

Research Article

The Cooperative Effect of In_2O_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_2O_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_2O_3 to In/HZSM-5 could improve the NO conversion. When a little In_2O_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_2O_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 NO_x by methane. Thus the activity of In/HZSM-5/ In_2O_3 for CH_4 -SCR of NO_x 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 NO_x , has attracted extra attention [6–9]. Li and Armor [6] reviewed the active catalysts for the SCR of NO_x 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 NO_x under a dry atmosphere over 500°C . They also found that In/HZSM-5 (ion exchange) and In_2O_3 /HZSM-5 (physically mixing) were equally active in CH_4 -SCR of NO_2 [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]. Gutierrez et al. [13] reported that addition of Pd improved the catalytic performance of PdInHM with high In loadings for CH_4 -SCR NO_x 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 NO_x 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_2O_3 case for In-containing HZSM-5. In our previous work [16], we prepared the In/HZSM-5/ In_2O_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_2O_3 to the In/HZSM-5 catalyst could effectually improve the conversion of NO and heighten the selectivity of methane to NO_x . 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_2O_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 NO_x 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 NO_x 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

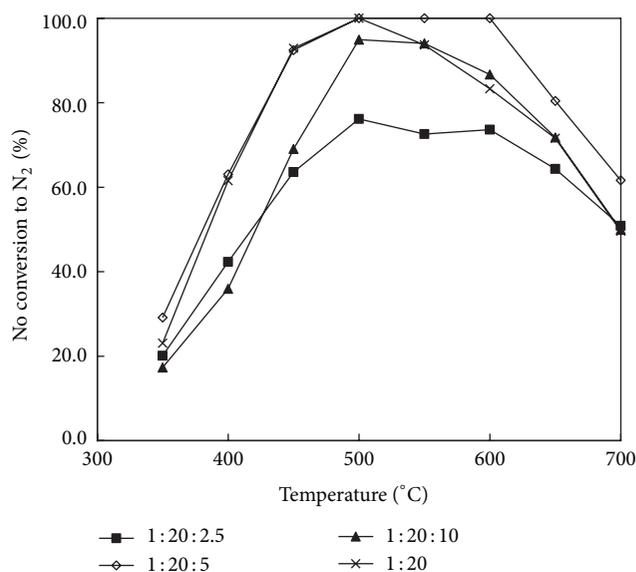


FIGURE 1: Conversion of NO to N₂ as a function of reaction temperatures over In(5%)/HZSM-5 and In/HZSM-5/In₂O₃ with different In : HZSM-5 : In₂O₃ proportions. Feed gas: 2500 ppm NO, 2000 ppm CH₄, 2.0% O₂, and balance of He; GHSV = 3600 h⁻¹.

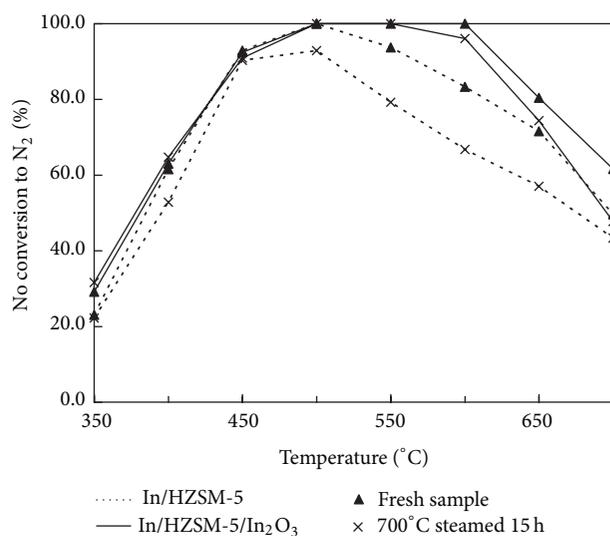


FIGURE 2: Effect of being pretreated with steam at high temperature for the activity of In/HZSM-5 and In/HZSM-5/In₂O₃. The sample was steamed with 4.0% H₂O in He at 48 mL·min for 15 h prior to SCR run. Feed gas: 0.25% NO, 0.2% CH₄, 2.0% O₂, and the balance of He; GHSV = 3600 h⁻¹.

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 NO_x over the whole catalyst.

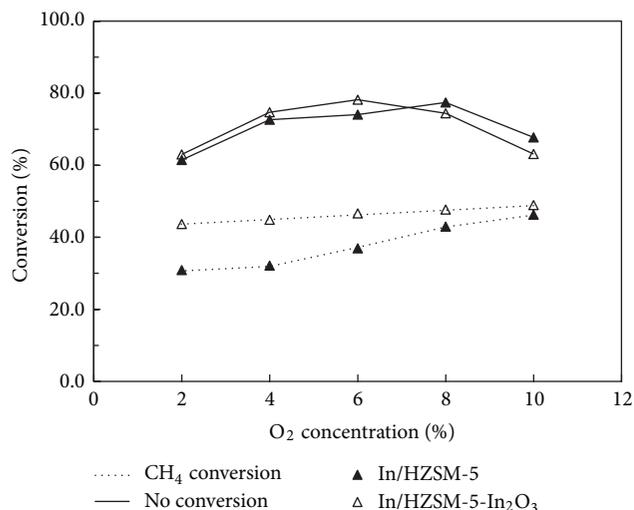


FIGURE 3: Effect of O₂ concentration on NO conversion to N₂ (solid line) and CH₄ conversion to CO₂ over In/HZSM-5 and In/HZSM-5-In₂O₃ at 400°C. Feed gas: 0.25% NO, 0.2% CH₄, and the balance of He; GHSV = 3600 h⁻¹.

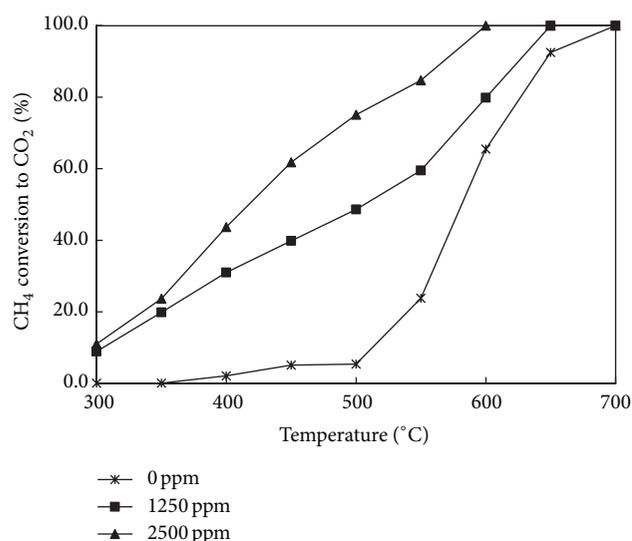


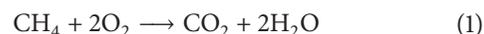
FIGURE 4: Effect of NO content on CH₄ conversion to CO₂ over In/HZSM-5-In₂O₃. Feed gas: 2.0% O₂, 0.2% CH₄, and the balance of H; GHSV = 3600 h⁻¹.

Figure 2 compares the activity of the catalysts before and after pretreatment with steam at 700°C for 15 hours. After presteaming, the NO conversion decreased significantly over In/HZSM-5 but had little effect on In/HZSM-5-In₂O₃. This indicated that the addition of In₂O₃ can protect the active sites and avoid the loss of activity of In/HZSM-5 under the condition of water.

3.2. Test of the Activity of the In/HZSM-5/In₂O₃. Figure 3 shows the changes of NO and CH₄ conversions with respect to O₂ concentration over In/HZSM-5 (1:20) and In/HZSM-5/In₂O₃ (1:20:5) catalyst at 400°C, respectively. The changes

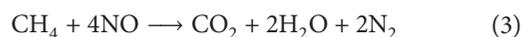
of the NO conversion over In/HZSM-5/In₂O₃ had the same trends with that over In/HZSM-5. Moreover, the difference in CH₄ concentration between these two catalysts was remarkable; CH₄ conversion over In/HZSM-5/In₂O₃ was higher than that over In/HZSM-5, although both conversions increased slightly with the increase of the O₂ concentration. This implies that In₂O₃ addition is favorable for CH₄ activation.

We also studied the effect of NO content on the conversion of CH₄ over In/HZSM-5/In₂O₃ (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



From Figure 4 we can see that the CH₄ conversion improved as the content of NO increased, which can correlate with that methane is consumed by the SCR reaction. Over In/HZSM-5/In₂O₃ 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 O₂ both exist.

Figure 5 investigates the conversion of the NO to NO₂ and N₂ without CH₄ over In/HZSM-5/In₂O₃. From the results, we can find that NO easily reacts with O₂ to form NO₂ at low temperatures. As the temperature increased, the amount of NO₂ reduced gradually, and N₂ 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 N₂ and CH₄ conversion to CO₂ without O₂ over In/HZSM-5/In₂O₃ (Figure 6). For this reaction system, CH₄ combustion would be avoided. The conversion of methane is mainly denoted by the reduction of NO. The detailed reaction is shown as follows:



However, from our results, the conversion of CH₄ was very low, and the conversion of NO to N₂ increased rapidly as the temperature increased. The production of N₂ clearly does not totally come from the CH₄-SCR NO. From Figure 5 we can see that direct NO decomposition partly leads to the production of N₂, which became the main resource of the N₂ 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/O₂-TPD. Figure 7 shows the TPD profiles in flowing He after NO adsorption over In/HZSM-5/In₂O₃ 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,

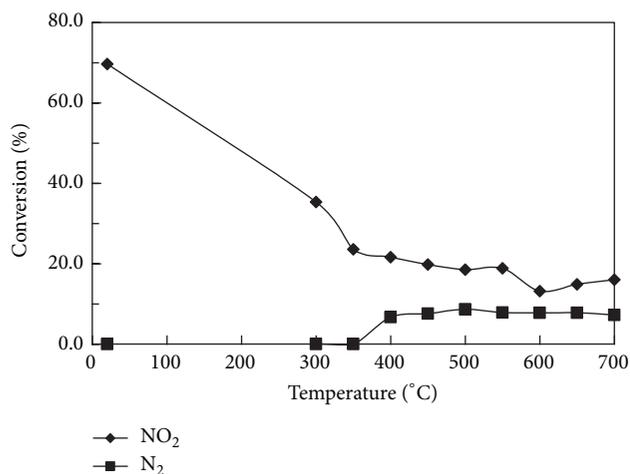


FIGURE 5: Conversion of the NO to NO₂ and N₂ as a function of reaction temperatures over In/HZSM-5/In₂O₃. Feed gas: 0.25% NO, 2.0% O₂, and the balance of He; GHSV = 3600 h⁻¹.

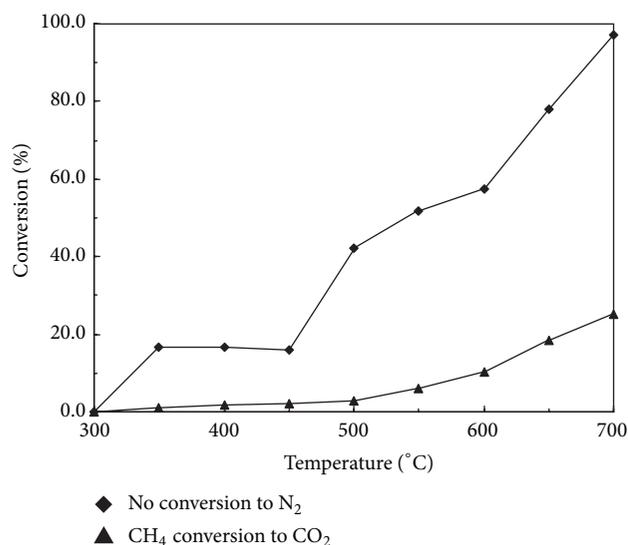


FIGURE 6: NO conversion to N₂ and CH₄ conversion to CO₂ without O₂ over In/HZSM-5/In₂O₃. Feed gas: 0.25% NO, 0.2% CH₄, and the balance of He; GHSV = 3600 h⁻¹.

desorption of N₂O and N₂ was observed. Obviously, a surface decomposition reaction likely occurred over In/HZSM-5/In₂O₃. Desorption of oxygen and NO₂ was not detected in this case. The TPD profiles after coadsorption of NO and O₂ are shown in Figure 8. Similarly, the NO desorption peak at 100°C was ascribed to the weakly bounded NO_x 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. Concomitantly, O₂ and NO₂ desorption peaks were observed, respectively. Thus, it is suggested that NO₂ is formed over the In/HZSM-5/In₂O₃ catalyst during NO/O₂ coadsorption. Part of the NO₂ is decomposed to NO and O₂, corresponding to

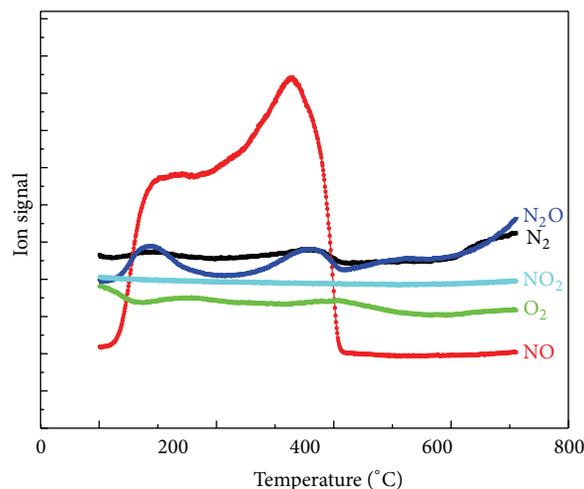


FIGURE 7: TPD profiles in flowing He after NO adsorption over the In/HZSM-5/In₂O₃ catalyst.

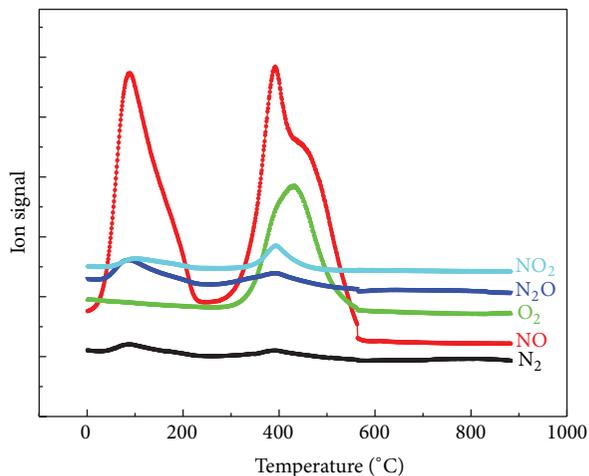


FIGURE 8: TPD profiles in flowing He after NO and O₂ coadsorption over the In/HZSM-5/In₂O₃ catalyst.

the desorption peaks of NO and O₂ at 100°C, 400°C, and 430°C. From Kikuchi's research [11], we know that NO₂ is the key for the whole SCR reaction. Combined with the result of Figure 5, we can easily conclude that NO₂ can be easily produced when NO and O₂ both exist over In/HZSM-5/In₂O₃.

3.4. Characterization of the Catalysts. The H₂-TPR results of the In/HZSM-5 and In/HZSM-5/In₂O₃ 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 In₂O₃ 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 H₂-TPR profile for In/HZSM-5/In₂O₃ with the different In₂O₃ addition quantities (Figure 10). When a little In₂O₃ is added to In/HZSM-5, the reduction peak at 600°C appears. As the quantity of the

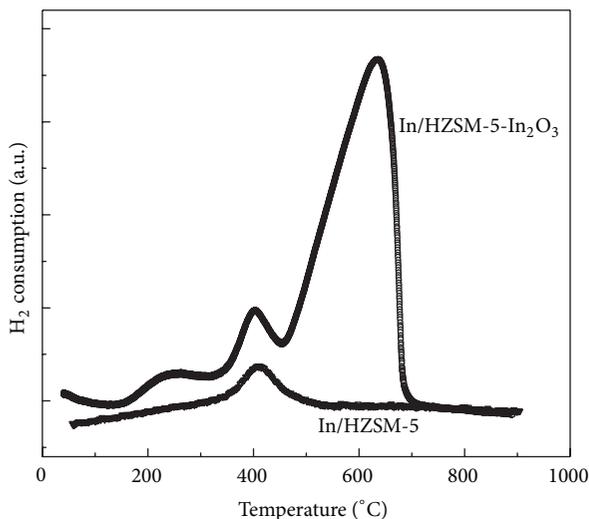


FIGURE 9: H_2 -TPR profiles over In/HZSM-5 (1:20) and In/HZSM-5/ In_2O_3 (1:20:5) catalysts with different ratios.

In_2O_3 increased to 1:20:5, the low temperature reduction peak appears. Then with the increasing of the In_2O_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_2O_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 NO_x [17–19]. The 600°C reduction peak can be attributed to the reduction of bulk In_2O_3 phase dispersed at the internal surface of HZSM-5. When the content of In_2O_3 exceeded to 10%, the dispersed bulk In_2O_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_2O_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_2O_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_2O_3 catalyst. In/HZSM-5/ In_2O_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 12 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 Brønst acid site, respectively [8, 20–22]. When 5% of In was loaded on the HZSM-5, the desorption peak at the Brønst acid site disappeared. This means that B-acid sites had been replaced by In^{3+} Proton for

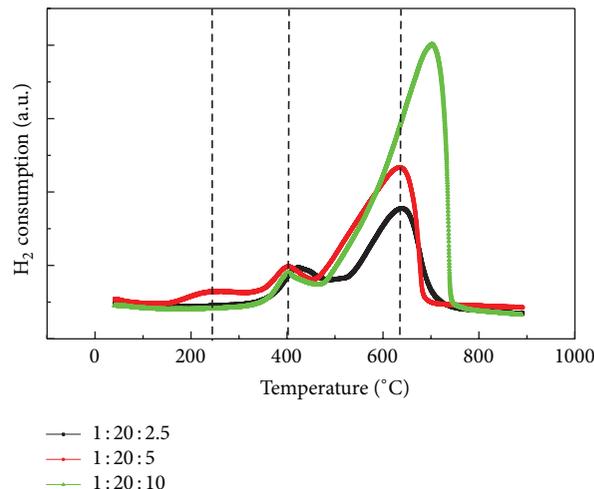


FIGURE 10: H_2 -TPR profiles over In/HZSM-5/ In_2O_3 catalysts with different In : HZSM-5 : In_2O_3 weight ratios.

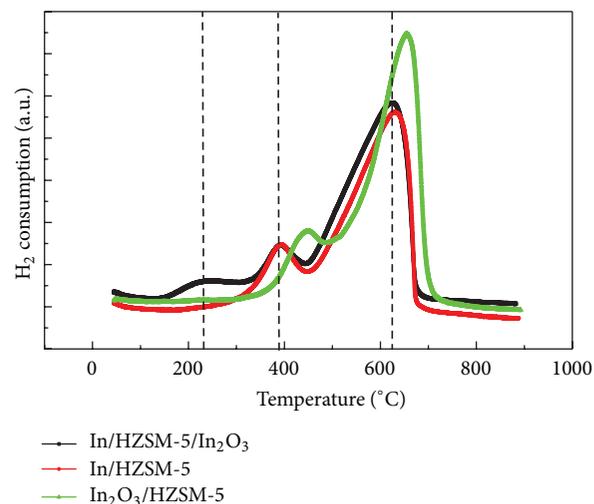


FIGURE 11: H_2 -TPR profiles over In/HZSM-5, In/HZSM-5/ In_2O_3 , and In_2O_3 /HZSM-5 catalysts. (In content equals 20% for all three catalysts.)

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 Brønst acid at HZSM-5. The Kikuchi group [8, 9] indicated that the addition of In_2O_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_2O_3 to In/HZSM-5 catalyst will provide more InO^+ sites and also contribute to the In_2O_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 NO_x 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

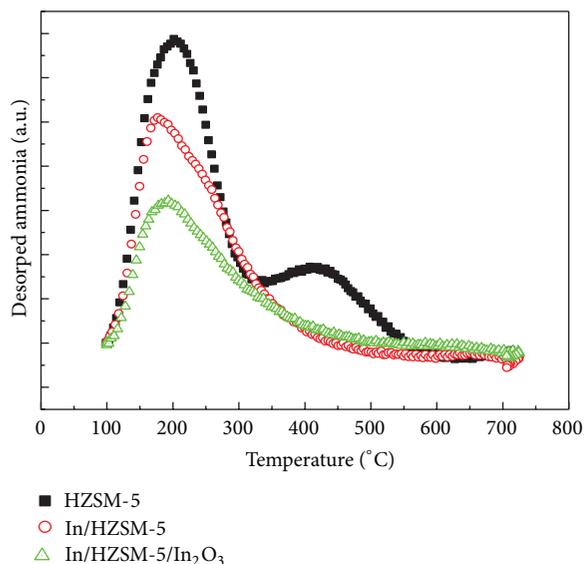


FIGURE 12: NH_3 -TPD profiles over HZSM-5, In/HZSM-5, and In/HZSM-5/ In_2O_3 .

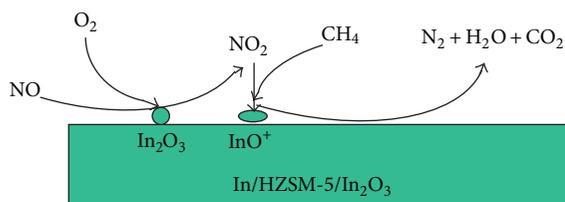


FIGURE 13: Schematic diagram for NO reduction by methane over In/HZSM-5/ In_2O_3 .

be explained by the results of Figures 5 and 9. Lónyi et al. [7, 26, 27] pointed out that the selective catalytic reduction of NO by methane required two catalytic functions: one for initiating the oxidation of NO to NO_2 (NO-COX) and another for the N_2 -forming reaction (CH_4/NO -SCR). The NO-COX reaction proceeded over the Brønsted acid sites and, if present, also over metal-oxide clusters. So we consider that the addition of a little In_2O_3 to In/HZSM-5 can accelerate the dispersion of the oxide In species at the internal surface of HZSM-5 and raise the InO^+ active sites. In_2O_3 highly dispersed at the internal surface of HZSM-5 would benefit the oxidation of NO to NO_2 . Results of Figures 5 and 9 show that NO_2 can be easily produced when NO and O_2 both exist over In/HZSM-5/ In_2O_3 . On the other hand, the increasing of InO^+ active sites contributed to the adsorption of NO_2 on the catalyst; the adsorption of NO_2 further enhanced the activation of methane. So the possible pathway of NO reduction by methane over In/HZSM-5/ In_2O_3 was suggested as Figure 13.

4. Conclusions

In conclusion, In/HZSM-5/ In_2O_3 (1 : 20 : 5) 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 CH_4 -SCR of NO_x compared with In/HZSM-5. The addition of In_2O_3 promoted the reaction of NO to NO_2 and increased the formation of InO^+ active sites of the In/HZSM-5. Thus, the adsorption of NO_2 on the catalyst was accelerated. Adsorbed NO_2 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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