Selective catalytic reduction of nitric oxide with ammonia in presence of oxygen over Mn-ZSM5
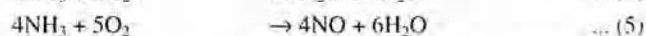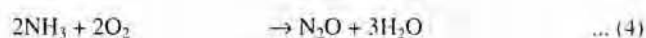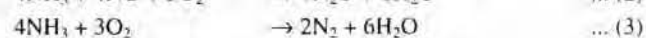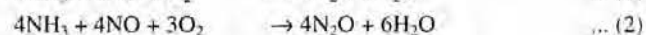
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Selective catalytic reduction of NO with NH₃ in the presence of oxygen with and without humid conditions has been studied over Mn-ZSM5 and H-ZSM5. The Mn-ZSM5 has been prepared by wet impregnation method, characterized by X-ray diffraction technique, atomic absorption spectroscopy and BET surface area. Mn-ZSM5 shows better NO_x reduction than H-ZSM5. H-ZSM5 alone is a poor catalyst for NO_x reduction with NH₃, but metal incorporated catalyst becomes active. In the presence of humid condition Mn-ZSM5 gives lower NO_x and NH₃ conversions. It may be concluded that the dispersed manganese species are the active centres for the selective catalytic reduction of NO with NH₃ in the presence of oxygen.

The catalytic reduction of nitric oxide in the presence of oxygen is an important process, aiming at cleaning of diesel and lean burnt exhaust gas. The selective catalytic reduction of NO_x with NH₃ is the technique applied in stationary sources. Many investigators have attempted NO reduction by CO, H_2 and hydrocarbons[1-4], but ammonia is still considered as a suitable reductant for NO in the presence of excess oxygen. Hamada and others[5] have reported that H-ZSM5 is a good catalyst for NO_x reduction by hydrocarbons. The promising reports of Cu-ZSM5[6-7] for NO_x reduction have given an impetus for a variety of zeolites to be investigated. The different possible catalytic reactions between NO and NH₃ in the presence of O_2 are shown below.

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad \ldots (1)$$
$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad \ldots (2)$$
$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad \ldots (3)$$
$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad \ldots (4)$$
$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad \ldots (5)$$
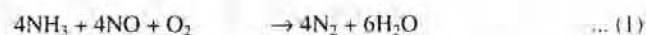
Catalytic reduction of NO with NH₃ in the presence of O_2 seems to be more suitable as far as selective catalytic reduction is concerned.

Experimental

H-ZSM5 was supplied by Alsi-Penta Zeolithe and all other chemicals used were from Fluka. The preparation of Mn-ZSM5 was carried out by wet impregnation method. Appropriately weighed quantity of manganese nitrate was taken with H-ZSM5 (Si/Al = 20) so that the total metal content in ZSM5 was around 3.25% by weight. Weighed quantity of H-ZSM5 powder was added slowly to the continuously stirred dilute metal nitrate solution. The mixture was then continuously stirred at 70°C for about 15 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 550°C for 5 h.

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 CX). The amount of transition metal in the zeolite was determined by atomic absorption spectroscopy.

Catalytic activity was measured using a feed gas composition of 1200 ppm of NO and 1200 ppm of NH₃ in N_2 with 6.5% O_2 by volume. The same reaction was also studied in humid condition allowing 5% water vapour by volume in the reaction mixture. The total Gaseous Hourly Space Velocity (GHSV) was around 180000 h^{-1}. 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 flow meters (MKS). The feed gases and the products were analysed 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 multichannel recorder (LPD-12, Linseis) for continuous monitoring of these gases.

Results and discussion

The X-ray powder diffractograms of H-ZSM5 and Mn-ZSM5 showed no qualitative change in the XRD patterns. The gross crystal structure appeared to be unaffected after manganese wet impregnation with H-ZSM5.

Figure 1 shows NO_x and NH_3 fractional conversions and N_2O formation with respect to the catalyst temperatures. The maximum NO_x conversion at 600°C is 62% and that of NH_3 is 95%, indicating that the reaction is not 1:1. However, at lower temperature up to 350°C the NO_x and NH_3 conversions are almost 1:1 as seen in Fig. 1. This clearly shows that the selectivity of the reaction is temperature-dependent. At lower temperature (below 350°C) the reactions 1 and 2 as cited above may be predominant whereas at higher temperature (above 350°C) the reactions 3 to 5 may also take place.
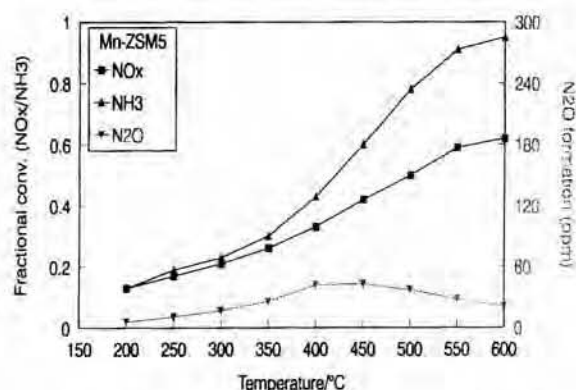
Bradley et al[8]. found that at low temperature (below 350°C) both NO and NH_3 have long enough residence time on the surface to react and form N_2, but with an increase in temperature the surface residence time of NO and NH_3 decreases. Kapteijn et al.[9] reported that at higher temperatures part of NH_3 is no longer available for selective catalytic reduction and can be converted into NO, resulting in decrease of the apparent NO conversion. The N_2O formation is maximam at 450°C around 43 ppm and subsequently falls with the temperatures. Above 400°C, N_2O formed may get further reduced to N_2. It is reported[10] that the selectivity of N_2O formation observed at an early stage of the reduction of NO reflects the difference in adsorptivity between NO and N_2O. The adsorption of NO is stronger than N_2O at lower temperatures. The NO and N_2O on the catalyst will establish an adsorption equilibrium and the N_2O is displaced by NO before it is converted to N_2. As the temperature is raised the N_2O formed on the catalyst will be reduced to N_2 before the displacement by NO. There is a report[11] that NH_3 is not able to reduce N_2O over the maganese catalyst, but instead the NH_3 is oxidised by oxygen and the distribution of the reaction products are the same as those of the NH_3 oxidation.

Figure 2 depicts the NO_x and NH_3 conversions along with the formation of N_2O over Mn-ZSM5 in humid condition by admitting 5% water vapour in the reaction mixture. It is observed that both NO_x and NH_3 conversions are lower and also the formation of N_2O is negligible as compared to Fig. 1. Another noticeable observation is that the conversion ratio of NO_x and NH_3 is quite close to 1:1. It is suspected that
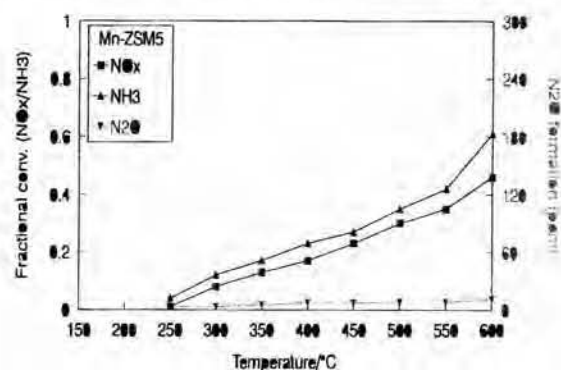

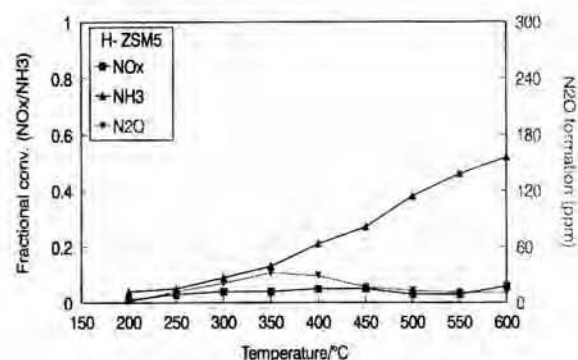
Fig. 1 : NOx, NH3 conversions with N2O formation over Mn-ZSM5.

Fig. 2 — Conversions and N₂O formation over Mn-ZSM5 with H₂O

Fig. 3 : NOx, NH3 conversions along with N2O formation over H-ZSM5.

Table 1 — Summary of NO_x and NH_3 conversions with N_2O formation at 500°C over the catalysts.

Catalyst	Surface area (m^2/g)	% Conversion		Formation of N_2O (ppm)
		NO_x	NH_3	
Mn-ZSM5	402	50	78	37
Mn-ZSM5 (with H_2O)	402	30	35	8
H-ZSM5	411	6	36	11

water vapour produces more new Bronsted acid sites on the surface which result in a strong chemisorption of NH_3, thus preventing it from getting oxidized easily and favouring reaction with NO_x. In spite of low conversion, reaction given in Eq.1 is predominant in the presence of water vapour. It is clear that in humid condition the reaction selectivity does take place over this catalyst. Water vapour inhibits the reaction reversibly, since upon removing the water vapour the NO and NH_3 conversions return back to the original higher values. The literature reports also mention that water suppresses especially N_2O formation[11], thus increasing the selectivity. Though water is the product of the reactions, it does not inhibit the reaction, but addition of external water vapour affects the reactions.

Figure 3 shows the NO_x and NH_3 fractional conversions along with the formation of N_2O over H-ZSM5 without metal impregnation. It is noticed that H-ZSM5 is a poor catalyst for NO_x coversion and at higher temperature showed only NH_3 oxidation. However, catalytic activity increases appreciably after metal incorporation.

Table 1 shows the BET surface area of the samples and percentage conversions of NO_x and NH_3 along with the N_2O formation over Mn-ZSM5 with and without vapour at 500°C. This is compared with H-ZSM5 which showed poor catalytic activity.

Kotmatsu et al.[12] proposed that the nitrate species is the reactive intermediate in the reduction of NO with NH_3 in the presence 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[14] as the key step in the mechanism of NO reduction on V-TiO_2. 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. Kapteign et al.[9] have stressed that the product of the reaction between NO, NH_3 and O_2 over manganese oxide 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) or (-N) species can only react with NO to give N_2O. A model reaction scheme has been proposed elsewhere[15] based on the observed products.

It may be concluded that the selectivity of NO reduction by NH_3 in the presence of O_2 is temperature dependent. Mn-ZSM5 showed better catalytic activity than H-ZSM5. A humid condition inhibits NO_x and NH_3 conversions reversibly and also low selectivity of N_2O formation. It is observed that below 500°C NH_3 takes part in NO_x reduction, whereas above this temperature also favours oxidation with O_2. The NO reduction is strongly dependent on the O_2 partial pressure. In the absence of O_2 the reaction rate drops drastically. The formation of N_2 and N_2O most probably takes place at different catalyst sites.

Acknowledgement

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