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REACTIVITY OF NO WITH NH₃ IN THE PRESENCE OF O₂ OVER Ce-ZSM5 WITH AND WITHOUT MOISTURE

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Abstract

Cerium based ZSM5 catalysts are used to study NO reduction with NH₃ in the presence of oxygen with and without moisture. The Ce-ZSM5 was prepared by wet impregnation method and characterized by X-ray diffraction technique, BET surface and SEM. Ce-ZSM5 showed better NO_x reduction than H-ZSM5 which is a poor catalyst for NO_x reduction with NH₃. The metal incorporation in H-ZSM5 has increased the catalytic activity. The catalytic activity showed significant difference in NO_x conversion with and without moisture. The disperse Ce species are the active centers for the reduction of NO with NH₃ in the presence of oxygen.

Keywords : Catalytic reduction of NO_x, ammonia, Ce-ZSM5 with and without moisture

INTRODUCTION

The NO, NO₂ and N₂O are significant pollutants in the environment discharged by transportation and other stationary sources of pollution. The metal based zeolite catalysts have been shown to be active catalysts for NO_x reduction by ammonia [1-3]. The catalytic reduction of nitric oxide in 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, H₂ and hydrocarbons [4-7], but ammonia type reductants are generally

more effective for NO_x reduction than hydrocarbons [8,3]. Ammonia is comparatively less reactive toward oxygen than hydrocarbons [9]. The promising report of Cu-ZSM5 [10,11] for NO_x reduction has given an impetus to a variety of zeolites to be investigated. In presence of oxygen, NO reacts with NH_3 giving out different products such as N_2 , N_2O and H_2O . It is also more important to prevent the formation of N_2O , which is also one of the significant contributors to the greenhouse effect and the oxidation of ammonia. Catalytic reduction of NO with NH_3 in presence of O_2 seems to be more suitable as far as selective catalytic reduction is concerned. In the present work the activity and selectivity of NO_x reduction by NH_3 over Ce on H-ZSM5 (designated as Ce-ZSM5) and H-ZSM5 with and without moisture are presented and discussed.

EXPERIMENTAL

H-ZSM5 was supplied by Alsi-Penta Zeolithe; all other chemicals used were from Fluka. The preparation of Ce-ZSM5 was carried out by the wet impregnation method. Appropriately weighed quantity of cerium nitrate was taken with H-ZSM5 (Si/Al = 20) so that the total metal content in ZSM5 was around 3.25 wt.%. Weighed quantity of H-ZSM5 powder was added slowly to the continuously stirred dilute metal nitrate solution. The mixture was then continuously stirred at 343 K 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 a furnace at 823 K for 5 h.

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

H-ZSM5 was heated to 673 K before use as a catalyst and for SEM micrographs. 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 then solidified and the sample surface side was polished to smoothness followed by gold metallization in vacuum.

Catalytic activity was measured using a feed gas compositions of 1200 ppm of NO and 1200 ppm of NH_3 in N_2 with 6.5 vol. % O_2 . The same reaction was also studied in moist conditions allowing 5 vol. % water vapor in the reaction mixture. The total Gaseous Hourly Space Velocity (GHSV) was around $180,000 \text{ h}^{-1}$. 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 quartz wool.

The individual gas flow rates were controlled using 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 a multichannel recorder (LPD-12, Linseis) for continuous monitoring of these gases.

RESULTS AND DISCUSSION

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

SEM micrographs of H-ZSM5 and Ce-ZSM5 were scanned and it was observed that after heat treatment and wet impregnation better crystallinity was developed.

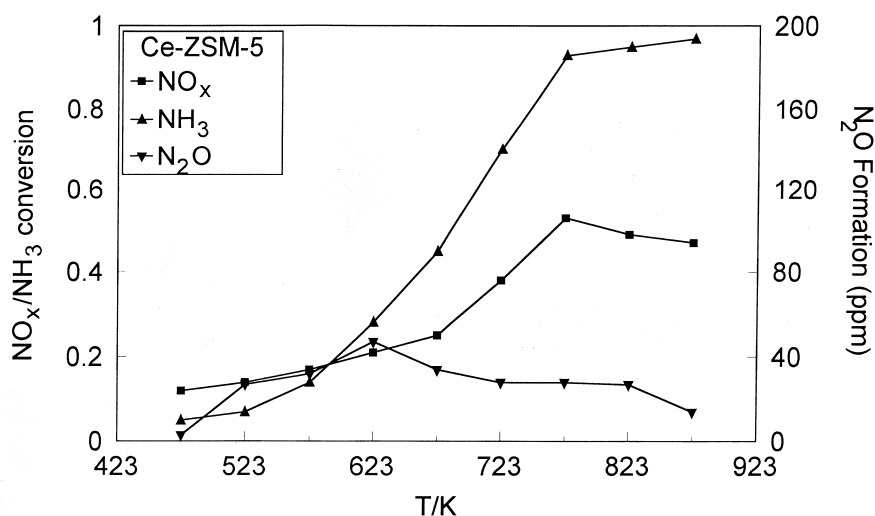
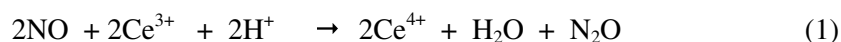


Fig. 1. Fractional conversions of NO_x, NH₃ with N₂O formation over Ce-ZSM5

Figure 1 shows NO_x and NH₃ fractional conversions and N₂O formation with respect to the catalyst temperatures. The maximum NO_x conversion at

773 K is 53% and that of NH₃ is 93%, indicating that the reaction is not 1:1. Beyond 773 K it is observed that the NO_x reduction falls, showing a declined trend as observed by many other investigators [9,12]. Another noticeable thing is that below 598 K, the NO_x showed higher conversion rate than NH₃. This may be because of disproportionation of NO over Ce-ZSM5, giving out N₂O and H₂O according to eq. 1. The redox couple of Ce³⁺/Ce⁴⁺ may be responsible for showing higher conversion than NH₃ below 598 K.



Bradley *et al.* [13] found that at low temperature (below 673 K) both NO and NH₃ have long enough 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.* [14] 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. The N₂O formation is a maximum at 673 K around 43 ppm and subsequently falls with the temperatures. Above 673 K, the N₂O formed may get further reduced to N₂. It is reported [15] 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 formation of N₂O over Ce-ZSM5 in humid conditions by admitting 5% water vapor in the reaction mixture. It is observed that both NO_x and NH₃ conversions are lower and also the formation of N₂O is less as compared to Fig. 1. Above 773 K, NO_x reduction is not lowering but increases with temperature unlike in Fig. 1. It is suspected that water vapor produces more new Brönsted acid sites on the surface, which results in a strong chemisorption of NH₃ and does not get oxidized easily but favors reaction with NO_x. Another noticeable observation is that in the presence of moisture it did not show higher conversion of NO_x below 598 K. This indicates that humidity suppresses the disproportionation of NO_x unlike in Fig. 1. It is clear that in humid conditions the reaction selectivity does take place over this catalyst. Water vapor inhibits the reaction reversibly, since upon removing the water vapor, the NO and NH₃ conversions return back to the original higher values. The literature reports also mention that water suppresses especially N₂O formation [16], thus increasing the selectivity. In spite of being the product water does not inhibit the reaction, but only on the addition of external water does vapor affect the reactions.

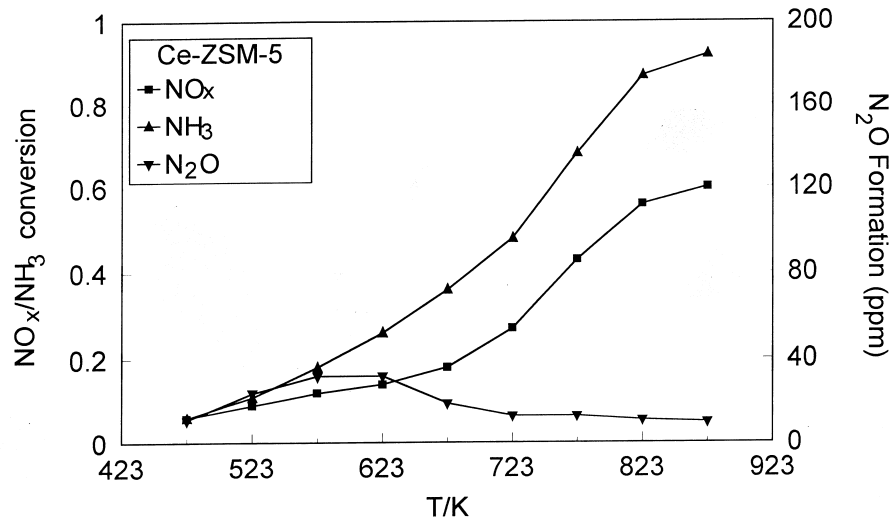


Fig. 2. Fractional conversions of NO_x , NH_3 and N_2O formation over Ce-ZSM5 with H_2O

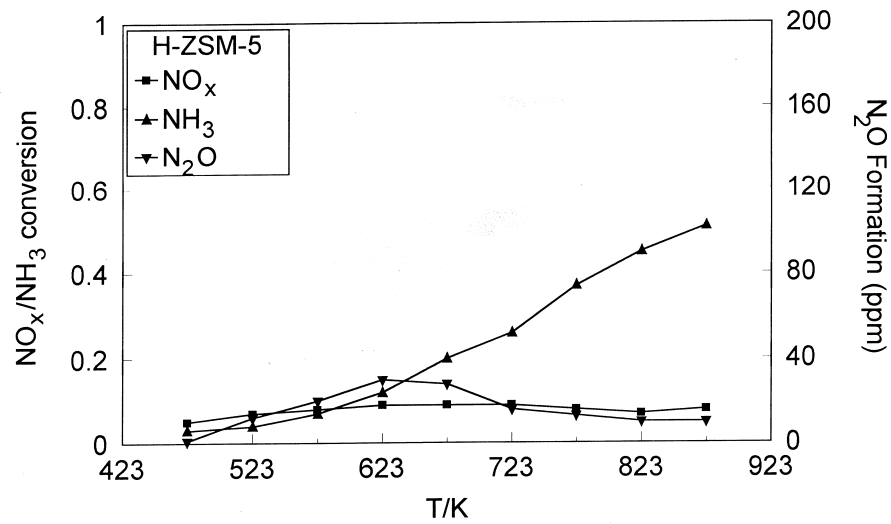


Fig. 3. Fractional conversions of NO_x , NH_3 along with N_2O formation over H-ZSM5

Figures 3 and 4 show the NO_x and NH_3 fractional conversions along with the formation of N_2O over H-ZSM5 without and with water vapor respectively. Ammonia oxidation is prominent in absence of water but NO_x reduction is negligible, indicating poor catalytic activity. In the presence of moisture NH_3 oxidation also fell down which further confirms that moisture prevents NH_3 oxidation. However, catalytic activity increases appreciably after metal incorporation.

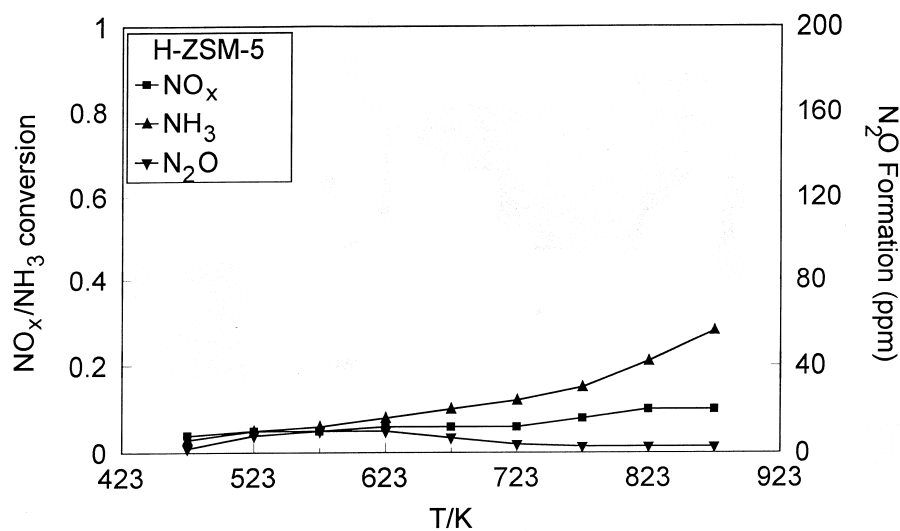


Fig. 4. Fractional conversions along with N_2O formation over H-ZSM5 with H_2O

Table 1 shows the BET surface area of the samples, rate of NO_x reduction and percentage conversions of NO_x and NH_3 along with N_2O formation over Ce-ZSM5 with and without vapor at 773 K. This is compared with H-ZSM5 which showed poor catalytic activity.

Kotmatsu *et al.* [17] 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 [18] reported that the mechanism of NH_3 conversion to N_2 involves a first step of heterolytic dissociative chemisorption of NH_3 to form $-\text{OH}$ and $-\text{NH}_2$ species. The formation of an $-\text{NH}_2$ species has been suggested [19] 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 $-\text{NH}_3$ or

-NH₂ species to directly yield N₂ and H₂O. The intermediate species (-NH₂) can react with NO to form N₂. Kapteign *et al.* [14] have stressed that the product of reaction between NO, NH₃ and O₂ can be explained by a model where the NH₃ is successively dehydrogenated by surface oxygen species. In this model, the intermediate species can react with NO to form N₂, while (-NH) or (-N) species can only react with NO to give N₂O. A model reaction scheme has been proposed elsewhere [20] based on the observed products. The catalytic activity may be ascribed to the redox ability of Ce³⁺/Ce⁴⁺ and the strong oxidizing property of Ce⁴⁺. The Ce³⁺ ions are oxidized by O₂ and Ce⁴⁺ activates NO to NO₂ promoting catalytic cycle [9].

Table 1

Summary of NO_x and NH₃ conversions with N₂O formation and rate of NO_x reduction at 773 K over the catalysts

Catalyst	Surface area (m ² /g)	NO _x Conv. (%)	Rate (mol/m ² s)	NH ₃ Conv. (%)	Formation of N ₂ O (ppm)
Ce-ZSM5	398	53	1.336x10 ¹⁵	93	28
Ce-ZSM5 (with H ₂ O)	398	43	1.084x10 ¹⁵	68	13
H-ZSM5	411	9	2.198x10 ¹⁴	36	13
H-ZSM5 (with H ₂ O)	411	8	1.953x10 ¹⁴	15	4

It may be concluded that the selectivity of NO reduction by NH₃ in presence of O₂ is temperature dependent. Ce-ZSM5 showed better catalytic activity than H-ZSM5. Moisture inhibits NO_x and NH₃ conversions reversibly and also gives a low selectivity of N₂O formation. Below 773 K NH₃ takes part in NO_x reduction, whereas above this temperature also favors oxidation with O₂. The NO reduction is strongly dependent on the O₂ partial pressure. In absence of O₂ the reaction drops drastically. The formation of N₂ and N₂O most probably takes place at different catalyst sites.

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