

Catalytic properties of Ru-mordenite for NO reduction

Nitin Labhsetwar^{a,*}, H. Minamino^b, M. Mukherjee^a, T. Mitsuhashi^b, S. Rayalu^a, M. Dhakad^a,
H. Haneda^b, J. Subrt^c, Sukumar Devotta^a

^a Environmental Materials Unit, National Environmental Engineering Research Institute, Nehru Marg, Nagpur 440020, India

^b Advanced Materials Laboratory, National Institute for Materials Science, 1-1, Namiki, Tsukuba, Ibaraki 3050044, Japan

^c Institute of Inorganic Chemistry, ASCR, CZ-250 68 Řež, Czech Republic

Received 14 November 2005; accepted 2 August 2006

Available online 12 September 2006

Abstract

The reduction of NO by CO over H and Na forms of Ru exchanged mordenite has been studied with ruthenium content of 0.2, 1 and 3 wt.%. The catalysts were characterized with respect to X-ray diffraction, BET surface area, temperature programmed oxidation, and temperature programmed desorption of ammonia. These catalysts have been evaluated for their activity for NO–CO reaction using a steady state gas laboratory evaluation assembly. The catalysts show high activity for NO reduction and almost 100% conversion of NO to N₂ was observed below 400 °C. The activity was found to be a factor of ruthenium content, however, Ru-mordenite in Na form was observed to be relatively more active than Ru-mordenite in H form, probably due to the electron donation from sodium to ruthenium sites. New zeolite phases with improved hydrothermal stability, high surface area and reasonable cation exchange properties can be potential materials for catalytic reduction of NO_x. Introduction of active metal ions through ion exchange insures their high dispersion in zeolite supports, which also offer tailoring possibilities for DeNO_x catalysts.

© 2006 Elsevier B.V. All rights reserved.

Keywords: NO reduction; Catalyst; Ru-zeolite; Mordenite; DeNO_x

1. Introduction

Nitric oxide (NO) is one of the major air pollutants having serious environmental and health impacts and their concentration in urban areas has an increasing trend. It is estimated that $(35\text{--}38) \times 10^6$ tonnes of NO are emitted from the exhaust gases of automobiles every year in the world [1]. Nitrogen oxides (NO_x) not only cause the formation of acid rains, but are also responsible for photochemical smog. The removal of NO_x remains to be a challenging problem for both research and practical applications. The common methods of NO treatment include liquid or solid absorption, NO reduction by CO and HCs, selective catalytic reduction of NO with NH₃. Since 1980s, intensive research is underway for development of highly efficient DeNO_x catalysts to eliminate NO through reductive mechanism. A range of catalytic materials has been reported for NO decomposition and reduction under lean and stoichiometric conditions including both transition and noble metal-based

catalytic materials [2–19]. Catalyst activity, selectivity, stability and cost remain the important parameters for this application as well. Therefore, search for new catalysts with improved properties has always been a research interest, both for academic and commercial reasons.

Ruthenium has long been recognized as an efficient catalyst in both metallic and oxide forms for a large number of reactions of commercial and environmental importance. However, its poor thermal stability under the oxidizing conditions and low surface area of unsupported ruthenium restricted its catalytic applications for high temperature applications. Efforts have been made towards preparation of thermally stable ruthenium catalysts, including those perovskite type materials [5,11]. However, such materials often possess very low surface area, which is a major limitation for this application. Excellent dispersion of ruthenium is possible on zeolites through ion exchange. It is therefore, worth exploring metallo-zeolites, especially after the development of hydrothermally stable zeolites phases, quite suitable even for auto-exhaust applications. Chang et al. studied the effect of Ru loading on the performance of Ru-NaZSM-5 catalyst prepared by ion exchange with ruthenium content as high as 20–100% for decomposition of nitrous oxide [7]. Li

* Corresponding author. Tel.: +91 712 2247828.

E-mail address: nitin_neeri@yahoo.com (N. Labhsetwar).

and Armor also reported that Ru-ZSM-5 is very active for the decomposition of nitrous oxide at low temperature [6]. Piertse et al. studied SCR activity over ZSM-5, mordenite, FER and BEA and observed that mordenite-based catalyst maintain the highest SCR activity over the long period of time [8]. They also observed that mordenite has the highest overall activity.

The objective of this work is to study the ruthenium exchanged mordenite catalysts for reduction of NO by CO under the stoichiometric conditions. The effect of co-cation, viz. Na and H on NO reduction activity has also been investigated, while TPO and ammonia-TPD studies were carried out to understand the properties of these materials for further investigations.

2. Experimental

Commercial grade mordenite zeolite procured from Zeolyst Corporation, USA with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 33.4$ was treated with 1 M aq. NH_4NO_3 solution for 2 h at 30°C , followed by filtration and washing with deionized water. This ammonium-exchanged zeolite was then oven dried at 110°C and calcined in a muffle furnace at 550°C to obtain H form mordenite. The H-mordenite was exchanged with Na^+ ions using an aqueous solution of NaNO_3 by following the same process used to prepare the ammonium form of mordenite. Ru-mordenite was prepared with 0.2, 1 and 3 wt.% Ru loading on H and Na forms of mordenite using ion exchange procedure. Mordenite zeolite was treated with 0.1 M $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ for 2 h at 30°C followed by filtration and drying at 110°C and subsequent temperature programmed oxidation (TPO) to obtain Ru-mordenite in H and Na forms. The maximum temperature of 500°C was used for TPO treatment. The catalyst with 0.2, 1 and 3% ruthenium on H-mordenite were designated as RH-0.2, RH-1 and RH-3 respectively whereas the catalyst with 0.2, 1 and 3% ruthenium on Na-mordenite were designated as RN-0.2, RN-1 and RN-3.

The catalyst samples were characterized for chemical composition using both wet chemical analysis and ICP-AES technique. Powder X-ray diffraction data were recorded at room temperature on a Rigaku Rint-2200HF machine, using Bragg–Brentano geometry with $\text{CuK}\alpha$ radiation (40 kV, 50 mA). XRD data were analyzed for phase identification, presence of impurity phase, as well as for structural damage if any during the catalyst preparations. BET surface area of samples was determined following the standard nitrogen adsorption method using Micromeritics ASP-200 instrument. Thermal stability experiments were performed by heating the catalysts at temperatures ranging from 500 to 700°C , under air atmosphere. Isothermal heating of the catalysts at 700°C has also been carried out to study the thermal study. These post-heated catalysts were investigated by XRD and weight loss during the heating as ruthenium is prone to form volatile oxides at higher temperatures. Thermal stability experiments were also performed using TG technique in the same temperature range, mainly to study the possibility of thermal loss by the formation of volatile ruthenium oxides. These experiments were conducted using Rigaku-TAS-200, Thermal Analyzer, by heating the samples up to 700°C in air atmosphere. The oxygen temperature programmed desorption (O_2 -TPD) was carried out using BEL-TPD instrument, equipped with both ther-

mal conductivity detector (TCD) and quadruple mass spectrometer (Q-mass). The sample was pre-treated by heating at 600°C followed by evacuation and oxygen exposure with decreasing temperature. The desorption was carried out by controlled heating in He flow up to 700°C with simultaneous determination of oxygen release by Q-mass.

3. Catalytic evaluations

The catalytic evaluations have been carried out using a pure gas laboratory evaluation assembly equipped with precise gas flow control and heating system. Gas analysis was carried out using an auto-sampling PC controlled, MTI-P-200, GC system and chemiluminescence-based NOx analyser. Some catalytic evaluations have also been carried out using a Bell TPD instrument equipped with Q-mass analyzer, and precise flow control and heating facilities. Catalytic evaluations were carried out in a quartz reactor using 0.2 g of catalyst (20 mesh sieve fraction). The reaction conditions used were $\text{NO} = 1000$ ppm, $\text{CO} = 1000$ ppm and balance helium using $\text{GHSV} = 3900 \text{ h}^{-1}$. The catalyst was pretreated at 550°C for 1 h in He flow followed by pretreatment with feed gas for 30 min. The reactants were stabilized at every temperature for 15 min and the products were analyzed using a NOx analyzer and gas chromatograph.

4. Results and discussion

Table 1 represents the data of original zeolite used. The original mordenite has high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, which is responsible for its high hydrothermal stability. However, the alumina content is enough for the cation exchange properties. The X-ray diffraction pattern of H-mordenite and Na-mordenite zeolite and Ru exchanged zeolite are shown in Figs. 1 and 2. The X-ray diffraction patterns of H-mordenite and Na-mordenite zeolite used for the preparation of catalysts matches well with JCPDS database and therefore confirm the mordenite phase. The X-ray diffraction patterns of Ru exchanged show intact structure of mordenite after the ion-exchange experiments. It was possible to identify the presence of RuO_2 in 1 and 3 wt.% Ru containing samples where the XRD peaks of RuO_2 becomes intense as the ruthe-

Table 1
Properties of original mordenite

Name	H-mordenite powder
Chemical composition	
SiO_2 (wt.%) dry basis	95.1
Al_2O_3 (wt.%) dry basis	4.83
Na_2O (wt.%) dry basis	0.03
$\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio	33.4
EDS data	
Si	45.963
Al	2.648
Na	0.203
O	96
Si/Al	17.358
BET surface area (m^2/g)	374.31

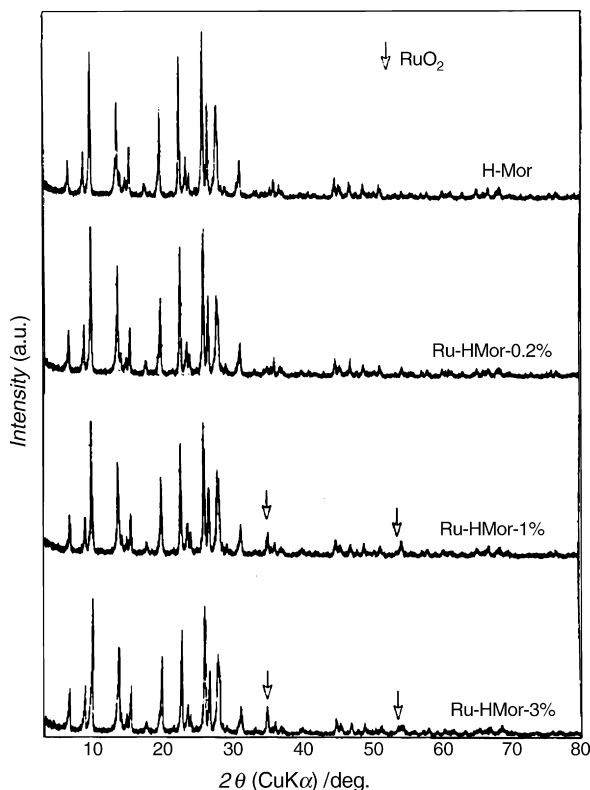


Fig. 1. XRD of H-Mor and Ru-H Mor.

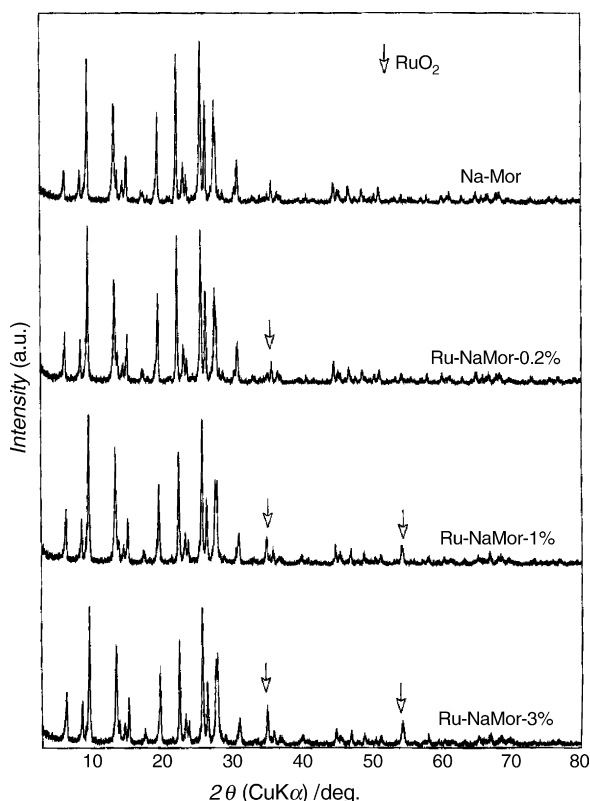


Fig. 2. XRD of Na-Mor and Ru-Na Mor.

Table 2
BET surface area results

Sample name	BET surface area (m ² /g)
RH-0.2	362.42
RH-1	357.68
RH-3	354.12
RN-0.2	360.04
RN-1	355.01
RN-3	352.79

nium loading increases. RuO₂ peak was not detected in sample containing 0.2 wt.% ruthenium, due to its low content and high dispersion. The XRD data, therefore, confirmed the presence of RuO₂ and unaffected structure of mordenite in catalysts.

The BET surface area results are shown in Table 2, which suggest the high surface area of catalytic materials even after calcination at higher temperature. There was no considerable impact of Ru loading on surface area, which, also indicate the high dispersion of Ru on exchange sites of mordenite. Results for temperature programmed desorption of ammonia are shown in Fig. 3. Original mordenite shows a peak for strong acid sites at 470 °C while another peak for weak acid site was observed at 153 °C. A shift towards lower temperature was observed for strong acid sites after Ru loading, in both H and Na forms of mordenite. The peak at 470 °C was shifted to 395 and 251 °C, respectively, while the peaks also become more intense as the Ru loading increases. A very intense peak was observed for RN-3 sample, while there is no change observed in weak acid sites

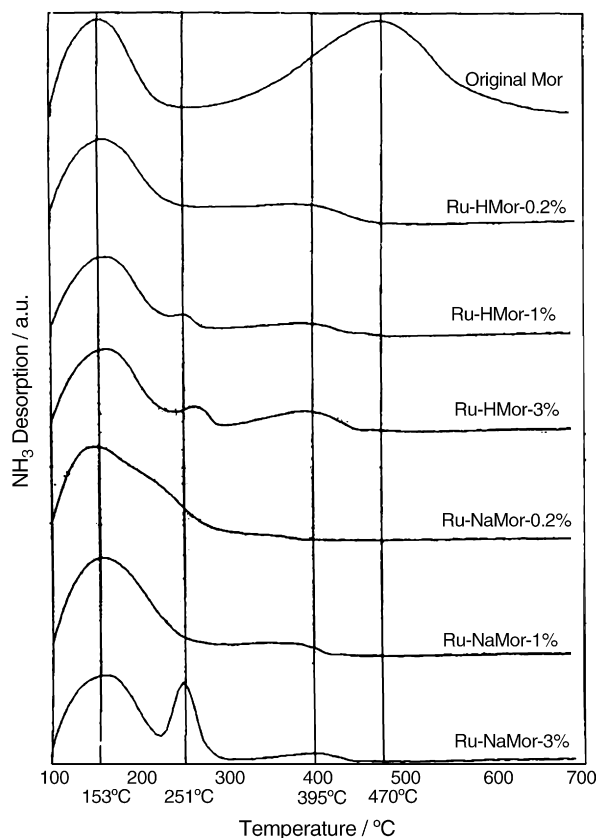


Fig. 3. TPD curve of Ru-Mor.

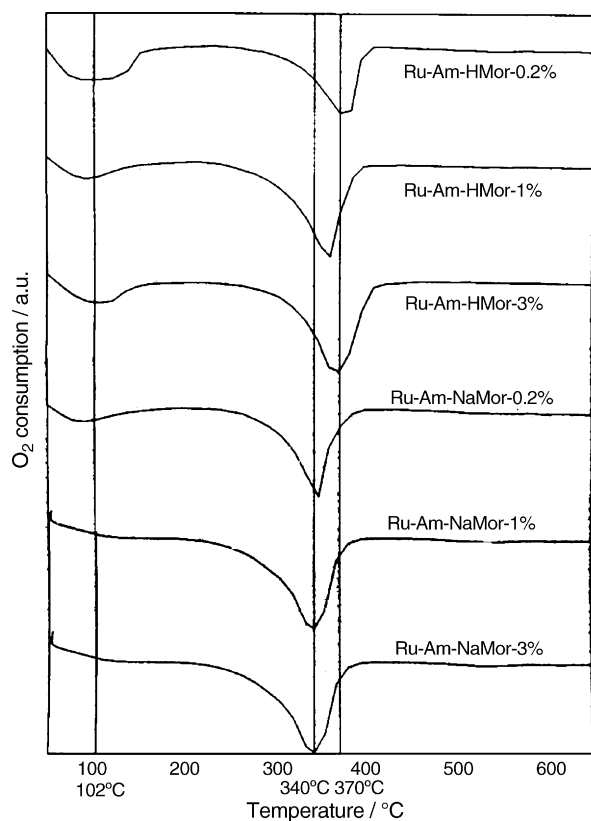


Fig. 4. TPO curves for Ru-Am-HMor and Ru-Am-NaMor.

with Ru loading. The decrease in surface acidity observed could be due to the oxidation of exchanged Ru to RuO_2 as well as due to the interaction of RuO_2 with support. Also high calcination temperature can result in aggregation of isolated oxide molecules into larger particles, which also leads to decrease in acidity [9].

The formation of RuO_2 mordenite was followed by temperature programmed oxidation (TPO) studies. Fig. 4 shows the TPO of Ru-Am-mordenite, the precursor for RuO_2 containing mordenite catalysts. A small peak was observed at 120°C and a broad peak around 340°C . The ammonium complex of ruthenium precursor is expected to decompose and result in ruthenium metal, which is oxidized to RuO_2 at higher temperature. As the ruthenium loading increases the oxygen consumption also increases. This is in accordance with observations of Chang et al. [6] that small metal clusters formed within zeolite pores require more than stoichiometric amount of oxygen to get oxidized. Ruthenium present at exchange sites may be oxidized at relatively higher temperature than that is required for the ruthenium present as adsorbed on surface.

Fig. 5 shows the catalytic activity of various catalysts for the reduction of NO to N_2 by using CO as a reducing agent. RH-0.2 shows light-off temperature around 200°C for NO reduction and reaches T_{90} above 300°C whereas, for the Na-MOR form, the reaction starts at around 170°C and reaches T_{90} conversion at 300°C . This indicates the promotional effect of Na ions on catalytic activity. This effect

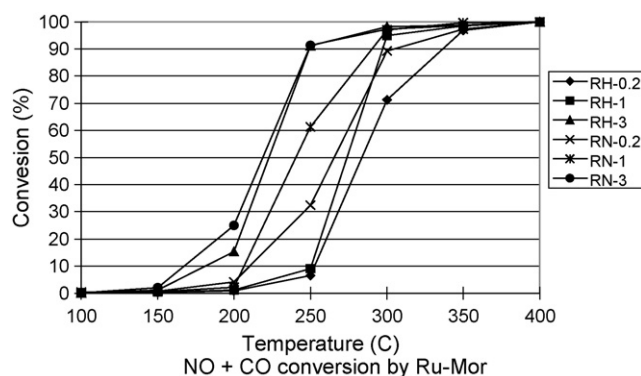


Fig. 5. NO+CO conversion by Ru-Mor.

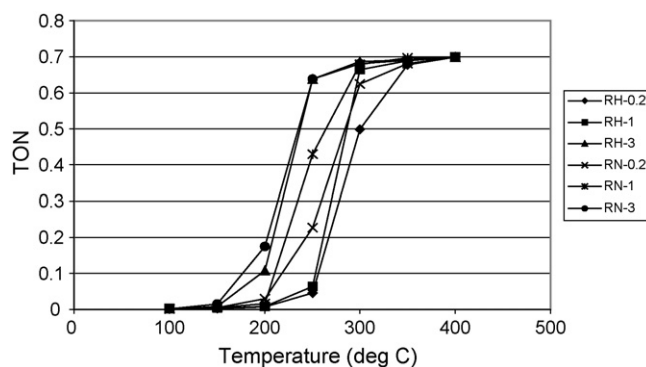


Fig. 6. TON vs. temperature for Ru-HMor and Ru-NaMor.

was even more pronounced for 1% Ru-MOR catalysts. The conversion of NO over RN-1 reaches T_{90} at 278°C while over RH-1 T_{90} was observed at 286°C . The conversion of NO over RN-3 starts around 160°C and reaches T_{90} at 225°C . The conversion increased with reaction temperature and reached about 100% around 350°C over RN-3. Fig. 6 shows change in TON versus temperature. TON is calculated as millimoles of NO converted per gram of catalyst per unit time. Maximum 0.7 mmol of NO is converted per gram of catalyst per hour. RN-3 shows the maximum conversion at 350°C . RH-0.2 converts 0.5 mmol of NO at about 300°C whereas RH-3 and RN-3 shows the same conversion at 210°C . Moles of NO converted increases with increase in ruthenium content, which is in line with previous discussion (Fig. 7).

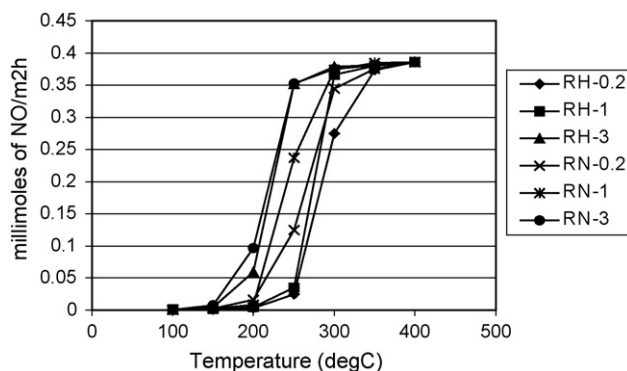


Fig. 7. Millimoles of NO converted per gram of catalyst per unit time.

It is therefore clear from the catalyst evaluation results that Na mordenite-based catalysts show much better activity than H mordenite based catalysts. Also it is evident that catalytic activity is a function of ruthenium content, which appears to provide the active sites for adsorption of both CO and NO. We propose to explain this reaction using MVK type mechanism, commonly used for mixed oxide type catalytic materials. Oxidation of CO on ruthenium has been investigated in details by Over and Muhler which suggest a CO oxidation mechanism through dissociative adsorption of oxygen [9]. However, as the present studies were performed under the stoichiometric conditions and in absence of oxygen, it is more appropriate to follow the MVK mechanism. CO molecules appear to be adsorbed on RuO₂ surfaces of catalysts, with their subsequent oxidation to CO₂ and reduction of catalyst surface. NO molecules are then adsorbed on this reduced catalyst surface followed by the reduction of NO in to nitrogen and consequent oxidation of reduced catalyst through replenishment of oxygen. In this way a simple redox mechanism can explain this reaction.

It is interesting to observe the promotional effect of Na for this reaction. As suggested by Chang et al. [7], sodium cations in Na mordenite serve as electron donating sites. The donation of electrons from sodium sites to ruthenium sites cause the ruthenium cations to become electron rich, which in turn, lead to electron transfer to nitrogen oxide and weakening of the N–O bond in the nitrogen oxide molecule. In this way Na promotes the activity for the second step involving NO reduction and oxidation of catalyst surface, which seems to be the rate limiting step for this reaction. We did not observe this promotional effect of Na for CO oxidation activity of catalysts, which further substantiate the proposed mechanism. It is, therefore, possible to tailor the catalytic properties of metals and metal oxides by supporting them on zeolites. Further studies on mechanistic aspects are in progress as these catalysts appear to be potential for practical applications related to NO reduction.

5. Conclusion

Ru-mordenite shows good catalytic activity for the reduction of NO with CO under stoichiometric conditions. Ion exchange method results in excellent dispersion of ruthenium in mordenite and does not affect its crystallinity, if pH of the solution is maintained properly during the synthesis. Ru-Mor with 3 wt.% ruthenium content shows excellent catalytic activity, and suggests the direct role of ruthenium content on catalytic activity for NO–CO reaction. The high catalytic activity of these catalysts is due to the high surface area and excellent dispersion of ruthenium in zeolites as compared to other support, which do not possess the ion exchange properties. An MVK type redox mechanism can explain the NO–CO reaction as the Ru is present in RuO₂ oxide form. The Na form of mordenite is found to be more active for NO–CO reaction than the H form, probably due

to the electron donation from sodium sites to ruthenium, which in turn weaken the N–O bond. Hydrothermally stable zeolites appears to be excellent support for the high dispersion of active metals like ruthenium while their catalytic properties can also be tailored by introduction of suitable co-cation. Their surface area is also equally responsible for their high catalytic activity, while their cation exchange capacity, although relatively very low, is very useful for the excellent and uniform dispersion of active cations.

Acknowledgements

This work was carried out under the CSIR Network project No. CORE(08) 1.3 as well as under the research cooperation between NEERI, India and NIMS, Japan. Some characterization studies were carried out in the framework of the bilateral cooperation between CSIR India and the Academy of Sciences of the Czech Republic. Thanks are due to the ICT, Hyderabad for providing the necessary research facilities.

References

- [1] J. Xiaoyuan, D. Guanghai, L. Liping, C. Yingxu, Z. Xiaoming, *J. Mol. Catal. A: Chem.* 218 (2004) 187–195.
- [2] P.J. Godowski, J. Onsgaard, A. Gagor, M. Kondys, Z.S. Li, *Chem. Phys. Lett.* 406 (2005) 441–445.
- [3] R. Nickolov, N. Stankova, M. Khristova, D. Mehandjiev, *J. Colloid Interface Sci.* 265 (2003) 121–128.
- [4] Y.-S. Ma, I.I. Rzeznicka, T. Matsushima, *Appl. Surf. Sci.* 244 (2005) 558–562.
- [5] N.K. Labhsetwar, A. Watanabe, T. Mitsuhashi, H. Haneda, *J. Mol. Catal. A: Chem.* 223 (2004) 217–223.
- [6] Y.-J. Li, J.N. Armor, *Appl. Catal. B* 1 (1992) L21–L29.
- [7] Y.-F. Chang, J.G. McCarty, E.D. Wachsman, *Appl. Catal. B: Environ.* 6 (1995) 21–23.
- [8] J.A.Z. Pieterse, R.W. van den Brink, S. Booneveld, F.A. Bruijn, *Appl. Catal. B: Environ.* 46 (2003) 239–250.
- [9] H. Over, M. Muhler, *Progr. Surf. Sci.* 72 (2003) 3–17.
- [10] A.L. Kustov, V.G. Kessler, B.V. Romanovsky, G.A. Seisenbaeva, D.V. Drobot, P.A. Scheglov, *J. Mol. Catal. A: Chem.* 216 (2004) 101–106.
- [11] N.K. Labhsetwar, A. Watanabe, T. Mitsuhashi, *Appl. Catal. B* 40 (2003) 21.
- [12] M. Misono, K. Kondo, *Chem. Lett.* (1991) 1001.
- [13] K. Yogo, S. Tanaka, M. Ihara, T. Hishiki, K. Kikuchi, *Chem. Lett.* (1992) 1025.
- [14] S. Sato, H. Hirabayashi, H. Yahiro, N. Mizuno, M. Iwamoto, *Catal. Lett.* 12 (1992) 193.
- [15] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki, T. Ito, *Catal. Lett.* 6 (1990) 239.
- [16] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, M. Tabata, *Appl. Catal.* 70 (1991) L15.
- [17] G. Zhang, T. Yamazaki, H. Kawakami, T. Suzuki, *Appl. Catal. B* 1 (1992) L15.
- [18] H. Hirabayashi, H. Yahiro, N. Mizuno, M. Iwamoto, *Chem. Lett.* (1992) 2235.
- [19] A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno, H. Obuchi, *Appl. Catal. B* 2 (1993) 71.