

# Selective Adsorption of NO<sub>x</sub> from Hot Combustion Gases by Ce-Doped CuO/TiO<sub>2</sub>

W. B. Li and R. T. Yang\*

Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109

K. Krist

Basic Research Group, Gas Research Institute, Chicago, Illinois 60631

J. R. Regalbuto

Department of Chemical Engineering, University of Illinois, Chicago, Illinois 60607

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CuO/TiO<sub>2</sub> has been shown to be a superior sorbent for selective, reversible adsorption of NO from hot combustion gases. High NO<sub>x</sub> adsorption capacities at 200 and 300 °C were obtained with a 5% CuO/TiO<sub>2</sub> sorbent, and the NO<sub>x</sub> desorbed rapidly at 450 °C. Doping with 2% Ce on the CuO/TiO<sub>2</sub> sorbent further increased both uptake rates (50% increase in initial rate) and NO<sub>x</sub> capacity (by 30%). In a direct comparison with the most promising known sorbent, MnO/ZrO<sub>2</sub> (1:1 molar ratio), reported by Eguchi et al. (*J. Catal.* **1996**, *158*, 420), the Ce-CuO/TiO<sub>2</sub> sorbent showed both higher uptake rates (by 100% in initial rate) and higher NO<sub>x</sub> capacity (by 15%). The effects of CO<sub>2</sub>, H<sub>2</sub>O, and SO<sub>2</sub> on NO<sub>x</sub> sorption on the Ce-CuO/TiO<sub>2</sub> sorbent were studied at 200 °C. CO<sub>2</sub> slightly decreased the initial uptake rate but increased the NO<sub>x</sub> capacity. H<sub>2</sub>O coadsorbed with NO<sub>x</sub> on different sites, both reversibly (i.e. desorbed at 450 °C). SO<sub>2</sub> irreversibly adsorbed (likely to sulfate the surface of TiO<sub>2</sub>) and decreased the NO<sub>x</sub> capacity by approximately 20%. The BET surface area of the TiO<sub>2</sub> support was 50 m<sup>2</sup>/g. Further studies with TiO<sub>2</sub> of higher surface areas are in progress.

## Introduction

Selective catalytic reduction (SCR) of NO<sub>x</sub> has been the most effective means for NO<sub>x</sub> abatement. V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> has been the main commercial catalyst for SCR with NH<sub>3</sub> for stationary sources,<sup>1</sup> whereas Pt-Rh-Pd is the catalyst for SCR (mainly by CO) used in automobiles.<sup>2,3</sup> The noble metal catalyst is effective as a three-way catalyst; however, it suffers from severe loss of activity for NO reduction in the presence of excess oxygen, which is the prevalent condition for diesel or lean-burn engines. Cu-ZSM-5<sup>4,5</sup> and Co-ZSM-5<sup>6</sup> have attracted interest as hydrocarbon SCR catalysts. These catalysts, however, are deactivated rapidly by moisture and SO<sub>2</sub>.<sup>6–8</sup> The most promising hydrocarbon SCR catalyst has been Cu<sup>2+</sup>-exchanged pillared clays, with high activities and low deactivation by H<sub>2</sub>O and SO<sub>2</sub><sup>9</sup> discovered in our laboratory.

A promising alternative for hydrocarbon SCR is NO<sub>x</sub> trapping, or adsorption/absorption of NO<sub>x</sub> at high tem-

peratures. For this purpose, a very specific sorbent is needed. The sorbent must be able to selectively adsorb NO<sub>x</sub> from oxygen-rich combustion gases that contain NO<sub>x</sub>, O<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub>. The desired temperature range for the NO<sub>x</sub> trapping is 300–400 °C, although temperatures outside this range may be prevalent depending on the specific application. The sorption rates must be high, e.g. suitable for applications at space velocities >3000 1/h. The sorption must be reversible either by increasing temperature or decreasing pressure, so a desorption stream concentrated in NO<sub>x</sub> can be obtained.<sup>10</sup> The concentration stream can be recycled to the combustion zone for NO decomposition into N<sub>2</sub>. Alternatively, desorption/decomposition can be accomplished by injecting a reducing gas. Still another alternative, applicable to lean-burn engines, is to dope noble metals in the sorbent and to run the engine with pulses of "rich-burn" conditions, during which time the adsorbed NO<sub>x</sub> decomposes into N<sub>2</sub>.<sup>11a,b</sup>

Indeed, there has been a long search for such a sorbent for NO<sub>x</sub>, as reviewed recently.<sup>12,13</sup> The more promising sorbents have been supported transition metal oxides,<sup>14–18</sup> ZSM-5 or MFI zeolites exchanged by

\* Author to whom correspondence should be addressed.

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Cu<sup>2+</sup> and other cations,<sup>19</sup> Fe<sub>2</sub>O<sub>3</sub> dispersed on activated carbon fibers,<sup>20,21</sup> zeolites,<sup>22,23</sup> Y-Ba-Cu-O,<sup>24,25</sup> mixed metal oxides,<sup>11a,b,26,27</sup> and carbon.<sup>28</sup> The most promising sorbent, in terms of NO<sub>x</sub> capacity and rate of uptake, appears to be Mn-Zr (1:1 molar ratio) mixed oxides, reported recently by Eguchi et al.<sup>27</sup>

In this work, we report sorbent characteristics of the new sorbents CuO/TiO<sub>2</sub> and Ce-CuO/TiO<sub>2</sub> and show that this sorbent is superior to the Mn-Zr oxides by a direct comparison.

## Experimental Section

**Adsorption/Desorption Measurements.** A thermogravimetric analyzer (TGA, Cahn 2000 system 113), equipped with a programmed temperature control unit, was used to study the adsorption/desorption of NO on various sorbents. All experiments were performed in flowing gases. The sample was held in a quartz bucket suspended in the heated zone of the quartz tube. A thermocouple was placed as close to the bucket as possible to indicate the temperature of the sample. The gas mixtures were obtained by blending gas streams of controlled flow rates. Helium (high purity grade, 99.9%, from Metro Welding) was used as the carrier. Water vapor was introduced by saturating the carrier through a gas wash bottle. Under the experimental conditions, the uptake rates were controlled by the sorption, with film diffusion playing a minimal role.

Sorption rates were measured at 200 and 300 °C. Desorption was measured at 450 °C, by heating the sample quickly to 450 °C, while the sample was in contact with the same gas flow. All samples were pretreated at 450 °C in He, followed by cooling to 300 or 200 °C for adsorption measurements. Calibrations for all step changes (in gas composition or temperature) were made to accurately account for differences in buoyancy and friction losses.

**Preparation of TiO<sub>2</sub>.** The TiO<sub>2</sub> used was obtained from Degussa in powder form. Pellets of TiO<sub>2</sub> were made by a densification procedure: One gram of titania powder was thoroughly mixed with 1.75 mL of distilled water. The resulting paste was air-dried in an oven at 60 °C for 24 h and at 120 °C for 72 h, before crushing and sieving to collect the 80–100 mesh fraction. The collected fraction was subsequently calcined at 450 °C in air for 12 h. The BET area of the TiO<sub>2</sub> support was 50 m<sup>2</sup>/g.

**Preparation of CuO/TiO<sub>2</sub> and Ce-CuO/TiO<sub>2</sub>.** CuO/TiO<sub>2</sub> was prepared from the Degussa TiO<sub>2</sub> and copper nitrate (from Aldrich). The 5% CuO/TiO<sub>2</sub> sample was prepared by using

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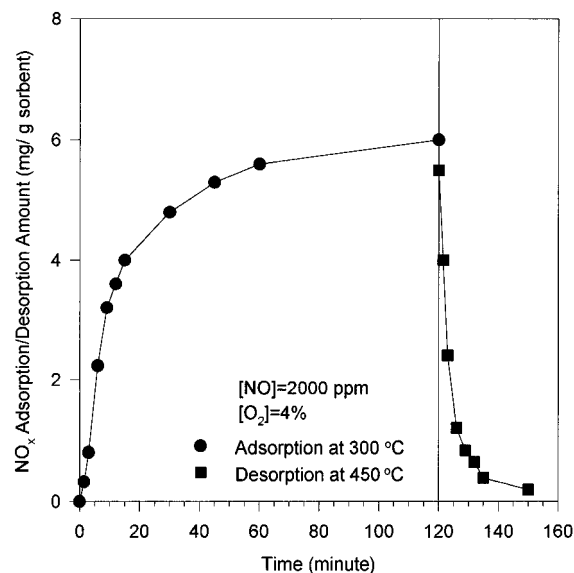
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**Figure 1.** Adsorption and desorption of NO<sub>x</sub> on 5% CuO/TiO<sub>2</sub>. Desorption was achieved by heating to 450 °C in 2 min in the same gas flow.

incipient wetness impregnation with aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O. The impregnated sorbent was first dried at 110 °C for 5 h followed by calcination at 450 °C for 10 h. The amount of CuO was kept at 5% (by wt) of TiO<sub>2</sub>.

A 2% Ce–5% CuO/TiO<sub>2</sub> was prepared by the incipient wetness procedure with aqueous cerium nitrate solution (on the 5% CuO/TiO<sub>2</sub>). The amount of Ce was kept at 2% (by wt of Ce) of the CuO/TiO<sub>2</sub> sample. The sample was then dried at 110 °C for 5 h and subsequently calcined at 450 °C for 10 h.

## Results and Discussion

CuO supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has been studied for NO<sub>x</sub> adsorption at room temperature.<sup>15</sup> We chose not to use  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the support because it is known that in the presence of SO<sub>2</sub> and O<sub>2</sub>, sulfation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> takes place at elevated temperatures resulting in pore closure due to an increase of the crystalline volume upon sulfation.<sup>29–31</sup> In our work on V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> for NH<sub>3</sub> SCR,<sup>32</sup> it was observed that NO at 1000 ppm did not chemisorb on V<sub>2</sub>O<sub>5</sub> at temperatures above 300 °C. It was found, however, that NO chemisorbs on sulfated TiO<sub>2</sub> surface (the sulfated TiO<sub>2</sub> was formed by exposure of TiO<sub>2</sub> to SO<sub>2</sub> and O<sub>2</sub> at low concentrations) at temperatures as high as 400 °C.<sup>32</sup> Therefore, TiO<sub>2</sub> was chosen as the support for CuO in this work.

**Adsorption/Desorption on CuO/TiO<sub>2</sub>.** The adsorption/desorption measurements were performed with the TGA microbalance as described above. A gas flow containing a mixture of NO/O<sub>2</sub>/He was used. Typical concentrations and flow conditions were as follows: NO = 2000 ppm, O<sub>2</sub> = 4%, balance = He, total flow rate = 50 mL/min, sample amount = 20 mg.

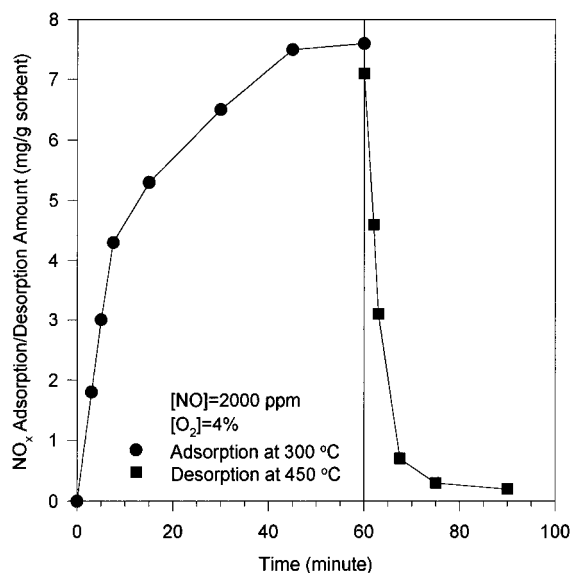
The results of NO<sub>x</sub> uptake at 300 °C are shown in Figure 1. From the uptake rates and adsorption amounts (in terms of isotherm), it is a routine matter to calculate the breakthrough curves for fixed bed adsorbers.<sup>10</sup> The amount adsorbed and the uptake rate

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**Figure 2.** Adsorption and desorption of NO<sub>x</sub> on Ce-CuO/TiO<sub>2</sub> (2% Ce, 5% CuO by wt). Desorption was achieved by heating to 450 °C in 2 min in the same gas flow.

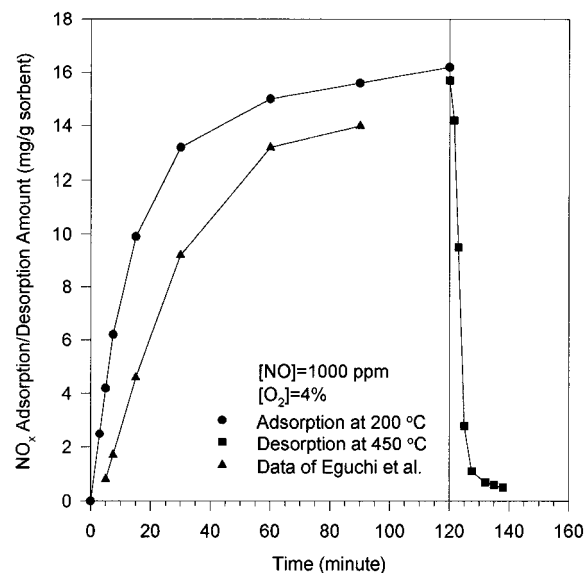
shown in Figure 1 were both very high for adsorber operation to obtain a high-purity effluent. As will be discussed shortly, adsorber breakthrough experiments were performed with the Mn-Zr oxide sorbent, with high-purity products (i.e. low NO<sub>x</sub> in the effluent) at high gas throughputs,<sup>27</sup> even though both the adsorption rate and NO<sub>x</sub> capacity on the Mn-Zr oxide sorbent were lower than those of our CuO/TiO<sub>2</sub> sorbent.

Results of desorption of NO<sub>x</sub> at 450 °C, in the same gas flow, are also shown in Figure 1. Heating from 300 to 450 °C took approximately 2 min, during which time a small amount of NO<sub>x</sub> was desorbed, as shown in Figure 1. The results showed that rapid desorption was accomplished at 450 °C. The working capacity of the sorbent, i.e., the reversible amount, depends on the time of desorption. It is clear from Figure 1 that well over 95% of the amount adsorbed was desorbed rapidly.

**Adsorption/Desorption of NO<sub>x</sub> on Ceria-Doped CuO/TiO<sub>2</sub>.** CeO<sub>2</sub> is known to be an effective promoter for the NO SCR reaction, both with NH<sub>3</sub><sup>33</sup> and with hydrocarbon.<sup>9</sup> The effect of CeO<sub>2</sub> dopant (at 2% by wt as Ce) on NO<sub>x</sub> adsorption/desorption is shown in Figure 2. The experimental conditions for the Ce-CuO/TiO<sub>2</sub> sorbent were identical to those for CuO/TiO<sub>2</sub>; thus, the results in Figures 1 and 2 can be compared directly.

From a comparison of Figures 1 and 2, it is seen that the CeO<sub>2</sub> dopant increased substantially both the NO<sub>x</sub> capacity and the uptake rate. The sorbent capacity, under the conditions in the experiment, was increased from approximately 6 to 7.7 mg/g, or approximately a 30% increase. The initial sorption rate was increased from 3.4 to 5.0 mg/g, both at  $t = 10$  min, or a 50% increase. The chemisorption rate was clearly the controlling step in the uptake, and the CeO<sub>2</sub> dopant substantially increased the chemisorption rate.

The significant increase in both chemisorption rate and sorption amount was attributed to the unique oxygen storage property as well as the redox property of Ce. The chemisorbed NO<sub>x</sub> species were predominantly NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> species on Cu<sup>2+</sup>-exchanged



**Figure 3.** Adsorption and desorption (in the same gas flow) on Ce-CuO/TiO<sub>2</sub> (2% Ce, 5% CuO by wt) compared with the MnO/ZrO<sub>2</sub> (1:1 molar ratio) sorbent of Eguchi et al.<sup>27</sup> under the same conditions except O<sub>2</sub> = 10% in their work (which yielded larger adsorption than 4% O<sub>2</sub>).

pillared clay<sup>34</sup> and on the Cu<sup>2+</sup>-exchanged zeolites (as reviewed in ref 33). The predominant species was NO<sub>3</sub><sup>-</sup> on metal oxides, particularly on oxides of base metals.<sup>27</sup> Oxidation of NO is involved in the chemisorption of NO in the presence of O<sub>2</sub>; in fact, O<sub>2</sub> enhances the sorption of NO<sub>x</sub>.<sup>11a,b,27</sup> However, it is also known that CeO<sub>2</sub> alone does not chemisorb NO at elevated temperatures.<sup>35</sup> Therefore, CeO<sub>2</sub> was only a promoter and its redox property facilitated the chemisorption of NO<sub>x</sub>.

#### Comparison of CeO<sub>2</sub>-CuO/TiO<sub>2</sub> with MnO/ZrO<sub>2</sub>.

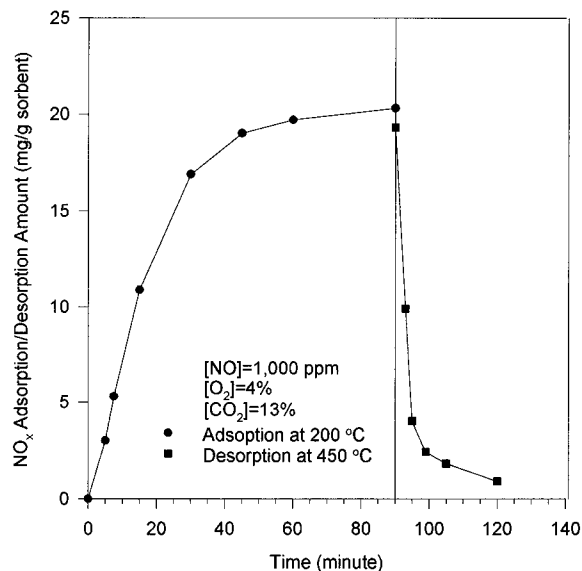
The most promising NO<sub>x</sub> sorbent reported in the literature was that of Eguchi et al.<sup>27</sup> It was reported that MnO/ZrO<sub>2</sub> (1:1 molar ratio) had a high sorption rate and capacity for NO<sub>x</sub> at 200 °C, 900–1000 ppm of NO in 10% O<sub>2</sub>. To make a direct comparison with their sorbent, the CeO<sub>2</sub>-CuO/TiO<sub>2</sub> was subjected to the same sorption conditions, i.e., 1000 ppm of NO and 200 °C. A lower O<sub>2</sub> concentration of 4% was used, however. The lower O<sub>2</sub> concentration would only lower the NO<sub>x</sub> sorption rate and capacity;<sup>27</sup> hence, the comparison was a conservative one for our sorbent. The amount of sorbent and the flow rate in the TGA experiment were not given by Eguchi et al.<sup>27</sup> However, it was expected that the chemisorption rate was the controlling step in uptake and the uptake was not limited by film diffusion or the NO supply rate.

The results with the two different sorbents are compared in Figure 3. The comparison shows that both sorption rate and capacity were significantly higher for the Ce-CuO/TiO<sub>2</sub> sorbent. The initial uptake rate was more than doubled with our sorbent, while the final capacity was higher by approximately 15%. The final NO<sub>x</sub> capacity for the Ce-CuO/TiO<sub>2</sub> sorbent corresponded to approximately 12 Å<sup>2</sup>/NO<sub>2</sub> or NO<sub>3</sub>. Obviously, the NO<sub>x</sub> capacity is limited by the surface area of the sorbent. Further work on high-surface-area TiO<sub>2</sub> prepared by the

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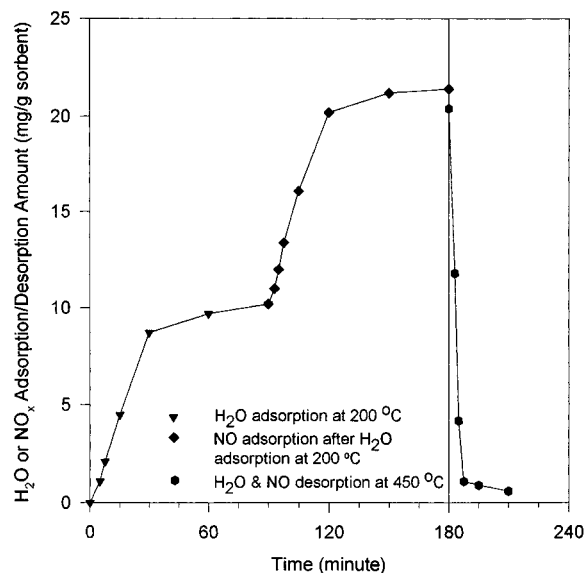


**Figure 4.** Adsorption and desorption (in the same gas flow) on Ce-CuO/TiO<sub>2</sub>, showing the effects of CO<sub>2</sub>.

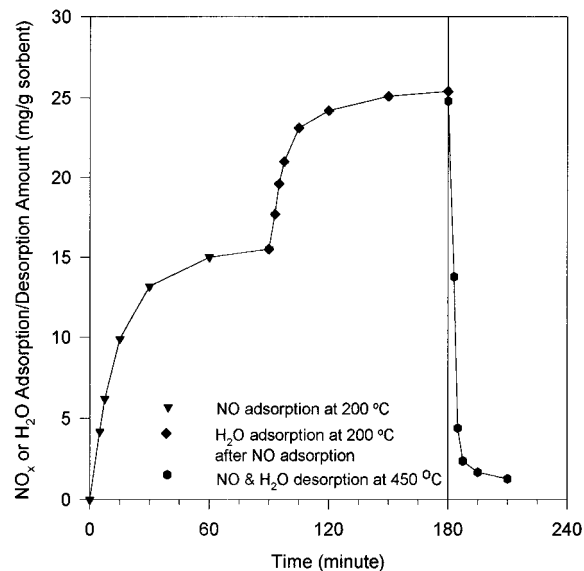
sol-gel technique and characterization of the surface NO<sub>x</sub> species is in progress.

**Effect of CO<sub>2</sub> in NO<sub>x</sub> Adsorption.** The effect of CO<sub>2</sub> was a major concern for metal oxide sorbents due to the formation of carbonates.<sup>11a,b,13,24-27</sup> The effects of CO<sub>2</sub> were investigated for the Ce-CuO/TiO<sub>2</sub> sorbent at 200 °C, since any effects of CO<sub>2</sub> would become less at higher temperatures. The sorbent was first exposed to a gas flow containing 13% CO<sub>2</sub> and 4% O<sub>2</sub> (in He). No uptake or weight change was observed. However, when 13% CO<sub>2</sub> was added to the gas flow containing NO and O<sub>2</sub>, changes in both NO<sub>x</sub> sorption rate and capacity were observed. The uptake and desorption results are shown in Figure 4. The NO<sub>x</sub> sorption was changed by CO<sub>2</sub> in two ways. First, a small, but clear, decrease in the initial sorption rate was observed. Second, the NO<sub>x</sub> capacity increased by over 25% due to the presence of CO<sub>2</sub>. These changes are shown by comparing Figures 3 and 4. Since the uptake rates were measured only by weight gain, the surface species were not known. Further studies to identify the surface species and possibly the role played by CO<sub>2</sub> are in progress. No changes were observed in the desorption due to CO<sub>2</sub>.

**Effect of H<sub>2</sub>O on NO<sub>x</sub> Adsorption.** The effect of H<sub>2</sub>O was also studied at 200 °C. The adsorption of H<sub>2</sub>O was first measured with 2.7% H<sub>2</sub>O in He, shown in Figure 5. The water adsorption was completely reversible. The effects of H<sub>2</sub>O on NO<sub>x</sub> adsorption were studied by presaturation of H<sub>2</sub>O. As shown in Figure 5, adsorption of H<sub>2</sub>O was allowed for 90 min at 200 °C, followed by the introduction of a flow containing 2.7% H<sub>2</sub>O, 1000 ppm of NO, and 4% O<sub>2</sub>. The presorbed H<sub>2</sub>O did cause a reduction in the NO<sub>x</sub> capacity; however, the rapid uptake of NO<sub>x</sub> on the H<sub>2</sub>O-presaturated sorbent was similar to that without H<sub>2</sub>O presorption, as shown in Figure 3. The final amount of NO<sub>x</sub> adsorbed on the H<sub>2</sub>O-presorbed sample was approximately 72% of that without H<sub>2</sub>O presorption. This result indicates that the H<sub>2</sub>O adsorption and NO<sub>x</sub> adsorption take place on two different sites. As a result, the presence of H<sub>2</sub>O caused only a small reduction of NO<sub>x</sub> adsorption. This is similar to the Cu-ZSM-5.<sup>6</sup>



**Figure 5.** Adsorption of H<sub>2</sub>O (2.7% H<sub>2</sub>O in He) followed by adsorption of NO<sub>x</sub> (1000 ppm of NO, 4% O<sub>2</sub>, 2.7% H<sub>2</sub>O, in He) and desorption (in the same gas flow) on Ce-CuO/TiO<sub>2</sub>.

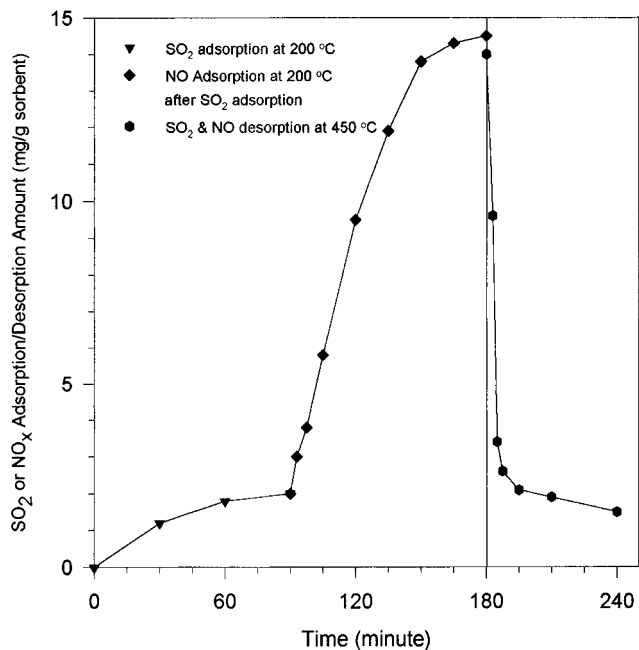


**Figure 6.** Adsorption of NO<sub>x</sub> (1000 ppm of NO, 4% O<sub>2</sub> in He) followed by adsorption of H<sub>2</sub>O (2.7% H<sub>2</sub>O, 1000 ppm of NO, and 4% O<sub>2</sub> in He) and desorption (in the same gas flow) on Ce-CuO/TiO<sub>2</sub>.

When the sample was heated rapidly to 450 °C in the same gas flow that contained H<sub>2</sub>O, NO, and O<sub>2</sub>, both H<sub>2</sub>O and NO<sub>x</sub> desorbed rapidly. Therefore, the Ce-CuO/TiO<sub>2</sub> sorbent coadsorbed H<sub>2</sub>O and NO<sub>x</sub> both reversibly.

The effect of H<sub>2</sub>O was also investigated by reversing the sequence of adsorption. In this experiment, the Ce-CuO/TiO<sub>2</sub> sorbent was first exposed to 1000 ppm of NO and 4% O<sub>2</sub>, followed by the addition of 2.7% H<sub>2</sub>O in the mixture. The results are shown in Figure 6. These results showed, again, that NO<sub>x</sub> and H<sub>2</sub>O adsorbed nearly independently; that is, they adsorbed on different sites. Also, the coadsorbed NO<sub>x</sub> and H<sub>2</sub>O were adsorbed reversibly.

**Effects of SO<sub>2</sub> on NO<sub>x</sub> Adsorption.** SO<sub>2</sub> is known to decrease the NO SCR activities;<sup>1</sup> hence, it is important to investigate its possible effects on NO<sub>x</sub> adsorption. Such effects were studied for the Ce-CuO/TiO<sub>2</sub> sorbent at 200 °C. Typical conditions for this series of experi-



**Figure 7.** Adsorption of SO<sub>2</sub> (1500 ppm of SO<sub>2</sub> and 4% O<sub>2</sub> in He) followed by adsorption of NO<sub>x</sub> (1000 ppm of NO, 1500 ppm of SO<sub>2</sub>, 4% O<sub>2</sub> in He) and desorption (in the same gas flow) on Ce-CuO/TiO<sub>2</sub>. Adsorption of SO<sub>2</sub> is irreversible at 450 °C, whereas that of NO<sub>x</sub> is reversible.

ments were as follows: 1000 ppm of NO, 1500 ppm of SO<sub>2</sub>, and 4% O<sub>2</sub>, with He as the carrier gas. The sorbent was first exposed to SO<sub>2</sub> + O<sub>2</sub>. An uptake of approximately 2 mg/g was observed in 90 min, as shown in Figure 7. Following the SO<sub>2</sub>/O<sub>2</sub> uptake, NO was introduced to the gas flow, i.e., 1000 ppm of NO, 1500 ppm of SO<sub>2</sub> and 4% O<sub>2</sub>. A rapid uptake of NO<sub>x</sub> was observed. However, the NO adsorption was reduced by the adsorbed SO<sub>2</sub>. The NO<sub>x</sub> capacity was reduced by approximately 20%, i.e., to an uptake of 12.1 mg of NO<sub>x</sub>/g of sorbent in 90 min at 200 °C (Figure 6).

Desorption was accomplished by rapid heating (in 2 min) to 450 °C in NO/SO<sub>2</sub>/O<sub>2</sub>/He. As also shown in Figure 7, rapid desorption was possible at 450 °C. However, compared to the case when SO<sub>2</sub> was absent (Figure 3), a significant amount of adsorbate was not desorbed at 450 °C. This amount was 2 mg/g, equal to that of the presorbed SO<sub>2</sub>/O<sub>2</sub>.

Cyclic NO<sub>x</sub> adsorption–desorption in the presence of SO<sub>2</sub> was also performed. In this experiment, the sorbent was cooled to 200 °C in SO<sub>2</sub>/O<sub>2</sub>/He, after desorption at 450 °C. NO was reintroduced to the gas mixture at 200 °C. The same uptake curve as shown in Figure 7 was obtained. The desorption curve at 450 °C was also reproduced. This result strongly suggested that the resident amount of adsorbate (after desorption at 450 °C) was SO<sub>2</sub> (or SO<sub>x</sub>). The adsorbed SO<sub>2</sub> was clearly irreversibly adsorbed at 450 °C. It is known that the TiO<sub>2</sub> surface is sulfated by SO<sub>2</sub> + O<sub>2</sub> in the temperature range of this study and that the surface sulfate cannot be desorbed at 450 °C.<sup>31</sup> It seems likely that the irreversible uptake in Figure 7 was due to surface sulfate on TiO<sub>2</sub>, whereas the NO<sub>x</sub> was bonded to Cu<sup>2+</sup> sites.

### Conclusion

CuO/TiO<sub>2</sub> (5% by wt) and its Ce-doped form have been developed as selective adsorbents for NO<sub>x</sub> at 200 and 300 °C. The sorbent capacity for the Ce-doped form was approximately 15.6 mg of NO<sub>x</sub>/g of the solid sorbent at 300 °C, 2000 ppm of NO, and 4% O<sub>2</sub>. Effects of CO<sub>2</sub> and SO<sub>2</sub> on NO<sub>x</sub> sorption on the Ce-CuO/TiO<sub>2</sub> sorbent were studied at 200 °C. CO<sub>2</sub> slightly decreased the initial NO uptake rates, but increased the NO<sub>x</sub> capacity. H<sub>2</sub>O coadsorbed with NO<sub>x</sub> on different sites. SO<sub>2</sub> was irreversibly adsorbed and decreased the NO<sub>x</sub> capacity by approximately 20%.

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