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PROGRESS REPORT

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2. PERIOD COVERED BY REPORT: January 1, 1995 - March 31, 1995
3. TITLE OF PROPOSAL: SIMULTANEOUS SO_2/NO_x ABATEMENT USING ZEOLITE-SUPPORTED COPPER.
4. NAME OF INSTITUTION: Clark Atlanta University
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ABSTRACT

We have significantly improved on our earlier results with a copper-impregnated alumina, obtaining reproducible results for the impregnation procedure and linear behavior with solution concentration of the precursor. The copper acetylacetonate precursor is adsorbed molecularly onto the alumina surface, with no noticeable decomposition. The adsorbed complex appears to form layers on the alumina surface, similar to results found using the same complex with a silica substrate. The materials start out as light blue powders, and after oxidation are light green. Using infrared spectroscopy, we have examined the *in situ* adsorption and oxidation of SO_2 on the oxidized sorbent, which is dispersed copper oxide supported on aluminum oxide, and have observed that the initial species formed correspond to aluminum sulfite and aluminum sulfate. The sulfate is formed at temperatures much lower than similar experiments studying SO_2 adsorption on alumina and sodium-doped alumina. As a result of oxidation, the adsorbed sulfur species, which begin as aluminum sulfite and sulfate, are converted to copper sulfate.

EXPERIMENTAL

The sorbents were prepared by copper acetylacetonate (Aldrich, used as received) in acetonitrile (Fisher Scientific, dried with molecular sieves), adding γ-alumina (from Goodfellow, 99.995%, 150 m^2/g, < 0.1 μm particle size) and stirring at room temperature for 24 hours. The sorbents were then vacuum filtered and dried in a vacuum oven at 80C for 24 hours. For SO_2 adsorption studies, the sorbent was calcined in air at 500C for 2 hours. Elemental analyses of the sorbents were performed by Galbraith Laboratories, Knoxville, TN.

For the infrared 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 μm particle size sieve, mixed with dried, sieved KBr very gently (to avoid impregnating the sorbent with potassium) 10% by weight, placed in the DRIFTS sample cup, and carefully leveled with a spatula.

Before starting the SO_2 adsorption experiments, the sorbent/KBr was heated to 400C in slowly flowing oxygen to remove any water or organics adsorbed after calcination. The sample was then cooled to the adsorption temperature and exposed to 10 torr of pure SO_2 (Matheson, research grade, used as received) for 30 minutes. The cell was evacuated for 10 minutes, and an infrared spectrum of the chemisorbed SO_2 was then obtained. The samples were then heated in 200 torr of pure oxygen at 400C for 30 minutes to oxidize the adsorbed species, and another spectrum was obtained.

RESULTS

Figure 1 shows the adsorption isotherm calculated from the batch impregnation of copper acetylacetonate on γ-alumina. The atomic adsorption analyses of the impregnated alumina provided the data for the weight percent copper adsorbed, while the weight percent copper in solution was calculated from the initial solution concentrations of copper acetylacetonate used to prepare the sorbents. The data has been fit to a straight line, even though two different adsorption regimes are apparently involved: formation of the first layer, followed by formation of the second and subsequent layers. One could propose that a break occurs at approximately 3.5 wt% in solution, but it is not clear that there are enough data points to support such a break in a definitive way.

Figure 2 is a plot of the amount of carbon measured on the surface of the support vs. the amount of adsorbed copper. The slope of the plot, which should be equal to the ratio of carbon to copper in the supported complex, is measured to be 10.5, within experimental error of the expected value of 10. The non-zero intercept is excess carbon on the surface, presumably from adsorption of acetonitrile during impregnation.

Figure 3 is a plot of the 1800 - 1200 cm^{-1} region of the DRIFT spectra of the supported complex as a function of the measured weight loading of copper on the support. In our earlier studies of copper acetylacetonate on silica, the presence of a band at 1553 cm^{-1} and another band at 1356 cm^{-1} were used to indicate the formation of multiple layers of copper acetylacetonate on the support.[1] In the present studies, the 1553 cm^{-1} band is not observed, but the 1356 cm^{-1} band can be seen to grow in as a function of copper weight loading. This band can be observed as a weak shoulder in the spectrum of the 4.04 wt% copper sample, so it is assumed that monolayer coverage is achieved between 2.35 wt% and 4.04 wt% copper on the support. This band continues to grow in relative intensity as a function of copper loading, and is seen clearly in the 9.44 wt% copper sample.

Figure 4 contains the infrared spectra of SO_2 chemisorbed on the 2.35 wt% copper sorbent after oxidation of this sorbent to remove the ligands. The band at 1057 cm^{-1} can be assigned to an aluminum sulfite species and the band at 1190 cm^{-1} to aluminum sulfate.[2] These assignments are based on our earlier results with adsorption of SO_2 on alumina and sodium-doped alumina. The other prominent bands in the spectra are not due to aluminum species and must be assigned by comparison with other spectra. The broad band at approximately 1120 cm^{-1} agrees well with frequencies associated with copper sulfate. The bands at 1250 and 1321 cm^{-1} must also be due to copper species, by elimination. One of the most noticeable results from the spectra is the prominence of the 1190 cm^{-1} absorption, due to aluminum sulfate, at adsorption temperatures greater than 150C. This band was observed before addition of oxygen. For pure alumina and sodium-doped alumina, the formation of aluminum sulfate was not observed without addition of oxygen until 300C, and then only occurred as a small side reaction. In these experiments, it appears that the major product formed at temperatures above 150C before oxidation is aluminum sulfate.

Figure 5 shows the spectra obtained after oxidizing chemisorbed SO_2 (adsorption at 150C, which was found to give the largest amount of adsorbed SO_2 in earlier studies) at three different weight loadings of copper on alumina. The sorbent with 1.12 wt% copper is well below monolayer coverage of the precursor, 2.35 wt% copper was just under monolayer coverage, and the 5.78 wt% copper sorbent was above monolayer coverage for the precursor. Two characteristics are notable in these spectra. The first is that the 1123 cm^{-1} feature dominates the spectrum, regardless of weight loading of copper, and that feature is due to copper sulfate. The intensity of this band as a function of copper loading increases as expected for this assignment. The second is that the intensity of the 1196 cm^{-1} feature, which is due to aluminum sulfate, decreases as the copper loading increases, and appears to be gone at the 5.78 wt% loading. The feature at 1037 cm^{-1} also follows this trend, but the nature of the species which is responsible for this absorption is not clear at this time.

DISCUSSION

In earlier attempts to prepare copper on alumina using copper acetylacetonate, we used another alumina, also from Goodfellow, to prepare the sorbents. The only difference in the description in the catalog from the company was that the new sorbent had a particle size of approximately 45 μm, closer to that used by other researchers in this field. Thus, in order to compare our results more directly with theirs, we began using the new alumina. Our initial consultation with the company did not yield any information which told us what might be giving the anomalous results. However, after we continued to see copper loadings which did not correlate well with solution concentration, we asked more specific questions and found out that the new alumina was an alpha alumina. Alpha alumina has a significantly lower surface area than γ-alumina, and different surface site densities. These differences apparently accounted for our poor results in the earlier attempts, because our results using the "old" alumina give excellent results for adsorption of copper acetylacetonate from acetonitrile solution. This is encouraging, because we initially thought that the alumina surface, which is more acidic than the silica surface, might not adsorb the copper acetylacetonate complex molecularly. The linear adsorption isotherm and the C/Cu ratio of approximately 10, indicate that the adsorption chemistry is predictable and that the complex is adsorbing molecularly.

The results from the SO_2 adsorption and oxidation studies allow us to propose a sequence for the adsorption of SO_2 on alumina-supported copper oxide. It appears that the initial form of the adsorbed SO_2 involves association with aluminum on the surface, either as aluminum sulfite or sulfate. At adsorption temperatures of 150C and greater, the predominant form of adsorbed SO_2 on the surface is aluminum sulfate, even without added oxygen. When oxygen is added at high temperature, 400C, the chemisorbed SO_2 is converted to copper sulfate, with a small amount of the adsorbed species remaining as aluminum sulfate. The amount of aluminum sulfate on the surface after oxidation decreases as the copper loading increases. Thus, in excess oxygen, the preferred form is copper sulfate, but in the absence of added oxygen, the adsorbed species appears to be associated with aluminum.

More experiments need to be carried out to clear up questions regarding the adsorption mechanism and the nature of the different adsorbed species. But clear progress has been made regarding the nature of this important flue gas cleanup sorbent.

REFERENCES

1) Mitchell, M. B.; Chakravarthy, V. R.; White, M. G. *Langmuir*, **1994**, *10*, 4523.

2) Mitchell, M. B.; Sheinker, V. N.; White, M. G. submitted to *J. Phys. Chem.*

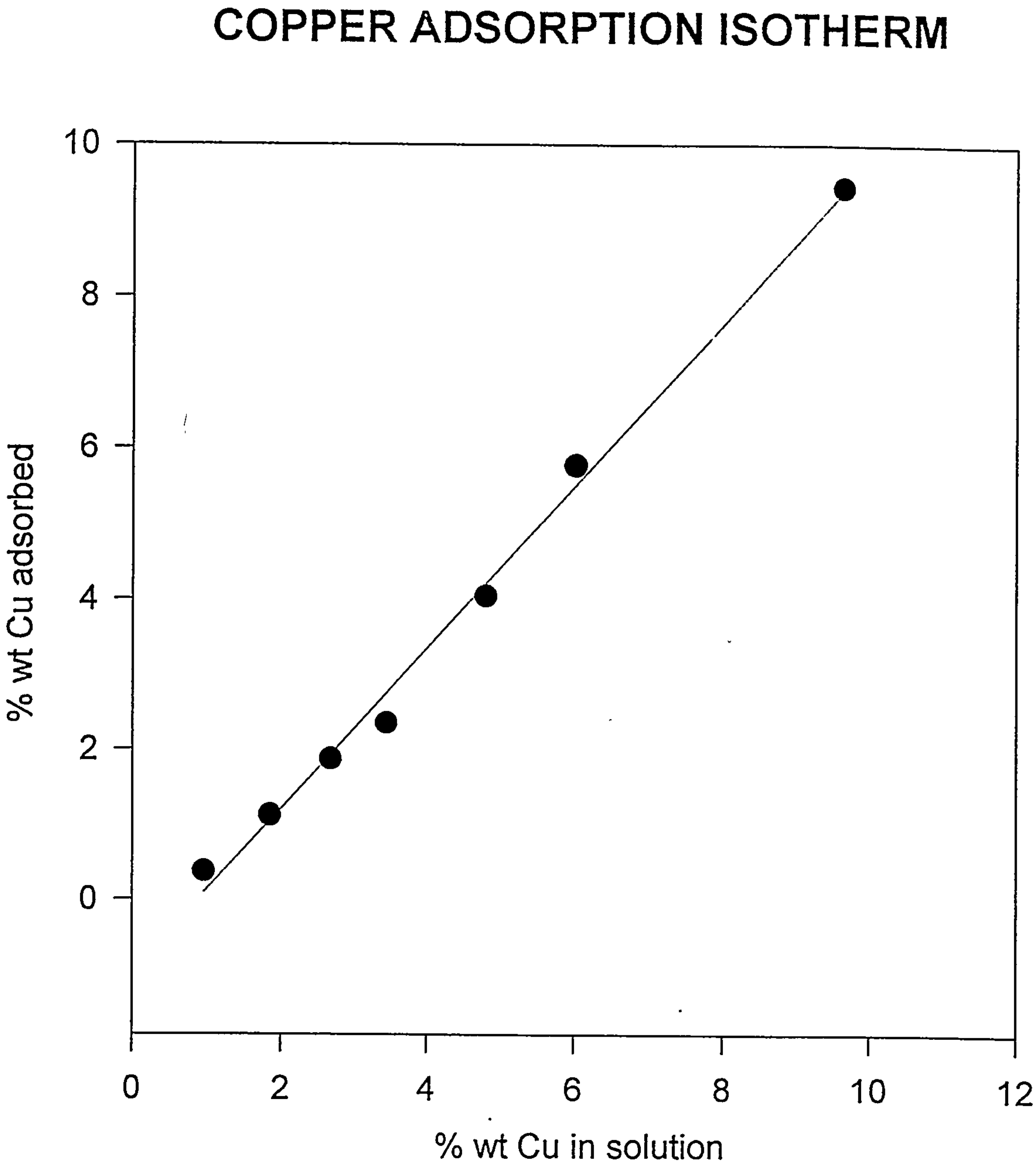

Figure 1. Adsorption Isotherm for Copper Acetylacetonate on Alumina from Acetonitrile Solution.

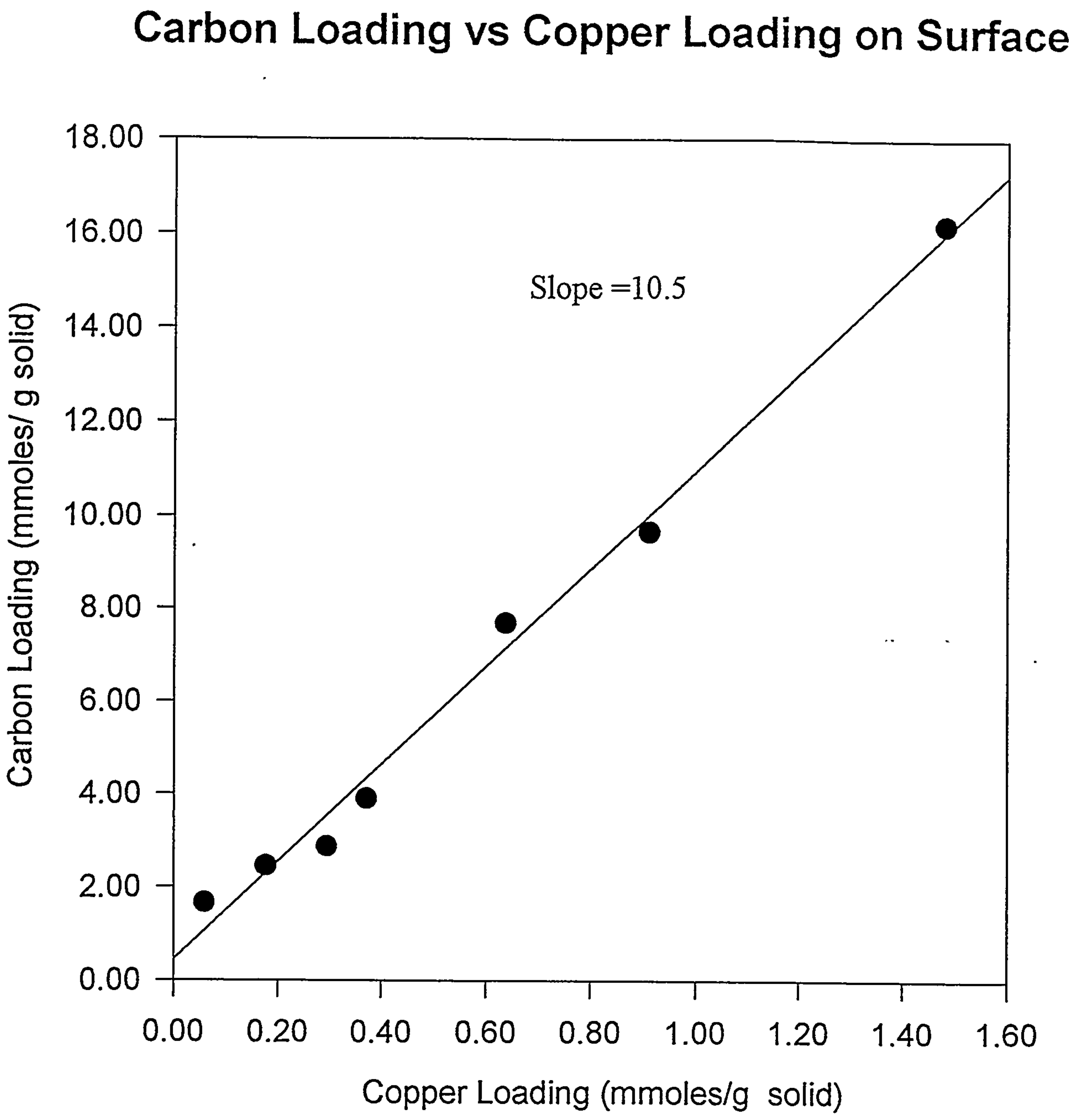

Figure 2. Plot of the measured concentration of carbon vs copper found in the copper acetylacetonate on alumina sorbent precursor.

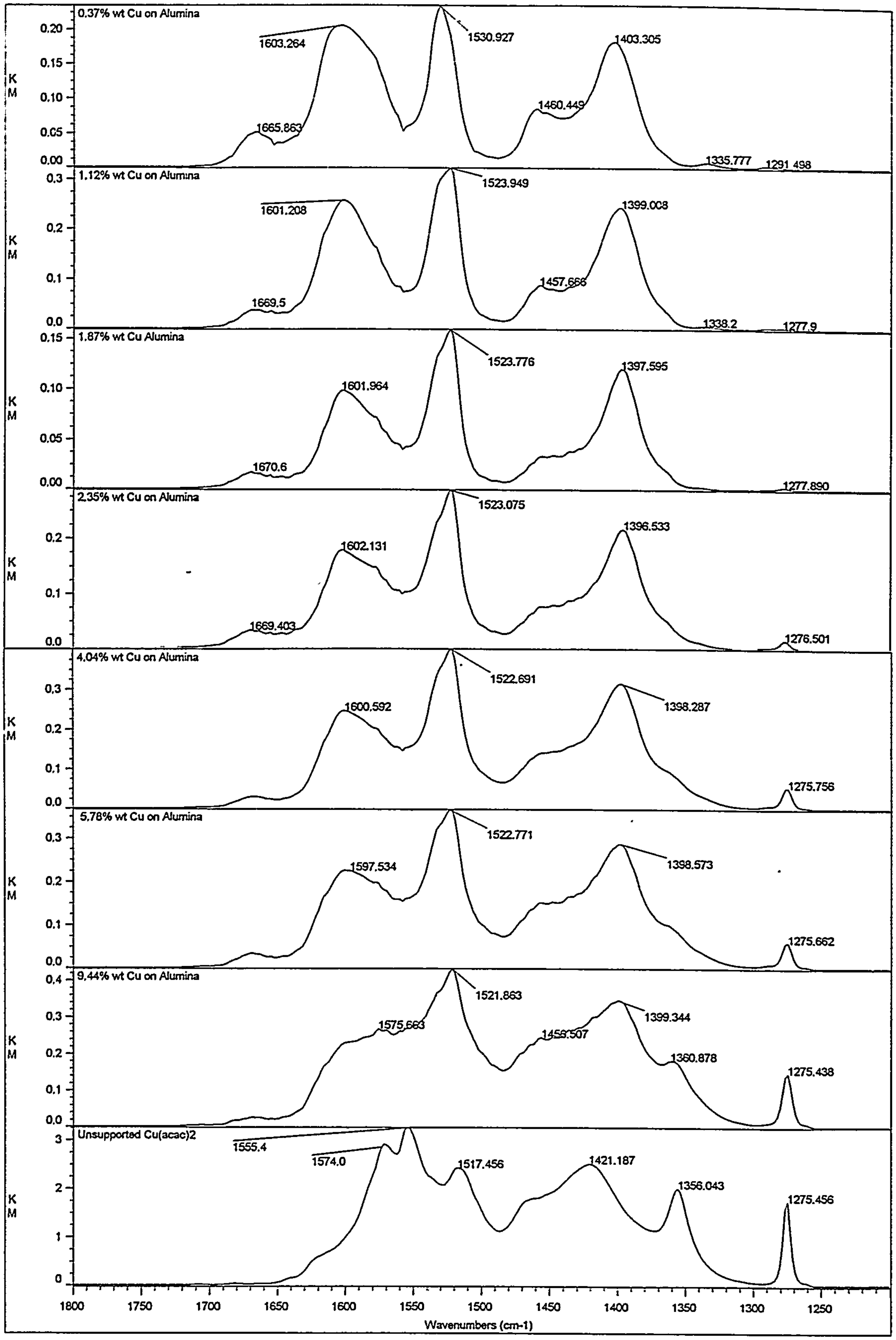

Figure 3. Infrared diffuse reflectance spectra of the copper acetylacetonate-impregnated alumina samples as a function of weight loading of copper.

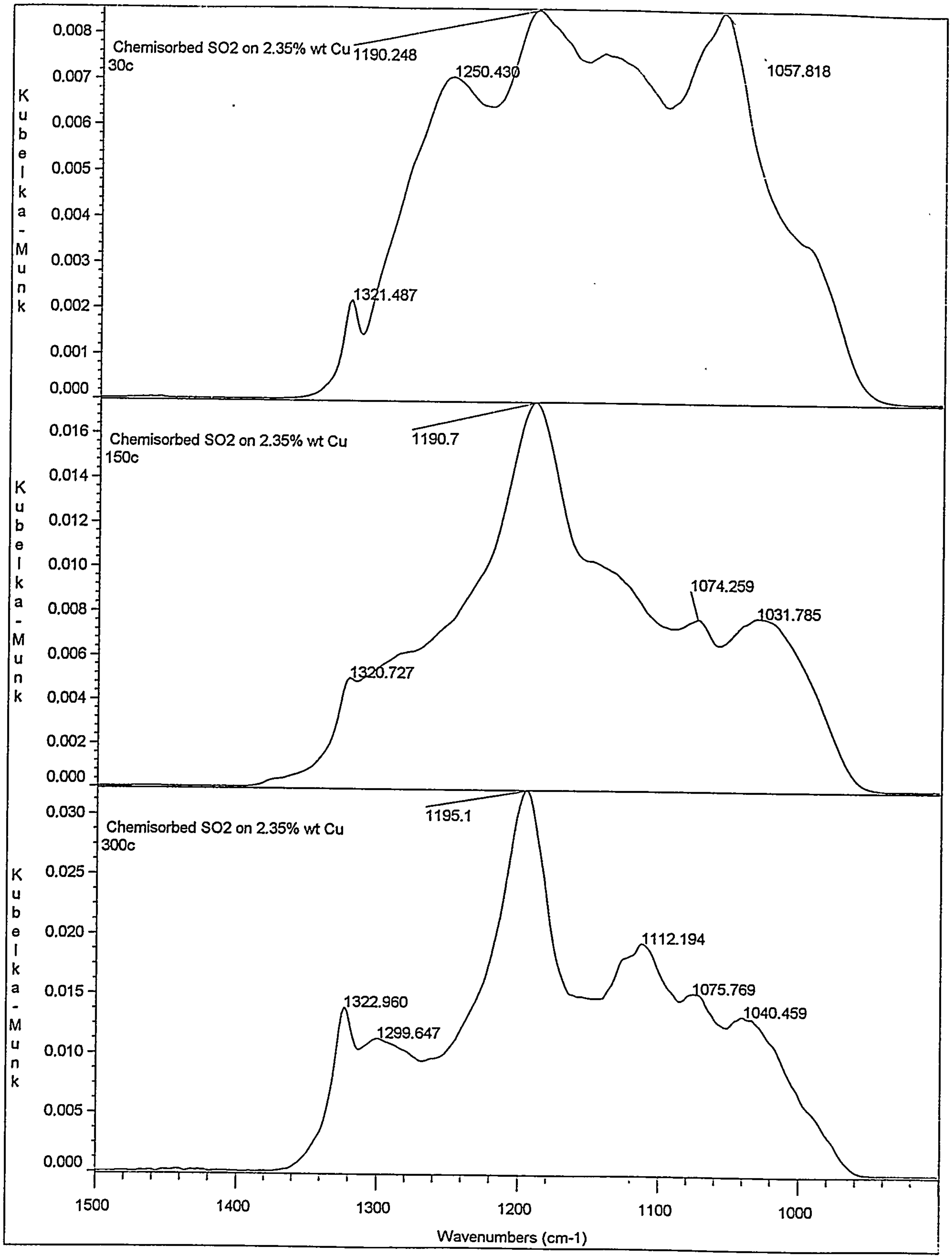

Figure 4. Infrared diffuse reflectance spectra of the samples after being exposed to 10 torr SO_2 for 30 minutes, after evacuation of physisorbed SO_2.

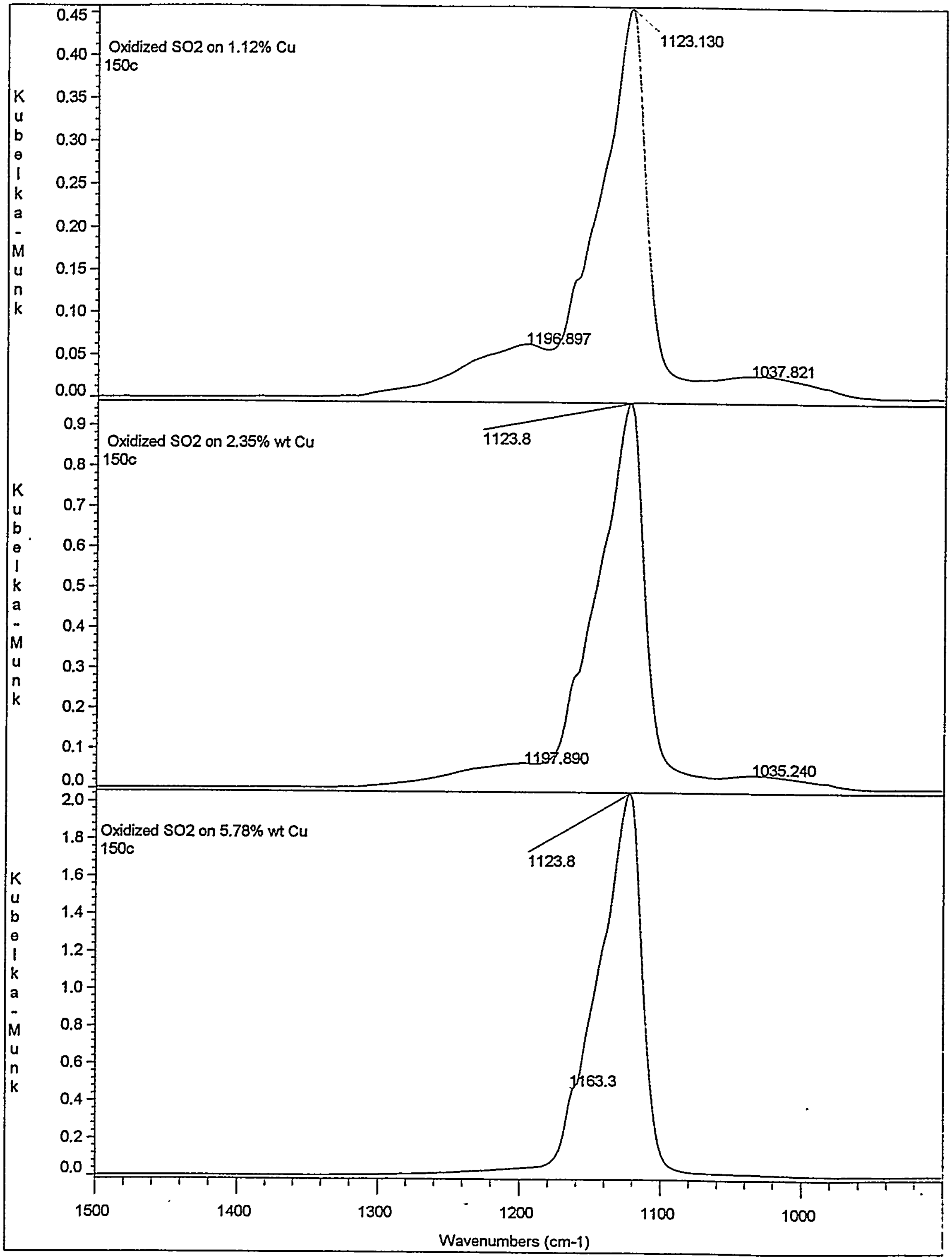

Figure 5. Infrared diffuse reflectance spectra of chemisorbed SO_2 on sorbents with different copper loadings, after oxidation of the chemisorbed SO_2.