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Superior Catalysts for Selective Catalytic Reduction of Nitric Oxide

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by

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During the past reporting quarter, progress was made in two separate tasks. First, TPD techniques were employed to study the reaction mechanism of the selective catalytic reduction (SCR) of NO with ammonia over iron oxide pillared clay catalyst. Second, a sulfur dioxide resistant catalyst, $\text{Fe}_2\text{O}_3/\text{TiO}_2$, was developed for the SCR of NO with ammonia by doping Fe_2O_3 on a high surface area TiO_2 support made by the sol-gel route.

Task 1. Mechanism of SCR of NO by NH_3 on Pillared Clay Catalyst: Temperature Programmed Desorption (TPD) Studies

We have used TPD techniques during the past three months to study the mechanism of the SCR reaction on the pillared clay catalyst. Before our studies, TPD results on the vanadia type catalyst in the literature showed that NH_3 chemisorbs strongly at the reaction temperatures (i.e., above 300°C), whereas NO does not. For the pillared clay catalyst, NH_3 also chemisorbs strongly at the reaction temperatures. Therefore, NO chemisorption would provide key information on the understanding of the SCR reaction on this catalyst.

Temperature programmed desorption (TPD) of NO_x on pillared clay was carried out in the same apparatus as that used for measuring the kinetic data of the SCR reaction, which was reported in details in earlier reports. Before NO was adsorbed on the catalyst surfaces, the catalysts were heated to 400°C in N_2 and were kept at this temperature for 2 hrs. As stated in the following text, some of the TPD experiments were conducted after the catalysts were subjected to the SCR reaction for a given time. In all of the TPD experiments, the heating rate was kept at $10^\circ\text{C}/\text{min}$ and the sample amount was 0.4 g. Nitrogen gas was used as the purge/carrier gas, at 350 ccSTP/min. Before measurement for the TPD signal, the gas phase NO was purged by N_2 until the base-line reached a steady state. The concentrations of NO or NO_2 were monitored by the chemiluminescent NO/ NO_x analyzer. Both clay and pillared clay were included in our TPD studies.

The TPD characteristics were significantly different for NO chemisorbed on the montmorillonite clay and that on the Fe_2O_3 -pillared clay, so they will be discussed separately.

The first observation was that the chemisorption of NO was substantially enhanced in the presence of O₂, for both montmorillonite clay and the Fe₂O₃-pillared clay. Figure 1 shows the TPD profile of NO adsorbed on the clay (in the absence of O₂). The equivalent TPD profile for NO adsorbed in the presence of 2% O₂ is showed in Figure 2. The amount of NO chemisorbed on the clay was increased by the presence of O₂ by approximately a factor of 7-8. Although the amounts were vastly different, the TPD peak positions were essentially the same. The peak desorption temperatures for NO chemisorbed in the absence of O₂ were: 75, 330 and 600°C, and that in the presence of O₂ were: 61, 340 and 600°C.

The TPD profile for NO (chemisorbed in the presence of O₂) from the delaminated Fe₂O₃-pillared clay is shown in Figure 3. A major difference between the TPD profiles from the clay and the pillared clay was apparent. The large peak at 330-340°C for the clay sample was substantially reduced and shifted toward a lower temperature (225°C), while the large peak at 75°C and the small peak at 600°C remained. For the Fe₂O₃-PILC TPD, a large amount of NO₂ was desorbed.

In order to obtain insight into the relationship between the TPD characteristics and the SCR activity, a series of NO TPD experiments were performed after the SCR reaction or NO adsorption both at 400°C. The PILC catalyst was heated to 400°C and was kept at this temperature for 30 minutes. A gas containing 1,000 ppm NO and 2% O₂ in N₂ was passed through the catalyst bed for 30 minutes. After the gas phase NO was purged by N₂ for 30 minutes, 1,000 ppm NH₃ was passed through the catalyst bed to react with the adsorbed NO for 20 minutes. Before heating to 650°C, the catalyst was purged in N₂. The TPD profiles from these experiments were different from those in the previous ones. There were two peaks in these TPD profiles: one at about 420°C, the other at near 650°C. The temperature ramp between 400°C and 650°C was repeated after the first TPD run, without further NO or NH₃ treatments. Desorption of NO_x continued at the same peak temperatures during the ensuing ramps, with gradually decreasing peak intensities. Figure 4 shows the results from the first TPD ramp and the third ramp. The same results were obtained when TPD measurements were made after the

PILC catalyst was subjected to the SCR reaction at 400°C. This result indicated that the adsorbed species corresponding to TPD peaks at 420°C and 650°C were not active species for the SCR reaction, and that the NO was very strongly bonded to the pillared clay catalyst. Bonding of the NO_x molecules within the clay lattice was a possibility.

As mentioned, NO does not chemisorb on V₂O₅ at temperatures above 300°C, and this was the basis for the Eley-Rideal type mechanism proposed for the NO SCR reaction with NH₃ (see, e.g., Went et al. 1992; Topsøe et al., 1995).. From the TPD results for the Fe₂O₃-PILC catalyst, it is seen that a significant amount of NO_x is chemisorbed at temperatures up to 600°C, i.e., well above the SCR reaction temperature of 350-400°C. It is, therefore, reasonable to conclude that SCR reaction on the Fe₂O₃-PILC follows a different type of mechanism, i.e., that of the Langmuir-Hinshelwood type, involving both chemisorbed NO_x and NH₃ (or NH_x).

Task 2. SCR by Fe₂O₃/TiO₂ Catalyst

Fe₂O₃ is known to be an active catalyst for SCR of NO with NH₃ [3,4]. In particular, Fe₂O₃ pillared/delaminated clay is a very active catalyst for SCR of NO with ammonia [4]. However, intracrystalline diffusion limitation was very strong over the Fe₂O₃ pillared/delaminated clay catalyst for SCR of NO with ammonia as reported in the last quarterly report.

In order to minimize the diffusion resistance limitation as well as using the active component of Fe₂O₃ for the SCR of NO with ammonia, we explored another possible support with large pore dimensions through the sol-gel route to eliminate the diffusion limitation. The active catalytic component, Fe₂O₃, was supported on the sol-gel support, and its catalytic activity on the SCR of NO was tested.

It is well-known that some oxides with high specific surface areas and pore volumes can be obtained by sol-gel processes [5,6]. While there are numerous reports concerning the SCR of NO over supported TiO₂, particularly V₂O₅/TiO₂ [7]. Studies of the SCR of NO over catalysts prepared by the sol-gel process are rare except by Baiker et al. [8] and Ko et al. [9].

We first prepared a porous TiO_2 support by the sol-gel process, and supported Fe_2O_3 on this TiO_2 carrier. The Fe_2O_3 supported on TiO_2 ($\text{Fe}_2\text{O}_3/\text{TiO}_2$) was used as the catalyst for SCR of NO with ammonia. The experiments and results are as follows:

A. Preparation of TiO_2 Support by the Sol-Gel Process

The TiO_2 sample was prepared by adding dropwise 0.2 M HNO_3 solution to the titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$) diluted in CH_3OH under vigorous stirring. The concentration was adjusted carefully to yield the following final molar ratio; $\text{Ti}(\text{OBu})_4:\text{H}_2\text{O}:\text{CH}_3\text{OH} = 1:5:100$. The process was facilitated with HNO_3 as the catalyst. After the sol changed into gel, the sample was washed repeatedly with distilled water and covered with distilled water for aging that lasted for 24 hrs. The sample was finally dried and calcined at 400°C . The specific surface area of the resulting sample was measured by the BET method to be $120 \text{ m}^2/\text{g}$. This value was very high as compared with the value of $25 \text{ m}^2/\text{g}$ for the commercial Degussa TiO_2 .

B. SCR by Fe_2O_3 Supported on Sol-Gel TiO_2 Catalyst

The above TiO_2 sample was impregnated in the iron nitrate aqueous solution via incipient wetness method. After the sample was dried and calcined at 400°C , the SCR activities of NO with ammonia were tested in a quartz fixed bed reactor as described earlier. The typical reaction conditions were as follows: $[\text{NO}] = 1,000 \text{ ppm}$, $[\text{NH}_3] = 1,000 \text{ ppm}$, $\text{O}_2 = 2\%$, $\text{N}_2 =$ balance, total flowrate = 500 ml/min , catalyst weight = 0.40 g . The SCR activity as a function of temperature is shown in Table 1.

Table 1. SCR Activity by $\text{Fe}_2\text{O}_3/\text{TiO}_2$ (Sol-Gel) Catalyst

	NO Conversion (%)			
T, °C	250	300	350	400
without SO_2	2	50	71	40
with SO_2	--	48	70	--

The data obtained with the addition of 500 ppm sulfur dioxide into the feed flow are also shown in Table 1. Table 1 shows that NO conversion first increased with increasing reaction temperature, reached the maximum of 71% at 350°C, and then decreased with temperature. As compared with the NO conversion - temperature profile for Fe₂O₃-pillared/delaminated clay catalyst [4], the activity for Fe₂O₃ on Sol-Gel TiO₂ dropped rapidly at below 400°C. This was possibly due to the strong NH₃ oxidation activity on the much larger Fe₂O₃ particles on the TiO₂ support. The dispersion of Fe₂O₃ on the sol-gel TiO₂ was different from that on Fe₂O₃-pillared/delaminated clay catalyst. Another result shown in Table 1 was that the Fe₂O₃/TiO₂ catalyst was strongly resistant to sulfur dioxide. For example, with the addition of 500 ppm sulfur dioxide, the NO conversion remained almost unchanged as compared to that without sulfur dioxide. This is an important result for applications to high sulfur American coals.

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Figure Captions

- Figure 1.** Temperature programmed desorption profile of NO_x from montmorillonite clay (absorbed at room temperature, 1,000 ppm NO, 0.4 g clay, N_2 flowrate = 350 ccSTP/min, heating rate = 10°C).
- Figure 2.** Temperature programmed desorption profile of NO_x from montmorillonite clay (conditions were the same as in Figure 2 except the adsorption was in the presence of 2% O_2).
- Figure 3.** Temperature programmed desorption profile for NO_x from delaminated Fe_2O_3 -pillared clay (conditions were the same as that in Figure 3, also in 2% O_2). $\text{NO}_x = \text{NO} + \text{NO}_2$.
- Figure 4.** TPD profiles for delaminated Fe_2O_3 -pillared clay with NO adsorbed at 400°C followed by purge with NH_3 and then N_2 (both at 400°C). (See text for detailed conditions.) The top profile is from first temperature ramp and the lower profile is from the third ramp, with no NO or NH_3 treatment between successive TPD runs.

Fig. 1

Fig. 2

Fig. 3

Fig. 4