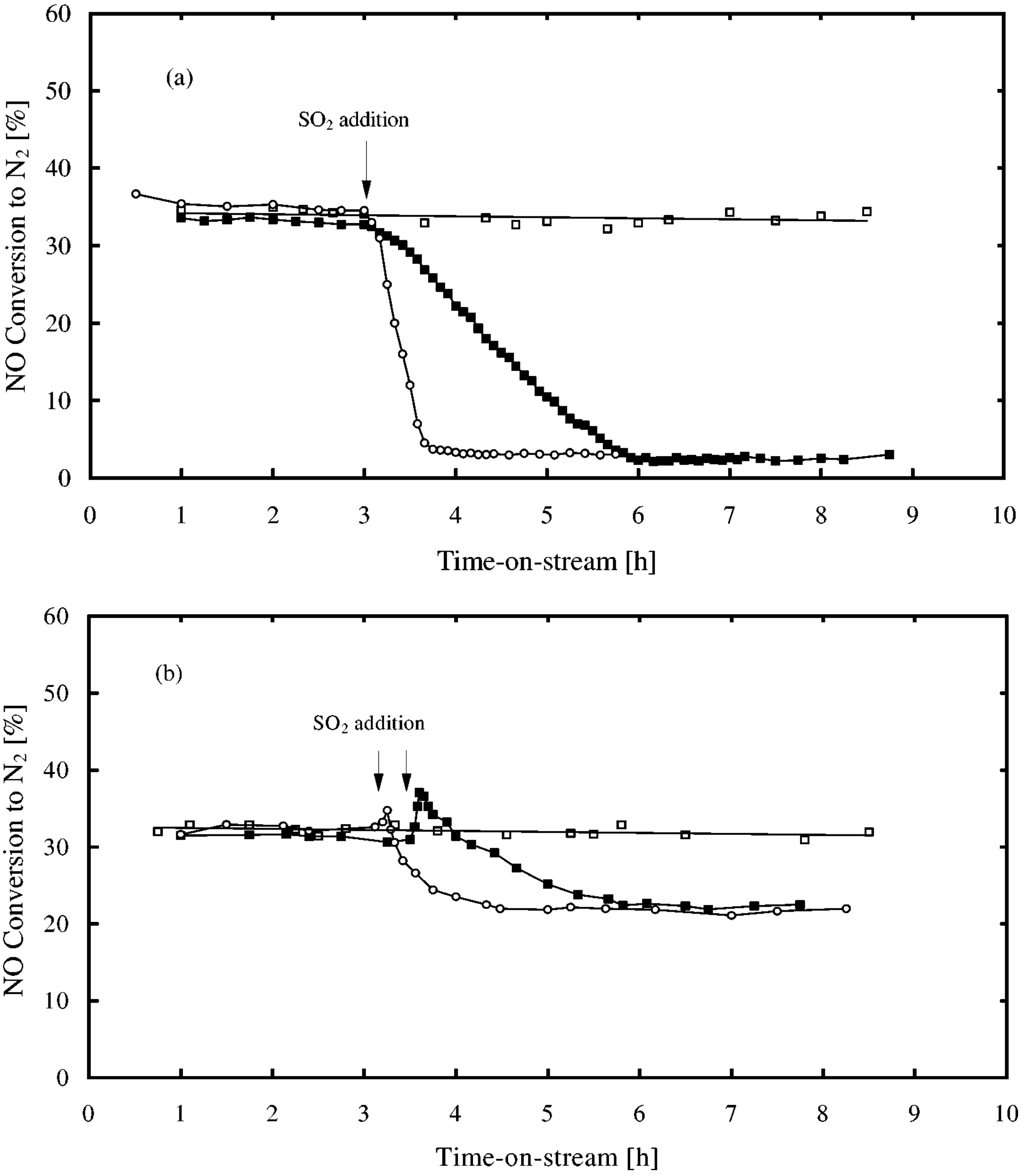


Figure 1. Effect of SO_2 on NO conversion to N_2 over γ-Al_2O_3 by (a) dimethyl ether and (b) methanol at 450 °C. (□) 0 ppm SO_2, (■) 17 ppm SO_2 and (○) 102 ppm SO_2. Conditions: 1700 ppm NO, 3400 ppm CH_3OH or 1700 ppm CH_3OCH_3 and 3% O_2; GHSV = 141000 h^{-1}.

450 °C, which corresponded to the temperature for maximum NO conversion to N_2 with dimethyl ether. The catalyst was exposed to a $NO/CH_3OCH_3/O_2$ feed gas for 3 h at 450 °C to establish a steady-state NO conversion in the absence of SO_2. Subsequently, SO_2 was added to the feed gas by replacing helium so that the total flow rate, and concentrations of the other compounds in the feed gas were unaffected.

The effect on NO conversion to N_2 in excess oxygen upon addition of 17 and 102 ppm SO_2, respectively, over γ-Al_2O_3 is plotted in figure 1(a). In the absence of SO_2, a steady-state NO conversion to N_2 of 34% at 450 °C was achieved (the GHSV was specifically chosen to maintain NO conversion below 40%). Addition of 17 ppm SO_2 to the feed gas initiated instantly a gradual decrease in activity over a period of 3 h resulting finally in a steady-state SCR conversion of approximately 3%. A similar decrease in SCR activity occurred upon addition of 102 ppm SO_2 to the feed gas, but the activity declined more quickly than for 17 ppm SO_2, and the same steady-state level of 3% NO conversion was reached after only 45 min. In contrast to methanol for SCR (see figure 1(b)) over the same γ-Al_2O_3 under identical conditions, no increase in the NO conversion to N_2 was observed upon addition of SO_2 to the feed gas. Near identical results were obtained using a second commercial γ-alumina (surface area: 238 m^2/g and NH_3-TPD: 1.80×10^{-3} mmol NH_3/m^2; (B) of [1]).

Figure 2 shows (applying a GHSV of 30700 h^{-1}) the steady-state SCR conversions in the temperature range 250–600 °C over γ-Al_2O_3 using a feed gas with and without SO_2. Addition of SO_2 to the gas mixture shifted the maximum NO conversion temperature from 460 to 540 °C, while

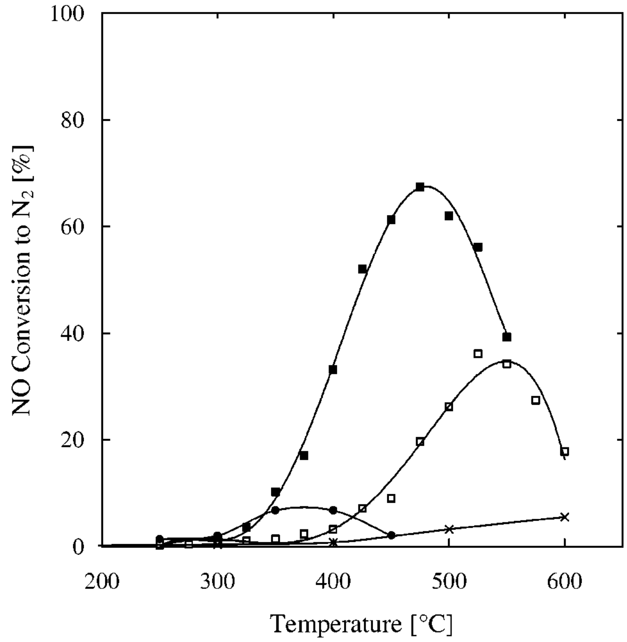


Figure 2. Steady-state NO conversion to N_2 by dimethyl ether under lean conditions over γ-Al_2O_3. (■) 0 ppm SO_2, (□) 102 ppm SO_2 and (×) blank reactor. Conditions: 1700 ppm NO, 1700 ppm CH_3OCH_3 and 3% O_2; GHSV = 30700 h^{-1}. (●) 1700 ppm NO, 3400 ppm CO, 5100 ppm H_2 and 3% O_2.

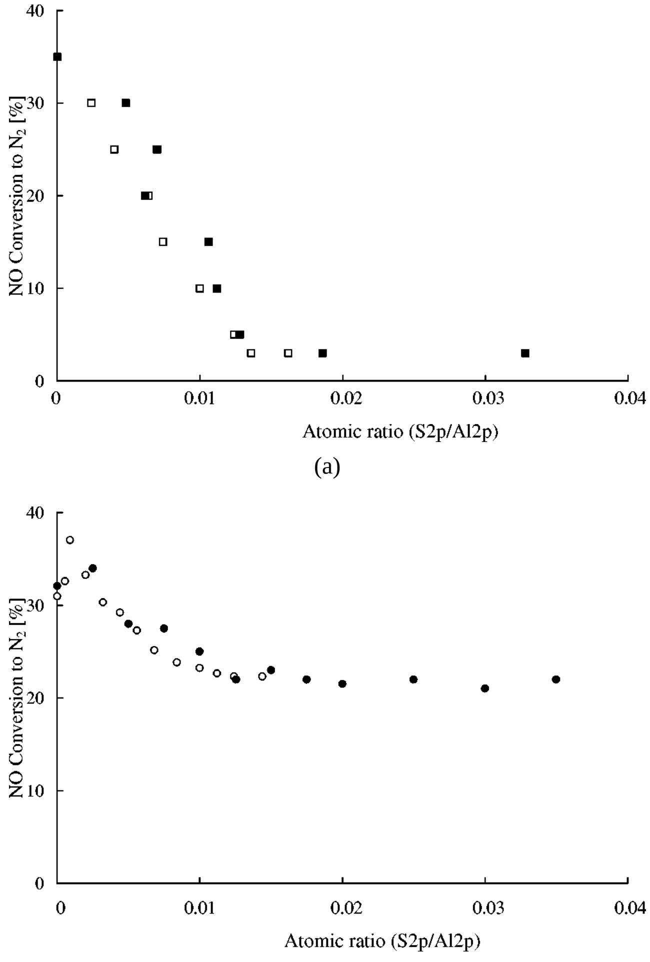
the NO conversion to N_2 was significantly reduced in the presence of SO_2. Virtually identical results were observed using different commercial γ-aluminas.

The results for dimethyl ether shown in figures 1(a) and 2 are in sharp contrast to our previous results using methanol as a reductant under identical experimental conditions [1]. For methanol, the temperature for maximum NO reduction increased by only 10 °C, and the steady-state SCR conversion was reduced by only a factor of 1.5 in the presence of SO_2. In addition, the initial activity using methanol was enhanced transiently upon exposure to SO_2, due to formation of Brønsted acid sites [5–7] which promotes methanol activation into methoxy [1]. This is discussed further below.

3.2. XPS analysis of sulphur accumulation

The accumulation of sulphur over γ-alumina was monitored at 450 °C by measuring the atomic ratio, S 2p/Al 2p, by XPS as a function of the exposure time to SO_2 using a feed gas with and without dimethyl ether included. The experimental protocol for SO_2 addition was identical to that described above. After exposing the catalyst to the SO_2 containing feed gas for a controlled duration, the feed gas mixture was instantly replaced by helium and cooled to ambient temperature, before transfer to the XPS instrument.

The atomic ratio, S 2p/Al 2p, was observed to be identical in the presence and in the absence of dimethyl ether, showing that dimethyl ether has no influence on the sulphation process. An analogous independence on the sulphation process was also observed for methanol. For the feed gas containing 102 ppm SO_2, the experimental atomic ratio curved strongly after 45 min of exposure, due to sulphate formation beyond a monolayer, corresponding to S 2p/Al 2p = 0.013 and 0.6 SO_4^{2-}/nm^2 (2.5 wt% SO_4^{2-}/Al_2O_3). This coincided with the approach to the lower steady-state activity level, shown in figure 1(a). Subsequently, the S 2p/Al 2p ratio gradually approached a constant value of 0.036. The maximum sulphate capacity (S 2p/Al 2p = 0.036) was 1.6 SO_4^{2-}/nm^2 (7 wt% SO_4^{2-}/Al_2O_3) which is in good agreement with the maximum sulphate capacity of 1.3 SO_4^{2-}/nm^2 for alumina reported by Saur et al. [6]. While using a lower SO_2 concentration (17 ppm SO_2), the monolayer capacity at S 2p/Al 2p = 0.013 was obtained after 180 min of exposure, which coincided with the approach to the same low degree of steady-state SCR activity, figure 1(a).



(a)

(b)

Figure 3. Catalyst deactivation as a function of the accumulated sulphur content (expressed as the atomic ratio, S 2p/Al 2p) over γ-Al_2O_3 at 450 °C. (a) (□) DME/NO/O_2/SO_2 (17 ppm) and (■) DME/NO/O_2/SO_2 (102 ppm). (b) (○) CH_3OH/NO/O_2/SO_2 (17 ppm) and (●) CH_3OH/NO/O_2/SO_2 (102 ppm).

In comparing the effect of SO_2 on methanol and dimethyl ether in SCR it is useful to consider the NO conversion into N_2 in relation to the accumulated sulphur content (described by the atomic ratio obtained from XPS), as shown in figure 3. The simultaneous occurrence of the sulphate monolayer and the permanently low DME-SCR activity is clearly illustrated by a break-point at S 2p/Al 2p $= 0.013$, figure 3(a). For methanol, the final steady-state SCR activity corresponded to $2/3$ of the activity displayed by the fresh γ-alumina, figure 3(b). In both cases, the decline in activity is related directly to the sulphur coverage on the γ-alumina surface and is independent of the SO_2 content in the feed gas mixture. The results shown in figure 3 demonstrate clearly the continued ability of sulphated γ-alumina to activate methanol above the monolayer coverage of sulphate, hence maintaining the system active for NO_x reduction, and the failure of sulphated γ-alumina to activate dimethyl ether in a similar way, thus resulting in very low steady-state activity.

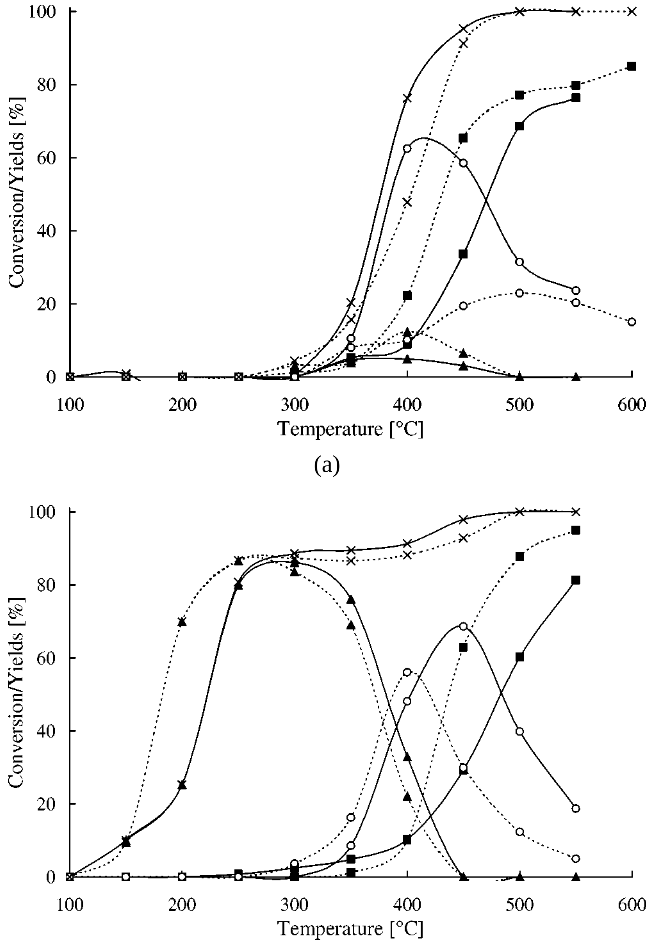
3.3. Dimethyl ether activation

To investigate further the discrepancy between the SCR performances of methanol and dimethyl ether for NO reduction over sulphated γ-alumina, the distribution of the carbon-containing products from DME/O_2 and $MeOH/O_2$ feed gases (balanced in helium) over fresh and sulphated γ-Al_2O_3 were determined and are shown in figure 4 (a) and (b). Methanol was converted selectively into dimethyl ether over γ-Al_2O_3 in the temperature range 100–300 °C, while for dimethyl ether, used as a reductant, conversion only commenced above 300 °C. For both methanol and dimethyl ether, CO was the main carbon-containing product formed between 300 and 475 °C. CO_2 was the predominant product above 400 °C. In addition, traces of methanol were detected from a DME/O_2 feed gas above 300 °C.

The formation of methanol (from DME/O_2) is attributed to protonation of dimethyl ether into a dimethyloxonium species, which subsequently eliminates methanol forming a methoxy species [8]. Based on our previous observations concerning the formation of Brønsted acid sites over sulphated γ-alumina [1], the increase in the methanol yield for the sulphated alumina was expected and entirely consistent with the literature [5–7].

DME-TPD studies by Chen and Falconer [9] have demonstrated that dimethyl ether is dissociatively adsorbed on γ-alumina into methoxy species and it is well documented that methanol is also absorbed on γ-alumina as methoxy species [10–13]. In the present case, dimethyl ether conversion commenced above 300 °C, whether used as a reductant or as product formed from methanol at low temperature. Hence, we can discount the presence of formate species [9], and the CO (and H_2) originates from decomposition of surface methoxy species. Consequently, the profiles for the CO yield from DME/O_2 and $MeOH/O_2$ are qualitatively similar over γ-alumina. Indeed, the results for the unsulphated γ-alumina, figure 4, are consistent with the TPD data reported by Chen and Falconer [9,10].

We note that decomposition of methoxy commenced slightly below the temperature required for NO conversion into N_2. A CO/H_2 mixture of composition corresponding to dimethyl ether decomposition displays low NO reduction capability over the γ-alumina, see figure 2. Therefore, it could be an intermediate formed during methoxy decomposition [12], which is involved and can intercept gas-phase NO_x according to an Eley–Rideal type mechanism, as proposed by Burch et al. [14], or react with adsorbed NO_x species following Langmuir–Hinshelwood kinetics, resulting in CO being detected only in traces in the presence of NO_x. The intermediate might be formyl, as methoxy is likely to decompose via sequential hydrogen loss [15]. Formyl has not been observed on a γ-alumina surface, since it would be a highly unstable, short-lived species.



(a)

(b)

Figure 4. Distribution of the carbon-containing products from (a) dimethyl ether/oxygen and (b) methanol/oxygen over (—) fresh γ-Al_2O_3 and (- - -) sulphated γ-Al_2O_3. (○) CO, (■) CO_2, (▲) CH_3OCH_3/CH_3OH and (×) overall CH_3OCH_3/CH_3OH conversion. (Detection of H_2 was not possible.) Conditions: 1700 ppm CH_3OCH_3 or 3400 ppm CH_3OH and 3% O_2; GHSV $= 30700\ h^{-1}$.

The CO and CO_2 distribution profiles from DME/O_2 were very different over the fresh and the sulphated γ-alumina. The enhancement of the CO_2 yield at lower temperatures might be due to the participation of sulphate in a redox process. Therefore, the combined effect of a higher temperature required for commencement of dimethyl ether conversion and an increase in CO_2 formation rate at lower temperatures, effectively eliminates the temperature region were methoxy is present in significant coverage on the sulphated surface. As a consequence, NO conversion to N_2 was strongly reduced compared to the unsulphated sample.

In contrast, the ability of the MeOH-SCR system to remain active in the presence of SO_2 is clearly due to the availability of surface methoxy above 300 °C, as evidenced by only a slight reduction in the CO yield compared to the unsulphated alumina. The difference in peak temperatures observed for the CO yield from MeOH/O_2 and the maximum SCR activity over sulphated alumina is probably related to NO activation, since the temperature required for maximum NO conversion by methanol is almost unaffected by the presence of SO_2.

4. Conclusions

The SCR activity of NO reduction by dimethyl ether is suppressed upon exposure of the γ-alumina catalyst to SO_2. This is attributed to the combined effect of a higher temperature required for dimethyl ether conversion and a decrease in the temperature required for CO_2 formation, leading to the limited availability of surface methoxy. Thus the DME-SCR system has a low sulphur tolerance compared to MeOH-SCR, where surface methoxy is present in a broad temperature region.

Acknowledgement

SGM is grateful for receiving the Christian og Ottilia Brorsons rejselegat for yngre videnskabsmænd og-kvinder scholarship, Copenhagen.

References

[1] S.G. Masters and D. Chadwick, Catal. Lett. 57 (1999) 155.
[2] S.G. Masters and D. Chadwick, Appl. Catal. B, to be published.
[3] D. Briggs and M.P. Seah, in: *Practical Surface Analysis*, Vol. 1, *Auger and X-ray Photoelectron Spectroscopy*, 2nd Ed. (Wiley, New York, 1992) p. 627.
[4] S.G. Masters and D. Chadwick, Catal. Today 42 (1998) 137.
[5] W. Przystajko, R. Fiedorow and I.G. Dalla Lana, Appl. Catal. 15 (1985) 265.
[6] O. Saur, M. Bensitel, A.B. Mohammed Saad, J.C. Lavalley, C.P. Tripp and B.A. Morrow, J. Catal. 99 (1986) 104.
[7] M. Ziolek, J. Kujawa, O. Saur, A. Aboulayt and J.C. Lavalley, J. Mol. Catal. A 112 (1996) 125.
[8] T.R. Forester and R.F. Howe, J. Am. Chem. Soc. 109 (1987) 5076.
[9] B. Chen and J.L. Falconer, J. Catal. 147 (1994) 72.
[10] B. Chen and J.L. Falconer, J. Catal. 144 (1993) 215.
[11] G. Bercic and J. Levec, Ind. Eng. Chem. Res. 31 (1992) 1035.
[12] T. Matsushima and J.M. White, J. Catal. 44 (1976) 183.
[13] E.C. DeCanio, V.P. Nero and J.W. Bruno, J. Catal. 135 (1991) 444.
[14] R. Burch, E. Halpin and J.A. Sullivan, Appl. Catal. B 17 (1998) 115.
[15] D. Chadwick and K. Zheng, Catal. Lett. 20 (1993) 231.