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Determination of Ruthenium Surface Areas by Hydrogen and Oxygen Chemisorption

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The feasibility of using oxygen adsorption at ambient temperatures and using hydrogen–oxygen titration at 100°C to measure the specific surface area of alumina supported ruthenium catalysts has been evaluated by comparison with hydrogen adsorption data. All three methods give agreement for crystallite sizes greater than 40 ± 10 Å but not for small particles. Above 40 Å, the oxygen technique is fast and gives linear isotherms down to pressures of a few torricellis. The hydrogen–oxygen titration has the same crystallite size requirements as the oxygen adsorption techniques.

INTRODUCTION

Chemisorption techniques for the measurement of the surface area of ruthenium catalysts have been described in the literature using hydrogen (*1–4*), carbon monoxide (*4,5*), and oxygen (*5*) as the adsorbing gases. A comparison of particle size data from hydrogen adsorption and electron microscopy (*4*) has shown the appropriateness of the hydrogen adsorption technique. Carbon monoxide, on the other hand, cannot be used because it forms multiple bonds with the surface ruthenium atoms (*6,7*). A drawback to the hydrogen adsorption technique is that the rate of hydrogen chemisorption is slow (*4,8*).

The method of titrating adsorbed oxygen with hydrogen was developed for measuring the surface area of supported platinum catalysts with low metal loadings (*9*). The titration technique is more sensitive because more hydrogen is consumed (*9*). Recently this technique has been extended to rhodium (*10*) and palladium catalysts (*11*).

Buyanova *et al.* (*5*) have compared the volumetric and flow methods for ruthenium surface area determination by selective chemisorption of oxygen. The catalysts surveyed contained 1% or greater of ruthenium by weight (*5*).

The objective of the present work is to compare the oxygen chemisorption, hydrogen chemisorption, and hydrogen–oxygen titration techniques for surface area measurements for ruthenium samples with a range of metal loadings and dispersions.

EXPERIMENTAL METHODS

The apparatus used for the adsorption measurements was a conventional glass vacuum system except for a series of Hoke bellows valves which isolated the dosing volume. The vacuum line, gas inlet line, catalyst sample tube, and a MKS Baratron pressure gauge were all connected to the 15.59 cc dosing volume. The sample tube was a Pyrex U-tube connected to the vacuum via a Swagelok fitting and had a needle valve on the other end to permit catalyst pretreatment under flowing hydrogen. A small (2.5 cm i.d.) furnace was used to heat the catalyst and the temperature was controlled by a Hewlett Packard temperature programmer (Model 240).

The hydrogen used for both catalyst pretreatment and chemisorption was purified by passage through a purifier (Bishop, Model A-1-DH). Research grade oxygen was used as received and Matheson UHP helium used for the dead space determinations was purified by passing it through a charcoal trap at −195°C.

The supported ruthenium catalysts were prepared by the impregnation of preformed 0.125 in. alumina spheres (Kaiser KC/SAF, surface area = 260 m^2/g) with aqueous solutions of ruthenium chloride ($RuCl_3 \cdot 1\text{-}3\ H_2O$, Alpha Inorganics). The catalysts were dried in air overnight at room temperature, then heated slowly in air (A samples), 5% H_2 in N_2 (B samples), or in N_2 (C samples) at 100°C to remove water vapor and finally heated for 4 hr at 500°C to decompose the ruthenium chloride. As is shown below, the air calcination sinters ruthenium; this technique was used to form the larger particle sizes. The metal loading was determined for each catalyst by X-ray fluorescence. The ruthenium powder was obtained from Fisher Scientific Co.

The procedure used for pretreating the catalyst samples prior to the adsorption measurements was to evacuate the samples for at least 4 hr at room temperature followed by reduction in 1 atm of flowing hydrogen (25 cc/min) for 2 hr at 400°C. Finally, the samples were heated under vacuum for an additional 2 hr at this same temperature. Comparable adsorption results were obtained for a sample reduced and evacuated at 200 and 400°C.

The hydrogen adsorption measurements were done at 100°C and an apparent dead volume was measured immediately following the adsorption measurements with the furnace still in place at 100°C. Oxygen adsorption measurements were made at ambient temperatures for all samples as well as at −78°C for two samples. For the titration of adsorbed oxygen with hydrogen, the sample with adsorbed oxygen was first evacuated for 30 min at ambient temperatures following the oxygen adsorption measurements. The sample was then isolated from the pumps and the temperature was raised to 100°C for the adsorption measurements and dead volume measurement. The time for the equilibration of each dose was usually 30 min and the value for the adsorption extrapolated to zero pressure is taken as the amount of chemisorption.

Adsorption isotherms were made for the alumina support using hydrogen, oxygen, and hydrogen–oxygen titration under the same conditions described for adsorption on the alumina supported ruthenium samples. The alumina had been soaked in a dilute solution of HCl, then dried at 150°C, and calcined at 500°C prior to the adsorption measurements. In each case, the adsorption isotherms were linear and extrapolation of the isotherms to zero pressure showed no evidence for chemisorption within the accuracy of the technique (0.1 μmole/g sample). Consequently, no correction for physical adsorption on the support was needed when the chemisorption was measured by extrapolation of the isotherms.

Crystallite sizes, 1, were calculated from the hydrogen adsorption data using the relation $1 = 6/Sd$ where S is the surface area and d is the density of ruthenium (*1*).

RESULTS AND DISCUSSION

Adsorption of Oxygen

Isotherms for the adsorption of oxygen on sample 236A at ambient temperature is presented in Fig. 1 for two separate experiments. Extrapolation to zero pressure gives a value of 1.2 μmoles/g sample indicative of a O/Ru_T atom ratio of 0.12 where Ru_T designates the total number of ruthenium atoms in the sample. Oxygen adsorption data for other samples is presented in Table 1. Evacuation of the oxygen at 23°C for 10 min followed by readsorption did not show any chemisorption

TABLE 1

ADSORPTION DATA

				Adsorption (μmoles/g sample)				Dispersion ratios		Crystallite size (Å)	
Sample No.	% Ru	Expt No.	BET (m^2/g)	H_2 100°C	O_2 23°C	H_2/O 100°C	O_2 −78°C	H/total Ru	O/total Ru	1[a]	1[b]
150A	0.081	1		0.6				0.15			61
		2				1.6					
		3			0.5				0.12	73	
236A	0.086	4a		1.2				0.28			32
		4b			1.2				0.28	32	
		4d				3.8					
		4e					1.0		0.24		
		6			1.1				0.26	35	
		7a			1.2				0.28	32	
		7b				2.6					
207A	0.37	8a		1.6				0.09			101
		8b			1.6				0.09	102	
		8c				4.3					
209A	0.82	9a		4.2				0.10			89
		9b			3.0				0.07	123	
		9c				11.5					
		10a		4.9				0.12			75
		10b			2.6				0.06	142	
		10c				9.5					
236B	0.086	11a		3.2				0.75			12
		11b			5.3				1.2		
		11c				13.2					
		11d			1.2						
207B	0.40	12					12		0.6		
		13a		11.0				0.55			16
		13b			27.5				1.4		
		13c				71					
183B	0.82	14a		20				0.49			18
		14b			41				1.0		
		14c				116					
		14d			46				1.1		
		15a				84					
		15b				85					
		15c		15.5							24
		15d			29.8						
300C	0.08	16a		1.2				0.3			36
		16b			1.9				0.5		
		16c				5.1					
Powder	100	17a		9.1							
		17b	0.91								
		17c			8.0						
		17d	0.87								

[a] Determined from oxygen chemisorption data.

[b] Determined from hydrogen chemisorption data.

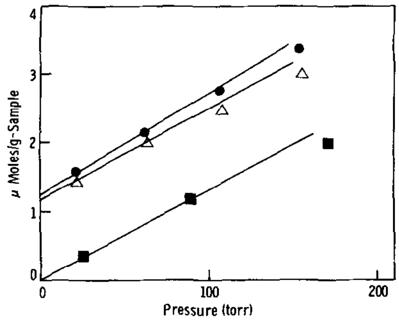

FIG. 1. Oxygen adsorption on sample 236A at 23°C. (△) Expt 7a; (●) Expt 4b; (■) readsorption of oxygen following Expt 4b.

as indicated by the zero value for the adsorption upon extrapolating to zero pressure. The chemisorbed oxygen was held strongly and could not be removed at 23°C. Only physisorbed oxygen was removed by evacuation. Furthermore, oxygen adsorption was rapid as shown in Fig. 2 for the adsorption at 50 Torr on sample 236A. After the rapid initial uptake a slow adsorption, which was probably on the support, amounted to an additional 0.4 μmoles/g for sample 150A when it was exposed to 175 Torr oxygen for 15 hr.

The appropriateness of using oxygen adsorption to monitor the number of available ruthenium sites, as well as the stoichiometry of the chemisorption, was determined by comparing oxygen chemisorption on a sample of ruthenium powder at 23°C with the total surface area as determined by the BET technique using N_2 adsorption at −195°C. The value for the oxygen chemisorption was 8.0 μmoles/g. The BET surface area of the powder was 0.87 m^2/g taking 16.2 $Å^2$ for the area occupied by a N_2 molecule. To determine the ruthenium site density, the BET area was divided by the area of a ruthenium site. For the area occupied by a ruthenium atom, we have used 9.03 $Å^2$ which is the average of the values given by Kubicka (*2*) for the (001), (110), and (100) planes. Equating the chemisorption data and the site density then gives an O/Ru ratio for the powder of 1.0. The stoichiometry of the chemisorption is then given by Eq. (1).

$$Ru_S + 1/2\ O_2 \rightarrow Ru_S\text{-}O. \qquad (1)$$

Here Ru_S designates a surface ruthenium atom.

Table 1 lists the oxygen adsorption both as the micromoles adsorbed and the ratio of oxygen atoms adsorbed to ruthenium atoms in the sample for all the samples examined. This ratio is the dispersion only when the oxygen adsorption data can be used to monitor the surface area. For the A samples, which were prepared by decomposition of the ruthenium chloride in air, the dispersion determined by oxygen

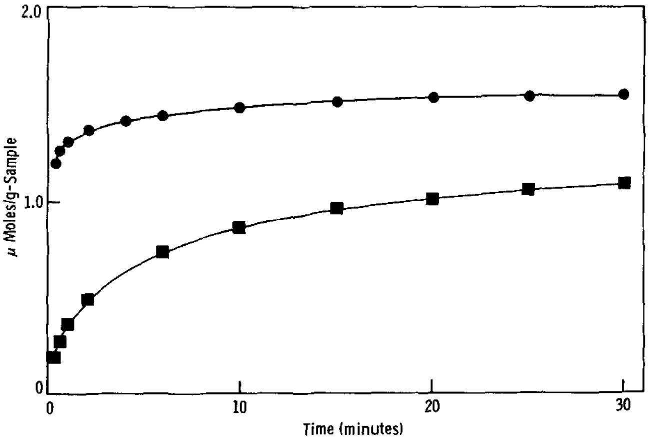

FIG. 2. Time dependence of oxygen and hydrogen adsorption on sample 236A. (●) O_2 adsorption at 23°C, 23.5–22.8 Torr O_2, Expt 4b; (■) H_2 adsorption at 100°C, 113.1–110.9 Torr H_2, Expt 4a.

adsorption was low (typically between 0.06 and 0.3) as expected for the sintered particles. On the other hand, the B samples, which were prepared by decomposition of the ruthenium chloride in hydrogen, showed a large rapid uptake of oxygen at room temperature which for some experiments exceeded the ruthenium content of the catalyst assuming the oxygen–ruthenium stoichiometry is unchanged. More likely, this stoichiometry does not hold for the smaller particles. This oxygen uptake could be repeated following a second sample pretreatment (Expt 14d); therefore, room temperature oxygen adsorption does not sinter the sample. Furthermore, titration of the chemisorbed oxygen with hydrogen indicates that the high value for the oxygen chemisorption was not the reaction with residual hydrogen from the pretreatment. Experiments 15a and 15b are duplicate titrations on the same sample.

Several experiments were carried out which compare the oxygen adsorption for large and small particle sizes in order to characterize particle size effects. Experiments 4b and 4e on sample 236A show that the oxygen adsorption is essentially the same at 23°C and −78°C for the sintered sample. On the other hand, experiments 12 and 13b on sample 207B show a much smaller value for the oxygen adsorption at −78°C (12 μmoles/g sample) compared to 23°C (27 μmoles/g sample). The −78°C oxygen adsorption now gives an O/Ru$_T$ ratio of 0.6. While Expts 12 and 13b were not carried out on the same sample, it is unlikely that the variability between 3 g samples would exceed a factor of two. We conclude that most of the additional adsorption for the B samples may be eliminated by carrying out the adsorption at a lower temperature.

Figure 3 compares the rate of oxygen adsorption on sample 207B at 23°C and −78°C. The slow uptake (over 39 min) at 23°C did not occur at −78°C. Also, the oxygen adsorption isotherm determined for sample 183B at 23°C (Expt 14b) was curved at lower pressures when each dose was equilibrated for 30 min which suggests that chemisorption sites were not saturated at the lower pressure. Figure 4 shows that a 2 hr equilibration time gave greater adsorption especially at low pressure.

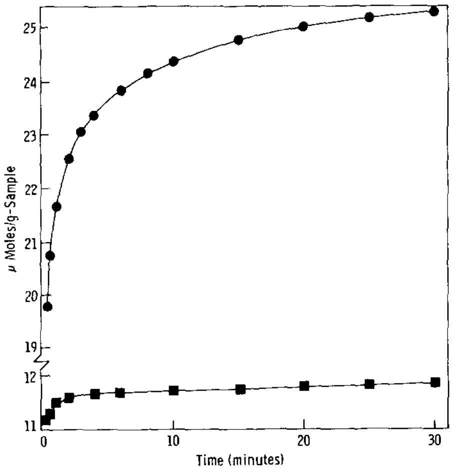

FIG. 3. Oxygen adsorption on sample 207B at 23°C and −78°C. (●) Expt 12, −78°C, O_2 pressure fell from 1.5 to 0.13 Torr; (■) Expt 13b, 23°C, O_2 pressure fell from 12.7 to 0.1 Torr.

Adsorption of Hydrogen

Isotherms for the adsorption of hydrogen at 100°C on samples 209A and 236A are presented in Fig. 5. The adsorp-

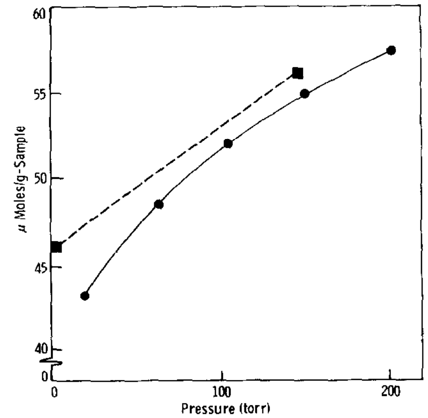

FIG. 4. Oxygen adsorption on sample 183B at 23°C. (●) 30 min equilibration for each dose; (■) 120 min equilibration.

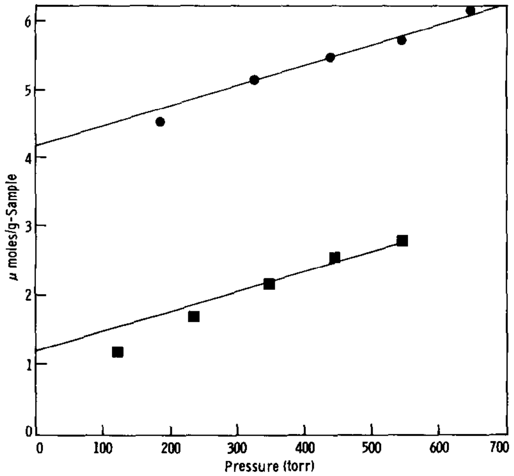

FIG. 5. Hydrogen adsorption on samples 209A and 236A at 100°C. (●) Sample 209A, Expt 9a; (■) sample 236A, Expt 4a.

tion isotherms are linear only above 200 Torr so the extrapolation to zero pressure does not include the lower pressure data. The longer time required for hydrogen to adsorb compared to oxygen is shown in Fig. 2. For sample 236A essentially the same value was obtained for the hydrogen chemisorption extrapolated to zero pressure at 23 and 100°C and therefore the same stoichiometry is considered to hold at both temperatures. The hydrogen adsorption was carried out at 100°C rather than at 23°C in the present work since the adsorption equilibration was faster at the higher temperature. Thirty minutes was not sufficient time for the equilibration at 23°C. Dalla Betta (*4*) has handled this difficulty by measuring hydrogen desorption isotherms following overnight equilibration at ambient temperatures. The relatively weak chemisorption of hydrogen was demonstrated in our work by an adsorption–evacuation–readsorption experiment. Three quarters of a monolayer was adsorbed following evacuation of a 1% Ru–Al_2O_3 sample with chemisorbed hydrogen for 1 hr at room temperature.

The stoichiometry of the hydrogen adsorption was determined by comparison of the hydrogen adsorption at 100°C on a sample of ruthenium powder with the total surface area of the powder determined by the BET technique (Expts 18a and 18b). In this case, a H/Ru_S ratio of 1.1 was calculated using the same assumptions made in calculating the O/Ru_S ratio. Hydrogen chemisorption on all the samples is listed in Table 1 as both micromoles per gram of sample and as the ratio of hydrogen atoms chemisorbed to the total ruthenium content of the samples.

The dispersion *D*, which is defined as the fraction of the total number of metal atoms which are at the surface of the metal particles, was determined using the hydrogen chemisorption data for each sample in Table 1 assuming that the stoichiometry of the chemisorption can be represented by a H/Ru_S ratio of 1.0 as given in Eq. (2).

$$Ru_S + 1/2\ H_2 \rightarrow Ru_S\text{-}H. \qquad (2)$$

It is also convenient to calculate an approximate particle size l from the chemisorption data by assuming the particles are all cubes of uniform size though it is understood that the sample is made up of a distribution of shapes and sizes. Particle sizes calculated from the hydrogen chemisorption data for all the samples and from the oxygen chemisorption data for the A samples are given in Table 1.

The A samples showed generally the same values for hydrogen chemisorption at 100°C as for oxygen chemisorption at ambient temperature. The B samples, on the other hand, showed much less hydrogen adsorption than oxygen adsorption. The highest dispersion determined by hydrogen adsorption for a B sample was 0.75 for sample 236B. The applicability of the hydrogen adsorption technique to the measurement of ruthenium surface areas has been demonstrated by Dalla Betta (*4*) by comparison of adsorption data and electron microscopy data. The smallest particles for which the comparison was made were 42 Å. Oxygen and hydrogen chemisorption give a different result for smaller particles. We have made the assumption that the hydrogen technique is appropriate for metal surface area measurements on small particles. The room temperature oxygen adsorption for the B samples, on the other hand, gives values that are too large based on the O/Ru_S ratio determined for the powder. The magnitude of the oxygen adsorption suggests either multiple adsorption on ruthenium surface sites or penetration below the surface layer. We conclude that the oxygen data cannot be used to measure the surface area of ruthenium particles which are smaller than 40 ± 10 Å. A change in the O/Pt_S stoichiometry from 1.0 for large crystallites to 0.5 for small platinum particles has been reported (*12,13*). For ruthenium crystallite sizes larger than 30–40 Å, the oxygen adsorption technique in addition to being fast has the advantage that the extrapolation to zero pressure can be made using isotherm data taken below 100 Torr. The uncertainty in the result arising from the dead space measurement will affect only the slope of the isotherm. The uncertainty is less for oxygen isotherms than for hydrogen isotherms where only data taken above 200 Torr is used for the extrapolation.

The oxygen adsorption result for sample 207B at −78°C is in reasonable agreement with the hydrogen adsorption data which suggests that the oxygen technique is applicable to small particles if the adsorption is carried out at reduced temperatures.

Sample 300C prepared by the decomposition of ruthenium chloride in nitrogen is intermediate in chemisorption properties between the A and B samples. The hydrogen adsorption data compares with that for 236A (which was calcined in air) but the oxygen chemisorption exceeded the hydrogen adsorption. The crystallite size range 30–50 Å appears to be the region where the oxygen adsorption property of the metal changes.

We were mostly interested in the ruthenium catalysts with low metal loadings (~0.1%) for catalyst applications (*14*), however, the chemisorption studies were carried out on higher metal loadings to test the applicability of the chemisorpiton techniques. The oxygen uptake was lower than the hydrogen uptake on sample 209A and this same result was obtained twice. The ruthenium powder showed similar hydrogen and oxygen chemisorption. Possibly sample 209A was not well reduced. Freel (*15*) has reported that a supported platinum sample given a mild reduction showed less oxygen adsorption than hydrogen adsorption, whereas a well-reduced sample chemisorbed equal amounts of the two gases. The resolution of this discrepancy will be dealt with in a future publication.

Hydrogen Titration of Adsorbed Oxygen

The hydrogen uptake at 100°C measured upon titrating the adsorbed oxygen not removed by evacuation at ambient temperature is listed in Table 1 for all the samples. Hydrogen titration of a presorbed oxygen layer is subject to the same limitations as the oxygen adsorption method for measuring ruthenium surface areas. For ruthenium samples with both a low metal loading and dispersion, the increase in the hydrogen uptake for a titration compared to hydrogen or oxygen adsorption alone may be useful.

Even for the A samples oxygen chemisorption not oxidation must precede the titration. X-Ray data has shown that oxidation of ruthenium samples with metal content higher than 0.3% leads to RuO_2 formation. Neither a metal nor an oxide was detectable in sample 150A; however, a sample pretreated only by outgassing at 400°C showed a hydrogen uptake of 9.2 μmoles/g of sample which corresponds to reaction with three layers of RuO_2. The depth of penetration was estimated by comparing the hydrogen uptake on sample 150A after a reduction pretreatment.

The titrations carried out here, however, serve as a check on the hydrogen and oxygen chemisorptions. The micromoles of hydrogen used per gram for the titration was generally equal to twice the extrapolated value for the oxygen adsorption plus the extrapolated value for the hydrogen chemisorption as indicated by Eq. (3).

$$\text{Ru–O} + 3/2\ H_2 \rightarrow \text{Ru–H} + H_2O. \quad (3)$$

This stoichiometry for the B samples means that the excess oxygen adsorbed is also strongly held and not removed by the room temperature evacuation. If the greater oxygen adsorption on the small particles were the result of residual hydrogen from the pretreatment this stoichiometry would not be expected to hold.

CONCLUSIONS

The method of oxygen chemisorption to measure the surface area of alumina supported ruthenium catalysts has been shown to have the advantage of being faster than hydrogen adsorption. Since low pressure data may be used in the extrapolation of the oxygen isotherms to zero pressure, the oxygen method is more accurate than the hydrogen method. Room temperature oxygen chemisorption is only applicable for ruthenium crystallite sizes greater than 40 ± 10 Å. Oxygen chemisorption at −78°C may be used for smaller crystallites. Hydrogen–oxygen titration also measures surface ruthenium sites since room temperature evacuation of an oxygen covered surface removes only physisorbed oxygen from the metal and the support. Titration with hydrogen at 100°C then measures only the strongly held oxygen. The titration technique has the same limitations as both the oxygen and hydrogen adsorption techniques.

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