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The Effect of Reduction Temperature on the Chemisorptive Properties of Ru/SiO_2: Effect of Chlorine

Chemisorption techniques are frequently used to determine the surface areas of supported metal catalysts. In the case of Ru, hydrogen adsorption (*1–8*), oxygen adsorption (*4, 5, 11*), and CO adsorption (*5–10*) have been used. However, it has also been reported (*12, 13*) that Ru catalysts derived from the reduction of $RuCl_3 \cdot 3H_2O$ contain residual chloride following reductive pretreatment in hydrogen. Because we suspect that this residual chloride may in part be responsible for inconsistencies in the reported values of the adsorption of both hydrogen and CO, we have performed a chemisorption study aimed at clarifying these inconsistencies. In this note we report on the effect of catalyst pretreatment temperature on the adsorptive properties of Ru/SiO_2 as a function of residual chloride concentration.

The silica-supported catalysts used in this study were prepared by standard impregnation techniques. Initially, the appropriate weight of $RuCl_3 \cdot 3H_2O$ (Mitsuwa Chemical Co., Japan) was dissolved in an amount of deionized water sufficient to ensure the complete wetting of the support. The solution was mixed with SiO_2 (Aerosil 380, Japan Aerosil Co.) until a slurry having the consistency of a thin paste was formed. The slurry was dried in a vacuum desiccator at room temperature for several days and stirred regularly during the drying process to ensure uniformity.

The dried catalyst was crushed and sieved. The fractions between 60 and 200 mesh were used for the chemisorption study. A rather high Ru metal loading (1.2 mmol Ru/g or 10.8 wt%) was used in order to facilitate the analytical measurements.

Chemisorption measurements were performed at room temperature using the dynamic pulse technique (*14*). The gases used in this study were all research grade or better. The carrier gas, 99.999% argon (Nipson Sanso) or 99.99% helium (Showa Denko), was purified by passing it over a heated copper catalyst at 500 K backed up by a molecular sieve, 5 Å. The purity of the carrier gas was confirmed by means of an O_2–CO titration technique (*15*). In this method, the carrier gas is circulated over a Pt/SiO_2 catalyst for periods in excess of that required to perform an experiment. The oxygen content in the carrier gas can be obtained by measuring the CO_2 evolved following titration of the Pt surface with CO.

$$\mathrm{Pt(s)} + \tfrac{1}{2}\,\mathrm{O_2(g)} \rightarrow \mathrm{Pt(s){-}O} \qquad (1)$$

$$\mathrm{Pt(s){-}O} + 2\mathrm{CO} \rightarrow \mathrm{Pt(s){-}CO} + \mathrm{CO_2(g)} \qquad (2)$$

PROCEDURE

The sample was first evacuated at room temperature for 10 min. The temperature was then increased to 400 K in vacuum and outgassed at that temperature for 1 h. Hydrogen was passed over the catalyst at a rate of 30–60 ml/min and the temperature was increased at a rate of 10 K/min to each of the reduction temperatures used in this study. Reduction was carried out in flowing hydrogen at each temperature for 3 h, followed by evacuation at the same temperature for 30 min. The catalyst was then cooled to room temperature. The hydrogen was purified by passing it through a reduced MnO trap and a molecular sieve to remove oxygen and traces of water.

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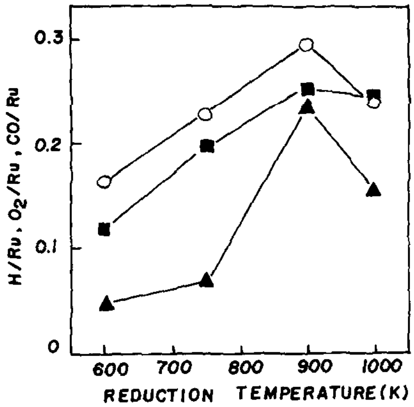

FIG. 1. Hydrogen, oxygen, and CO chemisorption of Ru/SiO_2 as a function of reduction temperature. ▲, hydrogen adsorption (H/Ru); ■, oxygen adsorption (O_2/Ru): ○, CO adsorption (CO/Ru).

TABLE 1

Metal Particle Size of Ru/SiO_2 Reduced at Various Temperatures Estimated by X-ray Line Broadening and Chemisorption of H_2, CO, and O_2

Reduction temperature (K)	Particle size of Ru (Å)				
	X-ray	H-ads	Co-ads	O_2-ads	CO + Cl[a]
600	25–30	216	65	92	25
750	25–30	164	50	58	24
900	25–30	43	37	42	27
1000	30–35	64	44	43	36

[a] The particle size of Ru is estimated on the assumption that CO + Cl represents the total number of surface Ru atoms.

The choline content of the catalysts was measured using an X-ray fluorescence spectrometer (Rigaku XDF-DS).

RESULTS AND DISCUSSION

Chemisorption experiments. The adsorption of CO and hydrogen as a function of reduction temperature is show in Fig. 1. The adsorption of CO and O_2 tracked one another quite closely as the reduction temperature was increased. However, the chemisorption of hydrogen was strongly suppressed when the reduction temperature was 600 K. For all of the gases studied, the amount of chemisorption increased markedly as the reduction temperature was increased. A chemisorption maximum was observed at a reduction temperature of 900 K.

Particle size as measured by X-ray diffraction line broadening was almost constant when the reduction temperature was less than 900 K (Table 1). An increase in particle size was observed following reduction in H_2 at 1000 K. This increase in particle size is undoubtedly due to sintering of the metal particles at the higher reduction temperatures.

The adsorption of CO as a function of both reduction temperature and residual chloride concentration is shown in Fig. 2. It is immediately apparent from these data that the adsorption of CO is strongly dependent on the concentration of residual chloride left on the catalyst following reduction. If it is assumed that Ru sites occupied by chloride do not chemisorb CO in the presence of an argon carrier gas, the total number of exposed Ru sites can be calculated as the sum of the CO chemisorbed and the residual chloride. These data are also shown in Fig. 2 and are remarkably constant over the 600–900 K reduction temperature range. The Ru crystallite size calculated using this assumption is shown in Table 1. The value is in very good agreement with the particle size obtained from X-ray line broadening. This is in marked contrast to

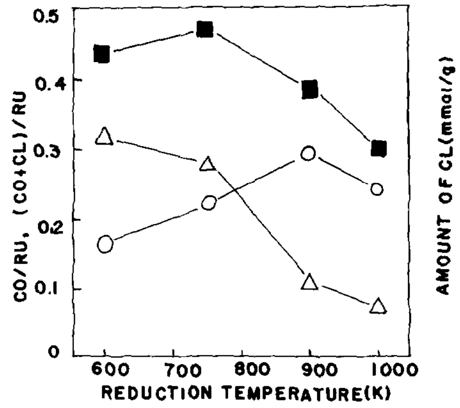

FIG. 2. CO chemisorption on Ru/SiO_2 as a function of residual chloride concentration and reduction temperature. △, chloride concentration (mmol of Cl/g of catalyst); ○, CO adsorption (CO/Ru); ■, sum of CO adsorption and residual Cl (CO + Cl/Ru).

crystallite sizes obtained from only chemisorption. For this reason, we suggest that the chloride is intimately associated with the metal rather than with the support.

When the chloride concentration was decreased by reduction at 900 K, subsequent CO adsorption experiments following reduction at 600 K gave identical CO chemisorption results (Fig. 3).

Because hydrogen is dissociatively absorbed on Ru, it is reasonable to expect that dual-surface sites are required for hydrogen adsorption while single-surface sites suffice for CO and oxygen adsorption (surface stoichiometry: CO/Ru = 1 and O_2/Ru = 1). This means that the presence of chloride should inhibit the adsorption of hydrogen to a greater extent than CO, as is observed. This hypothesis was tested by plotting the fraction of the surface used for hydrogen adsorption, H/(CO + Cl), as a function of the fraction of the surface used for CO adsorption, CO/(CO + Cl). The resulting plot shown in Fig. 4 conforms to the parabolic relationship $y = x^2$. This suggests that the residual chloride blocks both hydrogen and CO chemisorption. Hydrogen adsorption is inhibited to a greater extent than CO due to the dual-site requirement.

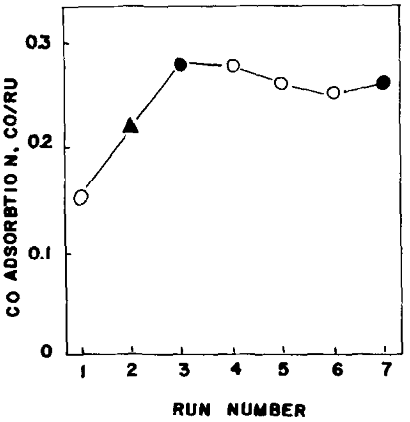

FIG. 3. Effect of the catalyst pretreatment history on CO chemisorption on Ru/SiO_2 reduced at different temperatures. ○, reduced at 600 K (CO/Ru); ▲, reduced at 750 K (CO/Ru): ●, reduced at 900 K (CO/Ru).

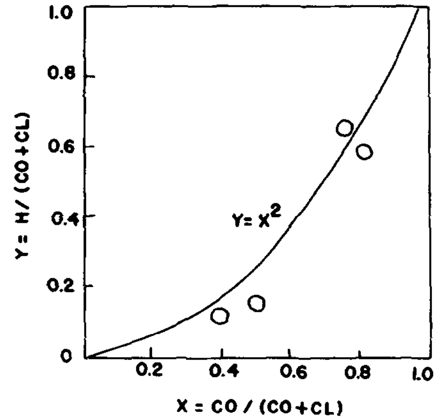

FIG. 4. Parabolic relationship between hydrogen and CO chemisorption y = H/(CO + Cl); x = CO/(CO + Cl). A $y = x^2$ fit is obtained.

The relatively large concentrations of chloride remaining on the surface following reduction in hydrogen at temperatures in excess of 700 K appear to be unique to Ru. Studies currently in progress in our laboratory on Pd/SiO_2, Rh/SiO_2, and Pt/SiO_2 show only trace amounts of chloride following reduction in hydrogen at 700 K. For the case of Pd/SiO_2 prepared by impregnation from $PdCl_2$ salts, reduction in hydrogen at 450 K eliminated virtually all of the chloride from the catalyst surface. Likewise, a 600 K reduction of Rh/SiO_2 reduced the chloride concentration to less than 1 at.% of Rh. Unlike alumina, silica does not incorporate chloride into its structure. Neutron activation studies show that the chloride concentration of Pt/Al_2O_3 catalysts prepared from $H_2PtCl_6 \cdot 6H_2O$ is about two orders of magnitude greater than that observed over a Pt/SiO_2 catalyst prepared and treated in the same way (*16*). For this reason, we are quite confident that the chloride is intimately associated with the Ru rather than with the support.

The relative reducibility in hydrogen of several noble metal chlorides is given by Anderson (*17*) as follows:

$$PtCl_2 > RuCl_3 > IrCl_2 > RhCl_3.$$

The relatively large surface energy of Ru compared to Rh and Pd should be taken into account. Anderson (*18*) reports that the relative surface energies for several catalytically important metals are as follows:

$$\text{Ru, Mo, Ir } (2.25) > \text{Rh } (2.00) > \text{Pt } (1.80) > \text{Pd } (1.5).$$

If we consider the following reduction reactions,

$$RuCl_3 + \tfrac{3}{2} H_2 \rightarrow \text{Ru (bulk)} + 3HCl \quad (3)$$

$$RuCl_3 + \tfrac{3}{2} H_2 \rightarrow \text{Ru (surface)} + 3HCl, \quad (4)$$

the relatively large difference in energy between bulk Ru and surface Ru requires that reaction (4) take place at considerably higher temperatures than reaction (3). In the case of Pd, the much lower difference between surface and bulk energy should enable reduction to be completed at much lower temperatures.

The important conclusion that emerges from this study is that unless the chloride content of a Ru/SiO_2 catalyst is reduced to a very low level, metal surface areas obtained using either CO, O_2, or hydrogen chemisorption grossly underestimate the total number of exposed Ru surface sites. The error is particularly severe for the case of hydrogen chemisorption measurements carried out at room temperature. This is undoubtedly due to the dual-site adsorption requirement for hydrogen. Chemisorption measurements using hydrogen carried out at higher temperatures are probably more accurate due to the greater mobility of hydrogen. However, the dynamic pulse method becomes difficult to use at higher temperatures so that the use of a static chemisorption technique becomes advisable.

There is no question that CO or O_2 chemisorption gives a more accurate measure of the Ru surface area. However, considerable underestimation results when the catalyst is reduced at temperatures below 900 K. We have found that steam treatment at 673 K was effective in reducing the chloride concentration considerably. Reduction in hydrogen at temperatures in excess of 900 K is impractical due to the onset of sintering. The use of nonchlorine-containing salts for the preparation of Ru/SiO_2 may be advisable if a chloride-free catalyst is desirable.

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