Catalysis Letters 39 (1996) 105–109

# Catalytic behaviour of $Cu/ZrO_2$ and $Cu/ZrO_2(SO_4^{2-})$ in the reduction of nitric oxide by decane in oxygen-rich atmosphere

G. Delahay [1], B. Coq, E. Ensuque and F. Figuéras [2]

*Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, URA 418 CNRS, ENSCM, 8 rue de l'Ecole Normale, 34053 Montpellier Cedex, France*

Received 5 October 1995; accepted 16 February 1996

The selective catalytic reduction (SCR) of NO by decane under an oxidising atmosphere has been carried out on $Cu/ZrO_2$ and $Cu/ZrO_2(SO_4^{2-})$. Zirconia-supported Cu catalysts were prepared by ligand exchange with Cu acetylacetonate followed by calcination at 773 K. The solids obtained were characterised by temperature programmed reduction (TPR) by hydrogen and temperature programmed desorption (TPD) of NO. $Cu/ZrO_2$ is active and selective in the reduction of NO by decane at low temperature ($< 600$ K) but oxidises NO to $NO_2$ between 640 and 770 K. By contrast, whatever the temperature, a total selectivity to nitrogen is obtained with $Cu/ZrO_2(SO_4^{2-})$. About 40% NO conversion to $N_2$ is observed with GHSV of 70 000 $h^{-1}$. The promoting effect of sulfate is attributed to the large increase of acidity and the strong interaction between copper and sulfur species which is evidenced by TPD of NO and TPR by $H_2$.

**Keywords:** nitric oxide; selective reduction; $Cu/ZrO_2$; sulfated-zirconia

## 1. Introduction

Most of the huge number of formulations claimed to be efficient for $NO_x$ removal combine a metal oxide and an acidic support, Cu/MFI being the archetype of this class of materials. There are numerous reports in the open literature which propose that these solids act as bifunctional catalysts [1–7], whereby NO could be oxidised to $NO_2$ on the metal oxide or cationic sites and the $NO_2$ will then react with an adsorbed hydrocarbon activated by the acid function.

On the other hand, solid acids exhibit some activity, as shown for hydrogen or cerium exchanged zeolites [8–12] and for some sulfate promoted metal oxides [13,14]. However, their activity remains lower than that of bifunctional catalysts. Hamada et al. [13,14] have indeed pointed out that, when $ZrO_2$, $TiO_2$ and $Fe_2O_3$ are doped with $SO_4^{2-}$ the resulting increase of acidity promotes the NO reduction at low temperature. This is especially true for $ZrO_2(SO_4^{2-})$, which was claimed to be a superacid solid when activated under air at high temperature [15].

Bethke et al. [16–18] have shown that Cu–Zr–$O_x$ catalysts prepared by co-precipitation of copper and zirconium salts are active and selective in the NO reduction by propene in presence of 1% $O_2$. For higher oxygen partial pressures, NO conversion decreases and was reduced by a factor of 5 under 8% $O_2$ atmosphere [16].

It thus appeared interesting to investigate the behaviour of $Cu/ZrO_2(SO_4^{2-})$ catalysts for the selective catalytic reduction (SCR) of NO by decane under $O_2$-rich atmosphere. It was indeed shown that the redox properties of Pt were modified when supported on $ZrO_2(SO_4^{2-})$ [19,20]; similar behaviour might be expected for $Cu/ZrO_2(SO_4^{2-})$.

## 2. Experimental

Zirconium hydroxide was obtained by adding dropwise concentrated $NH_4OH$ solution to a $ZrOCl_2 \cdot 8H_2O$ (Fluka) solution at a constant pH = 10. The precipitate was filtered, repeatedly washed with distilled water until no chloride ion was detected, and dried overnight at 393 K. The sulfated-zirconia was prepared by contacting 15 g of dried $Zr(OH)_4$ with 250 $cm^3$ of a 0.1 N $H_2SO_4$ solution; the slurry was then stirred for 6 h. After filtering the solid was dried overnight at 393 K. With this procedure a sulfur content just lower than a monolayer of sulfate was introduced. In order to prevent the modification of sulfur content of $ZrO_2(SO_4^{2-})$ by deposition of Cu salt in aqueous medium, and a high Cu dispersion, a dedicated procedure was used to introduce $Cu^{2+}$ on the supports. This method is based on ligand exchange as described by Boitiaux et al. [21] for preparing noble metal supported catalysts. Copper catalysts were obtained by contacting 3 g of the support ($ZrO_2$ or $ZrO_2(SO_4^{2-})$), dried overnight at 473 K under He, with 0.741 g of copper acetylacetonate (Janssen) in 200 $cm^3$ of acetylacetone solution (Prolabo) and stirring during 6 h. After filtration, the powder was dried at 393 K for 3 h and then calcined under air at 773 K for 3 h.

The catalysts were characterised by nitrogen sorption

---

[1] To whom correspondence should be addressed.

[2] Present address: Institut de Recherches sur la Catalyse du CNRS, 2 Avenue A. Einstein, 69626 Villeurbanne Cedex, France.

© J.C. Baltzer AG, Science Publishers

Table 1
Physico-chemical characteristics of the samples

| Sample | Cu content (wt%) | S content (wt%) | BET surface area ($m^2 g^{-1}$) | Structure |
|---|---|---|---|---|
| $Zr(OH)_4$ | 0 | 0 | 290 | – |
| $ZrO_2$ | 0 | 0 | 135 | tetr + mon [a] |
| $Cu/ZrO_2$ | 3.7 | 0 | 136 | tetr + mon [a] |
| $ZrO_2(SO_4^{2-})$ | 0 | 2.5 | 207 | amorphous |
| $Cu/ZrO_2(SO_4^{2-})$ | 4.0 | 2.5 | 230 | amorphous |

[a] tetr = tetragonal, mon = monoclinic.

at 77 K (Micromeritics ASAP2000), X-ray diffraction (CGR Theta 60 instrument using Cu K$\alpha$ monochromatic radiation), temperature programmed reduction by hydrogen (TPR) and temperature programmed desorption of NO (TPD). Some characteristics of the different solids prepared are listed in table 1.

The reducibility of copper species was examined by TPR as described elsewhere [22]. 0.085 g of the catalyst was activated at 673 K for 1 h under air, then cooled to room temperature under high purity He flow. Helium is then replaced by the reducing gas ($H_2/Ar$ 3/97 vol/vol, purity of both gases $> 99.995\%$), a linear temperature programme was then started from 293 to 773 K (ramp: 5 K $min^{-1}$, flow: 20 $cm^3 min^{-1}$).

The experimental setup of TPD (NO) was very similar to that used for TPR experiments, except for the detection device. The gases desorbed from the solids were monitored by using a quadrupole mass spectrometer (Balzers QMS421) calibrated with standard mixtures. The catalyst sample, usually 0.085 g, was placed in a quartz reactor and activated in an air stream at a flow rate of 100 $cm^3 min^{-1}$ at 673 K for 1 h. Thereafter, the reactor was cooled to room temperature and the air stream switched to a helium stream until no oxygen was detected in the effluent. NO was then adsorbed at room temperature in a flow of NO/He (1/99, vol/vol, purity of NO $> 99.95\%$) at a total flow-rate of 50 $cm^3 min^{-1}$ for 30 min. NO in the gas phase was then flushed with helium until no NO was detected in the effluent. TPD experiments were started from room temperature to 773 K at a heating rate of 10 K $min^{-1}$ and a helium flow rate of 50 $cm^3 min^{-1}$.

The SCR of NO by *n*-decane was performed in a flow reactor operating at atmospheric pressure. 0.052 g of the catalyst was activated in situ at 673 K for 1 h under air, then cooled to 298 K under He. The reaction gas contained 0.1 vol% NO (purity $> 99.95\%$), 0.03 vol% *n*-decane (purity $> 99.5\%$), and 9 vol% $O_2$ (purity $> 99.995\%$), the balance being He. The flow rate was 60 $cm^3 min^{-1}$ (space velocity: 70 000 $h^{-1}$) and the temperature ramped from 298 to 750 K (ramp: 5 K $min^{-1}$). The composition of the effluents was monitored continuously by sampling on-line to a quadrupole mass spectrometer Balzers QMS421 equipped with a Faraday detector (0–200 amu) and following the masses 28, 30, 44, 46 and 57. Nitrogen and carbon monoxide production was discriminated by analysing the products with a gas phase chromotograph (Varian) equipped with a katharometer and a 13X molecular sieve column.

## 3. Results

On zirconia-supported Cu catalysts, no diffraction line for CuO phase was detected. Only the patterns characteristic of tetragonal and monoclinic $ZrO_2$ were observed. This demonstrates that copper is present either as isolated cationic species, or as CuO aggregates smaller than approximately 3 nm. The sulfate promoted $ZrO_2$ retained higher surface area on heat treatment than did the unpromoted $ZrO_2$ (table 1). In line with these results, $ZrO_2(SO_4^{2-})$ remained amorphous while $ZrO_2$ was a mixture of crystallised phase (tetragonal + monoclinic). As previously reported, the addition of sulfate delays the crystallisation of zirconia [15].

When applied to the study of supported metal catalyst, TPR provides information about the reducibility of the active species and the extent of metal–support interactions. Under the conditions employed here, $ZrO_2$ and $ZrO_2(SO_4^{2-})$ do not show any reduction peak ($H_2$ consumption) below 590 K (fig. 1). On the other hand, one peak for copper reduction was observed for both

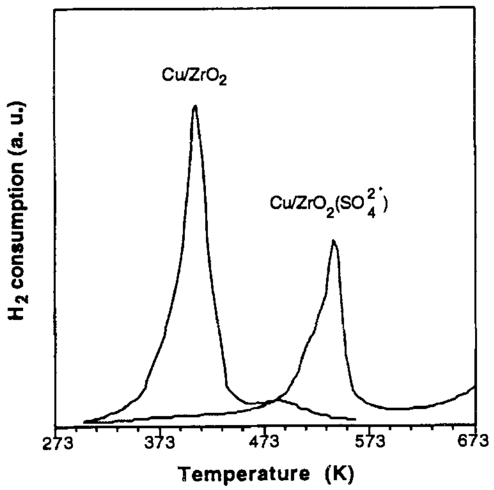

Fig. 1. Temperature programmed reduction by $H_2$ of $Cu/ZrO_2$ and $Cu/ZrO_2(SO_4^{2-})$. Conditions: $H_2/Ar$: 3/97, flow rate = 20 $cm^3 min^{-1}$, amount of catalyst = 0.085 g, heating rate = 5 K $min^{-1}$.

$Cu/ZrO_2$ and $Cu/ZrO_2(SO_4^{2-})$. This reduction occurs 132 K lower for $Cu/ZrO_2$ (407 K) than for $Cu/ZrO_2(SO_4^{2-})$ (539 K) and the amount of $H_2$ consumed is 1.0 and 0.8 per mole of copper respectively. The occurrence of only one reduction peak for zirconia-supported copper catalysts could be accounted for by either the one-step reduction of isolated $Cu^{2+}$ species to $Cu^0$, or the reduction of CuO to $Cu^0$ aggregates. The latter explanation should be considered more likely since the TPR of Cu/MFI or Cu/MOR, which contain isolated $Cu^{2+}$ species, exhibits two reduction peaks separated by more than 100 K, which correspond to the reduction of $Cu^{2+}$ to $Cu^+$ and $Cu^+$ to $Cu^0$ [22–24]. On the other hand, the easy reduction of $Cu/ZrO_2$ should be noted. It has been previously shown that the reduction temperature of $Cu/SiO_2$ decreases from 570 to 500 K when the dispersion of CuO increases [25]. However, the very low reduction temperature observed for $Cu/ZrO_2$ (409 K) cannot be accounted for only by a dispersion effect, but also by some kind of CuO–$ZrO_2$ interaction which facilitates the CuO reduction as proposed in the case of highly dispersed CuO clusters supported on titania [26]. Finally, the higher temperature needed to reduce CuO when supported on $ZrO_2(SO_4^{2-})$ could mean either that the presence of $SO_4^{2-}$ suppresses the CuO–$ZrO_2$ interaction, or decreases the reducibility of CuO by an electronic interaction as suggested in the case of $Pt/ZrO_2(SO_4^{2-})$ [19,20].

The TPD of NO shows that the copper free samples adsorb only very small amounts of NO (fig. 2 and table 2). NO desorbs from $ZrO_2$ as a broad peak centered around 550 K. On the other hand, $ZrO_2(SO_4^{2-})$ adsorbs three times less NO than $ZrO_2$. The introduction of Cu on both solids clearly increases the amount of NO taken up by the sample. On the $Cu/ZrO_2$ catalyst, three NO desorption peaks with maxima at 368, 494 and 710 K were observed (fig. 2). The latter NO desorption peak is accompanied by an equivalent amount of desorbed $O_2$ (table 2). After the thermal desorption, the colour of the sample is darker. During the TPD of NO from zirconia-supported copper catalysts, only trace amounts of $N_2O$ and $NO_2$ were detected (table 2).

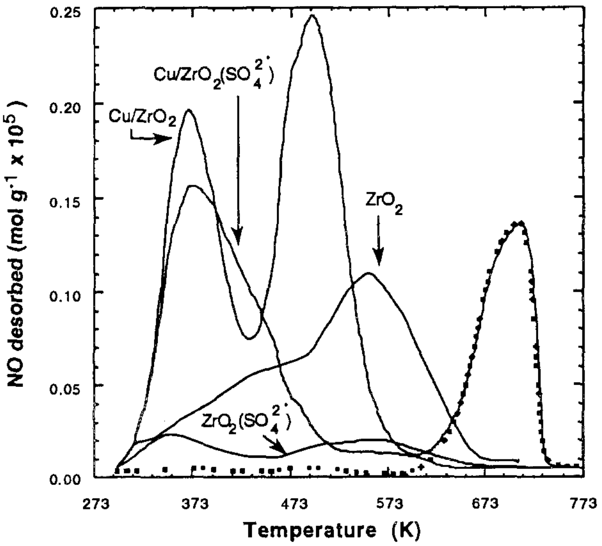

Fig. 2. Temperature programmed desorption of NO (—) and $O_2$ (▪▪▪) from $Cu/ZrO_2$, $Cu/ZrO_2(SO_4^{2-})$, $ZrO_2$ and $ZrO_2(SO_4^{2-})$. Conditions: He flow rate = 50 $cm^3$ $min^{-1}$, amount of catalyst = 0.085 g, heating rate = 10 K $min^{-1}$.

Table 2

Amount (mol $g^{-1}$ × $10^5$) of gases desorbed during NO TPD experiments. Conditions: He flow rate = 50 $cm^3$ $min^{-1}$, amount of catalyst = 0.085 g, heating rate = 10 K $min^{-1}$

| Compound | NO[a] | $O_2$ | $N_2O$ |
|---|---|---|---|
| $ZrO_2$ | 11 (553)[a] | – | traces |
| $Cu/ZrO_2$ | 10 (368), 15 (494), 7 (710) | 6.5 (710) | 0.5 (368) |
| $ZrO_2(SO_4^{2-})$ | 1.3 (360), 1.7 (570) | – | traces |
| $Cu/ZrO_2(SO_4^{2-})$ | 11 (364) | – | 0.7 (364) |

[a] Within parentheses, temperature (K) at which the desorption rate is maximum.

Similar NO TPD profiles have been obtained by Hierl et al. [27] on $Cu/Al_2O_3$. These authors proposed that the adsorption steps which occur during NO exposure near room temperature are the following:

$$Cu^{2+} + NO_{gas} \rightarrow Cu^{2+}\text{–}NO \tag{1}$$

$$Cu^{2+}\text{–}O^{2-} + NO_{gas} \rightarrow Cu^{2+} + ONO^- \tag{2}$$

Eqs. (1) and (2) correspond to the formation of surface mononitrosyl and nitrito complexes. When the temperature is increased, they attributed the three NO desorption peaks to [27]:

$$Cu^{2+}\text{–}NO \rightarrow Cu^{2+} + NO_{gas} \tag{3}$$

$$2Cu^{2+} + ONO^- \rightarrow Cu^{2+}\text{–}ONO_2^- + Cu^0 + NO_{gas} \tag{4}$$

$$Cu^{2+}\text{–}ONO_2^- \rightarrow Cu^0 + NO_{gas} + O_{2,gas} \tag{5}$$

The decomposition of copper nitrate species at high temperature to ($NO + O_2$) and $Cu^{II}$ species has been also proposed by Li and Armor [28] on Cu/MFI and by Shimokawabe et al. [29] on $CuO/SiO_2$. They suggest that nitrate species are formed by room temperature reaction between NO and oxygen atoms of CuO aggregates. However, it should be pointed out that Shimokawabe et al. [29] only reported two NO desorption peaks at 370 and 680 K, and did not observe the desorption peak at around 500 K.

The nature of the surface NO complex which desorbs at 570 K from $ZrO_2$ has not been identified but might be tentatively assigned to nitrito or nitrato surface complexes because of the high desorption temperature. Therefore, assuming that the same amount of NO adsorbs on $ZrO_2$ of the $Cu/ZrO_2$ sample, the amount of NO taken up by Cu species alone would be 210 $\mu$mol/g (table 2), which corresponds to NO/Cu = 0.36 (mol/

mol). It seems therefore that medium dispersion of Cu was obtained with CuO aggregates smaller than 3 nm.

Finally, on Cu/ZrO$_2$(SO$_4^{2-}$) the NO desorption peak at low temperature only remains and the amount of NO desorbed is very close to that found on Cu/ZrO$_2$. The presence of (SO$_4^{2-}$) strongly inhibits the formation and/or the decomposition of nitrito and nitrato species. Hierl et al. [27] have proposed that the formation of nitrito and nitrato species on Cu/Al$_2$O$_3$ involves a partial reduction of Cu$^{2+}$. The TPR by H$_2$ (fig. 1) has shown that copper species are more difficult to reduce when supported on ZrO$_2$(SO$_4^{2-}$) than on ZrO$_2$. This behaviour could explain the inhibition of nitrito and nitrato species on Cu/ZrO$_2$(SO$_4^{2-}$). The smaller amount of NO which desorbs from Cu/ZrO$_2$(SO$_4^{2-}$) might in turn be explained by the strong interaction between copper ions and sulfate species (modification of the copper environment). According to Zhang et al. [33], the pre-adsorption of SO$_2$ on Cu/ZSM-5 which can lead to the formation of sulfate species [34], decreases the quantity of NO adsorbed by this solid. A similar explanation could be put forward for the present system.

In the SCR of NO by *n*-decane, ZrO$_2$ and ZrO$_2$(SO$_4^{2-}$) exhibited no activity below 773 K. Two waves of NO conversion occurred on Cu/ZrO$_2$: (i) the first around 563 K where NO is selectively reduced to nitrogen and (ii) the second at higher temperature ($> 673$ K) where NO is mainly oxidised to NO$_2$ (fig. 3a). It should be noted that the oxidation of NO to NO$_2$ remained far from the thermodynamic equilibrium under the given conditions: 1000 ppm NO + NO$_2$, 9% O$_2$. This behaviour appears slightly different from that reported by Bethke et al. [16,17] for the SCR of NO by C$_3$H$_6$. They found a selective reduction of NO to N$_2$ between 480 and 680 K which went through a maximum for NO conversion at 580 K. However, the nature of the reductant, propene, and the O$_2$ concentration of 1%, which are different from our study, could be the reason for this discrepancy. On Cu/ZrO$_2$(SO$_4^{2-}$), NO is selectively reduced to N$_2$ and only traces of NO$_2$ were detected during the reaction (fig. 3b). On this catalyst a maximum of 42% NO conversion to nitrogen occurs at 658 K. On these supported Cu catalysts, the oxidation of *n*-decane to CO$_2$ (no CO detected) starts at a lower temperature than the NO reduction and rapidly reaches a conversion plateau of 85% (fig. 3c).

NO$_2$ was often claimed to be an important intermediate for the selective reduction of NO to N$_2$ by reacting with the activated hydrocarbon [1–7]. Anyway, if Cu/ZrO$_2$ is indeed selective for NO reduction at low temperature, it becomes unselective at high temperature. This is not the case for Cu/ZrO$_2$(SO$_4^{2-}$) which appears a little less active than Cu/ZrO$_2$ at low temperature, but remains selective for the NO reduction whatever the temperature investigated. This behaviour of Cu/ZrO$_2$(SO$_4^{2-}$) could be tentatively ascribed to either (i) the much higher acidity of ZrO$_2$(SO$_4^{2-}$) compared to ZrO$_2$ [15] which facilitates the reaction between activated decane and NO$_2$ through a nitration like mechanism leading ultimately to N$_2$ formation, or (ii) to the stabilisation, by the sulfate groups, of nitrito surface complexes which have a chance to be paired into N$_2$ before being desorbed. However, the latter explanation seems less likely since the TPD of NO from Cu/ZrO$_2$(SO$_4^{2-}$) did not show any decomposition of nitrito or nitrato surface complexes (fig. 2).

## 4. Conclusion

Cu/ZrO$_2$ is active in the catalytic reduction of NO to N$_2$ by decane in excess of oxygen only at low temperature ($T < 600$ K) and acts as an oxidising catalyst for temperature above 690 K. The pre-sulfation of zirconia

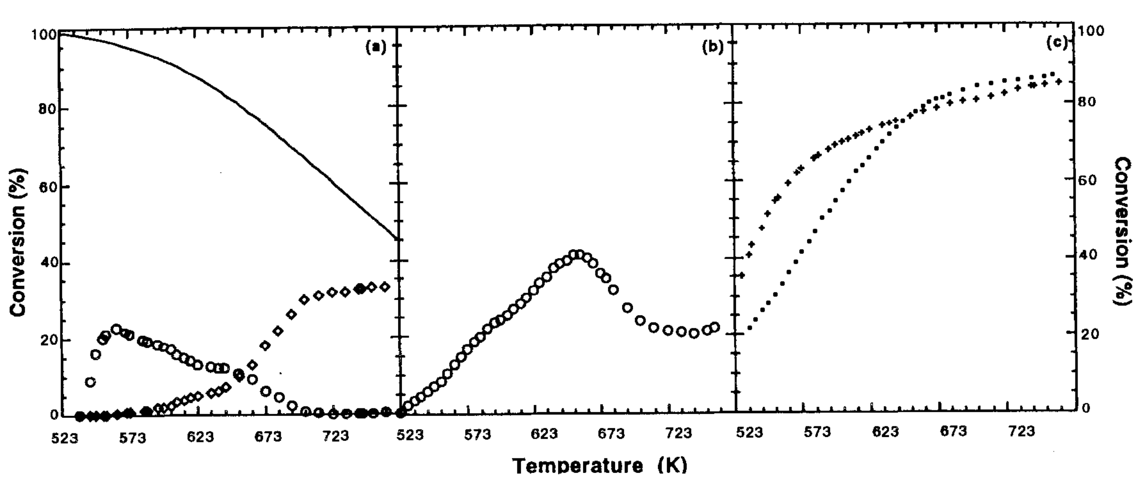

Fig. 3. Selective catalytic reduction of NO by decane on: (a) CuZrO$_2$: (○) NO conversion to N$_2$, (◇) NO conversion to NO$_2$, (—) thermodynamic equilibrium NO + $\frac{1}{2}$O$_2$ $\rightleftharpoons$ NO$_2$ with 1000 ppm NO + NO$_2$ and 9% O$_2$; (b) Cu/ZrO$_2$(SO$_4^{2-}$): (●) total NO conversion and NO conversion to N$_2$; (c) decane conversion on CuZrO$_2$ (+) and Cu/ZrO$_2$(SO$_4^{2-}$) (×). Conditions: feed: 1000 ppm NO, 3000 ppmC decane, 9% O$_2$, balance with helium, flow rate = 60 cm$^3$ min$^{-1}$, amount of catalyst = 0.052 g, heating rate = 5 K min$^{-1}$.

leads to a Cu/ZrO$_2$(SO$_4^{2-}$) catalyst fully selective in NO conversion to nitrogen in the whole range of temperatures. This effect has been attributed to the increase of acidity and/or strong interaction between copper and sulfur species.

## Acknowledgement

Support of this work by European Union (BRITE EURAM II contract No. BRE2-CT92-0192) is gratefully acknowledged.

## References

[1] M. Yasuda, T. Miyamoto and Misono, *207th National Meeting ACS*, San Diego (1994) p. 98.
[2] J.O. Petunchi and W.K. Hall, Appl. Catal. B 2 (1993) L17.
[3] H. Hamada, Y. Kintaichi, T. Yoshinari, M. Tabata, M. Sasaki and T. Ito, Catal. Today 17 (1193) 111.
[4] M. Shelef, C.N. Montreuil and H.W. Jen, Catal. Lett. 26 (1194) 277.
[5] C. Yokoyama and M. Misono, J. Catal. 150 (1994) 9.
[6] C. Yokoyama and M. Misono, Catal. Today 22 (1994) 59.
[7] M. Sasaki, H. Hamada, Y. Kintaichi and T. Ito, Catal. Lett. 15 (1992) 297.
[8] C. Yokoyama and M. Misono, Bull. Chem. Soc. Japan 67 (1994) 557.
[9] H. Hamada, Y. Kintaichi, M. Tabata, M. Sasaki and T. Ito, Chem. Lett. (1991) 2179.
[10] T. Inui, S. Iwamoto, S. Kojo and T. Yoshida, Catal. Lett. 16 (1992) 223.
[11] K. Yogo, M. Umeno, H. Watanabe and E. Kikuchi, Catal. Lett. 19 (1993) 131.
[12] Y. Li and J.N. Armor, J. Catal. 145 (1994) 1.
[13] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal. 64 (1990) L1.
[14] H. Hamada, Catal. Today 22 (1994) 21.
[15] K. Arata, Adv. Catal. 37 (1990) 165.
[16] M.C. Kung, K.A. Bethke and H.H. Kung, *207th National Meeting ACS*, San Diego (1994) p. 154
[17] K.A. Bethke, D. Alt and M.C. Kung, Catal. Lett. 25 (1994) 37.
[18] K.A. Bethke, C. Li, M.C. Kung and H.H. Kung, Catal. Lett. 31 (1995) 287.
[19] K. Ebitani, H. Konno, T. Tanaka and H. Hattori, J. Catal. 135 (1992) 60.
[20] K. Ebitani, H. Konno, T. Tanaka and H. Hattori, J. Catal. 143 (1993) 321.
[21] J.P. Boitiaux, J. Cosyns and S. Vasudevan, Stud. Surf. Sci. Catal. 16 (1982) 123.
[22] B. Coq, D. Tachon, F. Figuéras, G. Mabilon and M. Prigent, Appl. Catal. B 6 (1995) 271.
[23] Y. Lee and B.H. Ha, in: *Zeolites and Related Microporous Materials: State of the Art 1994*, eds. J. Weitkamp, H.G. Karge, H. Pfeifer and W. Holderich (Elsevier, Amsterdam, 1994) p. 1563.
[24] H. Exner and F. Fetting, Chem. Eng. Technol. 14 (1991) 428.
[25] A. Jones and B.D. Mc Nicol, Chem. Ind. 24 (1986) 129.
[26] F.S. Delk and A. Vavere, J. Catal. 85 (1984) 380.
[27] P. Hierl, H.-P. Urbach and H. Knözinger, J. Chem. Soc. Faraday Trans. 88 (1992) 355.
[28] Y. Li and J.N. Armor, Appl. Catal. 76 (1994) L1.
[29] M. Shimokawabe, N. Hatakeyama, K. Shimada, K. Tadokoro and N. Takezawa, Appl. Catal. 87 (1992) 205.
[30] M.C. Kung and H.H. Kung, Catal. Rev. Sci. Eng. 27 (1985) 425.
[31] J.L.G. Fierro and J.F. Garcia de la Banda, Catal. Rev. Sci. Eng. 28 (1986) 265.
[32] E. Ensuque, B. Coq, G. Delahay, F. Figuéras and J. Saussey, unpublished.
[33] W.X. Zhang, H. Yahiro, N. Mizuno, J. Izumi and M. Iwamoto, Langmuir 9 (1993) 2337.
[34] J.P. Chen and R.T. Yang, J. Catal. 139 (1993) 277.