

Combined NO_x selective catalytic reduction and NH₃-slip oxidation activity of composite [Fe-Beta + Fe(Mn)MCM-48] catalysts

Aleksandr Yu. Stakheev,^{*a} Dmitriy A. Bokarev,^a Alina I. Mytareva,^a
Rajesh K. Parsapur^b and Parasuraman Selvam^{*b}

^a N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation.
Fax: +7 499 135 5328; e-mail: st@ioc.ac.ru

^b National Centre for Catalysis Research and Department of Chemistry, Indian Institute of Technology-Madras, Chennai 600036, India. E-mail: selvam@iitm.ac.in

DOI: 10.1016/j.mencom.2014.09.023

A promising performance of dual-function catalysts such as [Fe-Beta + Fe(Mn)MCM-48] with various composition ratios for high NO_x conversion with a zero NH₃ slip has been demonstrated.

Low-cost nitrogen oxides (NO_x) after-treatment is one of the main challenges facing high-efficiency gasoline and diesel engines operating with lean mixtures. Selective catalytic reduction (SCR) is the most efficient process for removing NO_x. In this process, NO_x reacts with ammonia injected into exhaust gas in front of a catalyst to form molecular nitrogen gas and water vapor without creating secondary pollutants. In general, NO_x abatement can be achieved using a system of a zeolite–NH₃–DeNO_x catalyst (e.g., Fe-Beta or Cu-Beta) followed by an NH₃-slip catalyst, which usually contains expensive noble metal components such as Pt or Pd.^{1,2} In order to reduce the after-treatment cost, it is necessary to develop dual function catalysts comprising zeolite, which is active in NH₃-SCR, and a low-cost redox component for removing residual NH₃. Fe³⁺ cations existing in zeolites and mesoporous materials are active sites in ammonia oxidation processes.^{3,4} Likewise, Fe³⁺ incorporated into M41S-type (e.g., FeMCM-41 and FeMCM-48) mesoporous materials are employed as oxidation catalysts.^{5–8} Furthermore, according to our preliminary data, the modification of FeMCM-48 with manganese, i.e., Fe(Mn)MCM-48, increases the catalyst activity in oxidation processes. Here, we studied the NH₃-DeNO_x activity of composite catalysts prepared by the mechanical mixing of Fe-Beta zeolite and Fe(Mn)MCM-48 as a redox component.[†]

Figure 1(a) depicts the XRD data for Fe(Mn)MCM-48. The diffraction pattern shows all the reflections characteristic of a cubic MCM-48 structure.^{9,10} Specific surface areas and pore-size distributions were obtained by BET and BJH methods, respec-

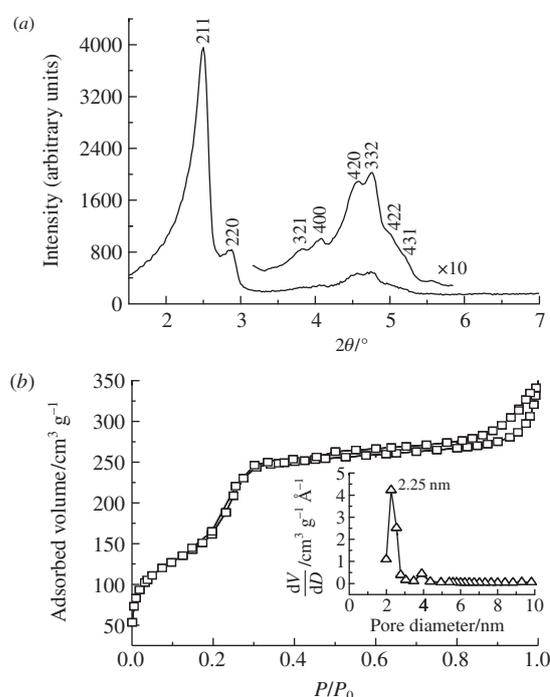


Figure 1 (a) XRD pattern; (b) N₂ adsorption–desorption isotherm, insert: pore size distribution of Fe(Mn)MCM-48.

tively. Figure 1(b) shows the nitrogen adsorption and desorption isotherms and pore size distribution of Fe(Mn)MCM-48. According to the IUPAC classification of physisorption isotherms,¹¹ this sample has a Type IV isotherm. It contains a hysteresis loop at relative pressures higher than $p/p_0 = 0.4$ that is typical of mesoporous materials.

Figure 2 shows the TEM image of Fe(Mn)MCM-48. The sample has a regular array of uniform channels, which confirms the periodicity and high crystallinity consistent with XRD results. It was shown earlier that Fe cations in Fe-Beta are located in cationic positions and the amount of iron oxide species is negligible.¹² On the other hand, the characterization data for Fe(Mn)MCM-48 clearly indicate isomorphous replacement of Si⁴⁺ with Fe³⁺ in the framework structure. The incorporation of Fe³⁺ ions into lattice positions is suggested by an increase in the unit cell parameters. This is well supported by DRUV-VIS and EPR studies.

[†] The microporous Fe-Beta zeolite catalyst was prepared by the incipient wetness impregnation of H-Beta (Si/Al = 12) with an aqueous solution of Fe(NO₃)₃·9H₂O followed by calcination at 550 °C in air flow. The Fe content was estimated at 0.7 wt% (AAS). On the other hand, the mesoporous Mn-modified FeMCM-48 (Si/Fe = 60) catalyst, designated as Fe(Mn)MCM-48, was prepared hydrothermally according to a procedure reported earlier⁹ with Fe₂(SO₄)₃·H₂O having trace amounts of Mn. The nominal iron content of the sample was 1.5 wt%. The catalysts were characterized by TEM, XRD, BET surface area, DRUV-VIS and EPR spectroscopy.

All samples were tested in NH₃-DeNO_x using a fixed-bed reactor with a feed gas containing NO (600 ppm), NH₃ (700 ppm), 10 vol% O₂ and 6 vol% H₂O balanced with N₂ at GHSV = 270 000 h⁻¹. An FTIR GASMET-4000 analyzer was used for the analysis of reaction products. Note that the reaction was carried out with an excess of NH₃ (100 ppm above reaction stoichiometry) for the evaluation of NH₃-DeNO_x and NH₃-slip removal efficiency.

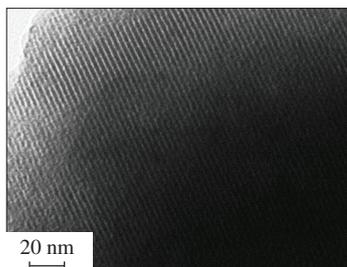


Figure 2 TEM image of Fe(Mn)MCM-48.

A typical reaction product distribution for the parent Fe(Mn)MCM-48 and Fe-Beta is shown in Figure 3. The catalytic tests of Fe(Mn)MCM-48 revealed significant activity in NH_3 oxidation, which started above 200°C , while its activity in NO_x SCR was marginal. The main reaction products were NO and N_2O [Figure 3(a)]. On the other hand, Fe-Beta demonstrated favorable NH_3 -De NO_x activity, whereas that in the oxidation of residual NH_3 was insufficient below 400°C [Figure 3(b)].

In order to combine the activity of Fe(Mn)MCM-48 in NH_3 oxidation and the favorable NH_3 -De NO_x performance of Fe-Beta, we used these components for the preparation of a [Fe-Beta + Fe(Mn)MCM-48] composite catalyst.[‡] The basic idea was to combine the NH_3 -De NO_x activity of Fe-BETA and the NH_3 oxidation activity of Fe(Mn)MCM-48 in one catalytic brick. Additionally, we attempted to improve the selectivity of NH_3 oxidation over Fe(Mn)MCM-48 due to the consumption of NO formed in reaction (1) in the secondary NH_3 -De NO_x reaction over Fe-Beta [reaction (2)]:

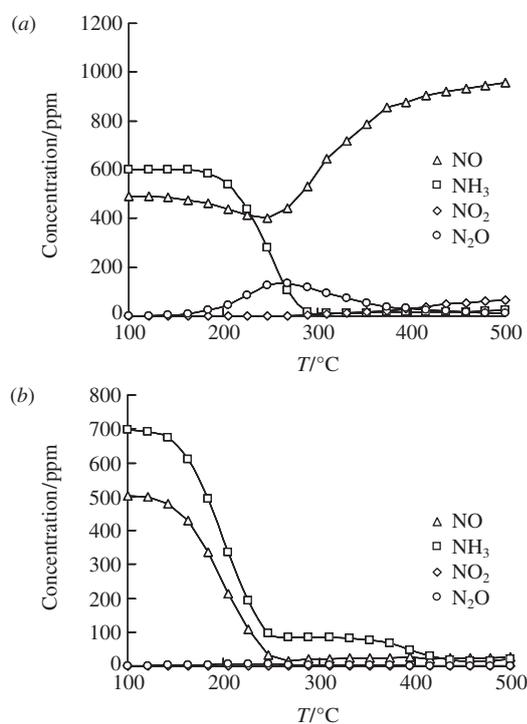


Figure 3 Reaction product distribution for (a) the parent Fe(Mn)MCM-48 and (b) Fe-Beta during NH_3 -De NO_x .

[‡] Composite [Fe-Beta + Fe(Mn)MCM-48] catalysts were prepared by the thorough mechanical mixing of both Fe-Beta and Fe(Mn)MCM-48 powders in an agate mortar followed by pelletization using a hydraulic die. The Fe-Beta:Fe(Mn)MCM-48 component ratio was varied from 1:1 to 5:1.

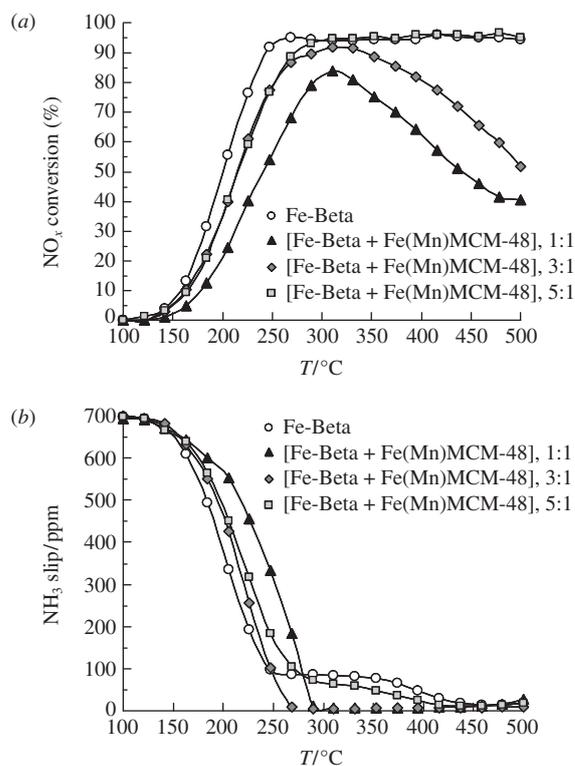


Figure 4 NH_3 -De NO_x performance of Fe-Beta zeolite and the composite [Fe-Beta + Fe(Mn)MCM-48] with different component ratios: (a) NO_x conversion and (b) outlet NH_3 concentration.

The NH_3 -De NO_x performance of Fe-Beta and the composite [Fe-Beta + Fe(Mn)MCM-48] catalysts having different component ratios are compared in Figure 4(a) and their efficiencies in NH_3 -slip removal are compared in Figure 4(b). The composite catalyst [Fe-Beta + Fe(Mn)MCM-48] with a weight component ratio of 1:1 demonstrates efficient NH_3 -slip removal above 260 – 270°C , when NH_3 oxidation over Fe(Mn)MCM-48 becomes significant [see Figure 3(a)]. However, the oxidation activity of this composition is excessive, as indicated by the downward bending of an NO_x conversion profile at $\sim 300^\circ\text{C}$. This bending originates from unfavorable NH_3 over-oxidation over Fe(Mn)MCM-48 leading to undesirable NO formation and NH_3 depletion. Evidently, the oxidation activity of Fe(Mn)MCM-48 is overbalanced in this composition. Varying the Fe-Beta:Fe(Mn)MCM-48 component ratio allowed us to minimize the unfavorable NH_3 over-oxidation and to balance activities in NH_3 -De NO_x and NH_3 oxidation. The favorable performance was attained for the composite catalysts with 3:1 and 5:1 ratios [cf. Figure 4(a)]. The data suggest that the performance can be optimized further by a careful adjustment of the component ratio.

Additional experiments demonstrated that the composite catalyst prepared by mechanical mixing provided better performance than a dual bed configuration with the front bed of Fe-Beta and the downstream bed of Fe(Mn)MCM-48. The mechanically mixed composition did not produce any N_2O emission at 200 – 300°C and lower NO formation above 280°C typical of Fe(Mn)MCM-48 [Figure 3(a)], as compared to the dual bed configuration. We believe that the advantage of the composite catalyst stems from intense secondary NH_3 -De NO_x over neighboring Fe-BETA in the composite catalyst [reaction (2)]. The NH_3 -De NO_x decreases the amount of NO and hinders the secondary reaction of N_2O formation:¹³



In conclusion, the data on the $\text{NH}_3\text{-DeNO}_x$ performance of the composite [Fe-Beta + Fe(Mn)MCM-48] catalyst indicate that the favorable NO_x -SCR activity and the efficient NH_3 -slip removal can be attained within a wide temperature range. The performance of the composite catalyst can be optimized by varying a ratio between Fe-Beta and Fe(Mn)MCM-48.

This work was supported by the Russian Foundation for Basic Research (grant no. 13-03-92711/IND_a) and the Department of Science and Technology, New Delhi (grant no. INT/RUS/RFBR/P-152). A. Mytareva acknowledges the support of Haldor Topsøe A/S in the framework of a Ph.D. student support programme.

References

- 1 Z. Hu, C. Z. Wan, Y. K. Lui, J. Dettling and J. J. Steger, *Catal. Today*, 1996, **30**, 83.
- 2 A. Scheuer, W. Hauptmann, A. Drochner, J. Gieshoff, H. Vogel and M. Votsmeier, *Appl. Catal. B*, 2012, **111–112**, 445.
- 3 T. Inui, H. Nagata, T. Takeguchi, S. Iwamoto, H. Matsuda and M. Inoue, *J. Catal.*, 1993, **139**, 482.
- 4 J. Patarin, M. Tuilier, J. Dun and H. Kessler, *Zeolites*, 1992, **12**, 70.
- 5 W. A. Carvalho, P. B. Varaldo, M. Wallau and U. Schuchardt, *Zeolites*, 1997, **18**, 408.
- 6 P. Selvam and S. K. Mohapatra, *J. Catal.*, 2006, **238**, 88.
- 7 P. Selvam and T. A. P. Paulose, *J. Nanosci. Nanotechnol.*, 2006, **6**, 1758.
- 8 H. Subramanian and R. T. Koodali, *React. Kinet. Catal. Lett.*, 2008, **95**, 239.
- 9 P. Selvam and S. E. Dapurkar, *Catal. Today*, 2004, **96**, 135.
- 10 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. C. Beck, *Nature*, 1992, **359**, 710.
- 11 K. S. W. Sing, *Pure Appl. Chem.*, 1982, **54**, 2201.
- 12 D. E. Doronkin, A. Yu. Stakheev, A. V. Kucherov, N. N. Tolkachev, M. Kustova, M. Høj, G. N. Baeva, G. O. Bragina, P. Gabrielson, I. Gekas and S. Dahl, *Top. Catal.*, 2009, **52**, 1728.
- 13 F. Kapteijn, L. Singoredjo, A. Andreini and J. A. Moulijn, *Appl. Catal. B*, 1994, **3**, 173.

Received: 30th January 2014; Com. 14/4299