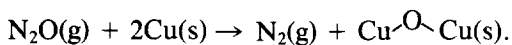


## Dispersion of Silica-Supported Copper Catalysts Determined by NMR of $^{63}\text{Cu}$

Determining the dispersion of supported copper catalysts is difficult because of the inertness of copper metal. Copper does not readily dissociate and adsorb hydrogen, and therefore, the traditional method of hydrogen chemisorption is not applicable in this case. The most widely used method of determining dispersion (or surface area) of supported and unsupported copper has been the reaction of copper surface atoms with nitrous oxide (1-6). The reaction is



The stoichiometry of one oxygen to two copper surface atoms has been inferred from the UPS study of Narita *et al.* (5).

We report here the use of solid state NMR of  $^{63}\text{Cu}$  in silica-supported copper catalysts as a new, independent method for determining copper dispersion. This method has an advantage over the nitrous oxide method in that it need not assume a stoichiometry for a reaction. The results are shown to agree with those obtained from the use of nitrous oxide when the stoichiometric ratio of copper to adsorbed oxygen in the above reaction is two.

A series of five silica-supported catalysts of varying metal loading were prepared. Three catalysts were prepared by using an aqueous impregnation method (7, 8), and two were prepared by using an ion exchange technique (9). All catalysts used Cab-O-Sil HS-5 silica as the support and  $\text{Cu}(\text{NO}_3)_2$  as the source of copper. Copper loadings were determined using atomic adsorption spectroscopy. All samples were reduced in flowing hydrogen (40 S  $\text{cm}^3/\text{min}$ )

at 573 K for 2 h and then either transferred to sample bulbs for nitrous oxide experiments or prepared for NMR studies.

The nitrous oxide method utilizing the technique described by Scholten and Konvalinka (2) was used as a basis of comparison for dispersions determined by NMR. The chemisorption/surface reactions were carried out on a modified Micromeritics 2100D volumetric adsorption apparatus having all-stainless-steel manifold, lines, and valve bellows. The system internal temperature was maintained at 307 K. Approximately 200 to 500 mg of reduced catalysts were placed in a sample bulb and attached to the apparatus. The samples were outgassed for 12 h at 473 K. Dead volumes for the sample bulb and an empty bulb were determined by using helium. The samples were reduced again in several static reduction/evacuation cycles. The samples were heated to 523 K in hydrogen and then outgassed at that same temperature for several hours. After the reduction/evacuation cycles the samples were outgassed for 6 h at 523 K. Each sample was cooled to between 343 and 363 K and held at that temperature. Approximately 350 Torr (1 Torr =  $133.3 \text{ N m}^{-2}$ ) of nitrous oxide was admitted to the manifold and allowed to equilibrate for several hours. The sample valve was then opened, as was the valve to the empty sample bulb. The final pressure, after about 3 h, was approximately 200 Torr. Liquid nitrogen was then applied to the empty sample bulb, freezing out the residual nitrous oxide in about 2 h. The final pressure, corresponding to nitrogen, was about 5 to 10 Torr. From this residual nitrogen pressure the copper dis-

TABLE I  
Comparison of Silica-Supported Copper  
Catalyst Dispersions Determined by Nitrous  
Oxide Reaction with Dispersion  
Determined by NMR

Catalyst (% Cu)	Dispersion (%)	
	Nitrous oxide	NMR
12 <sup>a</sup>	4	2
8 <sup>b</sup>	25	29
5 <sup>a</sup>	7	10
3 <sup>b</sup>	20	20
0.25 <sup>a</sup>	36	30

<sup>a</sup> Catalyst prepared by impregnation.

<sup>b</sup> Catalyst prepared by ion exchange.

persions were calculated, and the results are given in Table 1. Note that we have assumed the stoichiometry shown in the above equation.

The NMR study was performed on a home-built spectrometer described previously (10). The spectrometer operated at 5.167 T (220 MHz proton resonance) and gave the following resonances: <sup>63</sup>CuCl, 58.351 MHz; <sup>63</sup>Cu metal, 58.493 MHz; and <sup>23</sup>Na, 58.236 MHz (11, 12). The inductor in the NMR probe was wound from flat silver ribbon, and was 6 mm i.d. Copper (I) chloride solid was used as a tuning standard. The signals of both <sup>63</sup>Cu in CuCl, and Cu<sup>o</sup>, were maximized using 90° pulses, indicating that all three transitions of the quadrupolar <sup>63</sup>Cu nucleus ( $I = \frac{3}{2}$ ) were excited at a broadcast bandwidth of 160 kHz. The pulse lengths were approximately 3 μs. A dwell of 0.5 μs, which was well below the inverse of the Nyquist frequency, was used. The filter was set at 500 kHz half-band for spectra that contained both copper metal and copper (I) chloride and at 100 kHz for spectra containing only one resonance, or when the spectra were folded. The recycle time was set at 0.05 ms. No attenuation of signal was observed because of T1 saturation. Phase inversion of the preparation pulse on alternate scans was used to minimize baseline artifacts. Scans

numbering 10,000 to 30,000 were accumulated, depending on the copper loading of the catalyst.

Because of the large shifts involved in NMR of <sup>63</sup>Cu, the effect of frequency offset upon the spectrum was investigated. It was found that no significant attenuation of signal occurred for offsets less than 100 kHz. Consequently, the carrier frequency was set between the Cu(I)Cl and Cu<sup>o</sup> resonances, giving offsets of 50 and 40 kHz, respectively. Samples for the NMR investigation were placed in glass tubes (approximately 100 mg) and reduced in flowing hydrogen as described above. Samples requiring no additional treatment were cooled and then sealed in the glass tubes with approximately 400 Torr of hydrogen. The samples to be chlorided were reduced as described above and then cooled to 523 K. A mixture of hydrogen (50 S cm<sup>3</sup>/min) and HCl (20 S cm<sup>3</sup>/min) was then passed over the samples for 10 min. The flow was then switched to pure hydrogen and the samples were cooled. The glass tubes were sealed as described above. The temperature and time of exposure to HCl gas was optimized to give the maximum Cu(I) peak without decreasing the total copper signal due to conversion of copper to CuCl<sub>2</sub>, which is paramagnetic. The NMR of <sup>63</sup>Cu for the silica-supported catalysts are shown in Fig. 1.

Because both <sup>63</sup>Cu and <sup>65</sup>Cu are quadrupolar nuclei, there have been few investigations of small copper particles (13-15). Originally we had intended to use the variation of Knight shift in the surface region to quantify dispersion (13, 14). But only the highest dispersion sample showed a slight peak shape change due to this effect. The electric field gradient asymmetries near the surface are apparently sufficiently large such that surface nuclei are unobserved when the broadcasting and observation bandwidths of the present experiment are used. The adsorbates hydrogen and carbon monoxide provided no change in the spectra, indicating that no surface nuclei were

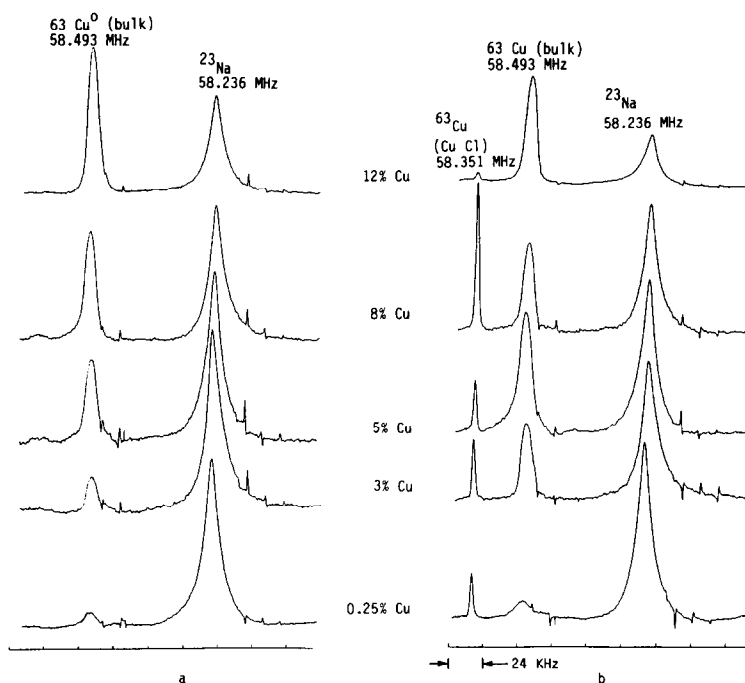


FIG. 1.  $^{63}\text{Cu}$  NMR of silica-supported copper catalysts: (a) reduced, (b) reduced and treated with HCl,  $\text{H}_2$  mixture for 10 min. The spectra of the chlorided samples were folded to eliminate attenuation of signal due to offset effects. The position of the peak is indicated by frequency.

observed with adsorption. Also, adsorption and reaction of the surface with  $\text{N}_2\text{O}$  did not change the spectra. Chloriding the surface of the copper particles to form  $\text{CuCl}$ , on the other hand, resulted in a peak in the position of that observed for  $\text{CuCl(s)}$  (Fig. 1b), in which the local symmetry of Cu is Td. In addition, the bulk copper signal intensity did not decrease in the chloriding process. In some cases there is a slight increase in the copper metal (bulk) peak. We interpret this to indicate that some additional reduction is occurring during the chloriding step. The resonance of  $^{23}\text{Na}$  in the NMR sample tube walls was used as an internal standard for a given catalyst loading.

The dispersions were calculated using the integrated intensities of peaks shown in Fig. 1b assuming the copper (I) chloride peak represented all the surface copper atoms and the copper metal peak represented the bulk copper atoms. The disper-

sions determined by this method are given in Table 1. There is good agreement with the dispersions determined from the nitrous oxide method.

When HCl gas is adsorbed on a copper surface, an interface between well-ordered metallic copper and surface-chlorided copper is formed. This interface could be characterized by a large electric field gradient making Cu in the interface invisible to  $^{63}\text{Cu}$  NMR. This possibility cannot be eliminated, but comparison of the catalysts before and after HCl treatment shows that the bulk copper peak does not decrease in intensity with chloriding even with the higher dispersion catalysts. The magnitudes of the observed dispersions and this fact both suggest that haliding the Cu surface produces a region below the halided surface layer that maintains essentially the same electric field gradient as that in bulk Cu and is therefore visible to NMR.

It may also be argued that both the NMR

approach and the nitrous oxide technique overestimate the dispersion. The copper chloride peak may represent more than a monolayer of copper and the nitrous oxide reaction may allow oxygen to intercalate into the top two or more layers of the copper particle. However, physical techniques have verified the nitrous oxide technique (2, 3, 6). Consequently, for catalysts in the dispersion range studied in this work the NMR technique gives reliable results.

From our results we conclude that NMR of  $^{63}\text{Cu}$  is a viable method of determining dispersions for supported copper catalysts. The results are consistent with the nitrous oxide method when the copper/oxygen stoichiometric ratio is two.

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