Catalytic reduction of NO$_x$ by ammonia over nickel and lanthanum supported on zeolite

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The effects of oxygen and water on the reduction of NO by NH$_3$ over metal supported H-ZSM-5 catalysts have been determined. The catalysts have been prepared by wet impregnation method and characterized by X-ray diffraction and BET surface area. Higher NO$_x$ reduction rate is obtained over Ni/ZSM-5 catalyst compared with La/ZSM-5 and H-ZSM-5. In presence of water vapour the NO$_x$ rate has been found to be lower than in the absence of water vapour. Oxygen promotes SCR reaction in forming reactive intermediate species for the reduction of NO by NH$_3$.

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The selective catalytic reduction (SCR) of nitric oxide with ammonia in the presence of oxygen and water vapour represents an important process of cleaning diesel exhaust or lean burn exhaust gases. This is the main technique which is applied for stationary NO$_x$ sources like power stations, chemical industries etc. Many investigators have tried NO$_x$ reduction employing the reductants like CO, H$_2$ and hydrocarbons[1-3], but NH$_3$ is still considered to be one of the suitable reductants in presence of excess oxygen[4,5]. Hamada and others[3,6] have reported that H-ZSM-5 is a fairly good catalyst for NO$_x$ reduction by hydrocarbons and after a promising report of Cu-ZSM-5[5-7], a variety of zeolite catalysts have been investigated. Generally most of the exhaust gases contain excess oxygen and water vapour, therefore it is necessary to develop the catalysts applicable in oxygen rich and humid atmospheres. It was felt worthwhile to carry out the reduction of NO by NH$_3$ in presence of oxygen over Ni and La on H-ZSM-5 designated as Ni/ZSM-5 and La/ZSM-5. Since most of the exhaust environments contain moisture, such as automobiles and industrial exhausts, it is important to see the effect with and without humidity on activity and selectivity of these catalysts.

Materials and Methods

The preparation of M/ZSM-5 (M = Ni and La) was carried out by wet impregnation method. Appropriately weighed quantities of Ni and La nitrate were taken with H-ZSM-5 (Si/Al ratio 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 773 K for 5 h. H-ZSM-5 was supplied by Alsi-Penta Zeolithe 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 Kα radiation filtered through Ni. The total BET surface areas of these samples were measured at liquid nitrogen temperature using Omnisorp (100 CP).

Catalytic activity was measured using feed gas compositions of 1200 ppm of NO and 1200 ppm of NH$_3$ in N$_2$ with 6.5% O$_2$ by volume. The same reaction was also studied in a humid 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 NH_3 and N_2O respectively. The out put signals of these instruments were fed to the multi-channel recorder (LPD-12 Linseis) for continuous monitoring of these gases. At every temperature the reaction was stabilized till constant yield of the products were achieved for about 20-30 min.

Results and Discussion

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

Figure 1 shows NO_x and NH_3 conversions as well as N_2O formation during SCR reaction over Ni/ZSM-5 in dry gas stream. The maximum NO_x conversion was observed around 823 K and a slight decrease in activity at higher temperatures. The NH_3 conversion reaches almost to completion at 873 K and N_2O formed is quite low, maximum 17 ppm at 623 K and further decrease at higher temperatures. It is also seen that NO_x and NH_3 conversions amount to 1:1 only up to 523 K.

Figure 2 indicates the NO_x and NH_3 conversions as well as the formation of N_2O during the SCR reaction in presence of water vapour over Ni/ZSM-5. The NO_x and NH_3 conversions have dropped down compared with the results in absence of water vapour. The maximum NO_x conversion of 65% in dry gas stream

has dropped to 21% conversion at 773 K and NH_3 conversion has also lowered from 89% to 36% respectively, but better selectivity to N_2O formation is observed. Less selectivity for N_2O formation is desired as it gives rise to greenhouse effect like CO_2, therefore, more yield of N_2O is not preferred in SCR reaction. The Cu-ZSM-5 catalyst however showed higher activity for NO_x and NH_3 conversions in presence of water vapour[7].

Figure 3 depicts the NO_x conversions over M/ZSM-5 and H-ZSM-5 in dry gas flow. The Ni/ZSM-5 catalyst gave higher conversion rate than the other catalyst, whereas H-ZSM-5 showed very poor activity. La/ZSM-5 catalyst did not show very promising activity as compared to Ni/ZSM-5. One possible reason is that the redox couple of Ni^{2+}/Ni^{3+} may be responsible for higher conversion, but La has only 3+ state. It is generally observed that multiple oxidation states of active metal catalysts contribute higher NO_x conversion rates as compared with metal having only 3+ oxidation state[7]. The formation of ion pairs in different oxidation states on account of mutual interaction giving reduced and oxidized species may also act as active sites for adsorption. The active site is Ni^{3+} which is reduced to Ni^{2+} after coupling between NO and NH_3. The regeneration of Ni^{2+} to Ni^{3+} is difficult and it occurs through the disproportion of NO_x to N_2 and N_2O and Ni^{2+} in turn may be oxidized to Ni^{3+} with O_2. The role of O_2 may be for the regeneration of Ni^{3+} active site in the process. Multiple valence states facilitate electron

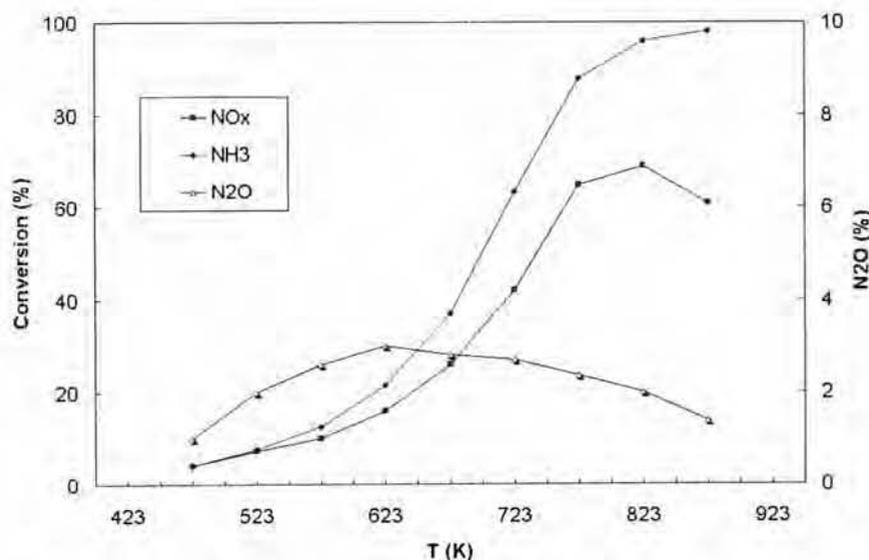Fig. 1—Percentage conversions of NO_x and NH_3 along with N_2O formation as a function of temperature over Ni/ZSM-5.
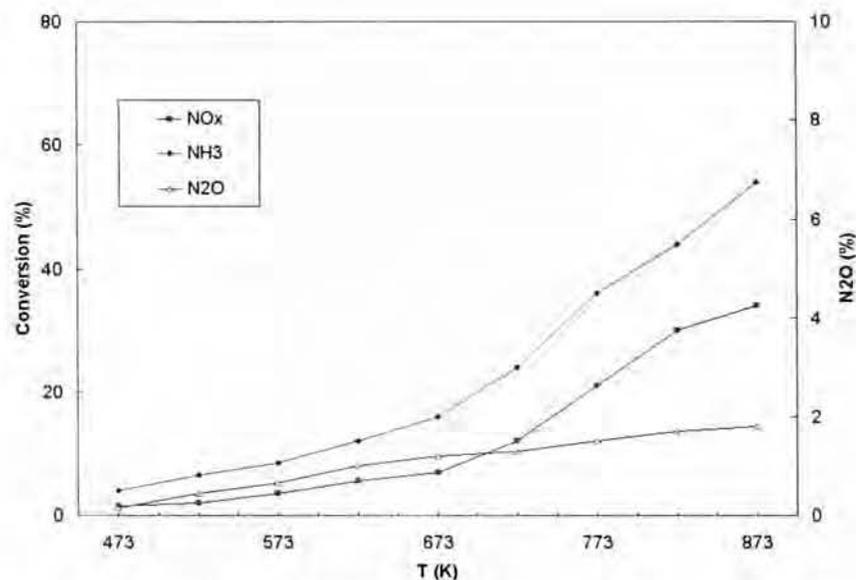
Fig. 2—Percentage conversions of NO$_x$ and NH$_3$ along with N$_2$O formation as a function of temperature over Ni/ZSM-5 with water vapour.
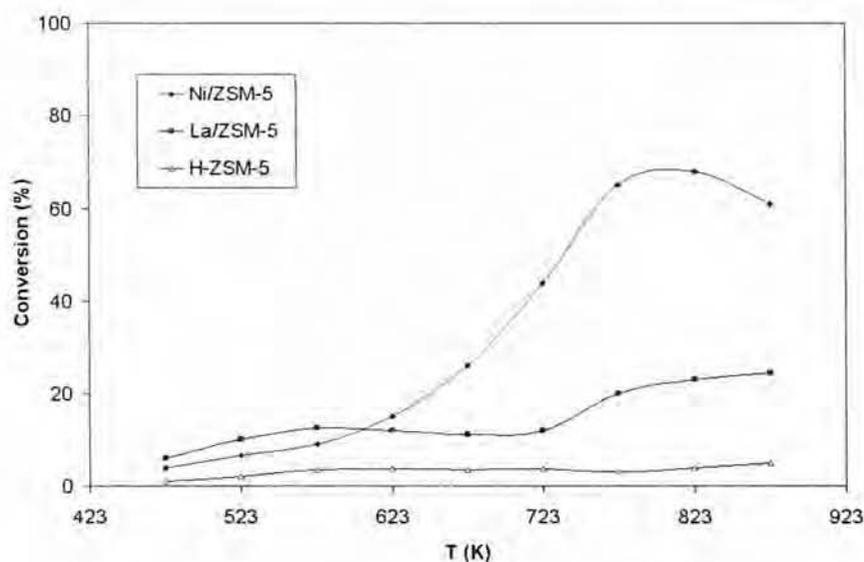

Fig. 3—Percentage conversion of NO$_x$ as a function of catalyst temperature.

transfer and adsorption of the reactants on the catalyst surface. Figure 4 shows the NO$_x$ reduction over these catalysts in presence of water vapour. It is seen that the conversion rate of NO$_x$ has decreased considerably. The only difference observed in La/ZSM-5 is that at 873 K it shows marginal higher NO$_x$ conversion than Ni/ZSM-5. In presence of water vapour less NO$_x$ is adsorbed on the catalyst than in the absence of water, hence low concentration of NO$_x$ is available for the reaction. H-ZSM-5 in the absence of

metal incorporation showed very poor activity with and without water vapour, indicating thereby that the metal incorporation enhances the activity. Activity also depends on the type of metal, its electronic property, oxidation state, bonding capacity besides other factors.

Table 1 shows the BET surface area of these catalysts and are almost in the range 400 m^2/g, except La/ZSM-5 is slightly lower. It also shows NO$_x$ reduction rate and NH$_3$ conversion along with N$_2$O
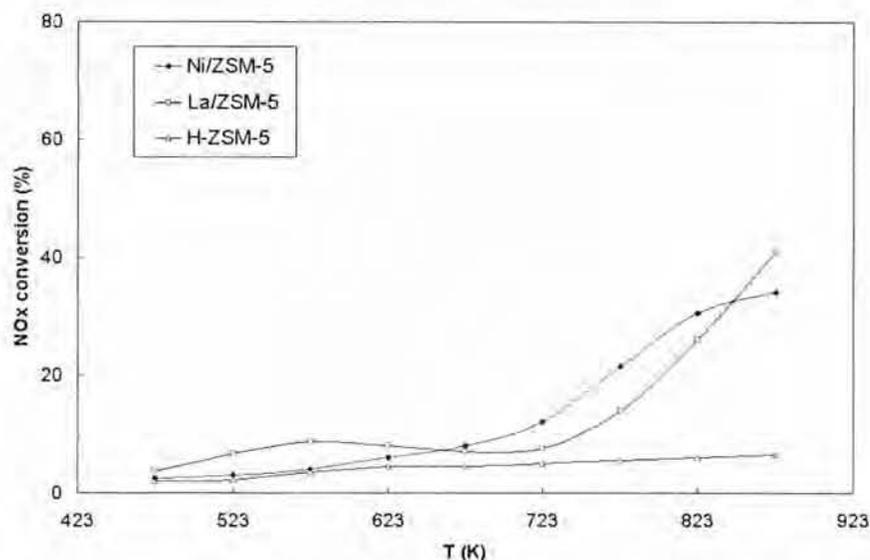
Fig. 4—Percentage conversion of NO_x as a function of catalyst temperature with water vapour.

Table 1—Summary of NO_x conversion with rate and NH_3 conversion along with N_2O formation over Ni/ZSM-5 and La/ZSM-5 with and without water vapour at 773 K

Catalyst	Surface Area (m^2/g)	NO_x conv (%)	Rate [a] (molec./m^2.s)	NH_3 conv. (%)	N_2O Yield (ppm)
Ni/ZSM-5	410	65	2.65×10^{15}	89	15
Ni/ZSM-5 (with H_2O)	410	21	8.26×10^{14}	36	08
La/ZSM-5	391	20	8.25×10^{14}	79	35
La/ZSM-5 (with H_2O)	391	14	5.77×10^{14}	48	11

[a]Rate is defined as the number of NO molecules converted per unit area (/m^2) per second.

formation with and without water vapour at 773 K. It is seen that the difference between NO_x and NH_3 conversions without water are more than those with water. It is clear that NO_x reduction is inhibited in presence of water. The La/ZSM-5 exhibited to be more oxidative type catalyst which showed higher NH_3 conversion rate than NO_x reduction and more N_2O yield as seen in Table 1. It is suspected that water vapour produces more new Brönsted acid sites on the surface, resulting in a strong chemisorption of NH_3 and does not get easily oxidized but favour reaction with NO_x. Due to increase in acidic sites on the surface, the NO_x adsorption will decrease due to acidic nature of NO_2. This indicates that water vapour suppresses the disproportion of NO_x unlike with dry condition. The literature reports also mention that water suppresses especially the selectivity of N_2O formation[8], thus increasing the selectivity of the reaction.

The trend of NO_x and NH_3 conversions are different from each other at higher temperatures (Fig.

1). In the case of Ni/ZSM-5 the decrease in NO_x conversion at 873 K may be because of side reaction like NH_3 oxidation giving NO as one of the products[9] leading to difference in NO_x and NH_3 conversions. There are several reports of NO decomposition over metal-zeolites[10,11] but the decomposition is inhibited by the presence of oxygen[12].

Komatsu[12] proposed that the nitrate species is the reactive intermediate in the reduction of NO with NH_3 in presence of O_2. Intermediate species can be nitrite complex, nitro complex or nitrato complex depending upon the type of the catalyst and the metal plays a key role in the orientation of the adsorbed species. These species fail to form in the absence of O_2. Centi and Parathoner[13] reported that the mechanism of NH_3 conversion to N_2 involves a first step of heterolytic dissociative chemisorption of NH_3 to form –OH and $-NH_2$ species. The formation of an $-NH_2$ species has been suggested as the key step in the mechanism of NO reduction[14]. At present, the view on the selective catalytic reduction mechanism of NO_x reacts with

surface $-NH_3$ or $-NH_2$ species to directly yield N_2 and H_2O. The intermediate species ($-NH_2$) can react with NO to form N_2. Kapteijn[15] 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 ($-NH_2$) or ($-N$) species can only react with NO to give N_2O.

Conclusion

The selectivity of NO reduction by NH_3 in the presence of O_2 with and without moisture is temperature dependent. The Ni/ZSM-5, La/ZSM-5 and H-ZSM-5 showed different activities with SCR of NO$_x$ by NH_3. The higher NO$_x$ conversion rate was obtained with Ni/ZSM-5. In presence of water vapour the NO$_x$ conversion rate decreased to certain extent whereas the adsorption rate of NH_3 on the catalyst was increased. Above 823 K the reaction rate of NO$_x$ over Ni/ZSM-5 starts declining and oxidation of NH_3 with surface oxygen becomes substantial leading to NO as one of the product. The NO reduction is strongly dependent on the O_2 partial pressure. In the absence of O_2 the reaction drops drastically. Oxygen plays an important role in forming the active intermediates species lowering the activation energy of the SCR reaction. The formation of N_2 and N_2O most probably takes place at different catalyst sites.

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