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Measurement of Ruthenium Metal Surface Area by Chemisorption

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Hydrogen adsorption isotherms were measured on unsupported and supported Ru catalysts and compared with argon BET surface areas and particle size distributions measured by electron microscopy. At 21°C and pressures above 120 Torr, the adsorption on Ru metal powder was consistent with a surface stoichiometry of $Ru_{(s)}$–H. Also, good agreement was obtained between particle size calculated from hydrogen adsorption and the particle size distribution observed by electron microscopy.

INTRODUCTION

Adsorption of hydrogen and carbon monoxide on ruthenium has been reported in the literature (*1–6*), although the use of adsorption to measure metal surface area has not been discussed in great detail. In several of these reports, hydrogen adsorption is used to measure metal surface area (*3, 5*); but no comparison of the adsorption results with other techniques was reported. On the other hand, the use of CO adsorption appears to be complicated by several CO molecules bonding to a single surface ruthenium atom (*4, 6*). In addition, there is interference from CO adsorption on the support.

This work presents data on the adsorption of hydrogen and carbon monoxide on unsupported and supported ruthenium catalysts. The adsorption results are compared with the BET metal surface area as measured by argon adsorption and with the particle size distribution measured by electron microscopy.

EXPERIMENTAL METHODS

Apparatus

Adsorption isotherms were measured with a conventional Pyrex glass constant volume adsorption system employing greased high-vacuum stopcocks. The system was pumped by a 115 liter s^{-1} oil diffusion pump backed by a rotary mechanical pump. The pumps were isolated from the adsorption system by liquid-nitrogen-cooled traps. Pressure was measured with a Texas Instruments quartz spiral Bourdon gage.

The sample was contained in a Pyrex or quartz cell of flow-through design to permit treatment of the sample in a flowing gas stream.

Electron micrographs were obtained with a Philips EM 200 electron microscope operating at 100 kV with a magnification of 250,000 including photographic enlargement. Catalysts were either ground in a mortar and supported on parlodion film or ground in a tissue grinder and sprayed onto a carbon support.

Materials

Liquid carbonic hydrogen, 99.95% minimum purity, was passed over an Engelhard Deoxo palladium catalyst to react trace amounts of oxygen. The water formed was removed by dehydrated 5A molecular sieve at 77°K. Matheson carbon monoxide, 99.5% pure, was passed through a trap at 195°K before use. Ultrahigh-purity argon, 99.999% was used as received.

The ruthenium powder was obtained

from J. A. Samuel and Co. Supported catalysts were prepared by impregnating the dry support with sufficient ruthenium trichloride solution, Engelhard Chemical Division, to just wet the catalyst. The supports were Cab-O-Sil HS-5, a silica produced by the flame hydrolysis of silicon tetrachloride, from G. L. Cabot Corp., and Dispal M colloidal alumina, from Continental Oil Co. The 0.5% Ru/Al_2O_3 catalyst was obtained from Engelhard Industries. The 0.1% Ru/Al_2O_3 (stabilized) catalyst contained 3% by weight of lanthanum to stabilize the Ru under high temperature oxidizing conditions (*7*).

RESULTS

Prior to adsorption measurements, each sample was reduced at 400°C in hydrogen at a space velocity of 100 min^{-1} for at least 2 hr. The sample was then evacuated at 400°C for another 2 hr unless noted otherwise. After evacuation, the pressure above the sample was less than 1×10^{-6} Torr (1 Torr = 133.3 N m^{-2}).

Supported catalyst samples, evacuated at temperatures of 500, 400, and 300°C for 2 hr, gave identical hydrogen uptakes, while evacuation at 200°C for 2 hr showed an uptake smaller by 7%. Thus, evacuation at 400°C for 2 hr was adequate to remove the adsorbed hydrogen from ruthenium metal.

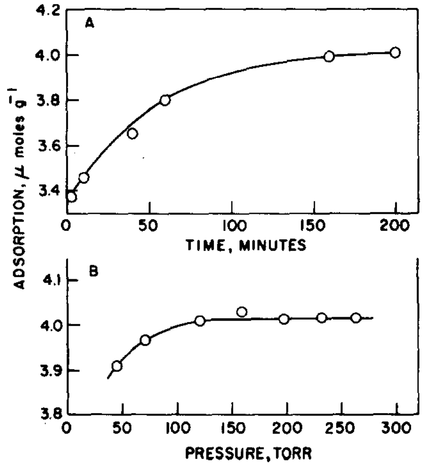

FIG. 1. Hydrogen adsorption on Ru metal powder at 21°C; (A) adsorption at a pressure of 266 Torr; (B) desorption isotherm.

Hydrogen adsorption on ruthenium approached equilibrium slowly at room temperature. Figure 1 shows typical adsorption data for ruthenium powder at 21°C. After approximately 200 min, further adsorption was negligible. The equilibrium isotherm points at lower pressures were obtained by decreasing the pressure. Desorption of hydrogen from the ruthenium was observed beginning at 120 Torr. The flat isotherm from 120 to 260 Torr indicates complete coverage of the ruthenium by hydrogen at a level of 4.01 μmoles H_2 g^{-1}. Argon adsorption at 77°K fitted to the BET equation gave a surface area for this ruthenium powder of 0.338 m^2 g^{-1}, assuming an argon area of 16.88 Å^2 (*8*).

A similarly slow adsorption was observed for carbon monoxide on ruthenium, giving a flat isotherm from approximately 100 to 260 Torr at a level of 5.06 μmoles CO g^{-1}.

A typical isotherm for hydrogen adsorption on a silica supported ruthenium catalyst, after reduction and evacuation at 400°C, is given in Fig. 2. The approach to equilibrium was slow as observed for the pure metal powders with apparent full coverage on the ruthenium being reached at about 120 Torr. In fact, it was observed that as the ruthenium particle size decreased, the rate of approach to equilibrium also decreased. In some cases the adsorption was carried out overnight. The apparent

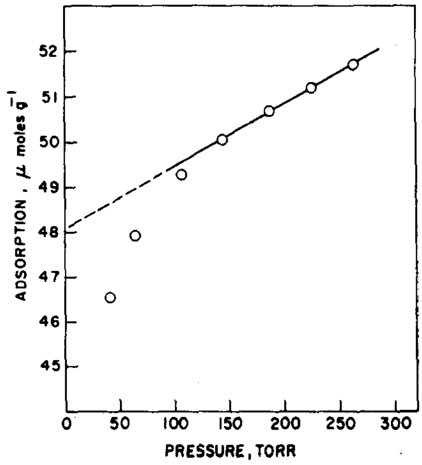

FIG. 2. Hydrogen desorption isotherm on 5% Ru/silica at 21°C.

TABLE 1
PARTICLE SIZE FROM HYDROGEN ADSORPTION AND ELECTRON MICROSCOPY

Catalyst	H_2 adsorption (μmoles/g)	d [adsorption (Å)]	[EM (Å)]	
			d_{surface}	d_{max}
5% Ru/SiO_2	48.6	43	42	30
5% Ru/SiO_2 (250°C, 4 hr, air)	39.0	53	47	45
5% Ru/Al_2O_3 (300°C, 4 hr, air)	24.5	85		60
5% Ru/Al_2O_3 (450°C, 12 hr, air)	21.2	98	98	83

nonzero slope above 120 Torr was due to physical adsorption of H_2 on the support as confirmed by a blank experiment.

The linear portion of the hydrogen adsorption isotherm above 120 Torr pressure was extrapolated to zero pressure, and the zero pressure intercept was taken as the hydrogen adsorbed on the metal. Hydrogen adsorption–desorption isotherms were measured on other silica supported ruthenium catalysts and several alumina supported samples; the results are presented in Table 1. Several of the samples were heated in air to increase the metal particle size.

The supported samples were examined by electron microscopy and the micrographs were analyzed to obtain particle size distributions. A particle size can be obtained from the surface area of the particles integrated over the particle size distribution (*9*). Since for several of the samples the distributions were incomplete at small particle size due to a lack of resolution, this procedure could not be used. A second particle size is that represented by the maximum in the distribution and for catalyst particle sizes distributed log-normally (*10*) the maximum in the distribution is close to the number average particle size.

DISCUSSION

Hydrogen adsorption on ruthenium is a relatively slow process, although steady-state coverages can be reached as noted in Fig. 1. Low and Taylor (*1*) studied the kinetics of this process on a supported catalyst and noted that measurable adsorption at 100°C took place in the time scale of hours. The adsorption kinetics followed the Elovich equation.

The steady-state coverage at room temperature in the pressure range of 120 to 250 Torr is adopted as a measure of the density of surface Ru atoms. The relation between the adsorbed hydrogen and the number of ruthenium atoms at the surface can be evaluated if the following assumptions are made concerning the crystal planes exposed by the ruthenium powder. The highest density plane for a hexagonal close-packed metal such as ruthenium ($a = 2.695$, $b = 4.273$) (*11*) is the basal plane (001) with an area of 6.29 Å^2/atom. The next highest density plane is (100), which has an area of 11.5 Å^2/atom. Assuming an equal number of surface atoms in these planes, the BET area exhibited by the ruthenium powder gives 6.31 μmoles of surface Ru/g of sample and a H_{ads}/Ru_s ratio of 1.27.

However, scanning electron microscope pictures of the ruthenium powder showed well-formed crystallites with a truncated hexagonal bipyramidal habit. The planes forming the sides of the bipyramid have an angle much greater than 90° to the basal plane, indicating the presence at the surface of planes other than the (100) plane which should be perpendicular to the basal plane. Such a plane, with an angle of 120° to the basal plane, is the (101). In itself, the surface density of atoms in the (101) plane is very low; but it is an open plane, so that the nearest neighbor atoms slightly below the surface are not fully coordinated and have to be included in the estimate. Actually, these atoms are coordinated to the same extent as those in the basal plane and therefore can also participate in chemisorption. The average area occupied by a Ru atom on a (101) plane in which the contribution of the nearest neighbors has been accounted for is 6.71 Å^2. An estimate of the amount of exposed surface atoms in the sample of Ru powder, assuming equal participation of the (001), (100), and (101) planes, or an average area of 8.17 Å^2/surface atom, gives a value of 6.87 μmoles g^{-1}, which corresponds to an H_{ads}/Ru_s ratio of 1.17. The deviation of this value from unity is considered to be reasonable in view of the uncertainties inherent in the assumptions concerning the cross section of the Ar atom used in the BET measurement, the absence of multiple adsorption, and the equal participation of the low index (001), (100), and (101) planes.

Based on the previous considerations, the assumptions of the overall applicability of $H_{ads}/Ru_s = 1$ was applied to a series of supported catalysts using this value and the previously used average area of 8.17Å^2/Ru atom. Crystallite size was calculated from the H_2 adsorption data assuming the particle to be cubic with five sides exposed to the gas phase. In Table 1 are listed the particle sizes calculated from the adsorption measurements as well as the particle sizes determined from electron micrographs. The particle size represented by the maximum in the distribution, d_{max}, is listed and where the distribution was sufficiently complete, the surface average particle size, $d_{surface}$, was also determined from the measured particle size distribution.

The agreement between the surface average particle diameter obtained from electron micrographs and that calculated from hydrogen adsorption data is excellent considering the assumptions involved.

The data on samples with lower Ru concentration and progressively increased dispersion (H_{ads}/Ru) are shown in Table 2. As the average particle size decreases and the dispersion increases, the ratio of the hydrogen atoms taken up and the total amount of Ru in the supported samples tends to unity. Even at the highest dispersion, there is no indication of substantial multiple adsorption. There are, however, indications that in supported Ru catalysts prepared so as to disperse the metal possibly to an atomic state, this may no longer hold (*12*).

TABLE 2
HYDROGEN ADSORPTION AT 21°C ON SUPPORTED RU CATALYSTS

Catalyst	H_2 adsorption (μmoles/g)	H/Ru (total)	d (Å)
5% Ru/SiO_2	48.6	0.20	43
5% Ru/Al_2O_3	70.5	0.29	30
1.6% Ru/Al_2O_3	27.1	0.34	25
0.5% Ru/Al_2O_3	15.3	0.62	14
0.1% Ru/Al_2O_3 (stabilized)	10.2	1.03	<10

Carbon monoxide adsorption on ruthenium powder was also slow with coverage at pressures above 100 Torr corresponding to a CO/Ru_s ratio of 0.74. Low CO adsorption implies the presence of bridge-bonded CO on ruthenium. However, values of Co_{ads}/Ru_s calculated from CO adsorption data on metal blacks reported in the literature vary from 0.2 to 1.5 (*2*, *6*). Further indication that CO adsorption is unsuitable for surface area determination is given by CO/Ru (total) values on supported catalysts reported as high as 1.9 for dilute metal–silica samples (*6*). In agreement, infrared bands in the 1750 to 2100 cm^{-1} region, observed for CO adsorbed on supported ruthenium catalysts, have been assigned to $Ru(CO)_2$ or $Ru(CO)_3$ type structures (*4*, *6*).

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