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NOTE

Characterization of Ru–Cu Catalysts Using H_2 Chemisorption at 77 K

Ru–Cu catalysts constitute an interesting catalytic system. Supported Ru catalysts are highly active for reactions involving hydrogen such as hydrogenolysis of alkanes and hydrogenation of CO. Cu, on the other hand, has negligible activity for these reactions. Thus, in Ru–Cu catalysts, Cu can be considered to be an inactive component (1). In early work by Sinfelt *et al.* (1), it was known that Cu could not alloy with Ru. However, due to the limitations of standard characterization techniques, it was difficult to access how Cu interacted with Ru. It was not clear what kind of intimate contact there was between Cu and Ru nor what the fraction of Ru atoms exposed was.

The dispersion of a supported metallic catalyst is an important parameter for comparing reaction results. The traditional way that dispersion is determined is by chemisorption, especially of H_2. At room temperature, Cu does not readily adsorb H_2. Unfortunately, it has been found that on Ru–Cu bimetallic catalysts hydrogen can spillover to Cu, which can lead to overcounting of Ru surface atoms (2–5). CO TPD, based on the assumption that CO does not spillover to Cu, has been used to measure the dispersion of supported Ru–Cu catalysts (6). However, CO has also been determined to migrate to Cu (5).

The only successful method to date for determining the number of surface Ru atoms in supported Ru–Cu catalysts has involved the use of H-NMR to identify quantitatively chemisorbed hydrogen on Ru vs that on Cu (7–8). Recently, Yates *et al.* (2) found that at 100 K hydrogen spillover is suppressed on a Cu-covered Ru(0001) surface and each Ru atom exposed chemisorbs a single H atom. This latter result suggests a means by which traditional volumetric H_2 adsorption can be applied to measure the number of surface Ru atoms in supported Ru–Cu catalysts without necessitating the use of H-NMR.

In this work, static volumetric H_2 chemisorption at liquid nitrogen temperature was used to measure the fraction of surface Ru atoms in highly dispersed Ru–Cu catalysts. The results are compared to those from H-NMR for a similar set of catalysts (7, 8) and to those for Cu-covered Ru(0001) (2).

A Ru/SiO_2 base catalyst was prepared using the incipient wetness impregnation method. $Ru(NO)NO_3$, dissolved in distilled water, was impregnated into Cab-O-Sil HS5 fumed silica. The catalyst precursor was dried at 363 K overnight and heated in flowing hydrogen at the heating rate of 1 K/min to 673 K and then reduced at this temperature for 8 h. After reduction, the catalyst was washed with boiling distilled water and filtrated at least five times in order to remove most of any Cl ions present. The catalyst was dried again at 363 K overnight. The catalyst contained 3% ruthenium (by weight). H_2 chemisorption at 298 K (see below) determined the percent dispersion and the average Ru particle size to be 36% and 2.4 nm, respectively, for this base catalyst. Different amounts of Cu were added to the Ru/SiO_2 base catalyst using the incipient wetness impregnation method and an aqueous solution of Cu nitrate. The Cu-modified catalysts were then re-reduced as mentioned above. Elemental analysis was done by Galbraith Lab., Inc. using atomic absorption (AA). Nomenclature used to identify the catalysts is Cu/RuS*xx*, where *xx* indicates the nominal Cu/Ru atomic ratio.

Static chemisorption was carried out in a Pyrex glass system. All the stopcocks were glass and were greased with Apizon-L (vapor pressure $<10^{-9}$ Torr, 1 Torr = 1 mm Hg = 133.3 Pa). A turbo-molecular pump backed by a mechanical pump was used to achieve a minimum pressure in the system of ca. 2×10^{-7} Torr.

Around 1 g of catalyst was loaded into a pyrex cell, then connected to the system. The catalyst was heated in H_2 (Research Grade, 99.99%, Liquid Carbonic) at 1 K/min to 673 K and kept at this temperature for 10 h. During this period, the catalyst was purged with pure H_2 three times in order to remove water vapor created during re-reduction. The catalyst was degassed for 2 h at 673 K, cooled to room temperature, and then further cooled to 77 K. Before introducing H_2, a system pressure $<2 \times 10^{-7}$ Torr was attained. Chemisorption measurement at room temperature was made following the procedure as described in (9). For adsorption at 77 K, the procedure was modified. Equilibrium was assumed when no pressure change could be noted within 24 h. Equilibrium adsorption

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TABLE 1

Composition of Ru–SiO$_2$ Catalysts

Catalyst	Nominal atomic ratio Cu/Ru	Atomic ratio Cu/Ru from AA[a]
Cu/RuS00	0.0	0.0
Cu/RuS05	0.05	0.04
Cu/RuS10	0.10	0.10
Cu/RuS20	0.20	0.18
Cu/RuS50	0.50	0.42

[a] Atomic absorption (Galbraith Lab., Inc.).

measurements were made for equilibrium pressures of 100–400 mm Hg. It took around 24 h for each equilibrium point after the first. The isotherms were extrapolated to zero pressure, and the difference was taken as a measure of irreversible hydrogen chemisorption.

Chemisorption experiments were done on both SiO$_2$ and Cu/SiO$_2$. No significant uptake of H$_2$ was detected under the conditions used.

A comparison of the actual and nominal Cu/Ru ratios is given in Table 1. The results show that the actual was close to the nominal. All calculations are based on the actual values.

The isothermal uptakes vs pressure on Cu/RuS00 and Cu/RuS50 at 298 and 77 K are given in Figs. 1–4. The irreversible uptakes for Cu/RuS00, the catalyst without any Cu, at the two different adsorption temperatures as shown in Table 2, are almost the same, suggesting that equilibrium chemisorption was able to be reached at 77 K within measurement time frame used. Table 2 also shows that, at 298 K, the irreversible uptake did not change much with Cu loading. This is what one would expect for hydrogen spillover onto the Cu decorating the Ru surface, and the Ru particle size distribution can be assumed to be approximately identical for all the catalysts. However, at 77 K, the irreversible uptake decreased greatly with an increase in Cu loading, suggesting that hydrogen spillover, occurring readily at room temperature, is suppressed at 77 K.

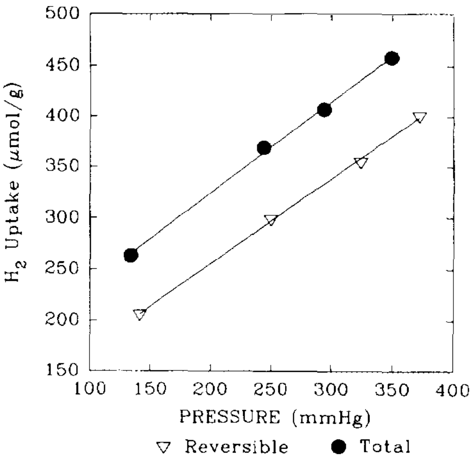

FIG. 2. Adsorption isotherm for H$_2$ on Ru/SiO$_2$ at 77 K.

The use of H-NMR to measure hydrogen chemisorption on Ru–Cu catalysts (7, 8) can be considered to be the most successful method to date for determining the number of Ru atoms exposed. The advantage of NMR is that different adsorption states of H can be identified. Three kinds of NMR peaks for H can be assigned: H adsorbed on Cu, irreversibly adsorbed H on Ru, and reversibly adsorbed H on Ru. Figure 5 shows a comparison between the results from NMR (7, 8), from this work for a similar series

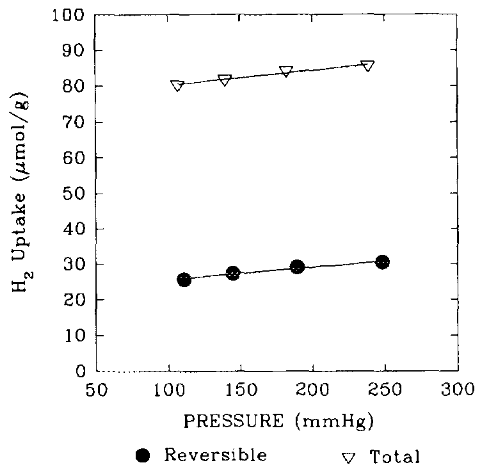

FIG. 1. Adsorption isotherm for H$_2$ on Ru/SiO$_2$ at 298 K.

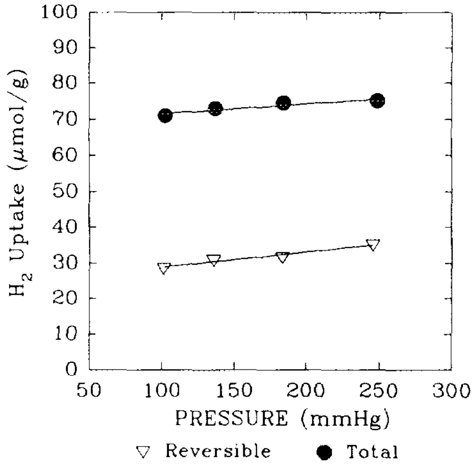

FIG. 3. Adsorption isotherm for H$_2$ on Ru–Cu/SiO$_2$ (Cu/RuS50) at 298 K.

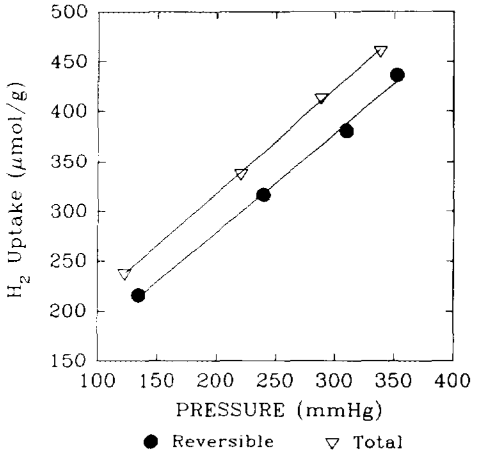

FIG. 4. Adsorption isotherm for H_2 on Ru–Cu/SiO_2 (Cu/RuS50) at 77 K.

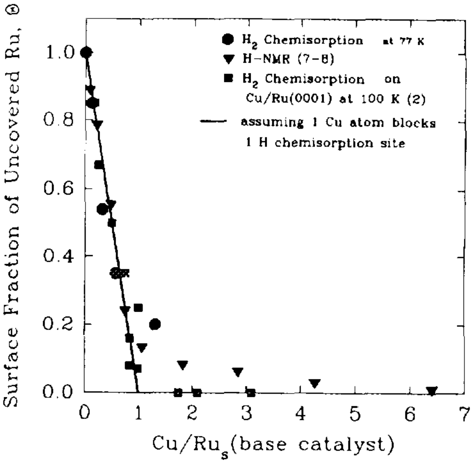

FIG. 5. Surface fraction of Ru versus Cu/Ru_s (base cat.).

of Ru–Cu–SiO_2 catalysts, and from H_2 chemisorption at 100 K on Cu/Ru(0001) (2). It shows the agreement among these methods in terms of relationships between the number of H_2 chemisorption sites and Cu coverage. As can be seen in Fig. 5, a monolayer coverage of Ru by Cu is predicted when the ratio of Cu/Ru_s (base catalyst) is around 1. However, based on Fig. 5, a monolayer coverage of Ru by Cu is not reached until higher loadings of Cu than the theoretical minimum. This is probably due to the fact that, while initially two-dimensional Cu islands are formed, with increasing Cu/Ru_s ratio three-dimensional Cu island formation or even Cu particle formation can occur, as speculated earlier by Wu *et al.*(8) and indicated by theoretical simulation (10). This appears to be the case especially where the Ru is dispersed on a high surface area support such as silica. Thus, high Cu/Ru ratios would be required before complete blockage of the Ru surface occurs. On a model surface such as Ru(0001), this would not appear to be the case, and full coverage of the Ru by Cu occurs for Cu/Ru_s = 1.

TABLE 2

H_2 Chemisorption on Ru–Cu/SiO_2

Catalyst	Irreversible H_2 uptake (µmol/g) 298 K	77 K	θ_{Ru}[a]
Cu/RuS00	54.0	56.4	1.00
Cu/RuS05	46.7	48.2	0.85
Cu/RuS10	39.7	30.2	0.54
Cu/RuS20	43.1	19.5	0.35
Cu/RuS50	44.2	11.5	0.20

[a] Assuming $H_{irrev}/Ru_s = 1$ at 77 K, $\theta_{Ru} = H_{irrev}(Cu/RuSxx)/H_{irrev}(Cu/RuS00)$.

The following conclusions can be drawn:

(1) The correlation between this work, H_2 chemisorption at 100 K (2), and H-NMR (7, 8) suggests that traditional volumetric H_2 chemisorption at 77 K can be used to measure accurately the number of exposed Ru atoms in supported Ru–Cu catalysts.

(2) The correlation between surface fraction of ruthenium and the coverage of Cu from three different methods strongly suggests that one Cu atom blocks one H chemisorption site as long as only two-dimensional Cu islands are formed.

(3) Three-dimensional Cu structures are able to form before monolayer coverage of Ru by Cu is complete.

(4) These results suggest a means for potentially characterizing other bimetallic systems, especially where there exists no alloy formation. Even when both metals can adsorb a gas, such as H_2, at room temperature, the kinetics of adsorption at low temperature on one of the metals may be sufficiently slow so that, in the absence of spillover, an accurate measurement can be made of adsorption on the surface atoms of the other metal.

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