

Zeolite supported iron catalyst for nitric oxide reduction by ammonia in the presence of oxygen

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Iron based H-ZSM-5 catalysts were used to study NO reduction with NH₃ in the presence of oxygen with and without humid conditions. The iron based H-ZSM-5 was prepared by wet impregnation method and characterized by X-ray diffraction technique, BET surface area and SEM. TPD experiments showed low and high temperature NH₃ desorption peaks. FTIR indicated only ammonia adsorbed species. Fe/ZSM-5 showed better NO_x reduction with NH₃ than H-ZSM-5 which was a poor catalyst for the NO_x reduction. The catalytic activity did not show significant difference in the NO_x conversion with and without water, but there was significant difference in NH₃ conversion. It may be said that the dispersed Fe species and acid sites were the active centers for the reduction of NO with NH₃ in the presence of oxygen.

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Automobile exhaust pollution control by three way catalyst is quite feasible, but in diesel engine exhaust it is difficult. Diesel engines give more amount of NO and the existing reducing agent is not sufficient in the exhaust environment for its reduction over the catalyst. Therefore, it is necessary to select external reducing agent for the reduction of NO over the catalyst. The metal based zeolite catalysts have been shown to be active for NO_x reduction with ammonia¹. The removal of NO_x from exhaust gas is the main issue to prevent pollution related health and environmental hazards. There is a need to develop a catalyst applicable in oxygen rich and humid atmosphere, aiming at cleaning diesel exhaust and lean burn exhaust gas. After promising reports²⁻⁵ on Cu-ZSM-5, a number of zeolite catalysts have been tried for NO_x reduction with NH₃ and hydrocarbons⁶⁻⁸. Ammonia type reductant is generally preferred which is much more effective for NO reduction, in presence of excess O₂, than hydrocarbons⁹. Hydrocarbons have some disadvantages such as carbon deposition, formation of oxide products like CO, CO₂ and HC consumption due to combustion. In the present investigation, evaluation of the activity and selectivity of NO reduction by NH₃ over iron based H-ZSM-5 (designated as Fe/ZSM-5), in the presence of O₂, in dry and humid conditions is reported. An attempt has been made to correlate the results of XRD, SEM, TPD

and FTIR.

Experimental Procedure

The preparation of Fe/ZSM-5 was carried out by wet impregnation method. Appropriately weighed quantities of ferric nitrate was taken with H-ZSM-5 (Si/Al = 20) so that the total metal content in ZSM-5 was around 3.5% by weight. Weighed quantity of H-ZSM-5 powder was added slowly to the continuously stirred dilute metal nitrate solution. The mixture was then continuously stirred at 343 K for about 5-7 h on a magnetic stirrer and then heated to dryness. The solid mass was homogenized in an agate mortar and then heated in the furnace at 823 K for 5 h. H-ZSM-5 was supplied by Alsi-Penta Zeolite and all other chemicals used were from Fluka.

The X-ray diffractograms of the samples were recorded on a Siemens Diffractometer (model D-500) using Cu K α radiation filtered through Ni. The total BET surface areas of these samples were measured at liquid nitrogen temperature using Omnisorp (100 CX).

H-ZSM-5 was heated to 773 K before using as a catalyst and for SEM micrograph. The morphology of these catalysts was analyzed by SEM on a Cambridge Stereoscanner S4-10 Microscope. The samples were prepared by spraying catalyst powder in resin melt (Technovit 4071) which was then solidified and the sample surface side was polished to smoothness followed by gold metallization in vacuum.

Catalytic activity was measured using feed gas compositions of 1200 ppm of NO and 1200 ppm of NH₃ in N₂ with 6.5% O₂ by volume. The same reaction was also studied in moist condition allowing 5% water vapour by volume in the reaction mixture. The total gaseous flow rate was around 50 mL/s. The reaction was studied in a continuous flow fixed bed quartz reactor in which around 0.2 g of the catalyst powder was loaded in between quartz wool. The individual gas flow rates were controlled using mass flow meters (MKS). The feed gases and the products were analyzed continuously on line employing a NO/NO_x Chemiluminescence analyzer for NO_x (915A/Beckmann Ind) and NDIR spectrometers (Binos HT 5.3/Leybold-Heraeus and Ultramate 5E/Siemens) for NH₃ and N₂O respectively. The output signals of these instruments were fed to the multi-channel recorder (LPD-12 Linseis) for continuous monitoring of these gases.

Experiments on temperature program desorption (TPD) of NH₃ and NO_x were carried out in a quartz reactor, loading about 0.15 g of the catalyst powder in between quartz wool, using an NDIR spectrometer for NH₃ and N₂O and a chemiluminescence NO/NO_x analyzer for NO_x *in situ*. The catalyst was initially maintained at 373 K in flowing N₂ (2 L/min) for about 30 min. NH₃/NO gas of about 1200 ppm was introduced for 30 min, then the adsorbing gas was stopped and only N₂ was allowed to flow till free from other gases. The catalyst was heated in a flowing N₂ at 10 K/min to obtain NH₃ / NO_x desorption.

FTIR spectra of adsorbed species on the surface of the catalyst were recorded. Adsorptions were carried out at 373 K with NH₃ and NO_x along with nitrogen. The catalyst was cooled in the same environment and then flushed with N₂ till free from other gases. Immediately the catalyst sample was mixed with KBr and mounted in the FTIR spectrometer for spectral recording (Magma 550 IR).

Results and Discussion

The X-ray powder diffractograms of H-ZSM-5 and Fe/ZSM-5 showed no qualitative change in the XRD patterns. The gross crystal structure appeared to be unaffected after iron wet impregnation with H-ZSM-5.

SEM micrograph of H-ZSM-5 and Fe/ZSM-5 were scanned and it was observed that after heat treatment and wet impregnation better crystallinity was developed. The average particle size of the sample was found to be less than 40 μm.

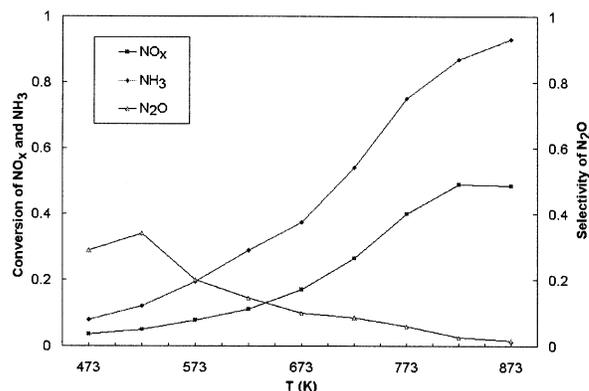


Fig 1—Fractional conversion of NO_x, NH₃ and selectivity of N₂O formation over Fe/ZSM-5.

Figure 1 shows fractional conversions of NO_x and NH₃ and the selectivity of N₂O formation with respect to the catalyst temperatures over Fe/ZSM-5. The maximum NO_x conversion at 773 K is 40% and that of NH₃ is 75%, indicating that the reaction is not 1:1 as seen in the figure. Beyond 823 K NO_x conversions level off whereas, NH₃ keep on showing higher conversions.

Bradley *et al*¹⁰ found that at low temperature (below 673 K) both NO and NH₃ have sufficient residence time on the surface to react and form N₂, but with an increase in temperature the surface residence time of NO and NH₃ decreases. Kapteijn *et al*¹¹ reported that at higher temperatures part of NH₃ is no longer available for selective catalytic reduction and can be converted into NO, resulting in a decrease of the apparent NO conversion. Above 673 K, N₂O formed may get further reduced to N₂. It is reported¹², that, the selectivity of N₂O formation observed at an early stage of the reduction of NO reflects the difference in adsorptivity between NO and N₂O. The adsorption of NO is stronger than N₂O at lower temperatures. The NO and N₂O, on the catalyst, will establish an adsorption equilibrium and the N₂O is displaced by NO before it is converted to N₂. As the temperature is raised the N₂O formed on the catalyst will be reduced to N₂ before the displacement by NO.

Figure 2 depicts the fractional conversion of NO_x and NH₃ along with the selectivity of N₂O formation over Fe/ZSM-5 in humid condition by admitting 5% water vapour in the reaction mixture. It is observed, that, NH₃ conversion is lower and also the selectivity of N₂O formation is less as compared to Fig. 1. It is also seen that above 823 K NO_x reduction is not leveling off but increases with temperature unlike in

Table 1—Catalytic performance of Fe/ZSM-5 with and without water vapour

Sr. No.	Catalyst	Temp. (K)	NO _x conversion (%)	N ₂ O yield (ppm)	Rate ^a (molec./m ² .s)	Turn Over Freq. ^b (TOF s ⁻¹)
1	Fe/ZSM-5	523	6	32	1.22×10 ¹⁵	1.38×10 ³
		623	11	32	2.23×10 ¹⁵	2.53×10 ³
		723	26	33	2.27×10 ¹⁵	5.98×10 ³
		823	48	18	9.73×10 ¹⁵	11.04×10 ³
2	Fe/ZSM-5(H ₂ O)	523	8	9	1.62×10 ¹⁵	1.84×10 ³
		623	14	9	2.83×10 ¹⁵	3.22×10 ³
		723	24	4	4.86×10 ¹⁵	5.52×10 ³
		823	44	3	8.92×10 ¹⁵	10.12×10 ³

^a Number of NO molecules converted per unit area (/m²) per second.

^b The number of NO molecules converted per Fe per second.

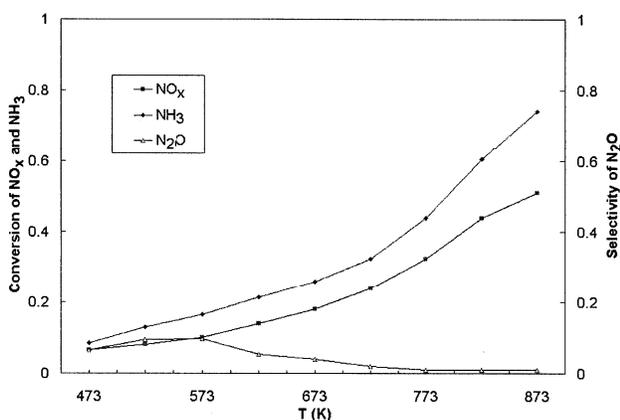


Fig 2—Fractional conversion of NO_x, NH₃ and selectivity of N₂O formation over Fe/ZSM-5 with H₂O.

Fig. 1. It is suspected that water vapour produces more new Brönsted acid sites on the surface which result in a strong chemisorptions of NH₃ and does not get oxidized easily. Humidity does not change much of the NO_x conversion, it has almost remained the same accept marginally lower conversion between 723 to 823 K. The literature reports also mention that water suppresses especially the selectivity of N₂O formation¹³, thus increasing the selectivity of the reaction.

H-ZSM-5 showed very low activity for NO_x reduction with and without moisture. Ammonia oxidation is prominent in absence of water but NO_x reduction is negligible indicating poor catalytic activity. In presence of moisture, NH₃ conversion also fell down which further confirms that moisture prevents NH₃ oxidation. However, catalytic activity increases appreciably after metal incorporation.

Table 1 shows the catalytic performance of Fe/ZSM-5 with and without water vapour along with the N₂O yield. It is also seen that the rate and turn

over frequency (TOF) increases with temperature as expected. However, catalyst did not show much difference in activity with and without water in agreement with the results reported previously¹⁴, but inhibited NH₃ conversion with water considerably.

Different ratio of NH₃/NO_x (NH₃:NO_x) versus NO_x conversion was carried out at different temperatures. It is observed that at 523 K a 1:1 ratio of NH₃ and NO_x gives maximum NO_x conversion, on increasing the ratio further the NO_x conversion remained the same, whereas by decreasing the ratio lower than 1:1 decreased the NO_x conversion. At higher temperatures more NH₃ is required that is higher ratio of NH₃ / NO_x. For example at 623 K, it gave maximum NO_x conversion with 1.25:1 of NH₃/NO_x ratio and at 723 K gave maximum conversion with 1.5:1, while at 823 K it was with 1.75:1. This indicates that different temperatures require different concentration of NH₃ to get maximum NO_x conversion. But beyond 873 K, further increase in NH₃ concentration has no impact on NO_x conversion.

Figure 3 presents the temperature programmed desorption (TPD) of NH₃ on Fe/ZSM-5 with and without water respectively. The TPD spectra of NH₃ shows two desorption peaks, one at around 460 K and other at 658 K. The low temperature peak is assigned as weak adsorption or physical adsorption of NH₃ and the high temperature peak is for the acid strength of the catalyst¹⁵. The high temperature peak has to be accounted for the acidity of the zeolite¹⁶. With water the high temperature peak gave 1.02 μmol/g.s NH₃ desorption compared to 0.92 μmol/g.s without water, indicating thereby that water has produced more acid sites resulting more NH₃ adsorption which also restricted NH₃ oxidation with water. Fe/ZSM-5 did not show any NO_x desorption in presence and absence of

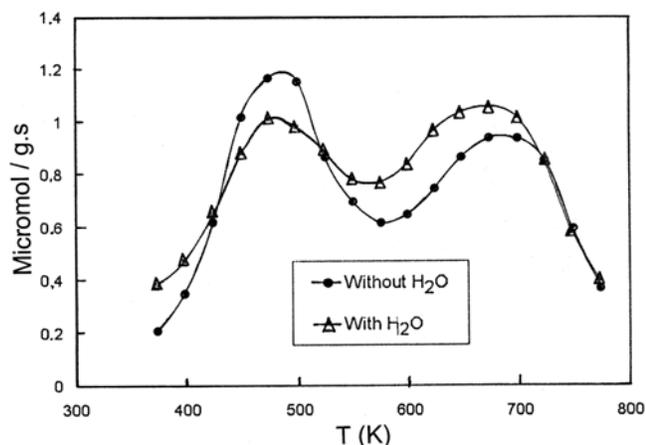


Fig 3—Temperature programmed desorption of NH_3 over Fe/ZSM-5 with and without H_2O .

humidity, also with and without O_2 .

Figure 4 depicts the FTIR absorption spectra, recorded at room temperature, of prior adsorbed NH_3 and NO_x species on this catalyst. The absorption bands at around 1406, 1460 and 3025 cm^{-1} are attributed¹⁷ to NH_4^+ (Fig. 4b). The NO adsorption was performed over this catalyst in presence and absence of O_2 , but no NO_x absorption band is observed and the spectra remained the same (Fig. 4c). In earlier studies⁵ Cu-ZSM-5 showed NO_x adsorption species in FTIR and NO_x desorption in TPD studies. Since this IR results are of adsorbed species recorded at room temperature rather than *in situ*, not all the species might have been detected here.

Komatsu *et al.*¹⁸ proposed that the nitrate species is the reactive intermediate in the reduction of NO with NH_3 in presence of O_2 . These species fail to form in the absence of O_2 . Centi and Parathoner¹⁹ reported that the mechanism of NH_3 conversion to N_2 involves a first step of heterolytic dissociative chemisorptions of NH_3 to form $-\text{OH}$ and $-\text{NH}_2$ species. The formation of the $-\text{NH}_2$ species has been suggested²⁰ as the key step in the mechanism of NO reduction on V-TiO₂. The selective catalytic reduction mechanism of NO_x reacts with surface $-\text{NH}_3$ or $-\text{NH}_2$ species to directly yield N_2 and H_2O . The intermediate species ($-\text{NH}_2$) can react with NO to form N_2 . Kapteijn *et al.*¹¹ have stressed that the product of the reaction between NO, NH_3 and O_2 can be explained by a model where the NH_3 is successively dehydrogenated by surface oxygen species. In this model, the intermediate species can react with NO to form N_2 , while ($-\text{NH}_2$) or

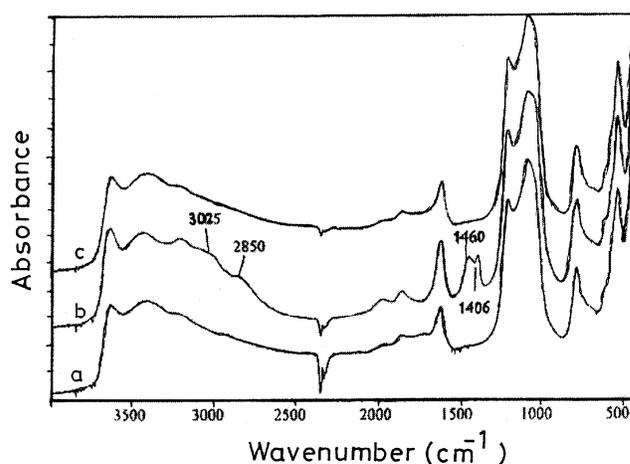


Fig. 4—FTIR absorbance spectra of adsorbed species over Fe/ZSM-5, (a) blank, (b) NH_3 adsorption at 373 K and (c) after NO adsorption with O_2 at 373 K.

(-N) species can only react with NO to give N_2O . Intermediate species formed can be nitrite complex, nitro complex or nitrate complex on the surface depending upon the type of the metal catalyst and the orientation of the adsorbed species that facilitates giving the particular selectivity of the reaction. Since in the present investigation, TPD and FTIR studies did not give indication of NO adsorbed species, it may be assumed, that, the reaction proceeds via Eley-Rideal mechanism²⁰ involving the reaction between adsorbed ammonia or NH_4^+ species with gaseous NO. However, many have reported the formation of NH_4NO_3 surface species^{18,21} which decomposes to N_2O or N_2 on a set of catalysts while others^{22, 23} showed the presence of several adsorbed NO species *in situ* IR studies. Long and Yang gave a possible reaction mechanism for NO reduction involving the reaction between one NO_2 molecule and two neighbouring NH_4^+ ions to form an active intermediate $\text{NO}_2(\text{NH}_4^+)_2$, which subsequently reacts with another NO to produce N_2 and H_2O . Therefore, it is tempting to say that the reaction proceeds via more than one mechanism depending upon the type of catalyst, catalyst composition, temperature, type of active and acidic sites on the surfaces.

Conclusion

The selectivity of NO reduction by NH_3 in the presence of O_2 with and without moisture is temperature dependent. Fe/ZSM-5 showed better catalytic activity than H-ZSM-5. A moist condition does not inhibit NO_x conversion much but inhibit NH_3

conversion reversibly, also low selectivity of N₂O formation. It is observed that below 773 K NH₃ takes part in NO_x reduction, whereas above this temperature it may favour oxidation with O₂. The NO reduction is strongly dependent on the partial pressure of O₂. In the absence of O₂ the reaction drops drastically. The formation of N₂ and N₂O most probably takes place at different catalyst sites. More than one mechanism is suspected at different temperatures.

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