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Activity, selectivity and durability of VO–ZSM-5 catalysts for the selective catalytic reduction of NO by ammonia

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Abstract

ZSM-5 zeolite was loaded with vanadyl ions (VO^{2+}) by treatment of Na–ZSM-5 with aqueous $VOSO_4$ solution at pH 1.5–2. The catalytic material was tested for the selective catalytic reduction of NO with ammonia at temperatures between 473 and 823 K and normal pressure using a feed of 1000 ppm NO, 1000 (or 1100) ppm NH_3 and 2% O_2 in He. The catalyst proved to be highly active, providing, e.g. initial NO conversions of >90% at $620\,l\,g^{-1}\,h^{-1}$ ($\approx 400\,000\,h^{-1}$) and 723 K, and selective, providing nitrogen yields equal to NO conversion at equimolar feed in a wide temperature range and only minor N_2O formation at NH_3 excess. Admixture of SO_2 (200 ppm) resulted in an upward shift of the useful temperature range, but did not affect the catalytic behaviour at temperatures $\geq$623 K. No SO_2 conversion was noted at $T \leq 723$ K and $450\,l\,g^{-1}\,h^{-1}$. The poisoning effect of water (up to 4.5 vol%) was weak at temperatures between 623 and 773 K. VO-ZSM-5 catalysts are gradually deactivated already under dry conditions, probably by oxidation of the vanadyl ions into pentavalent V species. This deactivation is considerably accelerated in the presence of water. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Selective catalytic reduction (SCR) of NO by NH_3; Vanadium; Zeolites; Activity; Selectivity; Durability

1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides has been a major topic in environmental catalysis over the last decade. This reaction has been intensively studied, both in the traditional, commercially established version with the reductant ammonia (SCR-NH_3) and with catalytic materials permitting the use of hydrocarbon reductants (SCR-HC). Owing to delayed progress in the search for stable catalysts for SCR-HC, the importance of the traditional ammonia technology has also increased by the recent commercial implementation of urea-based DENOX converters for heavy Diesel engines by Siemens [1].

Considerable progress has been made in the basic understanding of the SCR with ammonia over V/(W)/Ti/O catalysts, covering both, the refinement of the catalyst preparation and the elucidation of the reaction mechanism [2–8]. In the latter field, there are, however, divergent views about the requirements of the mechanism regarding the active site: while most mechanistic proposals (e.g. Ref. [7]) include the concerted action of two neighbouring V atoms in the surface, the amide-nitrosamide mechanism proposed by Ramis et al. [9] and modified by Lietti et al. [10] may proceed on isolated V sites.

It has been known for some time that SCR-NH_3 may be catalysed also by zeolites modified with redox elements as copper [11,12], cerium [13], or iron

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[12,14]. In a previous paper [15], we reported that ZSM-5 zeolites exchanged with vanadyl ions (VO^{2+}) exhibit an SCR activity well comparable with that of a V/Ti/O reference catalyst (Eurocat EL10 V1: 1% V_2O_5/TiO_2). The VO^{2+} ion, i.e. an isolated V(IV) species, could be established as the active site in this system by combining catalytic and spectroscopic investigations (EPR, XPS, UV-VIS). The present paper reports the influence of water and SO_2, which are typical ingredients in real flue gases, on the activity and the stability of a VO-ZSM-5 catalyst. Since the catalyst employed resulted from a modified preparation yielding superior SCR activity, the preparation and the catalytic properties of the improved VO-ZSM-5 catalyst will be described in detail.

2. Experimental

The catalyst was prepared by exchanging VO^{2+} ions into Na-ZSM-5 (Si/Al ≈ 14, Chemiewerk, Bad Köstritz, Germany) from a $VOSO_4$ solution (0.15 mol/l, 500 ml of solution for 10 g zeolite) at 348 K, keeping the pH value at 1.5–2 by adding sulphuric acid. Sixfold exchange under these conditions provided a vanadium content of 1.09 wt%, however, there was no significant increase of the V content already after the fourth exchange. The treatment of the zeolite with the acidic exchange solution resulted in some zeolite dealumination rendering the Si/Al ratio between 17 and 18, from which an exchange degree of ≈45% was calculated for the VO^{2+} ions. XPS measurements [16] showed that the dealumination of the external surface layer was much more intense ($(Si/Al)_{surf} = 30–40$). The material was dried in air at 393 K and used in the catalytic experiments without further treatment. A Eurocat EL10V1 sample (1%V_2O_5/TiO_2) was used as a reference catalyst. Its preparation has been described elsewhere [17].

The selective catalytic reduction (SCR) of NO with ammonia was investigated in a catalytic micro-flow reactor (i.d. 4 mm) at atmospheric pressure. The feed contained 1000 ppm NO, 1000 or 1100 ppm NH_3, and 2% O_2 in He. Poisoning effects and durability were studied by admixing 2.9 or 4.5 vol% H_2O and/or 200 ppm SO_2 to the feed. The SCR activity was measured at temperatures between 473 and 823 K (increasing order of reaction temperatures), charging 200 or 260 ml/min feed gas over 25–100 mg of catalyst (VO-ZSM-5 or Eurocat EL10V1, 620–120 $l\,g^{-1}\,h^{-1}$, or 400 000–170 000 vvh). The effluent was analysed by a combination of mass spectrometry (O_2, H_2O, NO, N_2O, N_2, NH_3) and non-dispersive IR-photometry (NO, NO_2). The nitrogen balance was in the range of 98–106% in the experiments without water admixture (‘dry conditions’), where the NH_3 signal at $m/e = 17$ could be reliably corrected for the contribution of fragmented H_2O. In the presence of water, the N balance was subject to much larger deviations, therefore we report here only NO conversions for these runs, which were consistently measured both by the IR and the MS techniques. The activity data will be reported in terms of conversions (X) for NO and NH_3, and yields (Y) for N_2 and N_2O.

SO_2 conversions under dry conditions were determined by mass spectrometry, measuring the SO_2 concentration in the effluent after trapping the SO_3 formed at 263 K. This temperature turned out to be too low for this purpose, since the water condensed at longer duration of the run may dissolve some SO_2. The SO_2 conversions, reported below, for the highest reaction temperatures (i.e. at the end of the run) should, therefore, be considered as upper limits.

3. Results

Fig. 1 compares the catalytic behaviour of VO-ZSM-5 prepared at an ion-exchange pH 1.5–2 (b, c) with that of the 1% V_2O_5/TiO_2 reference catalyst EL10V1. The experiment were performed with excess NH_3 (a, b) and with equimolar feed (c). Typical rates of NO consumption related to the V amount present (‘normalised reaction rates’) are summarised in Table 1 together with relevant selectivity data ($S_{N_2O} = 100\, Y_{N_2O}/X_{NO}$, %). As reported in Ref. [15], the Eurocat exhibits an activity maximum in a narrow temperature range around 623 K. Its tendency to oxidise ammonia at elevated temperatures and its unsatisfactory selectivity for nitrogen formation is confirmed, with N_2O selectivities increasing up to 60% at 723 K. The normalised reaction rate of the Eurocat reported in Table 1 is well consistent with our earlier data with equimolar feed [15]. Around the activity maximum, the NO conversion slightly exceeded that of NH_3 (by up to 8%). This could be due to N_2O formation,

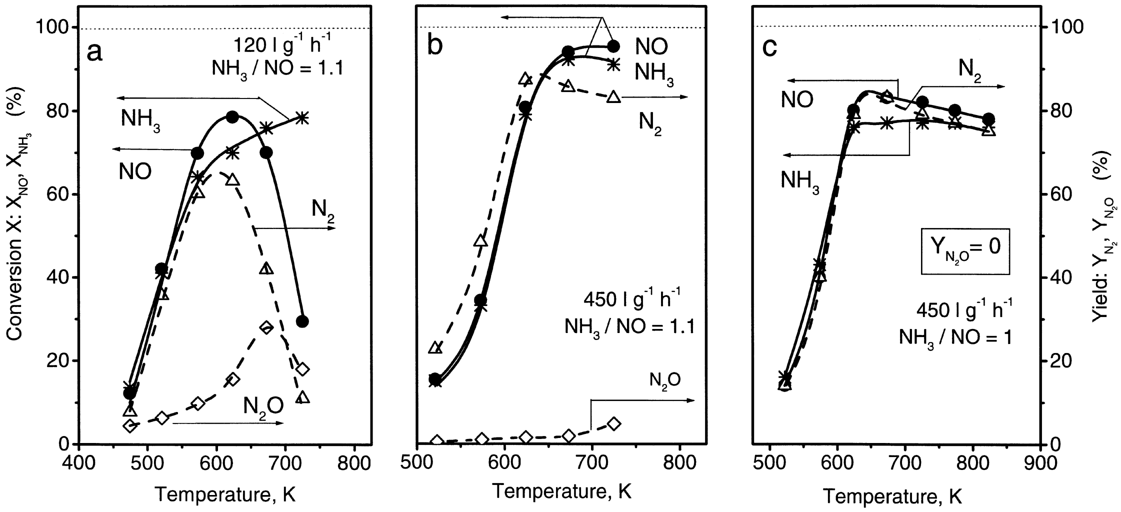

Fig. 1. SCR activity and selectivity of VO-ZSM-5 in comparison with V_2O_5/TiO_2–NO, NH_3 conversions and N_2, N_2O yields. Feed: 1000 ppm NO, 1100 or 1000 ppm NH_3, 2% O_2 in He. (a), 1%V_2O_5/TiO_2 (Eurocat EL10V1), NH_3 excess, 120 l g^{-1} h^{-1}; (b), VO-ZSM-5 (pH 1.5–2), NH_3excess, 450 l g^{-1} h^{-1}; (c), VO-ZSM-5 (pH 1.5–2), equimolar feed, 450 l g^{-1} h^{-1}.

Table 1
NO conversions and normalised reaction rates in the selective catalytic reduction of NO by NH_3 over VO-ZSM-5 catalysts. Feed: 1000 ppm NO, 1100 or 1000 ppm NH_3, 2%O_2 in He

Catalyst	Feed		T (K)	X_{NO}	r_{NO}/V (min^{-1})	S_{N_2O} (%)
	α[a]	(l g^{-1} h^{-1})				
Eurocat 1% V_2O_5	1.1	120	623	0.78 (max)	0.64	20
VO-ZSM-5 (pH 1.5–2)	1.1	450	623 (673)	0.81 (0.94)	1.26 (1.46)	2 (2)
	1.0	450	673[b]	0.83 (max)	1.22	0
	1.0	620	723[c]	0.95	2.58	–
	1.0	620	623[d]	0.47	1.28	–
VO-ZSM-5 (pH 2.7) [15]	1.0	94	673	0.64	0.62[e]	–
VO-ZSM-5 (pH 3) [15]	1.0	94	673	0.79	0.46[f]	–

[a] NH_3/NO.
[b] Deactivated during previous catalytic experiment.
[c] Initial activity.
[d] After 86 h time-on-stream.
[e] 0.37 wt% V.
[f] 0.62 wt% V.

predominantly from NO and NH_3 (instead of NO oxidation), but more likely, it is by experimental error since a similar difference occurred in an experiment with VOZSM-5 where N_2O was not observed at all (Fig. 1(c)).

On the contrary, the VO-ZSM-5 catalyst, which was studied at considerably larger space velocities, is highly selective for the SCR reaction. With equimolar feed (Fig. 1, c), the N_2 yield coincides with both, the NO and NH_3 conversions within the limits of experimental error, and N_2O is formed in low amounts only with excess NH_3 feed. Table 1 shows that preparation at pH 1.5–2 improves the activity of the VO-ZSM-5 catalyst considerably as compared with the preparation at higher pH values. The new preparation provides also much higher normalised reaction rates than the 1%V_2O_5/TiO_2 reference sample, although the zeolite catalyst requires a somewhat higher temperature to reach its maximum reaction rate. However, with the improved preparation, VO-ZSM-5 surpasses the

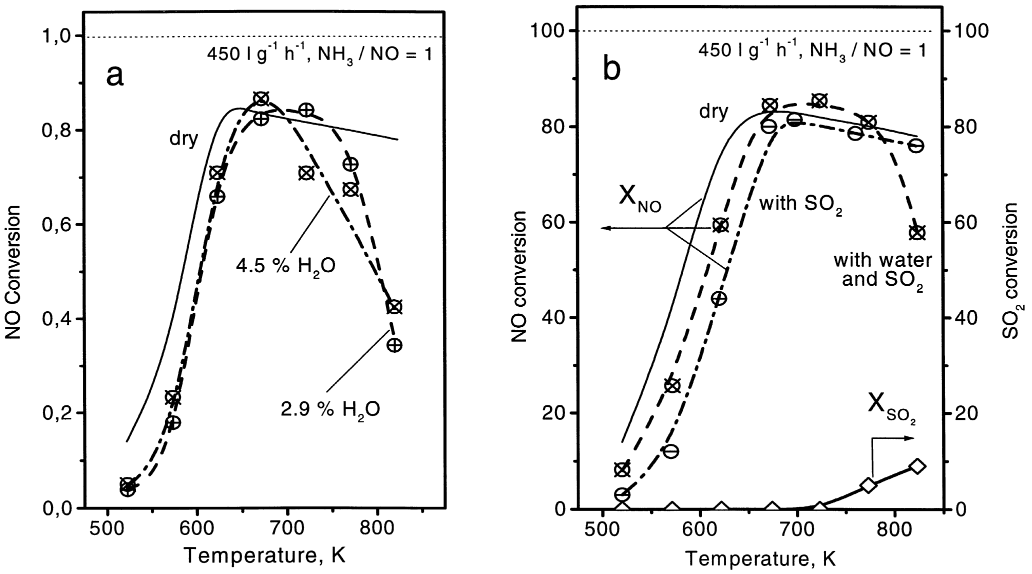

Fig. 2. Poisoning of VO-ZSM-5 (pH 1.5–2) by H_2O and SO_2. Feed: 1000 ppm NO, 1000 ppm NH_3, 2% O_2 in He at 450 l g^{-1} h^{-1} ('dry'). (a), Influence of moisture (2.9 or 4.5 vol% H_2O); (b). influence of SO_2 (200 ppm) under dry and moist (2.9 vol% H_2O) conditions; and SO_2 conversions measured without water admixed.

V_2O_5/TiO_2 catalyst even under the optimum conditions of the latter, both in activity and selectivity. Fig. 1 also shows that the vanadyl zeolite has a considerably broader useful temperature range than the reference V/Ti/O catalyst. It will be shown in the following that VO-ZSM-5 is subject to severe deactivation in the high-temperature region so that the initial activity would have been, certainly, sufficient to reach almost complete NO conversion above 673 K. Indeed, in a durability test at 723 K, an NO conversion of >90% was obtained with equimolar feed at a much higher space velocity of 620 l g^{-1} h^{-1}(Fig. 3), which results in the highest normalised reaction rate measured with VO-ZSM-5 so far (2.6 min^{-1}, cf. Table 1).

Fig. 2 summarises the influence of the typical catalyst poisons relevant for flue-gas catalysis. Fig. 2(a) shows that water effects a slight shift of the onset of catalyst activity to higher temperatures. More serious poisoning is indicated by a strong decrease of the NO conversion at temperatures >750 K, which is, however, at least partly due to an increased deactivation rate in moist media in this temperature region (vide infra). In a narrow range around 670 K, there is no poisoning even with 4.5 vol% water, and between 623 and 773 K the poisoning influence of water is absent at 2.9 vol%, and weak at 4.5 vol% H_2O.

Fig. 2(b) demonstrates that SO_2 is a catalyst poison only at low temperatures while the conversion curve coincides with that of the SO_2-free feed at $T \geq 673$ K. There was no SO_2 conversion up to 723 K. As noted in the experimental part, the SO_2 conversions measured at higher temperatures (up to 9%) may be erroneous due to SO_2 absorption in the SO_3 trap and should be considered as upper limits. An improved methodology for the investigation of the unwanted SO_2 oxidation reaction is currently being implemented in our experimental facilities. During the experiments reported in this paper (including durability test, Fig. 3), we did not note the formation of ammonium sulphate powder as experienced in similar experiments with other redox zeolites [16].

Fig. 3 reports results of durability tests performed with VO-ZSM-5 (preparation at pH 1.5–2). Already under dry conditions, the NO conversion decreases significantly with increasing time-on-stream (Fig. 3(a)). While this deactivation is more pronounced at 723 K, a still attractive residual activity appears to remain at 623 K, where the normalised reaction rate after almost 90 h still exceeds that of the reference

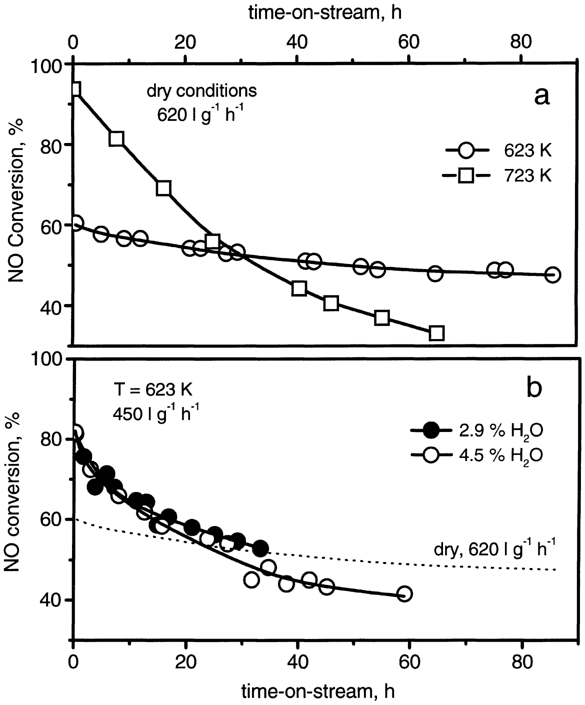

Fig. 3. Durability tests with of VO-ZSM-5 (pH 1.5–2). Feed: 1000 ppm NO, 1000 ppm NH_3, 2% O_2 in He ('dry'). (a), Influence of the reaction temperature on the deactivation under dry conditions ($620\,l\,g^{-1}\,h^{-1}$); (b), influence of the water content on the deactivation at 623 K ($450\,l\,g^{-1}\,h^{-1}$).

V_2O_5/TiO_2 catalyst (cf. Table 1). Moisture, however, accelerates the deactivation process considerably, with increasing damage occurring at increasing water contents (Fig. 3(b)).

4. Discussion

Exchange of VO^{2+} ions into ZSM-5 at pH 1.5–2 results in catalysts of very high activity for the SCR of NO with NH_3. In equimolar feed, these catalysts perform the SCR reaction selectively without oxidising ammonia to any significant extent either to N_2 or to N_2O. Moreover, no SO_2 oxidation activity could be detected with them at $T \leq 723$ K, which is compatible with observations about support effects on vanadium sites for the SO_2 oxidation reported by Dunn et al. [18].

It is not clear as yet why decreasing the pH of the exchange solution leads to a spectacular increase not only of the overall activity, but also of the reaction rate per vanadium site (cf. Table 1). Our earlier investigation of VO-ZSM-5 obtained at pH between 2.5 and 3 showed that preparations at pH <2.7 are practically void of intra-zeolite vanadium oxide clusters, which precipitate at higher pH values, i.e. they should contain predominantly VO^{2+} ions [15]. Our ongoing investigation on this question centres around the assumption that the dealumination, in particular, of the external surface region may have lead to the creation of mesoporosity, which may be favourable in a case where high reaction rates may lead to intra-zeolite transport limitations [19]. At the same time, we examine indications that an additional active site may have been formed, which may include aluminium extracted from the lattice during the exchange procedure [16].

The sensitivity of VO-ZSM-5 to the (reversible) influence of water and SO_2 is low. It has been often described in the literature that the SCR with ammonia is less affected by H_2O or SO_2 than the SCR with hydrocarbons, most likely due to the considerably stronger interaction of the NH_3 reductant with the surface. These 'poisons' have even been reported to act as promoters, e.g. H_2O with Cu-ZSM-5 [11] and Fe-ZSM-5 [14] or SO_2 with TiO_2-based systems [6]. Indeed, at temperatures around 670 K, the NO conversion under moist conditions usually slightly exceeds that under dry conditions (Fig. 2(a and b)), and the NO conversions for SO_2-containing mixtures are generally higher in the moist feed than under dry conditions (Fig. 2(b)). Although the differences appear to be small, a promotion by water in the temperature range around 670 K is quite likely to occur: since the runs were performed with identical time schedules, the moist conditions should have lead to more intense damage of the catalyst during the previous stages (cf. Fig. 3) so that the conversions measured under moist conditions are probably achieved with the catalyst in a more deteriorated state than under dry conditions.

The unsatisfactory stability of VO-ZSM-5 in the oxidising reaction medium was not quite unexpected. It has been shown in [15] that VO^{2+} ions are largely oxidised to inactive V(V) species during a 48-h calcination in air at 823 K, hence the question was whether there remains an acceptable residual activity under more moderate conditions. This is clearly the case at 623 K under dry conditions, but the acceleration of the deactivation by water (Fig. 3(b)) limits the perspectives of these catalysts with respect to industrial application. While the reason for the deactivation under dry conditions (oxidation of V(IV)) appears to be clear, the origin of the accelerating effect of water remains to be established. We did not investigate if the deactivation curves arrive at a stable level under moist conditions, which might be still attractive. Even then, the products formed in moist media from the VO^{2+} ions (now majority species) may give rise to unwanted side reactions, hence, the properties of such stabilised catalysts cannot be predicted without a thorough study.

While these results probably preclude the VO-ZSM-5 system from practical application in flue-gas purification units, the potential of this system as a model catalyst appears still attractive: It provides the chance to prepare a highly active species in a population, which is essentially undisturbed by side products, and this species is visible by ESR, which is a technique highly sensitive to coordination changes. Future will show if this potential will suffice to permit the elucidation of the SCR mechanism supported by this active species.

5. Conclusions

The selective catalytic reduction of NO by ammonia was studied with a catalyst obtained by exchange of VO^{2+} ions into Na-ZSM-5 at pH 1.5–2. The catalyst proved to be highly active, providing initial NO conversions of >90% at 723 K and a space velocity of $620\,l\,g^{-1}\,h^{-1}$ (1000 ppm each of NO and NH_3, 2%O_2) and selective, with NO conversions equaling those of NH_3 and no N_2O formed when NO and NH_3 are applied in an equimolar ratio. SO_2 added at a 200-ppm level poisoned the SCR activity at low temperatures, but had no influence at $T \geq 623$ K. No SO_2 conversion was found up to 723 K. Water at levels up to 4.5 vol% had little influence on the SCR rate between 623 and 773 K, while the NO conversions were significantly decreased below, and above, this temperature region. The SCR activity of VO-ZSM-5 is not stable even under dry reaction conditions. Deactivation is slow at 623 K and leaves an attractive residual activity; however, an admixture of water to the feed strongly intensifies the deactivation process.

References

[1] G. Fränkle, W. Held, W. Hosp, W. Knecht, L. Hofmann, W. Mathes, R. Neufert, J. Zürbig, VDI-Ber Ser. 12 306 (1997) 365.

[2] H. Bosch, F.J.J.G. Janssen, Catal. Today 2 (1988) 369.

[3] A. Baiker, P. Dollenmeier, M. Glinski, A. Reller, Appl. Catal. 35 (1987) 351.

[4] G.T. Went, L.-J. Leu, R.R. Rosin, A.T. Bell, J. Catal. 134 (1992) 492.

[5] L. Lietti, P. Forzatti, J. Catal. 147 (1994) 241.

[6] N.-Y. Topsøe, J.A. Dumesic, H. Topsøe, J. Catal. 151 (1995) 241.

[7] N.-Y. Topsøe, H. Topsøe, J.A. Dumesic, J. Catal. 151 (1995) 226.

[8] M.D. Amiridis, I.E. Wachs, G. Deo, J.-M. Jehng, D.S. Kim, J. Catal. 161 (1996) 247.

[9] G. Ramis, G. Busca, F. Bregani, P. Forzatti, Appl. Catal. 64 (1990) 259.

[10] L. Lietti, G. Ramis, F. Berti, G. Toledo, D. Robba, G. Busca, P. Forzatti, Catal. Today 42 (1998) 101.

[11] J.A. Sullivan, J. Cunningham, M.A. Morris, K. Keneavey, Appl. Catal. B7 (1995) 137.

[12] J.W. Byrne, J.M. Chen, B.K. Speronello, Catal. Today 13 (1992) 33.

[13] E. Ito, R.J. Hultermans, P.M. Lugt, M.H.W. Burgers, M.S. Rigutto, H. van Bekkum, C.M. van der Bleek, Appl. Catal. B4 (1994) 95.

[14] A. Ma, W. Grünert, J. Chem. Soc., Chem. Commun. (1999) p. 71.

[15] M. Wark, A. Brückner, T. Liese, W. Grünert, J. Catal. 175 (1998) 48.

[16] G. Piehl, A. Ma, W. Grünert, unpublished results.

[17] E. Garcin, F. Luck, R. Surantyn, Catal. Today 20 (1994) 1.

[18] J.P. Dunn, H.G. Stenger Jr., I.E. Wachs, paper presented at the 2nd World Congress on Environmental Catalysis, Miami Beach, USA, Nov. 15–20, 1998, submitted to Catal. Today.

[19] T. Tabata, H. Ohtsuka, Catal. Lett. 48 (1998) 203.