Research Article

The Cooperative Effect of In$_2$O$_3$ and In/HZSM-5 for Reduction of Nitric Oxide with Methane

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Compared with In/HZSM-5 catalyst, In/HZSM-5/In$_2$O$_3$ catalyst that contained two different kinds of In induced by the impregnation and the physical mixing method, respectively, has shown remarkable activity for methane selectively catalytic reduction (CH$_4$-SCR) of NO$_x$. The addition of In$_2$O$_3$ to In/HZSM-5 could improve the NO conversion. When a little In$_2$O$_3$ was added to the In/HZSM-5, the active sites of InO$^+$ which can adsorb NO$_2$ were increased. Moreover, at the internal surface of HZSM-5, highly dispersed In$_2$O$_3$ species could promote oxidation of NO to NO$_2$. The adsorption of NO$_2$ is the key step for the whole reaction, which benefits the activation of methane and the reduction of NOx by methane. Thus the activity of In/HZSM-5/In$_2$O$_3$ for CH$_4$-SCR of NOx was higher than that of In/HZSM-5.

1. Introduction

Extensive and intensive researches have been devoted to the selective catalytic reduction (SCR) by hydrocarbons, mainly on the automobile and autocatalyst industries [1–5]. Methane, the cheapest and most abundant hydrocarbon, as reducing agent for SCR of NOx, has attracted extra attention [6–9]. Li and Armor [6] reviewed the active catalysts for the SCR of NOx with CH$_4$ and concluded that Co, Cu, Ga, and In appeared to be more reactive than other transition metal ions. Kikuchi and Yogo [8] reported that Ga-H-ZSM-5 and In-H-ZSM-5 had high reactivity and selectivity for CH$_4$-SCR NOx under a dry atmosphere over 500°C. They also found that In/HZSM-5 (ion exchange) and In$_2$O$_3$/HZSM-5 (physically mixing) were equally active in CH$_4$-SCR of NO$_x$ [9, 10]. They indicated that InO$^+$ site was the important active site for In catalyst, which could chemisorb NO$_2$ and reduce it to N$_2$ with CH$_4$ [11]. They found that the addition of the novel metals especially Iridium could enhance NO conversion to N$_2$ over In/HZSM-5 [12]. They also thought that the addition of Ir could accelerate the oxidation of NO to NO$_2$ and NO$_2$ was reduced to N$_2$ by CH$_4$ on InO$^+$ [11, 12]. Gutiérrez et al. [13] reported that addition of Pd improved the catalytic performance of PdInHM with high In loadings for CH$_4$-SCR NOx and the promoting effect of palladium on InHmordenite catalysts was very sensitive to the In/Al ratio. Richter et al. [14] also compared the activity of the In/H-mordenite catalysts prepared by ion exchange and impregnation, respectively, for reduction of NOx by methane. They found that the preparation method did not affect the activity and the important active site was In on ion change positions, which had strong Lewis-acid character. Requejo et al. [15] indicated that there existed an important fraction of the indium present in the active sample coordinated as in the In$_2$O$_3$ case for In-containing HZSM-5. In our previous work [16], we prepared the In/HZSM-5/In$_2$O$_3$ catalyst that contained two different kinds of In induced by impregnation and physical mixing, respectively, and investigated the activity and selectivity for the removal of NO with CH$_4$ over this catalyst. Our results showed that the addition of In$_2$O$_3$ to the In/HZSM-5 catalyst could effectually improve the conversion of NO and heighten the selectivity of methane to NOx. In order to further elucidate the effect of the different In species located on the In-containing HZSM-5 catalyst, we performed more experiments and characterization tests.

2. Experimental

2.1. Catalyst Preparation. In/HZSM-5/In$_2$O$_3$ catalysts with different ratios were prepared by the impregnation and physical mixing method. For the detailed descriptions about the preparation method, please see our previous paper [16].
2.2. Catalytic Activity Test. The reactions of the selective catalytic reduction of NOx were studied in a single-pass flow reactor (i.d., 8 mm) made of quartz. All of the catalysts were palletized, crushed, and sieved to 32–60 mesh before use. 0.8 mL catalyst was loaded for each test. A typical inlet gas composition was 2,500 ppm NO, 2,000 ppm CH4, and 2.0% O2, and helium was used as the balance gas. The flow rate was 48 mL min⁻¹, which equals a space velocity of 3600 h⁻¹. All the results in this paper were obtained under similar conditions. The products were analyzed by a GC.

The NO conversion was calculated by the yield of N2, and the methane conversion was calculated by its consumption, which included the methane consumed by reacting with nitric oxide and oxygen. The extent of NOx conversion to N2 was used to evaluate the catalytic activity of a catalyst.

2.3. Catalyst Characterization. NO-TPD and NO/O2-TPD in pure He stream were measured on a flowing reaction system using a mass spectrometer (Omini-star, GSD-300) as the detector. Before adsorption the catalyst was first pretreated at 500°C in flowing He for 1 h. Then the catalyst was exposed to the gas stream of 0.2% NO or 0.2% NO–2% O2 in He at room temperature for 2 h. Then the catalyst was purged with pure He to remove the gas-phase NO and weakly adsorbed NO. Then the TPD program detected by the mass spectrometer was started from room temperature to 700°C at a ramping rate of 15°C min⁻¹.

Hydrogen temperature-programmed reduction (H2-TPR) in pure He stream was carried out using an Autochem 2910 (Micromeritics Co.). It was conducted according to the following steps. 100 mg fresh catalyst was loaded in a quartz reactor. Before the test, the catalyst was first pretreated at 300°C in flowing He for 1 h. When the temperature cooled close to room temperature, 10% H2/He with a total flow rate 50 mL min⁻¹ was used to change He. The temperature was increased linearly from room temperature to 900°C at a ramping rate of 10°C min⁻¹. The temperature-programmed desorption of ammonia (NH3-TPD) was performed on the same equipment with H2-TPR. The typical experiment was performed as follows. First 150 mg catalyst was placed in the quartz reactor and pretreated at 600°C in flowing He for 1 h so as to get clean surface. Then the catalyst was cooled down to 100°C and absorbed NH3 using an injector until saturation. Then the flow of He (40 mL min⁻¹) passed through the sample and the temperature was increased to 700°C at a ramping rate of 20°C min⁻¹. The ammonia desorption curve was recorded.

3. Results and Discussion

3.1. The Effect of In2O3 on the Activity of In/HZSM-5. Figure 1 shows the conversions of NO to N2 as a function of temperature for In/HZSM-5/In2O3 catalysts with different In2O3 ratios. When a little In2O3 (In : HZSM-5 : In2O3 = 1 : 20 : 2.5) was added to In/HZSM-5 catalyst, the conversion of NO to N2 slightly changed. As the quantity of In2O3 increased to 1 : 20 : 5, the catalytic activity clearly improved compared to In/HZSM-5. When the quantity of In2O3 further increased to 1 : 20 : 10, the conversion of NO to N2 began to decrease. So here within the scope of our investigation, the optimum ratio for In/HZSM-5/In2O3 should be 1 : 20 : 5. It was considered that when increasing the content of In2O3, the surface of In/HZSM-5 was covered completely by In2O3 powders. Hence, the active site could not exhibit its catalytic activity, which resulted in the decrease of the conversion of NOx over the whole catalyst.
of the NO conversion over In/HZSM-5/In$_2$O$_3$ had the same trends with that over In/HZSM-5. Moreover, the difference in CH$_4$ concentration between these two catalysts was remarkable; CH$_4$ conversion over In/HZSM-5/In$_2$O$_3$ was higher than that over In/HZSM-5, although both conversions increased slightly with the increase of the O$_2$ concentration. This implies that In$_2$O$_3$ addition is favorable for CH$_4$ activation.

We also studied the effect of NO content on the conversion of CH$_4$ over In/HZSM-5/In$_2$O$_3$ (1:20:5) catalyst (Figure 4). It is well known that there exist two competing reactions for the conversion of methane under our reaction conditions. They are

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \]  
(1)

\[ CH_4 + 2NO + O_2 \rightarrow CO_2 + 2H_2O + N_2 \]  
(2)

From Figure 4 we can see that the CH$_4$ conversion improved as the content of NO increased, which can correlate with that methane is consumed by the SCR reaction. Over In/HZSM-5/In$_2$O$_3$ catalyst, the enhancement of NO content can benefit the activation of methane. So for methane, it easily chooses NOx to react first when NO and O$_2$ both exist.

Figure 5 investigates the conversion of the NO to NO$_2$ and N$_2$ without CH$_4$ over In/HZSM-5/In$_2$O$_3$. From the results, we can find that NO easily reacts with O$_2$ to form NO$_2$ at low temperatures. As the temperature increased, the amount of NO$_2$ reduced gradually, and N$_2$ began to be produced. It means that the decomposition of NOx will happen when the temperature is up to 400°C. We also investigated the NO conversion to N$_2$ and CH$_4$ conversion to CO$_2$ without O$_2$ over In/HZSM-5/In$_2$O$_3$ (Figure 6). For this reaction system, CH$_4$ combustion would be avoided. The conversion of methane is mainly denoted by the reduction of NO. The detailed reaction is shown as follows:

\[ CH_4 + 4NO \rightarrow CO_2 + 2H_2O + 2N_2 \]  
(3)

However, from our results, the conversion of CH$_4$ was very low, and the conversion of NO to N$_2$ increased rapidly as the temperature increased. The production of N$_2$ clearly does not totally come from the CH$_4$-SCR NO. From Figure 5 we can see that direct NO decomposition partly leads to the production of N$_2$, which became the main resource of the N$_2$ as the temperature increased. Combined with the former results, it can be concluded that the existence of the oxygen is in favor of the activation of methane. And the reduction of NO with methane without oxygen is more difficult than that with oxygen.

3.3. NO-TPD and NO/O$_2$-TPD. Figure 7 shows the TPD profiles in flowing He after NO adsorption over In/HZSM-5/In$_2$O$_3$ catalyst. One NO desorption peak appeared at low temperatures of 100°C, which could be ascribed to the weakly adsorbed NO species. The other two overlapped NO desorption peaks appeared at much higher temperatures of 330°C and 380°C, which were attributed to the strongly adsorbed NO species. Accompanying with desorption of NO,
desorption of N$_2$O and N$_2$ was observed. Obviously, a surface decomposition reaction likely occurred over In/HZSM-5/In$_2$O$_3$. Desorption of oxygen and NO$_2$ was not detected in this case. The TPD profiles after coadsorption of NO and O$_2$ are shown in Figure 8. Similarly, the NO desorption peak at 100°C was ascribed to the weakly bounded NOx species. A continuous NO desorption started at 250°C, climbed up with temperature and gave the first maximum at 400°C, and then dropped slightly. After that, second desorption peak with a maximum at 430°C was observed. From Kikuchi’s research [11], we know that NO$_2$ is the key for the whole SCR reaction. Combined with the result of Figure 5, we can easily conclude that NO$_2$ can be easily produced when NO and O$_2$ both exist over In/HZSM-5/In$_2$O$_3$.

3.4. Characterization of the Catalysts. The H$_2$-TPR results of the In/HZSM-5 and In/HZSM-5/In$_2$O$_3$ are shown in Figure 9. For both In-containing HZSM-5 catalysts, the reduction peak near 400°C suggests the presence of In$^+$ at zeolite exchange positions [17, 18]. When In$_2$O$_3$ was added to In/HZSM-5, an obvious new peak appeared at about 600°C. Besides, there is another new peak at low temperature. To assign these peaks, we investigated the H$_2$-TPR profile for In/HZSM-5/In$_2$O$_3$ with different In$_2$O$_3$ addition quantities (Figure 10). When a little In$_2$O$_3$ is added to In/HZSM-5, the reduction peak at 600°C appears. As the quantity of the
In$_2$O$_3$ increased to 1:20:5, the low temperature reduction peak appears. Then with the increasing of the In$_2$O$_3$ content, the intensity of the 600°C reduction peak increases, while the low temperature peak disappears. It has been proposed that the 400°C reduction peak is caused by the reductive exchange of In$_2$O$_3$ with the HZSM-5. If this sample is later oxidized, (InO)$^+$ is produced and a subsequent TPR shows a signal shifted to lower temperature [19]. So the low temperature peak is ascribed to easily reducible dispersed indium phases (InO)$^+$, which is associated with the active species for the CH$_4$-SCR of NOx [17–19]. The 600°C reduction peak can be attributed to the reduction of bulk In$_2$O$_3$ phase dispersed at the internal surface of HZSM-5. When the content of In$_2$O$_3$ exceeded to 10%, the dispersed bulk In$_2$O$_3$ phase began to assemble, which made zeolite pores blocked. This could explain that the intensity of low temperature peak and 400°C peak both decrease for 10% In$_2$O$_3$ content compared with the low loading samples. We also investigated the H$_2$-TPR profile for the In-containing (20%; weight ratio) HZSM-5 catalysts prepared through the different methods (Figure 11). No matter which method, the reduction peak of In$^+$ at zeolite exchanged positions and bulk In$_2$O$_3$ phase dispersed at the internal surface of HZSM-5 appear. But the reduction peak of (InO)$^+$ species only appears on the H$_2$-TPR figure of In/HZSM-5/In$_2$O$_3$ catalyst. In/HZSM-5/In$_2$O$_3$ showed the highest catalytic activity for removal of NO by methane among the three catalysts [16]. That means (InO)$^+$ species plays an important role for the reduction of NO by methane. A combination of the impregnation and the physical mixing preparation method can produce the optimal catalytic result.

Figure 11 shows the NH$_3$-TPD results for different catalyst. For HZSM-5, there are two desorbed peaks at 200°C and 450°C, representing the two different strengths of acid center, Lewis acid site, and Brønsted acid site, respectively [8, 20–22]. When 5% of In was loaded on the HZSM-5, the desorption peak at the Brønsted acid site disappeared. This means that B-acid sites had been replaced by In$^+$ Proton for In/HZSM-5 [23]. Requejo et al. [15] pointed out that In would transform the InO$^+$ when it was added to HZSM-5, which would lead to the decrease of the Brønsted acid at HZSM-5. The Kikuchi group [8, 9] indicated that the addition of In$_2$O$_3$ not only accelerated the formation of InO$^+$ but also formed the oxidized In species dispersed at the internal surface of HZSM-5. Combined with the results of H$_2$-TPR and NH$_3$-TPD, we think that the addition of In$_2$O$_3$ to In/HZSM-5 catalyst will provide more InO$^+$ sites and also contribute to the In$_2$O$_3$ high dispersion at the internal surface of HZSM-5. NO$_2$ has been proposed by other researchers to be an important intermediate in the reaction scheme of SCR of NOx to N$_2$ [12, 24]. For In/HZSM-5 catalyst, the adsorption of NO$_2$ on the InO$^+$ sites was thought to be the key step for this reaction [10–12, 23, 25]. For NO and NO$_2$, methane preferred to react with NO$_2$ other than NO [12]. This also can
In conclusion, In/HZSM-5/In catalyst that contained two different kinds of In induced by the impregnation and the physical mixing method, respectively, had shown high catalytic performance for the CH₄-SCR of NOx compared with In/HZSM-5. The addition of In₂O₃ further enhanced the activation of methane. Consequently, the activity of the In/HZSM-5 for removal of NO with methane was increased.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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