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# LETTER TO THE EDITORS

## Detection and Role of Unreduced Copper Species in the Ring Opening of Cyclopropanes

In their recent paper (*1*) concerning the structure of $Cu/SiO_2$ catalysts prepared by ion exchange, Kohler *et al.* used diverse experimental methods, including temperature-programmed reduction (TPR) (*2*), and provided convincing evidence that a substantial portion of the Cu(II) ions in these catalysts can be reduced only to Cu(I) ions. These are ion-exchanged, isolated Cu(II) ions attached to the silica as individual atoms, which retain their isolated nature in the Cu(I) stage after reduction. These investigations are in line with the recently growing interest in the catalytic properties of copper. In this respect, the exact characterization of copper surfaces and the exploration of the active sites of the working catalysts have become a necessity. The efforts in this field have already revealed interesting properties of traditional catalysts (*3–10*) and newly developed amorphous copper–metal alloys (*11–14*), and have resulted in a still-continuing debate on the nature of the active sites of methanol synthesis catalysts (*15–17*).

As regards the TPR characterization of catalysts prepared by impregnation, the literature results indicate either total reduction without difficulty (*18*) or the presence of unreduced species (*19–21*). The studies also show that the reducibility of copper catalysts depends strongly on the nature of the support and the pretreatment conditions before reduction.

Our studies on the behavior of copper in heterogeneous catalytic transformations led to the recognition of interesting properties of this metal. New reactions and unusual activities and selectivities were observed in the transformations of oxygen-containing compounds (*22–25*), amino alcohols (*26, 27*), organosilanes (*28–31*), and hydrocarbons (*32, 33*).

Our recent studies relating to the surface characterization of copper revealed the role of copper oxide in the isomerization of methyloxirane (*25*) and a unique isomerizing activity of ion-exchanged copper catalysts (*34*), while the present study focuses on catalysts prepared by precipitation. These catalysts had been used and found to be active in certain transformations (*25, 28–33*); however, no information is available on their surface structure.

We have undertaken an investigation of Cu/Cab-O-Sil catalysts prepared by precipitation and have also sought a suitable probe molecule and test reaction which might be used to indicate differences in surface structure.

Our observations on ion-exchanged catalysts are similar to those of Kohler *et al.* (*1*). That is, $Cu/SiO_2$ catalysts prepared by the usual ion-exchange method (*35*) by using $Cu[(NH_3)_4]^{2+}$ solution and a large-pore silica gel (Strem, 340 $m^2/g$, 120–230 mesh), and decomposed at 773 K for 3 hr, contain a certain amount of unreduced copper species, the extent depending on the loading (Table 1). TPR experiments also revealed that, in contrast with earlier observations (*10*), this unreducible fraction of copper could not be reduced up to a temperature as high as 1073 K.

The other type of catalyst, which was prepared by precipitating basic copper carbonate onto a Cab-O-Sil M5 (BDH silica) support (*36*), exhibited similar behavior. TPR measurements on the fresh, noncalcined precursors revealed that they also contain increasing quantities of unreducible species with decreasing copper loading (Ta-

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TABLE 1

Characterization of Copper Catalysts by TPR Analysis

| Catalyst | Loading (wt%) | Dispersion[a] (%) | Hydrogen consumed[b] | Fraction of Cu(I) |
|---|---|---|---|---|
| Cu/SiO$_2$ | 6.36 | 14.3 | 0.93[c] | 0.07 |
| | 3.45 | 14.7 | 0.85 | 0.15 |
| | 1.91 | 16.9 | 0.71 | 0.29 |
| Cu/Cab-O-Sil | 46.8 | 6.7 | 1.16 | 0[d] |
| | 6.8 | 9.5 | 1.03 | 0.11[d] |
| | 6.8[e] | 9.5 | 0.99 | 0.01[f] |
| | 3.0 | 9.0 | 0.95 | 0.18[d] |
| | 1.1 | 7.6 | 0.89 | 0.23[d] |

[a] Determined with $N_2O$ titration at 363 K, by the pulse method.

[b] Molar ratio of hydrogen consumed to copper.

[c] Experimental error, ±5%.

[d] Values were calculated by assuming 1.16 : 1 stoichiometry, on the basis of the TPR curve and chemical analysis of the unsupported precursor.

[e] Calcined at 773 K for 3 hr in air.

[f] Value calculated by assuming 1 : 1 stoichiometry.

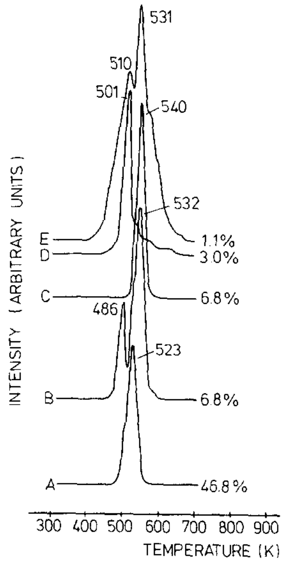
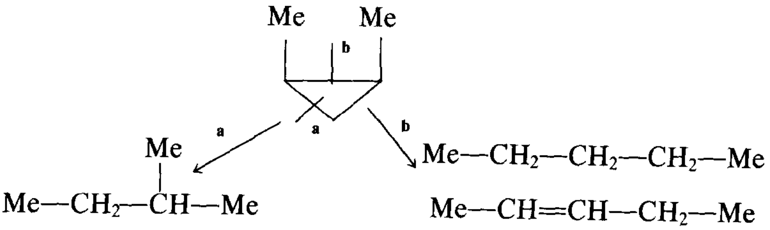


FIG. 1. TPR curves of supported copper catalysts. Sample quantities, 10–200 mg; carrier gas, 9% hydrogen in nitrogen; flow rate, 20 ml/min; temperature ramp, 11 K/min from room temperature to 723 K. Calibrations were made both with hydrogen gas pulses and by integration of the TPR curve of CuO pretreated at 973 K in air for 1 hr.

ble 1), with the TPR curves becoming more complex (Fig. 1). Heat treatment of the catalytic precursor at 773 K for 3 hr resulted in total reduction (Table 1, entries 5 and 6) and simplified TPR curves (Fig. 1, curves B and C). This difference in reducibility can be attributed to a strong interaction with the catalyst support. In the original preparation of this catalyst (*36*), kieselguhr was used as support and the precursor exhibited a facile decomposition into CuO in boiling water. In our case, however, no decomposition was observed under such conditions, and the precursor turned black, indicating the formation of CuO only after high-temperature calcination.

The search for a probe molecule led to *cis*-1,2-dimethylcyclopropane which proved to be a suitable indicator for the detection of ionic species of the catalysts. The ring opening of cyclopropanes is a well-known reaction on transition metal catalysts, whereas it has scarcely been studied on the catalysts of the IB group elements. On transition metals the usual products are saturated hydrocarbons, derived from rupture of the sterically less hindered C–C bond (*37*). On gold film, however, in the ring opening of *gem*-dimethyl- and *gem*-diethylcyclopropanes, isomerization occurred with rupture of the sterically hindered C–C bond at 648 K (*38*). Copper is also known to be capable of catalyzing the ring opening of three-membered hydrocarbon ring systems (*32*).

The transformation of *cis*-1,2-methylcyclopropane was studied in a circulation system in oxygen-free hydrogen at 523 K. Catalyst samples (30 mg) were reduced in flowing hydrogen (1 hr each at 473, 523, and 573 K, respectively) before the reaction. The product distribution was monitored with a Carlo Erba Fractovap 2150 GC. On the Cu on Cab-O-Sil catalysts used in this study, *cis*-1,2-dimethylcyclopropane opens in both the sterically less hindered **a** and the sterically hindered **b** directions (see scheme below), except on the specimen with 1.1% copper loading. Cleavage **a** yields isopentane, while cleavage **b** gives both *n*-pentane and 2-pentenes. On the 1.1% Cu/Cab-O-Sil catalyst, the hindered C–C bond breaks exclusively (Table 2),



*n*-Pentane and isopentane form on the atomic clusters of the catalysts consisting only of Cu(0) atoms. The olefins, however, may form on electrophilic centers of the surface. These active sites are not on the support, as it has proved to be inactive up to 573 K; i.e., they must be present on the metallic surface. The above results indicate that an increase in copper loading decreases the quantity of the unreduced species; accordingly, the higher the loading, the higher the chance of getting a surface with predominantly Cu(0) atoms. It also means that the extent of reaction due to the unreduced (electrophilic) species should decrease with increasing copper content of the catalysts.

Just such behavior was in fact observed on our catalysts. As the loading increases, the rate of formation of 2-pentenes decreases and hardly any alkene can be found on the catalyst with 46.8% copper (Fig. 2).

TABLE 2

Typical Product Distributions in the Ring Opening Reaction of *cis*-1,2-Dimethylcyclopropane over Cu/Cab-O-Sil Catalysts (30 mg) at Different $H_2$ Pressures at 523 K

| Loading (%) | $pH_2$ (kPa) | Quantity of products (mol%[a]) | | |
|---|---|---|---|---|
| | | Isopentane | *n*-Pentane | 2-Pentenes |
| 1.1 | 27 | 0 | 0.5 | 0.5 |
| | 66 | 0 | 1.5 | 0.3 |
| 3.0 | 27 | 0.6 | 12.4 | 0.2 |
| | 67 | 2.3 | 13.5 | 0.5 |
| 6.8 | 27 | 2.9 | 13.0 | 0.1 |
| | 66 | 3.2 | 12.6 | 0 |
| 46.8 | 39 | 1.0 | 11.5 | 0.2 |
| | 68 | 0.4 | 10.8 | 0 |

[a] Sampling is after 5 min.

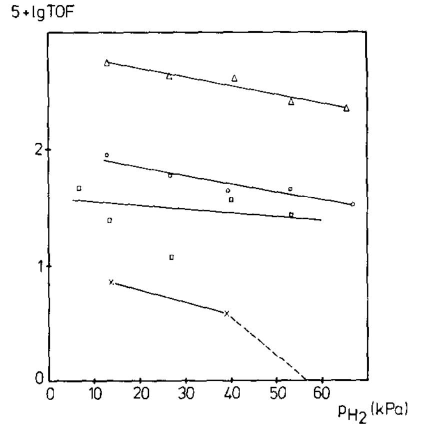


FIG. 2. Rate of formation of 2-pentenes as a function of hydrogen partial pressure on Cu/Cab-O-Sil catalysts (△, 1.1%; ○, 3.0%; □, 6.8%; ×, 46.8%). *Note.* There was no 2-pentene formation at 56.5 kPa $H_2$ pressure and above, over 46.8% Cu/Cab-O-Sil catalyst.

Although *n*-pentane could also be formed as a result of the readsorption and subsequent hydrogenation of the alkenes, direct hydrogen uptake (ring opening by hydrogenolysis) is more probable, as the quantity of 2-pentenes is negligible even at low hydrogen pressure.

To summarize, we have proved that

—the observation of Kohler *et al.* (*1*) on the unreducibility of a certain portion of copper in catalysts prepared by ion exchange also holds for catalysts prepared by precipitation;

—in contrast with earlier observations, the unreduced copper could not be reduced even at high temperatures;

—a correlation exists between the fraction of unreduced copper and the alkene-forming ability of the catalysts in the ring opening transformation of *cis*-1,2-dimethylcyclopropane.

It is worth emphasizing that this latter observation is a new example indicating that metallic Cu is not the only active species in transformations catalyzed by copper catalysts. Similar examples of our earlier findings are the activity of ion-exchanged $Cu/SiO_2$ catalysts in the double-bond migration of certain alkenes (*34*) and the ability of copper to catalyze the isomerization of methyloxirane to propanal (*25*).

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