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# QUARTERLY TECHNICAL PROGRESS REPORT

## 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  $\text{Fe}_2\text{O}_3$  on a high surface area  $\text{TiO}_2$  support made by the sol-gel route.

**Task 1. Mechanism of SCR of NO by  $\text{NH}_3$  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  $\text{NH}_3$  chemisorbs strongly at the reaction temperatures (i.e., above  $300^\circ\text{C}$ ), whereas NO does not. For the pillared clay catalyst,  $\text{NH}_3$  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  $\text{NO}_x$  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  $400^\circ\text{C}$  in  $\text{N}_2$  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  $\text{N}_2$  until the base-line reached a steady state. The concentrations of NO or  $\text{NO}_2$  were monitored by the chemiluminescent NO/ $\text{NO}_x$  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  $\text{Fe}_2\text{O}_3$ -pillared clay, so they will be discussed separately.

The first observation was that the chemisorption of NO was substantially enhanced in the presence of O<sub>2</sub>, for both montmorillonite clay and the Fe<sub>2</sub>O<sub>3</sub>-pillared clay. Figure 1 shows the TPD profile of NO adsorbed on the clay (in the absence of O<sub>2</sub>). The equivalent TPD profile for NO adsorbed in the presence of 2% O<sub>2</sub> is showed in Figure 2. The amount of NO chemisorbed on the clay was increased by the presence of O<sub>2</sub> 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 O<sub>2</sub> were: 75,330 and 600°C, and that in the presence of O<sub>2</sub> were: 61,340 and 600°C.

The TPD profile for NO (chemisorbed in the presence of O<sub>2</sub>) from the delaminated Fe<sub>2</sub>O<sub>3</sub>-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 Fe<sub>2</sub>O<sub>3</sub>-PILC TPD, a large amount of NO<sub>2</sub> 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% O<sub>2</sub> in N<sub>2</sub> was passed through the catalyst bed for 30 minutes. After the gas phase NO was purged by N<sub>2</sub> for 30 minutes, 1,000 ppm NH<sub>3</sub> 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 N<sub>2</sub>. 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 NH<sub>3</sub> treatments. Desorption of NO<sub>x</sub> 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<sub>x</sub> molecules within the clay lattice was a possibility.

As mentioned, NO does not chemisorb on V<sub>2</sub>O<sub>5</sub> at temperatures above 300°C, and this was the basis for the Eley-Rideal type mechanism proposed for the NO SCR reaction with NH<sub>3</sub> (see, e.g., Went et al. 1992; Topsoe et al., 1995).. From the TPD results for the Fe<sub>2</sub>O<sub>3</sub>-PILC catalyst, it is seen that a significant amount of NO<sub>x</sub> 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 Fe<sub>2</sub>O<sub>3</sub>-PILC follows a different type of mechanism, i.e., that of the Langmuir-Hinshelwood type, involving both chemisorbed NO<sub>x</sub> and NH<sub>3</sub> (or NH<sub>x</sub>).

#### **Task 2. SCR by Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> Catalyst**

Fe<sub>2</sub>O<sub>3</sub> is known to be an active catalyst for SCR of NO with NH<sub>3</sub> [3,4]. In particular, Fe<sub>2</sub>O<sub>3</sub> pillared/delaminated clay is a very active catalyst for SCR of NO with ammonia [4]. However, intracrystalline diffusion limitation was very strong over the Fe<sub>2</sub>O<sub>3</sub> 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 Fe<sub>2</sub>O<sub>3</sub> 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, Fe<sub>2</sub>O<sub>3</sub>, 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 TiO<sub>2</sub>, particularly V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> [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<sub>2</sub> support by the sol-gel process, and supported Fe<sub>2</sub>O<sub>3</sub> on this TiO<sub>2</sub> carrier. The Fe<sub>2</sub>O<sub>3</sub> supported on TiO<sub>2</sub> (Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>) was used as the catalyst for SCR of NO with ammonia. The experiments and results are as follows:

**A. Preparation of TiO<sub>2</sub> Support by the Sol-Gel Process**

The TiO<sub>2</sub> sample was prepared by adding dropwise 0.2 M HNO<sub>3</sub> solution to the titanium tetrabutoxide (Ti(OBu)<sub>4</sub>) diluted in CH<sub>3</sub>OH under vigorous stirring. The concentration was adjusted carefully to yield the following final molar ratio; Ti(OBu)<sub>4</sub>:H<sub>2</sub>O:CH<sub>3</sub>OH = 1:5:100. The process was facilitated with HNO<sub>3</sub> 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 m<sup>2</sup>/g. This value was very high as compared with the value of 25 m<sup>2</sup>/g for the commercial Degussa TiO<sub>2</sub>.

**B. SCR by Fe<sub>2</sub>O<sub>3</sub> Supported on Sol-Gel TiO<sub>2</sub> Catalyst**

The above TiO<sub>2</sub> 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: [NO] = 1,000 ppm, [NH<sub>3</sub>] = 1,000 ppm, O<sub>2</sub> = 2%, N<sub>2</sub> = 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 Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> (Sol-Gel) Catalyst**

	NO Conversion (%)			
T, °C	250	300	350	400
without SO <sub>2</sub>	2	50	71	40
with SO <sub>2</sub>	--	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 Fe<sub>2</sub>O<sub>3</sub>-pillared/delaminated clay catalyst [4], the activity for Fe<sub>2</sub>O<sub>3</sub> on Sol-Gel TiO<sub>2</sub> dropped rapidly at below 400°C. This was possibly due to the strong NH<sub>3</sub> oxidation activity on the much larger Fe<sub>2</sub>O<sub>3</sub> particles on the TiO<sub>2</sub> support. The dispersion of Fe<sub>2</sub>O<sub>3</sub> on the sol-gel TiO<sub>2</sub> was different from that on Fe<sub>2</sub>O<sub>3</sub>-pillared/delaminated clay catalyst. Another result shown in Table 1 was that the Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> 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  $\text{NO}_x$  from montmorillonite clay (adsorbed at room temperature, 1,000 ppm NO, 0.4 g clay,  $\text{N}_2$  flowrate = 350 ccSTP/min, heating rate =  $10^\circ\text{C}$ ).
- Figure 2.** Temperature programmed desorption profile of  $\text{NO}_x$  from montmorillonite clay (conditions were the same as in Figure 2 except the adsorption was in the presence of 2%  $\text{O}_2$ ).
- Figure 3.** Temperature programmed desorption profile for  $\text{NO}_x$  from delaminated  $\text{Fe}_2\text{O}_3$ -pillared clay (conditions were the same as that in Figure 3, also in 2%  $\text{O}_2$ ).  $\text{NO}_x = \text{NO} + \text{NO}_2$ .
- Figure 4.** TPD profiles for delaminated  $\text{Fe}_2\text{O}_3$ -pillared clay with NO adsorbed at  $400^\circ\text{C}$  followed by purge with  $\text{NH}_3$  and then  $\text{N}_2$  (both at  $400^\circ\text{C}$ ). (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  $\text{NH}_3$  treatment between successive TPD runs.



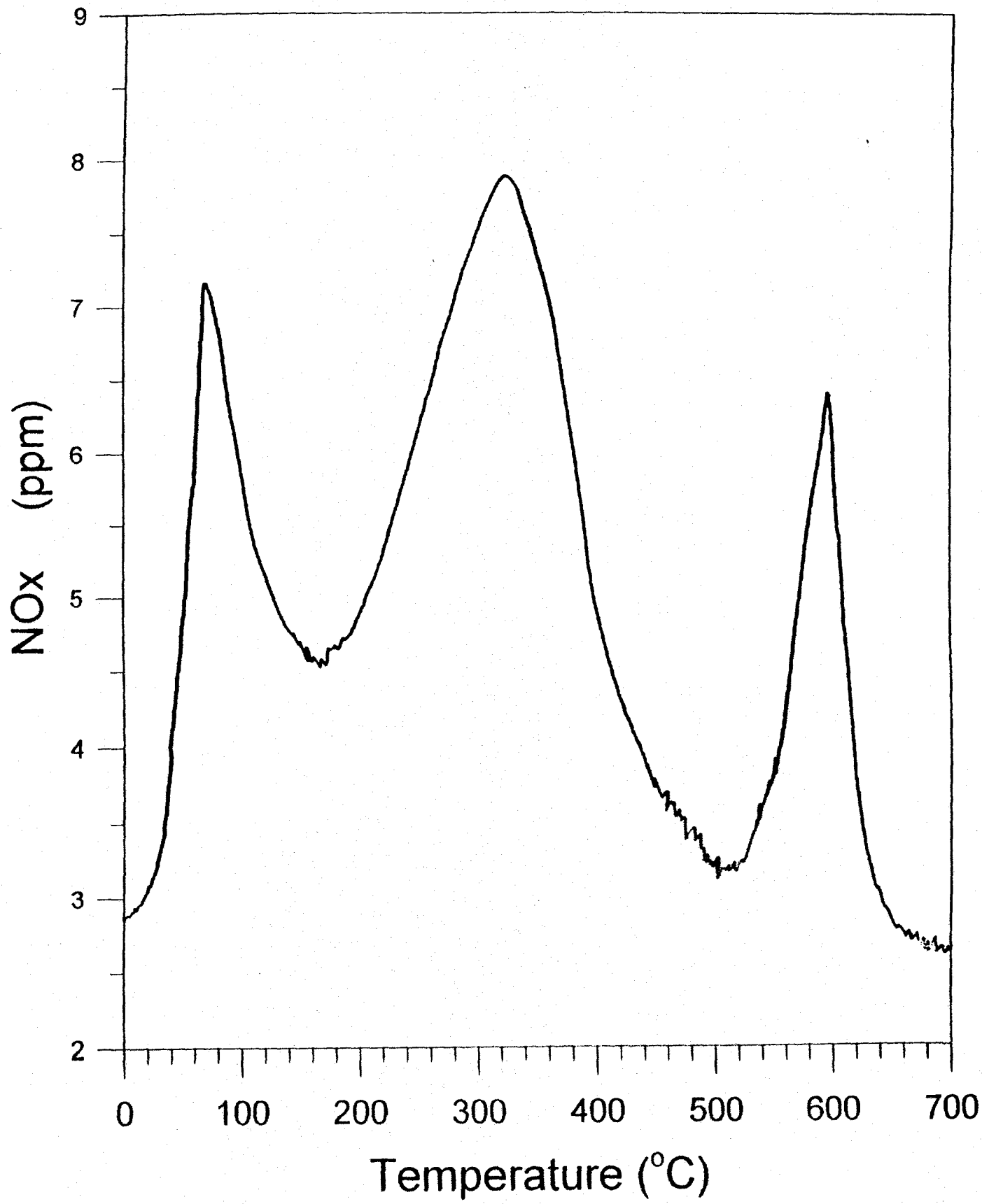


Fig. 1

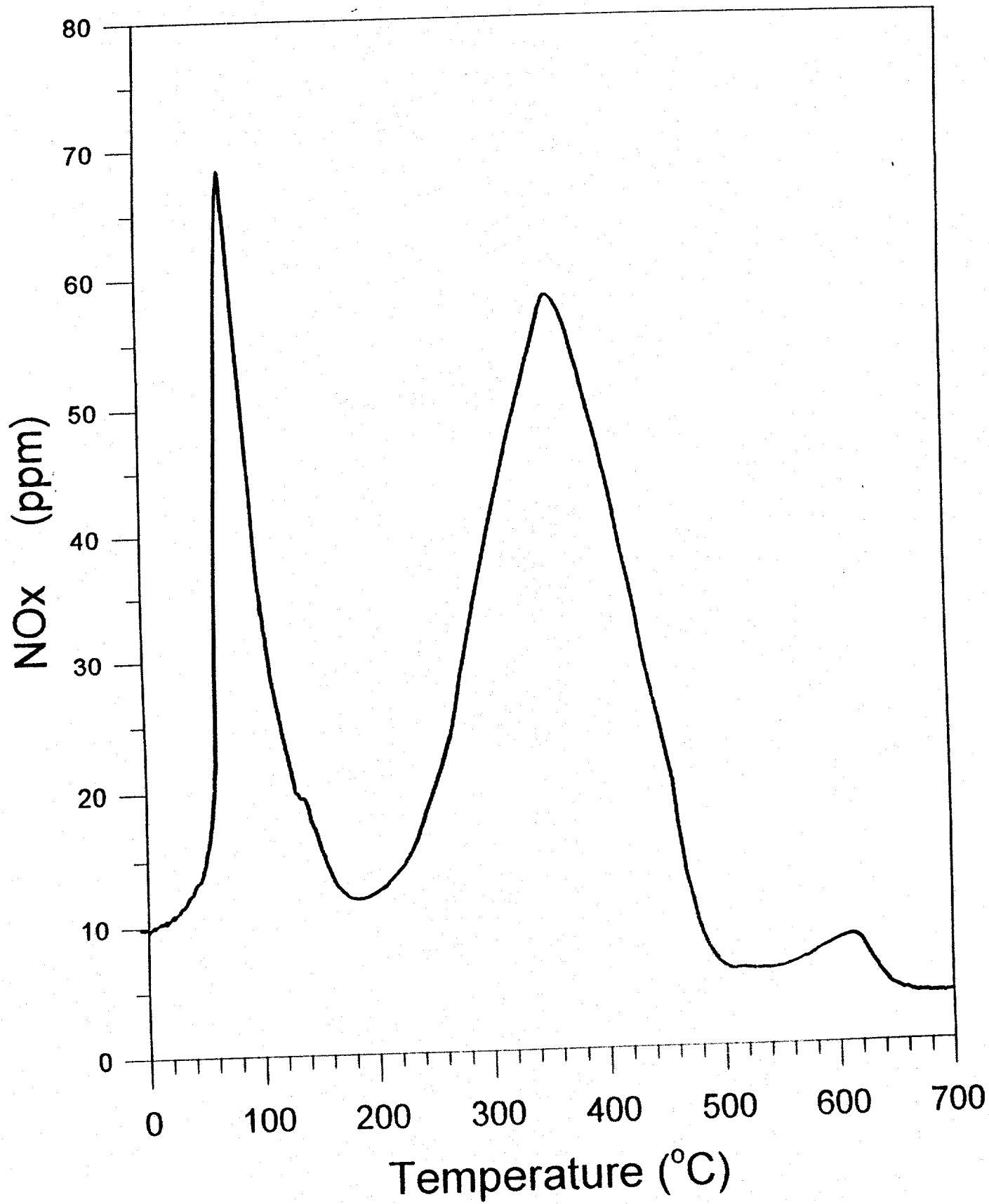


Fig. 2

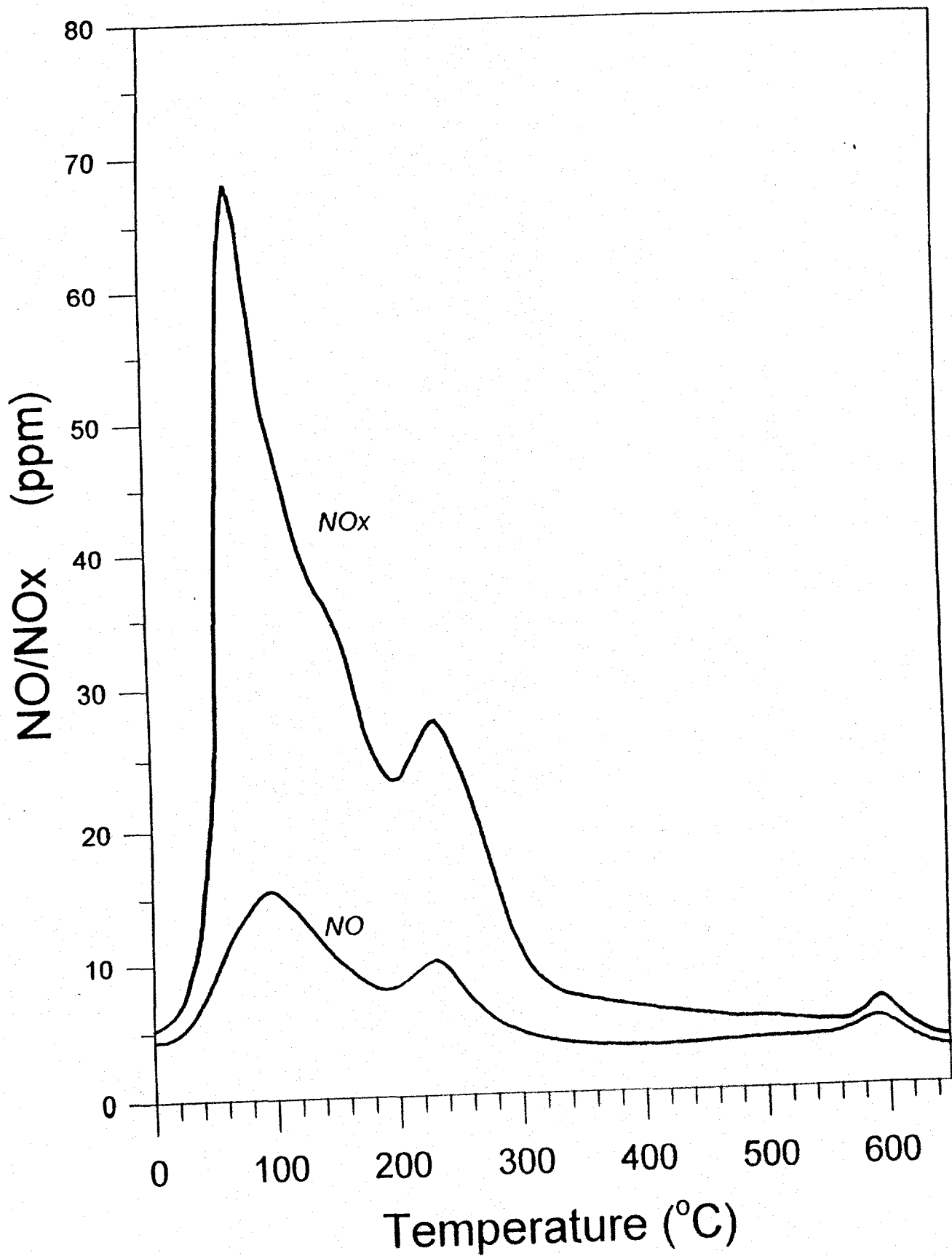


Fig. 3

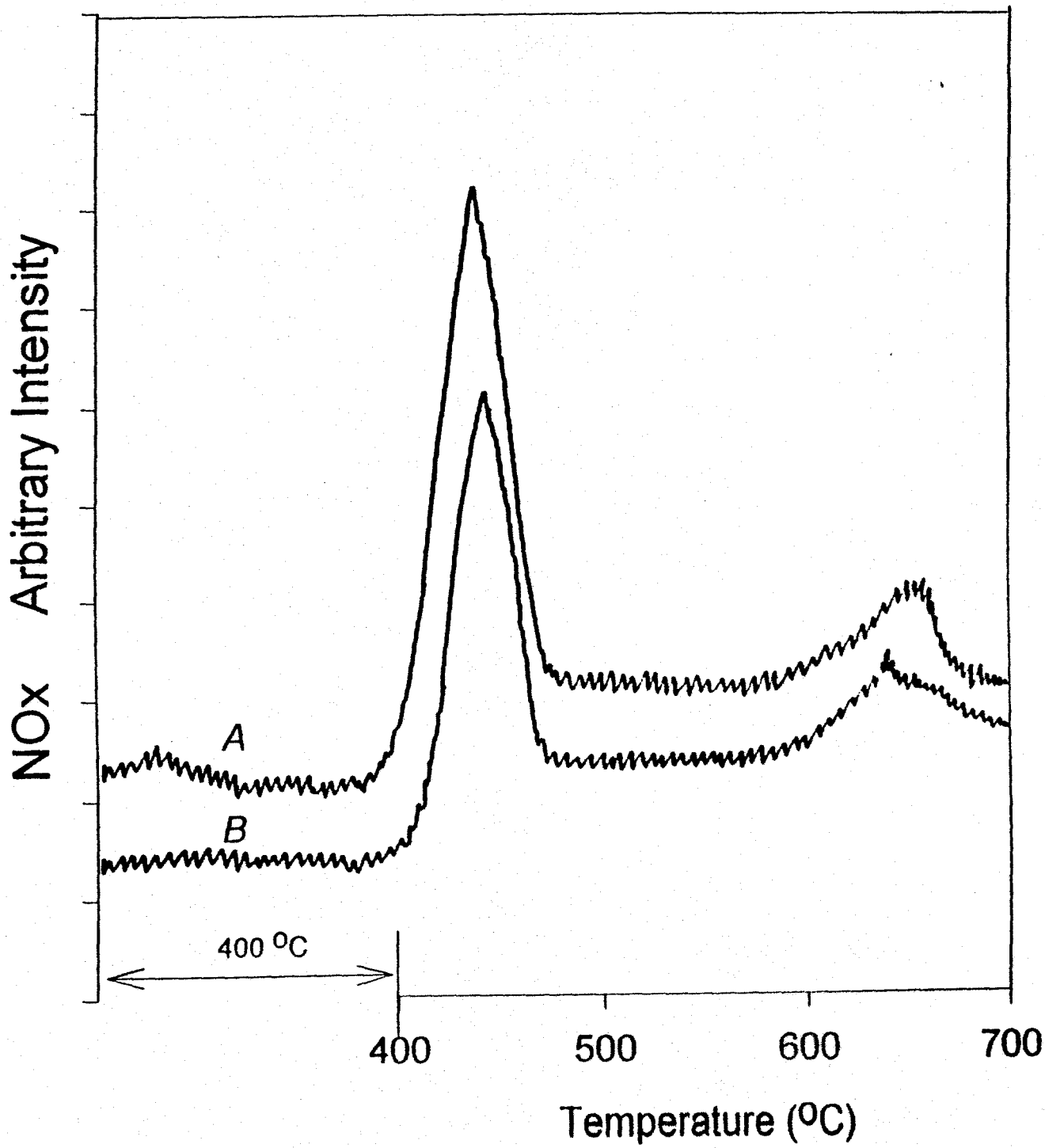


Fig. 4