

## Highly Disperse Ruthenium-Silica Catalysts

The most readily available chemical for the preparation of ruthenium catalysts is hydrated  $\text{RuCl}_3$ . Catalysts prepared by impregnation of  $\text{SiO}_2$  with solutions of  $\text{RuCl}_3$  typically do not have a dispersion exceeding 0.2 (1-4). Using  $\text{Al}_2\text{O}_3$  supports, higher dispersion is often obtained, which can approach unity for catalysts of low metal content (3, 5-8). This is not surprising, since these solutions undoubtedly contain ruthenium in the form of chloro-anions. Alumina has substantial anion exchange ability, whereas silica does not (9). There are isolated examples of somewhat higher dispersions obtained for  $\text{Ru-SiO}_2$  catalysts (10), but the reasons for the improved dispersion are not clear.

A very successful method of preparing  $\text{Pt-SiO}_2$  catalysts of high dispersion is the adsorption on  $\text{SiO}_2$  of cationic ammine complexes at high pH (11). This is apparently not feasible with  $\text{Ru(III)}$  amines, which are unstable, and yield anionic hydroxy complexes at the high pH values needed to ionize the  $\text{SiO}_2$  surface (12). An alternative is to use  $\text{Ru(II)}$  complexes. This has been done by Kobayashi and Shirasaki (13), but few details of the preparation are given, and the carbon monoxide adsorption results quoted suggest a much lower dispersion than obtained here.

A solution containing a mixture of  $\text{Ru(II)}$  ammine species is readily obtained by hydrazine reduction of aqueous  $\text{RuCl}_3$  (14). Our first attempts involved addition of  $\text{SiO}_2$  to such a solution, with occasional shaking while adsorption occurred. Adsorption was essentially complete in a few hours, and catalysts of about 0.4 dispersion were obtained. It was found, however, that higher dispersions ranging from 0.6 to 0.8 are achieved if the  $\text{SiO}_2$  is added to the  $\text{RuCl}_3$

prior to reduction and is present throughout the reduction process.

The following procedure was used for the preparation of catalysts containing 1 to 5%  $\text{Ru}$  by weight. We placed 0.5 to 2 g of  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  (42.1%  $\text{Ru}$ ) in a flask and dissolved it in 2 ml of  $\text{H}_2\text{O}$  per gram of  $\text{SiO}_2$ . The calculated amount of  $\text{SiO}_2$  (Davison 923, air-dried at  $250^\circ\text{C}$ ) was then added, and the mixture was shaken. Hydrazine hydrate, 0.8 ml per gram of  $\text{SiO}_2$ , was then added slowly, with constant shaking. When the evolution of  $\text{N}_2$  had subsided to a low level, the flask was stoppered and allowed to stand overnight at room temperature, with occasional shaking. After this period, the pH of the mixture was in the range  $9.3 \pm 0.2$ . This mixture was then filtered, and the catalyst was washed with cold 1 *M* ammonia. The filtrate and washings were combined and analyzed for  $\text{Ru}$  content by atomic absorption spectroscopy to obtain a value for the fraction of  $\text{Ru}$  incorporated in the catalyst. The catalyst was air-dried at  $100^\circ\text{C}$  and reduced in flowing  $\text{H}_2$  at 150-200 ml/min. The reduction temperature was  $100^\circ\text{C}$  for 2 hr, and was then raised slowly to  $350^\circ\text{C}$  and held for another 2 hr. The catalysts were cooled in  $\text{H}_2$  and stored in air.

Before use the catalysts were reduced in static  $\text{H}_2$  at  $100^\circ\text{C}$  until no further  $\text{H}_2$  consumption occurred. They were then pumped, heated to  $350^\circ\text{C}$ , and reduced at this temperature for a further 2 hr with  $P_{\text{H}_2} = 100$  Torr. The  $\text{H}_2$  consumption in this step was typically a few percent of that consumed in the initial reduction at  $100^\circ\text{C}$ . The catalysts were then pumped for 16 hr at  $350^\circ\text{C}$  before adsorption experiments. During the static reduction and pumping, a liquid  $\text{N}_2$  trap was present in close proximity to the sample to remove evolved water. At

TABLE 1  
Catalyst Characteristics

Composition <sup>a</sup>	Percentage Ru uptake	$d_{\text{H}_2}$ <sup>b</sup>	$d_{\text{O}_2}$ <sup>c</sup>	CO/H <sup>d</sup> uptake
1.00	98	0.81	0.49	1.5
2.03	99	0.78	0.55	1.7
2.95	96	0.70	0.60	1.9
5.02	98	0.61	0.64	2.3

<sup>a</sup> Weight percent Ru in the finished catalysts.

<sup>b</sup> Dispersion, measured by H<sub>2</sub> adsorption, assuming a surface stoichiometry of RuH (see text).

<sup>c</sup> Dispersion, measured by O<sub>2</sub> adsorption, assuming a surface stoichiometry of RuO<sub>2</sub>.

<sup>d</sup> Adsorbed CO molecules/H atoms (see text).

the end of high-temperature pumping, the dynamic vacuum was always better than 10<sup>-5</sup> Torr. Repetition of this reduction/pumping schedule on the same catalyst, followed by hydrogen adsorption, gave identical results within experimental error, indicating the adequacy of the initial reduction. The pumping time could be shortened to 1 hr by using a temperature of 450°C at the expense of a 10–20% loss in metal dispersion. The characteristics of the catalysts studied are given in Table 1.

Dispersions of the catalysts were measured by adsorption of H<sub>2</sub> and O<sub>2</sub>. There appears to be a good agreement among previous workers that the surface stoichiometry for hydrogen adsorption is RuH (1, 5, 8, 15). This stoichiometry is in agreement with electron microscopic particle size determinations, for dispersions approaching unity, in the case of Ru–Al<sub>2</sub>O<sub>3</sub> catalysts (1). In the case of O<sub>2</sub> chemisorption, the surface stoichiometry is less clear. Some workers favor a stoichiometry of RuO (5, 16) while others suggest RuO<sub>2</sub> (7, 8, 15, 17). There is no obvious reason for the discrepancies between these various results.

Hydrogen adsorption on the present catalysts is a slow process, as has been found by previous workers (1, 8, 18), and the adsorption kinetics are complex. An initial rapid adsorption is followed by a stage which obeys Elovich kinetics (linear rela-

tionship between amount adsorbed and log (time)). If the pressure is sufficiently high, a break eventually occurs in the  $n$  vs  $\log(t)$  plot, which is followed by a regime in which the slope is much lower, but generally non-zero. The time required to reach the break point decreases as the pressure is raised, and as the Ru loading of the catalyst is decreased.

The coverages at the break point, when plotted against pressure, have the appearance of an adsorption isotherm. We therefore interpret the break points as indicating termination of the surface adsorption process, and extrapolate the resulting nearly horizontal isotherm to zero pressure to obtain the hydrogen coverage. The above is a cumbersome process, since the time required is excessive. As an alternative, a single pressure measurement can be used. If adsorption is carried out at  $P = 200$  Torr, the break point occurs in less than 2 hr for all catalysts. The coverage at the break point is then corrected for physical adsorption on the support, measured on a sample of pure SiO<sub>2</sub>. The result agrees within 5% with the result of the extrapolation procedure. The dispersions given in Table 1 are calculated by the single-point procedure.

Oxygen, by contrast, adsorbs quickly on these catalysts, equilibrium being reached in a few minutes at room temperature. The isotherm saturates at a few Torr of pressure, and is nearly horizontal at higher pressures. The nearly horizontal section was extrapolated to zero pressure, in order to obtain O<sub>2</sub> uptakes. The dispersions in Table 1 were calculated from these uptakes assuming a surface stoichiometry of RuO<sub>2</sub>.

Adsorption of carbon monoxide was also studied on the catalysts. The initial stages of adsorption are fast, a coverage of one CO per surface atom (based on H<sub>2</sub> dispersion) being reached in minutes. Substantially more CO can be adsorbed, in times which increase with the amount adsorbed, but not in accord with Elovich kinetics. Table 1 gives the amount of CO adsorbed in 1 hr at 50 Torr at room temperature, cor-

rected for support adsorption. This amount is expressed as a ratio to adsorbed H atoms, determined from uptake measurements as above.

As can be seen from Table 1, neither the O/H nor CO/H ratio is constant in this series of catalysts. The dispersion calculated from RuO<sub>2</sub> stoichiometry agrees reasonably well with that obtained from hydrogen adsorption only in the case of the 5% catalyst. Discrepancies become progressively larger at lower metal content, i.e., at higher dispersions, assuming the correctness of the hydrogen dispersions. An assumed stoichiometry of RuO is untenable, as it would lead to dispersions greater than unity in three of the four cases studied. It seems best to conclude that O<sub>2</sub> adsorption cannot reliably be used for dispersion measurements on very finely divided Ru.

As can be seen from the table, all catalysts adsorb more than one CO molecule per surface atom, and more than two for the 5% catalyst. This is not surprising, as the presence of Ru(CO)<sub>2</sub> groups has been established by infrared spectroscopy (6, 19). Multiple CO adsorption per Ru requires small particles, as it is found not to occur on single-crystal surfaces (20–23) or on supported catalysts of low dispersion (6, 13, 16). On small polyhedral particles, the presence of many corner and edge atoms can permit the CO/Ru ratio to approach 3 or 4, as is found in the cluster carbonyls such as H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> or Ru<sub>3</sub>(CO)<sub>12</sub>.

In view of the above, the trend of CO coverage in Table 1 is, at first glance, surprising. As can be seen, the CO/Ru ratio decreases on the more disperse catalysts. The data in this table are, as noted, not equilibrium adsorption data. If the adsorption time is increased to 24 hr, the CO coverage in all cases increases by 10–20%, but the trend shown in the table remains. A simple explanation of this would be that, at the lower metal contents, a substantial fraction of the Ru is present as monatomic rafts. If these were reasonably large, they would present substantial close-packed ar-

reas on which CO/Ru would be less than unity, while still showing a high dispersion as measured by H<sub>2</sub> adsorption. The trends in the table could then be explained, either by a variation in raft size distribution with metal content or, more likely, by a variation of the relative proportions of rafts and polyhedra. There is some electron microscopic evidence (10) for the formation of rafts in Ru/SiO<sub>2</sub> catalysts of low metal content. It might also be the case that such variations in morphology with metal loading are responsible for some of the inconsistencies of O<sub>2</sub> adsorption noted above.

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