Selective catalytic reduction of nitrogen monoxide with methane over impregnated In/HZSM-5 in the presence of excess oxygen

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In/HZSM-5 catalyst prepared by the impregnation method was active for NO reduction with methane. Complete reduction of NO was obtained at 450°C over an In/HZSM-5 catalyst. The presence of oxygen in the feed greatly enhanced the NO reduction activity of In/HZSM-5. Co/HZSM-5 and Ga/HZSM-5 were less effective than In/HZSM-5. Cu/HZSM-5, In/Na-ZSM-5 and In_2O_3/Al_2O_3 were ineffective for NO reduction with CH_4. The NO reduction activity was proportional to the level of indium impregnated onto HZSM-5 but excess amounts of indium were detrimental to the catalytic activity. Phase analysis by XRD measurements demonstrated that there was a threshold value in the indium content, i.e., the maximum dispersion capacity of indium oxides. It is concluded that highly dispersed indium species are the active centers for the selective catalytic reduction of NO with CH_4.

Keywords: nitrogen oxide (NO); X-ray diffraction (XRD); indium (In); methane (CH_4); selective catalytic reduction (SCR); zeolite; ZSM-5

1. Introduction

Currently, the emission of NOx from transportation vehicles is controlled by the so-called three-way catalysts, and the reduction of NOx from stationary sources is commercially performed by selective catalytic reduction using NH_3 (NH_3-SCR) [1]. However, lean burn engines have higher fuel efficiency than the current engines. Three-way catalysts cannot efficiently control NOx emissions from lean burn engines because they work well only over a very narrow range of oxygen concentration and so does the NH_3-SCR because of inconvenience or poor economy.

The use of hydrocarbons to selectively reduce NOx (HC-SCR) has attracted increasing interest. Different reductants such as isobutane [2], propane [3], propene [4] and ethylene [5] and various catalysts have been selected for the title reaction. Zeolite-based catalysts have been reported to efficiently convert NOx to N_2 by HC-SCR.

Compared to the commercially practised selective catalytic reduction process which uses ammonia (NH_3-SCR), HC-SCR avoids many disadvantages associated with NH_3, such as transportation and storage of ammonia, equipment corrosion, ammonia slip and high operation cost. However, if methane can be used as the reducing agent for NOx, it will offer better system integration because natural gas (mainly methane) is readily available and widely used as a fuel for many electrical utilities and stationary combustion engines. Recently, methane has been reported to selectively reduce NOx over some catalysts, such as cobalt [6], gallium [7,8,11], and indium [9–11] ion-exchanged zeolites.

The aim of this paper is to evaluate the activity of In/HZSM-5 catalysts prepared by impregnation and to study the state of the indium species on In/HZSM-5 zeolite catalysts. We have studied the dispersion of indium species on the surface of HZSM-5 using X-ray diffraction (XRD).

2. Experimental

2.1. Catalyst preparation

All our catalysts were prepared by conventional wet impregnation of HZSM-5 or alumina powder with an aqueous solution of the corresponding metal nitrate as precursor except that In_2O_3/HZSM-5 (10 wt% In) was prepared by mechanically mixing HZSM-5 and In_2O_3 (Shanghai No.1 agent plant). Typically, an In/HZSM-5 catalyst was prepared by impregnating HZSM-5 ($SiO_2/Al_2O_3 = 25$, supplied by Nankai University) at ambient temperature by dissolving $In(NO_3)_3 \cdot 4.5H_2O$ (supplied by Beijing chemical plant) in a required amount of de-ionized H_2O. The mixture was stirred violently for 30 min and dried at 80°C for 4 h. The catalyst was calcined at atmospheric pressure from ambient temperature to 700°C and held at 700°C for 4 h, then cooled to ambient temperature. The indium loadings based on the total catalyst weight were 1, 3, 5, 10, and 20 wt%, respectively.

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2.2. Catalytic activity measurements

The catalytic activities were evaluated using a single-flow system with a micro-catalytic reactor in a steady-state plug flow mode. The reactor was a U-shaped quartz tube with 8.0 mm i.d. The catalysts were pelletized, crushed and then sieved to 30–60 mesh before use. 0.5 g of sample was used for activity evaluation. The usual flow-rate of the feed was 60 cm^3/min (GHSV = 3600 h^{-1}). The reaction mixture typically consisted of 2500 ppm NO, 2000 ppm CH_4, and 2.0% O_2 (helium as balance). The catalysts were pretreated in situ in flowing 10.0% O_2/He at 700°C for 1 h before reaction. The product analyses were performed with a gas chromatograph (GC) (102G, Shanghai analytical instrument plant) equipped with a thermal conductivity detector (TCD) and a Porapak QS column as well as a 13X zeolite column. The yield of N_2 was used to calculate the NO conversion, and the CH_4 conversion was calculated based on the change in CH_4 peak area. The selectivity was defined as the ratio of the consumption of CH_4 for NO reduction to the total consumption of CH_4 (the consumption of CH_4 for NO reduction and direct combustion).

2.3. X-ray diffraction (XRD)

XRD patterns were obtained using a Rigaku D/Max-rb X-ray diffractometer with Cu Kα radiation operated at 40 kV and 50 mA with a scan speed of 16 deg/min.

3. Results and discussion

Recently, cobalt, gallium and indium ion-exchanged ZSM-5 catalysts have been reported [6–11] to be effective for the SCR of NO with methane. In this study we found that In/HZSM-5 had a significantly higher catalytic activity than Co/HZSM-5 or Ga/HZSM-5 catalysts from 300 to 600°C, as shown in fig. 1. Above 450°C the NO conversion on Ga/HZSM-5 leveled off while that on Co/HZSM-5 dropped sharply. These results were similar to those on Ga–H-ZSM-5 and Co–H-ZSM-5 [8]. Copper ion-exchanged ZSM-5, a unique catalyst for the direct decomposition of NO [12] and the SCR of NO with ethylene [5], was a poor catalyst for the SCR of NO with CH_4 [6] because on Cu–H-ZSM-5 CH_4 preferably reacted with O_2 rather than with NO. Under our experimental conditions, the catalytic activity of copper impregnated HZSM-5 zeolite was even lower than that of HZSM-5.

Fig. 2 shows the effect of O_2 concentration on the NO reduction activity and CH_4 conversion and selectivity over an In/HZSM-5 catalyst at 450°C. Without the presence of O_2, the NO conversion was only about 49.0%, but addition of only 0.5% O_2 in the feed significantly enhanced the NO conversion to about 85.0%. A further increase of O_2 concentration up to 4% still elevated the NO conversion even to 100%. Interestingly, the CH_4 conversion was quite low (62% at 450°C) even in the presence of large amounts of oxygen (4% O_2) and the selectivity of CH_4 for NO reduction was especially high (100%), which meant that CH_4 reacted only with NO without the needless combustion. These results will be helpful in investigating the mechanism of the title reaction on In/HZSM-5.

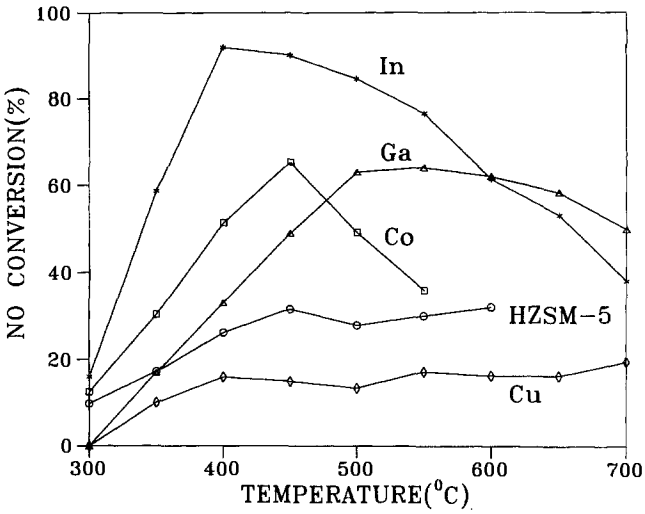

Fig. 1. Comparison of NO reduction with CH_4 over various metal impregnated HZSM-5 (SiO_2/Al_2O_3 = 25) catalysts. Metal loading 3 wt%, 2000 ppm NO, 2500 ppm CH_4, 2.0% O_2, total flow-rate 60 cm^3/min, catalyst weight 0.5 g.

Fig. 3 shows the activities of In/HZSM-5 catalysts with different SiO_2/Al_2O_3 molar ratios. It can be seen that the catalytic activity decreased with increasing SiO_2/Al_2O_3 ratio. Since, as reported [13], the acidity of silica–alumina increased with the content of aluminum, it is concluded that the proton acidity must have some effect on the activity of the catalyst.

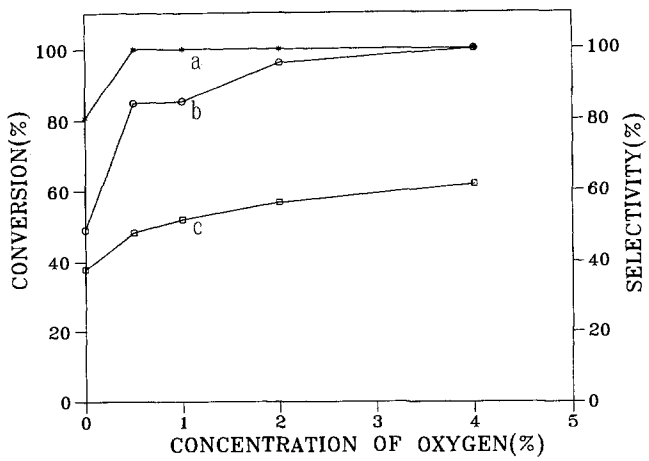

Fig. 2. Effect of O_2 on NO reduction with CH_4 over 5% In/HZSM-5 (SiO_2/Al_2O_3 = 25) catalyst. Temperature 450°C, 2500 ppm NO, 2000 ppm CH_4, flow-rate 60 cm^3/min, catalyst weight 0.5 g. (a) Selectivity of CH_4 for NO reduction, (b) NO conversion, (c) CH_4 conversion.

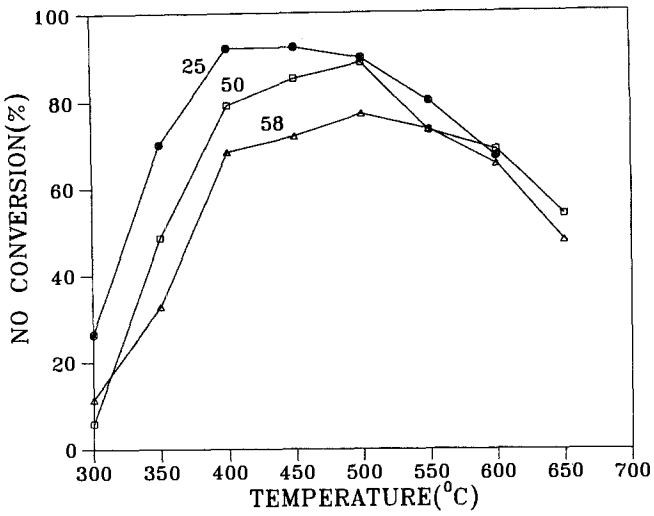

Fig. 3. Effect of SiO_2/Al_2O_3 molar ratio on NO reduction with CH_4 over 10% In/HZSM-5 catalysts. 2500 ppm NO, 2000 ppm CH_4, 2.0% O_2, total flow-rate 60 cm^3/min, catalyst weight 0.5 g.

As shown in table 1, indium impregnated Na-ZSM-5 catalysts did not show appreciable activities for the NO reduction and the NO conversions on In_2O_3/Al_2O_3 were much lower than those on In/HZSM-5. It is possible that the sodium ions prevented the fine distribution of In_2O_3 on the specific surface of HZSM-5 zeolite and that Al_2O_3 had lower specific surface area and thus less surface H^+ than HZSM-5. The mechanically mixed In_2O_3/HZSM-5 (10 wt% In) catalyst had much less activity than 10% In/HZSM-5 and 20% In/HZSM-5. It was concluded that supported In_2O_3 was less active than the highly dispersed indium species. The differences for the NO conversion shown on the different forms of indium illustrate the important role of highly dispersed indium species and surface H^+ of HZSM-5 zeolite. Because of the reported CH_4 adsorption [11,14] and activation [8,14] over HZSM-5 zeolite supported metal catalysts due to their proton acidic sites there may be some relationship between the activity of the In/HZSM-5 catalyst and its proton acidity.

Figs. 4 and 5 show the activities and the corresponding XRD patterns of In/HZSM-5 catalysts with different indium contents. Acting as a catalyst, HZSM-5 zeolite had some catalytic effect, but a little low. When 1% indium was impregnated onto HZSM-5, the activity of HZSM-5 was significantly enhanced. It is believed that the highly dispersed surface indium species are the active centers. When the indium content was between 5 and 10%, the catalyst showed the highest activity. However, the catalytic activity became lower again when the indium content exceeded 10%.

As reported by Xie and Tang [15], there is a threshold value for the maximum active compound content or, in other words, the maximum dispersion capacity of an oxide or a salt on carriers with considerable specific surface. The XRD patterns of In/HZSM-5 with different indium contents are consistent with this theory.

Normally, for crystalline transition metal compounds supported on carriers with highly specific surfaces, a content of the order of 1% is sufficient to give rise to sharp peaks in the XRD pattern [15]. However, in the case of In/HZSM-5, an indium content of up to 5% in a catalyst which did not lead to sharp peaks in the XRD pattern became the active component. Fig. 5 demonstrates that only a HZSM-5 phase was observed when the indium content was lower than 5%, while the XRD patterns of In/HZSM-5 with 10 and 20% In had sharp peaks (2θ = 30.64°, 35.48°, 51.16°, 60.8°) attributed to crystalline In_2O_3 (file No. 6-416). It is believed that the indium species were finely dispersed on the surface or located in the channels of the HZSM-5 zeolite when the indium content was lower than 5% and no isolated crystalline In_2O_3 could be detected in those samples. The threshold value of indium dispersion was located between 5 and 10%. As shown in fig. 4, the catalysts showed very high activities when the indium contents were below 5% and the most suitable indium loading was located between 5 and 10%. It is suggested that, when the content of indium oxide exceeded the maximum dispersion threshold, the surplus would exist in a crystalline state resulting in plugging of the zeolite channels and could not bring its function into full play, as shown by the decrease of the activity of the 20% In/HZSM-5 catalyst. In view of the high surface area of HZSM-5 zeolite and the considerable percentage, usually more than 5% by weight, of the heavy indium atoms in an In/HZSM-5 catalyst, one could suggest that the active centers were the highly dispersed indium oxide species on the surface

Table 1
Comparison of NO conversions on various catalysts. The reactions were run on a 0.5 g sample with a flow-rate of 60 cm^3/min (GHSV = 3600 h^{-1}) and 2500 ppm NO, 2000 ppm CH_4, and 2.0% O_2

Catalysts	Reaction temperature (°C)						
	350	400	450	500	550	600	650
HZSM-5	17.2	26.2	31.7	27.9	30.1	32.1	–
In/HZSM-5 [a]	58.6	91.9	90.6	84.5	76.5	61.4	53.1
In_2O_3/HZSM-5 [b]	33.4	49.2	57.3	63.1	64.6	47.3	30.2
In/Na-ZSM-5 [a]	–	6.7	6.1	8.2	–	12.7	13.8
In_2O_3/Al_2O_3 [a]	7.9	7.6	8.6	17.6	20.8	31.0	22.7

[a] In = 10 wt%.
[b] In = 10 wt%, prepared by directly mixing HZSM-5 and In_2O_3.

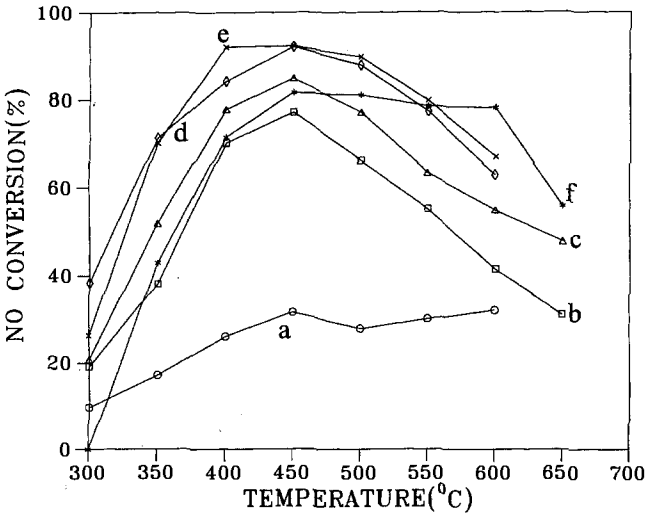

Fig. 4. Effect of indium loading and temperature on the NO reduction with CH_4 over In/HZSM-5 ($SiO_2/Al_2O_3 = 25$) catalyst. 2500 ppm NO, 2000 ppm CH_4, 2.0% O_2, total flow-rate 60 cm^3/min, catalyst weight 0.5 g. (a) HZSM-5, (b) 1% In/HZSM-5, (c) 3% In/HZSM-5, (d) 5% In/HZSM-5, (e) 10% In/HZSM-5, (f) 20% In/HZSM-5.

or in the channels of HZSM-5 zeolite. It is necessary to further investigate the interaction between surface H^+ of ZSM-5 zeolite and the surface indium species and their effects on the catalytic activity of In/HZSM-5 for the title reaction.

4. Conclusion

Impregnated In/HZSM-5 was an effective catalyst for selective reduction of NO with CH_4 in the presence of excess oxygen. A complete NO conversion to N_2 was obtained on an In/HZSM-5 catalyst at 450°C. Even when GHSV was 28800 h^{-1}, the NO conversion was still more than 60% at 450°C. The catalytic activity and selectivity did not decrease even after 12 h of continuous reaction. It is notable that the presence of O_2 was contributory to NO reduction with CH_4 and enhanced the selectivity of CH_4 for NO reduction. In addition, the presence of H^+ in zeolite was important; In/Na-ZSM-5 was almost inactive for the NO reduction and In_2O_3/Al_2O_3 was less active than In/HZSM-5. The proton acidity and the state of surface indium species in the zeolite were crucial factors for the catalytic performance. There seemed to be a synergism between the well-dispersed indium species and the H^+ in HZSM-5 zeolite with regard to NO reduction with CH_4. These suggestions are in agreement with the TPR and NH_3-TPD results [16]. The NO reduction activity was proportional to the level of indium impregnated onto HZSM-5 but excess amounts of indium were detrimental to the catalytic activity. There was a threshold value for the maximum indium content. The highly dispersed indium species were the active centers for the title reaction. When the content of indium oxide exceeded its maximum dispersion capacity, the surplus would exist in crystalline In_2O_3 state resulting in the plugging of the zeolite channels and could not bring its function into full play.

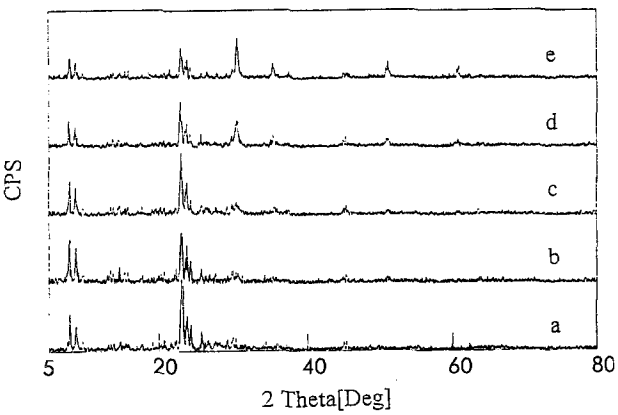

Fig. 5. XRD patterns of In/HZSM-5 ($SiO_2/Al_2O_3 = 25$) catalysts with different indium loadings: (a) HZSM-5, (b) 3% In/HZSM-5, (c) 5% In/HZSM-5, (d) 10% In/HZSM-5, (e) 20% In/HZSM-5.

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