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## Simultaneous SO<sub>2</sub>/NO<sub>x</sub> Abatement Using Zeolite-Supported Copper

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## ABSTRACT

We have continued the investigation of the adsorption of NO on the Cu/ $\gamma$ -alumina samples and have begun the study of the interaction of NO with sulfated Cu/ $\gamma$ -alumina. The interaction of NO with a sulfated surface is extremely important, since the copper sites in the most popular NO reduction catalyst, Cu/ZSM-5, also adsorb SO<sub>2</sub>, and the catalyst is poisoned by SO<sub>2</sub>. It may be possible to determine whether the poisoning mechanism is due to a chemical effect, or some other effect, and investigate measures which might alleviate the deleterious effects of surface sulfation on the adsorption/reduction process.

The results for NO interacting with the sulfated surface do not appear to result in the formation of any new species, but do show a dramatic change in the relative amounts of the NO species formed on the surface. The sulfation of the copper species apparently forces the copper species to remain as Cu<sup>2+</sup>, which gives rise to a strong band at 1850 cm<sup>-1</sup>, shifted to lower frequency from the 1863 cm<sup>-1</sup> absorption found for the unsulfated catalyst, but which is still probably due to the formation of a Cu<sup>2+</sup>/NO complex, given the small frequency shift. Two other infrared absorption bands observed for NO adsorbed on the un-sulfated catalyst are observed in the current study only weakly, and are due to the formation of adsorbed NO<sub>2</sub>, the NO oxidation product formed when Cu<sup>2+</sup> is reduced to Cu<sup>+</sup>, and to the Cu<sup>+</sup>/NO<sup>-</sup> complex. The relatively intense absorption due to the Cu<sup>2+</sup>/NO complex and the weak absorptions due to adsorbed NO<sub>2</sub> and the Cu<sup>+</sup>/NO<sup>-</sup> complex indicate that little reduction of the copper has taken place. Stabilization of the Cu species as Cu<sup>2+</sup> by the sulfate apparently prevents participation of the surface copper species in the redox cycle.

To our knowledge this is the first reported infrared spectroscopic study of NO interacting with a sulfated Cu/ $\gamma$ -alumina catalyst.

## EXPERIMENTAL

The copper on  $\gamma$ -alumina catalysts were prepared, as has been described before, using non-aqueous impregnation techniques. Copper acetylacetonate (Aldrich, used as received) was dissolved in acetonitrile (Fisher Scientific, dried with molecular sieves),  $\gamma$ -alumina (from Goodfellow, 99.995%, 150 m<sup>2</sup>/g, < 0.1  $\mu$ m particle size) was added, and the mixture was stirred at room temperature for 24 hours. The catalysts were then vacuum filtered and dried in a vacuum oven at 80 °C for 24 hours. The catalyst was then calcined in air at 500 °C for 2 hours. Elemental analyses of the catalysts were performed by Galbraith Laboratories, Knoxville, TN.

For the infrared spectroscopic studies, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used. A DRA-2C0 optical accessory from Harrick Scientific was used, with an associated controlled environment cell for the *in situ* studies. The sample was sieved using a 38  $\mu$ m particle size sieve, mixed with dried, sieved KBr very gently (to avoid impregnating the sorbent with potassium) 20% by weight, placed in the DRIFTS sample cup, and carefully leveled with a spatula.

For these experiments, the copper loading on alumina was not a variable. Of the three primary samples which have been studied in the previous work, 1.12 wt%, 2.35 wt%, and 5.78 wt% Cu on  $\gamma$ -alumina, the 5.78 wt% Cu/ $\gamma$ -alumina catalyst was used for these studies, because it

yields the highest degree of surface sulfation. Before beginning the NO adsorption experiments, the catalyst/KBr was heated to 400 °C in slowly flowing oxygen to remove any water or organics adsorbed after calcination. The catalyst was then cooled to 300 °C and exposed to 10 torr of pure SO<sub>2</sub> (Matheson, research grade, used as received) for 30 minutes. The cell was evacuated and then heated in 200 torr of pure oxygen at 400 °C for 30 minutes to oxidize the adsorbed SO<sub>2</sub>, and an infrared spectrum was measured. The sample was then cooled to 30 °C and exposed to 20 torr of a flowing 4% NO (balance He) gas mixture (Specialty Gas Southeast). The infrared spectrum was measured at 1, 20, 40, and 60 minutes after the flow was begun. The final spectra were obtained by subtracting the contribution of gas-phase NO.

## RESULTS

A Cu/γ-alumina catalyst which was prepared from a precursor which contained more than a monolayer of the copper acetylacetonate, corresponding to 5.78 wt % Cu, was chosen as the system to examine. The results are plotted in Figure 1 as a function of time to observe the formation of new species and changes in the intensities of the infrared bands with adsorption of NO.

Spectrum A in Figure 1 is the spectrum of the sulfated catalyst before addition of NO. Absorption bands at 2262, 2204, 2142, and 2079 cm<sup>-1</sup> are prominent. These bands are reproduced in subsequent spectra measured after the addition of NO, seen in spectra B, C, D, and E of Figure 1, measured after 1 min, 20 min, 40 min, and 60 min of exposure to flowing NO, respectively. The most intense band in these spectra is observed at 1850 cm<sup>-1</sup> with a shoulder at approximately 1860 cm<sup>-1</sup>. A medium intensity band is observed in the neighborhood of 1640 - 1627 cm<sup>-1</sup>, and a weak feature is observed at approximately 1700 cm<sup>-1</sup>. All of these bands, with the exception of those due to the surface sulfate species, disappeared upon evacuation. The frequencies of these bands are very similar to those observed for the unsulfated catalyst. However, the relative intensities are dramatically different.

For reference purposes, the results from the previous report on the adsorption of NO on the 5.78 wt% unsulfated Cu/γ-alumina catalyst are shown in Figure 2. On this catalyst, two new bands at approximately 1863 and 1640 cm<sup>-1</sup> appeared after 1 min exposure to flowing NO. At the completion of 1 hr exposure to flowing NO, these two bands were still present and were accompanied by a new band at approximately 1703 cm<sup>-1</sup> which began to appear after 20 min exposure time. Also, the 1640 cm<sup>-1</sup> peak had shifted to approximately 1629 cm<sup>-1</sup> at the end of one hour exposure. These peaks disappeared upon evacuation.

A review of the literature and a discussion of the frequency shifts associated with NO binding to copper was presented in the previous report and will not be reproduced here. The assignments of the bands observed for the unsulfated catalyst to particular species is presented in Table 1. The assignment of the 1863 cm<sup>-1</sup> vibrational mode to the Cu<sup>2+</sup>/NO complex is due to the observation that NO adsorbed on copper aluminate (a Cu<sup>2+</sup> species) gives rise to a strong absorption at this frequency, and this frequency is shifted only slightly down from the gas phase NO absorption at 1876 cm<sup>-1</sup>. Larger changes are expected to result from the ionization of the NO to form NO<sup>+</sup> or NO<sup>-</sup> as discussed in the earlier report.

Table 1. Assignment of Observed Absorptions to Surface Species.

<u>Observed Vibrational Frequency (cm<sup>-1</sup>)</u>	<u>Assignment</u>
1876	Gas-phase NO
1863 and 1850 (sulfated surface)	Surface Cu <sup>2+</sup> /NO
1700	Surface Cu <sup>+</sup> /NO <sup>-</sup>
1640 - 1627	Surface Cu <sup>+</sup> -ONO <sup>-</sup>

The observed assignments are consistent with a model for the chemisorption of NO on Cu/alumina sorbents proposed by Hierl, et al.<sup>1</sup> In this model, the authors proposed the following sequence of steps.



The reaction of equation 1 is proposed to give rise to the 1863/1850 cm<sup>-1</sup> absorption, while the species formed in reaction 2 is proposed to give rise to the 1640-1627 cm<sup>-1</sup> absorption. The band at 1700 cm<sup>-1</sup>, based on its low frequency and the predictions by Shelef<sup>2</sup>, is assigned to the formation of a surface Cu<sup>+</sup>/NO<sup>-</sup> species.

The results for NO interacting with the sulfated surface do not appear to result in the formation of any new species, but do show a dramatic change in the relative amounts of the NO species formed on the surface. The sulfation of the copper species apparently forces the copper species to remain as Cu<sup>2+</sup>, giving rise to the strong band at 1850 cm<sup>-1</sup>, shifted to lower frequency from the 1863 cm<sup>-1</sup> absorption found for the unsulfated catalyst, but which is still probably due to the formation of a Cu<sup>2+</sup>/NO complex, given the small frequency shift. Two other infrared absorption bands observed for NO adsorbed on the un-sulfated catalyst are observed in the current study only weakly, and are due to the formation of adsorbed NO<sub>2</sub> (present on the surface as Cu<sup>+</sup>-ONO<sup>-</sup>), the NO oxidation product formed when Cu<sup>2+</sup> is reduced to Cu<sup>+</sup>, and to the Cu<sup>+</sup>/NO<sup>-</sup> complex. The relatively intense absorption due to the Cu<sup>2+</sup>/NO complex and the weak absorptions due to adsorbed NO<sub>2</sub> and the Cu<sup>+</sup>/NO<sup>-</sup> complex indicate that little reduction of the copper has taken place. Stabilization of the Cu species as Cu<sup>2+</sup> by the sulfate apparently prevents participation of the surface copper species in the redox cycle.

## REFERENCES

1. Hierl, M.; Urbach, H.-P.; Knozinger, H. *J. Chem. Soc. Faraday Trans.*, **1992**, *88*, 355.
2. Shelef, M. *Chem. Rev.*, **1995**, *95*, 209, and references therein.

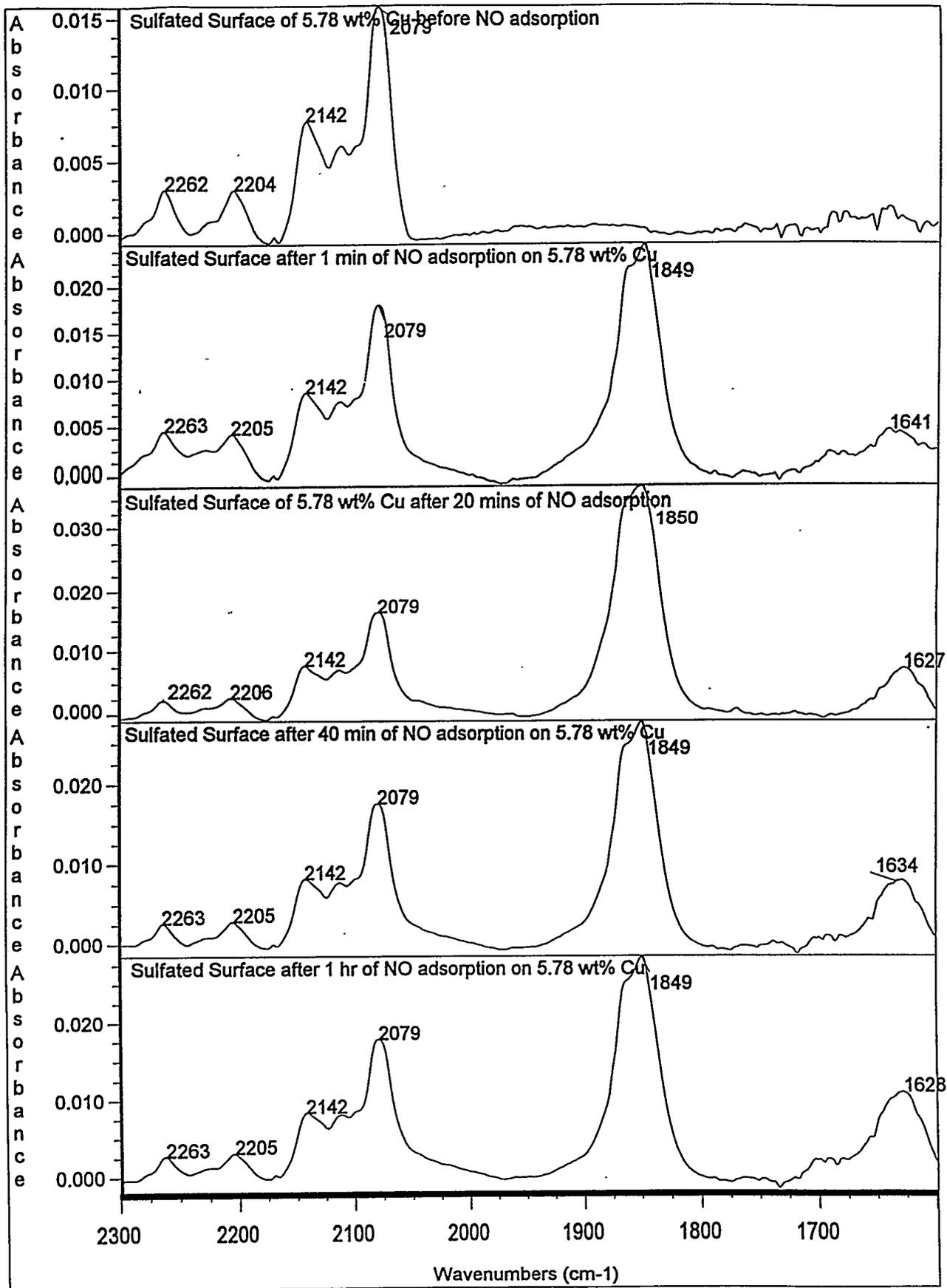


Figure 1.

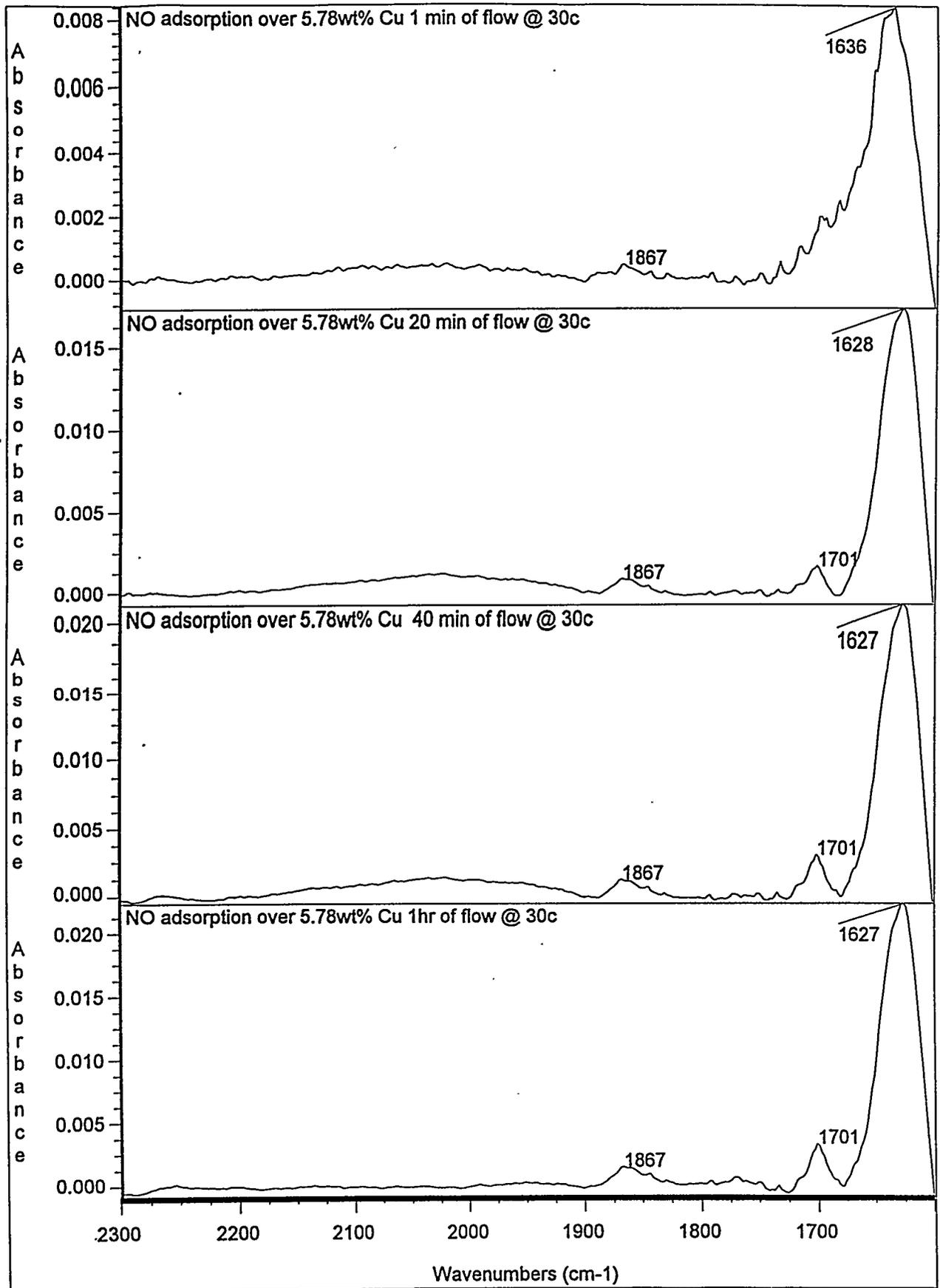


Figure 2.