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The chemical status of indium in indium impregnated HZSM-5 catalysts for the SCR of NO with CH₄

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Abstract

TPR and NH₃-TPD experimental results suggested that there was a strong interaction between surface indium species and the protonic acid sites of HZSM-5 zeolite during the preparation of In/HZSM-5 catalysts with conventional wetness impregnation method. A mechanism for the reduction of indium species on In/HZSM-5 catalysts has been proposed. © 1997 Elsevier Science B.V.

Keywords: Indium; Impregnation; ZSM-5; Zeolites; Selective catalytic reduction (SCR) of NO; Temperature-programmed process

1. Introduction

The selective catalytic reduction (SCR) of NO with hydrocarbon has attracted considerable attention because the traditional NH₃-SCR process has such disadvantages as ammonia slip, equipment corrosion and ammonia transportation and storage although it has been industrialized in Japan and Europe for many years [1].

Recently, indium ion-exchanged HZSM-5(In-H-ZSM-5) catalysts have been reported [2–4] to be efficient for the SCR of NO with CH₄ in the presence of excess O₂. However, the nature of the active centers and the interaction between indium species and the surface of the carrier have not been fully investigated. To gain full

understanding of these points, much study is still needed.

More recently we have found [5] that indium impregnated HZSM-5(In/HZSM-5) catalyst was very active and selective for the SCR of NO with CH₄ in the presence of excess O₂. In addition, we investigated the reduction behavior of indium species in In/HZSM-5 catalyst and the role of protonic acidity on the activity of In/HZSM-5 catalysts with TPR and NH₃-TPD methods. In this paper, the TPR and NH₃-TPD experimental results are presented. The aim of these studies was to identify the chemical nature of indium species on In/HZSM-5 catalysts prepared by wetness impregnation method and the interaction between indium oxide and surface protonic acid sites of HZSM-5 zeolite. A mechanism has been proposed for the reduction of indium species on In/HZSM-5 catalysts.

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2. Experimental

2.1. Catalyst preparation

The catalysts with various indium loadings (1–20 wt%) were prepared by incipient wetness impregnation of the supports, HZSM-5 and NaZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$, supplied by Nankai University, China), with a required amount of the solution (0.03 g In/ml) of $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ (from Beijing Chemical Plant, China). Catalysts were denoted by the ~ wt% of indium contents on the supports. The samples were dried at 80°C for 4 h and subsequently calcined in air at 700°C for 4 h. All catalysts were pelletized and crushed to 30–60 mesh before use.

2.2. Temperature-programmed reduction (TPR)

The temperature-programmed reduction (TPR) experiments were performed in a conventional apparatus with a gas chromatograph (GC) (102G, Shanghai Analytical Instrument Plant, China) equipped with a thermal conductivity detector (TCD). Typically, a sample of 20 mg (in the case of In_2O_3 , a sample of 10 mg was used) was placed in a U-shaped quartz tube with 5.0 mm I.D. and purged at ambient temperature in a 20 cm³/min 5% H_2/Ar flow. The temperature was then raised to 900°C at a rate of 11°C/min. The hydrogen consumption was monitored with the TC detector. The water formed during the TPR experiments was removed with magnesium perchlorate placed just before the TC cell.

2.3. Temperature-programmed desorption of NH_3 (NH_3 -TPD)

TPD experiments were carried out on 40 mg of the catalysts after adsorbing NH_3 with a U-shaped stainless steel reactor which was connected to a TCD. The samples were pretreated at 600°C in a dried helium (Tyt Air Products Pte, Singapore) flow for 0.5 h, then cooled to

150°C and saturated with NH_3 gas. After short purging in He gas flow the TPD experiments were performed by raising the temperature to 700°C at a rate of 25°C/min and in a helium flow-rate of 30 cm³/min.

3. Results and discussion

In the report [5] of our recent work, the In/HZSM-5 catalyst was an effective catalyst for the SCR of NO with CH_4 in the presence of excess O_2 . An addition of only 1 wt% of indium greatly enhanced the catalytic activity of HZSM-5 and the activity increased with the indium content. However, excess indium was detrimental to the activity. The highly dispersed indium species were suggested to be the active centers for the title reaction.

On the TPR curves of the indium impregnated ZSM-5 zeolites (Fig. 1), the high temperature peak (HTP) always appeared when pure In_2O_3 (Fig. 1d), In/HZSM-5 catalyst with high indium content (Fig. 1c), $\text{In}_2\text{O}_3/\text{HZSM-5}$ prepared by directly mixing In_2O_3 and HZSM-5 (Fig. 1b), or indium oxide loaded non-acidic materials like In/Na-ZSM-5 (Fig. 1e) were subjected to temperature-programmed H_2 reduc-

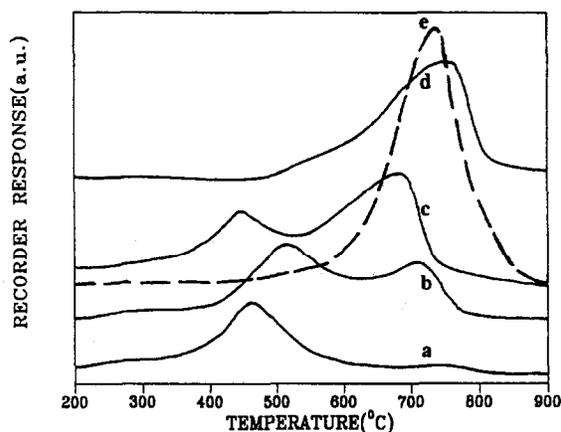


Fig. 1. TPR spectra for different indium-containing catalysts. (a) 10% In/HZSM-5 (b) 10% In_2O_3 /HZSM-5 (c) 20% In/HZSM-5 (d) In_2O_3 (10 mg) and (e) 10% In/NaZSM-5.

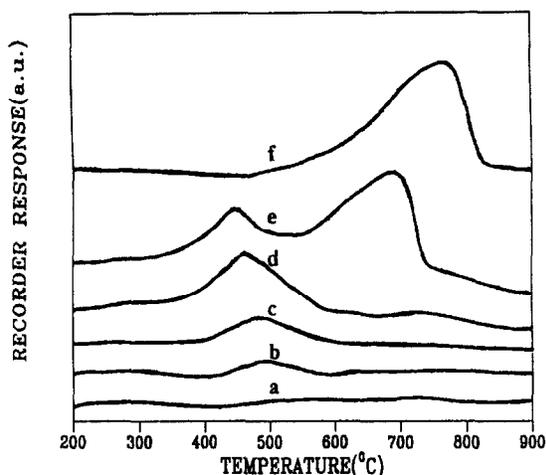


Fig. 2. TPR spectra for catalysts with different indium loadings. (a) 1% In/HZSM-5 (b) 3% In/HZSM-5 (c) 5% In/HZSM-5 (d) 10% In/HZSM-5 (e) 20% In/HZSM-5 and (f) In_2O_3 (10 mg).

tion. These peaks resulted from the reduction process of the surface crystalline In_2O_3 to indium metal.

Although the indium content in In_2O_3 /HZSM-5 catalyst was also 10 wt%, its HTP intensity was much greater than that of 10 wt% In/HZSM-5. The reason might be that the extent of indium dispersion in In_2O_3 /HZSM-5 catalyst was much lower than that in 10 wt% In/HZSM-5 catalyst and much crystalline In_2O_3 was formed.

In Fig. 2 the TPR spectra of In/HZSM-5 catalysts with different In loadings were depicted. Two peaks appeared on the TPR spectra, indicated as low (LTP) and high temperature peaks (HTP). Only the LTP of indium reduction appeared when In loadings were less than 5 wt%. The intensity of LTP increased with the indium loading until the maximum limit In loading for the dispersion capability of indium oxide on the surface of HZSM-5 zeolite was attained. By further loading with indium oxide the intensity of LTP practically did not change and a HTP appeared. Since the LTP did not appear on the TPR spectra of pure In_2O_3 and of 10 wt% In/NaZSM-5 (Fig. 1e), the appearance of LTP could be due to the reduction of the highly dispersed indium species formed during the preparation of In/HZSM-5 catalysts because of

the strong interaction between surface indium species and the protonic acid sites of HZSM-5 zeolite. It was suggested that only the one-dimensional network of indium species was formed on HZSM-5 zeolite surface at very low In loading, whereas at In loadings higher than 10 wt%, the formation of the surface crystalline In_2O_3 occurred.

As shown in Fig. 3, two NH_3 desorption peaks appeared on every TPD profile except on that of 10 wt% In/NaZSM-5 (Fig. 3f). The intensity of both the high and low temperature TPD peaks decreased as the In loading increased and the decreasing extent of the high temperature TPD peak was much greater than that of the low temperature TPD peak. The high temperature desorption peaks were suggested to result from strong protonic acid sites which were relevant to silanol (Si-OH-Al) [6]. We believed that the acid sites interacting with surface indium species were mainly protonic acid sites and that exchanges between indium ions

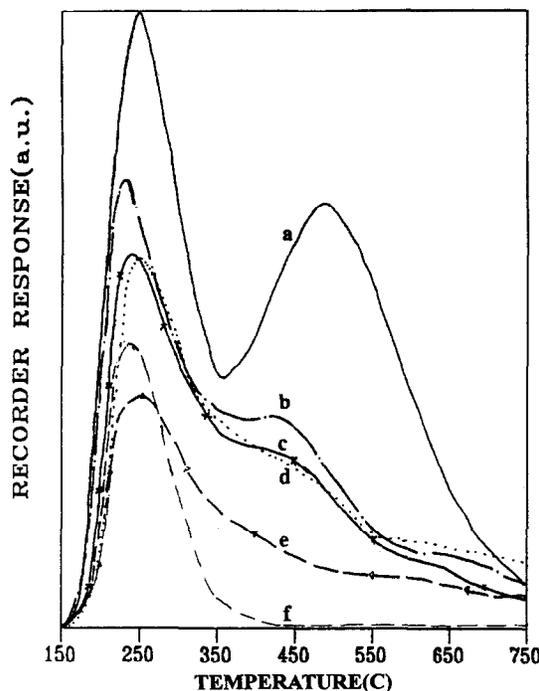
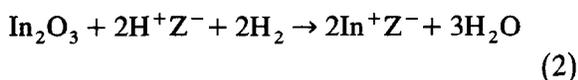
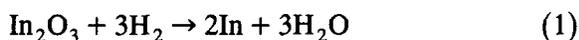


Fig. 3. Temperature programmed desorption ammonia profiles for different catalysts. (a) HZSM-5 (b) 3% In/HZSM-5 (c) 5% In/HZSM-5 (d) 10% In/HZSM-5 (e) 20% In/HZSM-5 and (f) 10% In/NaZSM-5.

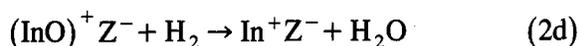
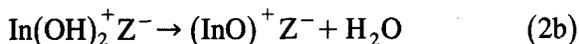
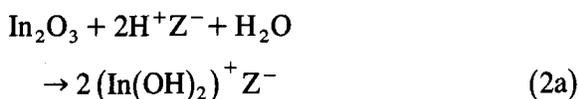
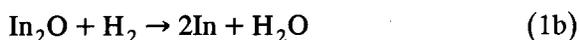
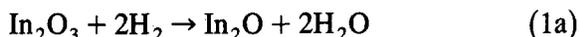
and protons of HZSM-5 occurred readily during the preparation of In/HZSM-5 catalysts.

It is generally accepted [7–9] that it is difficult to exchange trivalent ions into ZSM-5. Because the lattice is relatively hydrophobic and the anionic field is weak, precipitation of hydroxides and exchange of metal hydroxide ions such as $[M(OH)_2]^+$ would be possible.

Similarly to the recently reported [10–14] investigation on the status of gallium in gallium containing zeolites, a mechanism for the reduction of indium species in In/HZSM-5 catalysts has been proposed.



Eqs. (1) and (2) can be broken down into two and four steps, respectively, which is helpful to the understanding of these reduction processes.



Eq. (2a), or the presence of protons in HZSM-5 zeolite, were critical for the proceeding of Eq. (2). In the case of 10 wt% In/NaZSM-5, Eq. (2a) could not proceed and so there was no LTP in its TPR spectrum (Fig. 1e).

During the impregnation and calcination process, the solid-state ion exchange (Eq. (2c)) between the highly dispersed In_2O_3 and the protons of HZSM-5 zeolite could occur readily. After TPR experiments, the colors of the catalysts were from grey to black, which was due to In_2O or In^+Z^- , while the color of reduced In_2O_3 was white, the same as that of indium metal. It was believed that after reduction the

indium species in In/HZSM-5 catalysts at least partially existed as In_2O or In^+Z^- . Because of the striking feature that the In^{3+} ions were six coordinated in the bulk of In_2O_3 and only three coordinated on the surface of HZSM-5 zeolite, the $(\text{InO})^+$ had more mobility than the In^{3+} ions in the bulk of In_2O_3 and so the $(\text{InO})^+$ was easier to be reduced than the bulk In_2O_3 .

However, because of the synergism between indium species and protonic acid sites of ZSM-5 the In^+Z^- was very stable and more difficult to be reduced at 900°C. In addition, the In^+ was difficult to be sublimated although the sublimating temperature of In_2O is only 650–700°C. Thus there was no HTP in the TPR spectra of In/HZSM-5 catalysts with In loadings lower than 5 wt% (Fig. 2). When In loading exceeded the optimal indium content, a high temperature peak (HTP) appeared due to the reduction of bulk In_2O_3 itself according to Eq. (1). Infrared transmission (IR) study of chemisorbed pyridine to investigate the interaction between surface indium species and protonic acid sites of HZSM-5 and XPS measurements to further study the status of indium in In/HZSM-5 catalysts have also been initiated in our laboratory.

4. Conclusions

Flow reactor TPR experiments along with TPD of ammonia indicated that indium ions exchanged with the protons of HZSM-5 zeolite when HZSM-5 was impregnated with indium nitrate solution and then calcined. These processes resulted in the great decrease of protonic acidity, the formation of highly dispersed indium species which were suggested to be the active centers for the SCR of NO with CH_4 in the presence of O_2 and a strong interaction between the indium species and the protonic acid sites of the zeolite framework. The presence of protons in zeolite support was a prerequisite for appearance of LTP in the TPR spectra of In/HZSM-5 catalysts and for the

formation of active centers for the title reaction. The $(\text{InO})^+$ was easier to be reduced than the bulk In_2O_3 while the In^+Z^- was more difficult to be reduced than In_2O .

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