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Characterization of Highly Dispersed Ru Catalysts by Chemisorption

Stoichiometries for H_2 chemisorption and H_2–O_2 titration on Ru are somewhat in doubt based on the literature. In addition, little or no work has been done on highly dispersed (75–100%) Ru catalysts. In order to be able to better charcterize such types of catalysts, H_2 chemisorption and H_2–O_2 titration on highly dispersed Al_2O_3- and zeolite-supported Ru have been investigated. The findings suggest that H_2 chemisorption may be the best method for determination of the Ru surface-area/dispersion. For such dispersed catalysts the ratio H_{ads}/Ru(s) was found to be slightly larger than 1.0.

INTRODUCTION

The analysis of catalytic results using supported metal catalysts necessitates as complete a characterization of the catalysts as possible. Of particular interest is the determination of the specific metallic surface area and the dispersion [(no. of surface metal atoms/no. of total metal atoms) × 100%]. This is normally accomplished by selective chemisorptive measurements where the chemisorbed species absorbs with a specific stoichiometry on the surface metal atoms but does not adsorb on the support. Typical gases used are H_2 and CO. More recently the H_2–O_2 titration method has been suggested to be perhaps a more accurate way of active surface area determination for Pt (*1*), Rh (*2*), Pd (*3*), and Ru (*4, 5*) due to the greater consumption of gases. H_2–O_2 titration follows this set of reactions

$$M_s + \frac{x}{2}\,O_2 \rightarrow M_sO_x$$

$$M_sO_x + \frac{2x + y}{2}\,H_2 \rightarrow M_sH_y + xH_2O \text{ (trapped)}$$

where M_s is a surface metal atom and x and y are experimentally determined numbers which in principle are constant.

The most common method for determination of the surface area and dispersion of Ru catalysts has been H_2 chemisorption (*4–12*). Dalla Betta (*10*), Taylor (*4*), and Kubicka (*8*) have all studied in some detail H_2 chemisorption on Ru powder to determine the number of H atoms chemisorbing per Ru surface atom. Kubicka (*8*), assuming an equal contribution from the (001), (110), and (100) planes, calculated an average value of 1.50 for H/Ru(s). Dalla Betta (*10*), based on SEM results, assumed an equal number of Ru surface atoms to be in the (001), (100), and (101) planes and determined H/Ru(s) = 1.17. Taylor (*4*), also assuming the area occupied by a surface Ru atom to be an average of those for the (001), (110), and (100) planes, determined H/Ru(s) to be 1.1. Given the assumptions made for that calculation and the errors inherent in experimental measurement it was suggested that the actual ratio of adsorbed H atoms to surface Ru atoms was one (*10*). This ratio seems to hold for supported Ru particles as small as 4.3 nm in diameter (*10*). There is no information available in the literature which indicates whether this ratio does or does not also hold for even smaller Ru particles. From theoretical considerations there are indications that H/M(s) may increase with a decrease in metal particle size (*13–15*).

A surface area determination technique more recently applied to Ru is H_2–O_2 titration (*4, 5*). There is disagreement in the literature, however, as to the number of O atoms chemisorbed on Ru surface atoms—one (*4*) or two (*5*). Taylor (*4*) found that the stoichiometry of oxygen chemisorption on Ru was O/Ru(s) = 0.5–1.0 provided the Ru particle diameter was >4 nm. For her samples with particles <4 nm the stoichiometry

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of O/Ru(s) ranged from 0.86–2.55. Kubicka (*5*) has studied the oxygen and hydrogen chemisorption and oxygen–hydrogen titration on Ru powder and has found that oxygen chemisorption results in the formation of a surface oxide close to RuO_2, i.e.

$$Ru(s) + O_2 \rightarrow Ru(s)O_2$$

and that the surface processes during titration may be represented by

$$Ru(s)O_2 + 5\tfrac{1}{2}H_2\,(g) \rightarrow Ru(s)H + 2H_2O(g)$$

Kubicka suggested that the lower oxygen adsorption and/or higher hydrogen uptake found by Taylor would be expected for metal surfaces which had not been completely reduced or which had been recontaminated with oxygen.

Thus, there are conflicting views in the literature as to the stoichiometries of the various chemisorption techniques used to determine the dispersion of supported Ru. In addition, little or no study of the stoichiometries for highly dispersed Ru has been made. For highly dispersed systems chemisorption characterization is especially crucial since the utility of X-ray diffraction is minimal when particles are <3 nm and since a large fraction of the metal particles may be even below the resolution limit of most transmission electron microscopes. Therefore, in order to be better able to characterize highly dispersed (~100%) Ru catalysts, a study was undertaken to clarify stoichiometries for H_2 chemisorption and H_2–O_2 titration on surface Ru atoms present in such systems.

EXPERIMENTAL

Three types of Ru catalysts were prepared making use of two different supports and two different preparation techniques.

NaY zeolite-supported Ru catalysts containing ~3.2 wt% Ru were prepared by ion-exchange using $Ru(NH_3)_6Cl_3$ and are designated as RuY. The complex was decomposed under vacuum by heating the catalyst slowly (0.4 K/min) to 693 K and holding it at that temperature for 2 hr. The catalyst was then reduced in H_2 at 700 K for 1.5 hr and, finally, heated under vacuum at this temperature for 1.5 hr to desorb the hydrogen before chemisorption measurements were begun.

Ru/NaY catalysts were prepared by impregnation via the vapor phase of $Ru_3(CO)_{12}$ of NaY zeolite, previously dried under vacuum at 773 K. This impregnation process took place in an evacuated, sealed Pyrex cell held at a temperature of 353 K for several weeks. This temperature ensured that the vapor pressure of $Ru_3(CO)_{12}$ was high enough for reasonably rapid adsorption of it on the zeolite but was not high enough to cause decomposition of the carbonyl (*16*). The supported carbonyl was then decomposed under vacuum at 703 K. The resulting catalyst was in a reduced state vis-à-vis H_2. Chemisorption studies were carried out on one sample (0.58 wt% Ru) without any treatment beyond decomposition. Another catalyst (1.34 wt% Ru) was treated under H_2 and then desorbed under vacuum at 703 K.

A Ru/Al_2O_3 catalyst was prepared also from $Ru_3(CO)_{12}$. After impregnation of the alumina by $Ru_3(CO)_{12}$ the catalyst was heated at 573 K under vacuum to decompose the carbonyl and form the reduced supported metal.

Chemisorption and titration measurements were made at 298 K using a standard, static gas volumetry set-up. Equilibrium was assumed when no pressure change could be noted over a 2-hr period. For H_2 chemisorption a period of approximately 4–5 hr was required for equilibrium to be realized for the initial measurement at the lowest pressure. Additional measurements at higher pressures required only approximately 2 hr to achieve equilibrium. The quantity of gas (chemisorbed or reacted + chemisorbed) was found by subtracting the quantity of gas uptake on the physisorption isotherm from that on the initial adsorption/reaction isotherm—both at a pressure of 20 kPa. In every case the two isotherms were parallel, as expected. Both

H_2 titration of a Ru surface covered by oxygen and O_2 titration of a Ru surface covered by hydrogen were carried out.

The Ru concentrations in the catalysts were determined by atomic absorption spectroscopy. Transmission electron microscopy (TEM) was utilized to characterize three catalysts following gas volumetric measurements. Samples were prepared for TEM by both cross section of the support particles and replica of the surfaces of those particles. Multiple samples were prepared by both methods for each catalyst. The resulting micrographs were examined to estimate the maximum Ru particle size and the relative distribution of metal particle sizes occurring within the support particles and on their outside surfaces.

DISCUSSION OF RESULTS

As can be seen in Table 1, hydrogen chemisorption on totally dispersed Ru (catalysts A and B) yields a H/Ru (total) ratio of 1.13–1.15. An electron microscopy study of these catalysts (Table 2) confirmed that the Ru was totally dispersed (catalyst B is for all intents and purposes so). The fact that all the Ru atoms present in catalysts A and B were available for chemisorption suggests that ratios greater than 1 are possible, are not just due to errors in measurement or surface atom density, and are probably due to multiple adsorption of hydrogen on certain Ru sites. Dalla Betta (*10*) has also found indications that H/Ru(s) may be greater than 1 when Ru is highly dispersed. An alternate possibility would be that hydrogen spillover occurs. However, given that H/Ru(s) was found greater than 1.0 in every case for unsupported Ru powder, multiple adsorption on certain Ru sites would seem to be indicated. In any case, it has been suggested that hydrogen spillover from supported metals should be minimized by operating at 298 K and relatively low H_2 pressure (*17*).

For the measurements made here for both H_2 chemisorption and H_2 titration it was not possible to extrapolate the initial adsorption isotherm to $P = 0$ to determine the amount of H_2 chemisorbed and/or reacted. This was due to the fact that, for all catalysts, the adsorption isotherm for reversibly adsorbed H_2 did not extrapolate to zero adsorption at $P = 0$ (Fig. 1). This extrapolation procedure has previously been utilized for Ru catalysts having a

TABLE 1

Chemisorption and Titration Results

Catalyst	Wt% Ru	H_2 chemisorption $[H_{ads}/Ru(total)]$	Dispersion	Oxygen chemisorption via O_2 chemisorption or O_2 titration $[O_{ads}/Ru(s)]$	H_2 chemisorption via H_2 titration $[H_{ads}/Ru(s)]$
A. Ru/Al_2O_3	1.04	1.146	100%	3.50	0.89
				2.33[a]	1.51
B. Ru/NaY	0.58	1.13	100%	2.68	0.61
C. Ru/NaY	1.34	0.75	75%[b]	2.45	1.05
				2.14	1.13
D. RuY	3.20	0.84	84%[b]		
E. RuY	3.24	0.66	66%[b]	3.12	1.02
				3.29	
				Avg = 2.79	Avg = 1.04

[a] Via O_2 chemisorption.

[b] Assuming $H_{ads}/Ru(s) = 1$.

TABLE 2

Electron Microscopy Results

Catalyst	Wt% Ru	$H_{ads}/Ru(T)$	Description of Ru particles
A. Ru/Al_2O_3	1.04	1.146	Maximum particle size of 1.0 nm
B. Ru/NaY	0.58	1.13	*Exterior*—most had diameters ~1.0 nm (detection limit) with a few larger (up to 3.0 nm) *Interior*—all particles detected were at the limit of detection of 1.0 nm
C. Ru/NaY	1.34	0.75	*Exterior*—most < 2.0 nm with a few ~3.0 nm and a very few up to 6.0 nm in diameter *Interior*—most 1.0 nm or less with a few at 1.5–2.0 nm

much lower dispersion (*4*, *10*). Taylor (*4*) noted that for adsorption on Al_2O_3 alone there was no evidence of chemisorption. Both Taylor (*4*) and Kubicka (*5*) have noted reversible adsorption of H_2 on supported and unsupported Ru following evacuation of the catalysts for 1 hr at 298 K. If the amount of reversibly adsorbed H_2 had not been subtracted from the total in this study, however, the H/Ru (total) determined by extrapolation for the totally dispersed catalysts A and B would have been 1.53 and 1.94, respectively, for the initial H_2 adsorption measurements.

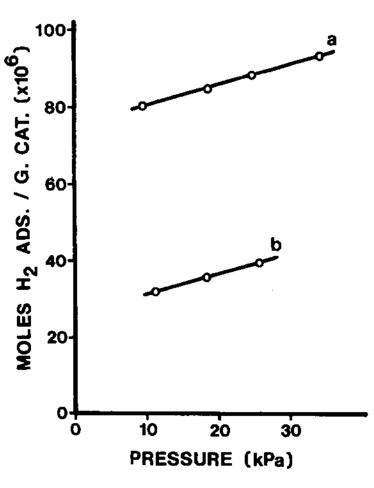

FIG. 1. H_2 adsorption isotherms for Ru/NaY (1.34 wt% Ru). (a) Reversible and irreversible adsorption; (b) Reversible adsorption.

The results for O_2 chemisorption on a desorbed Ru surface or O_2 titration onto a Ru surface covered by chemisorbed hydrogen (Table 1) illustrate the difficulty with using either of these techniques to determine the dispersion. Values for O/Ru(s) varied between 2.14 and 3.5, and, even on the same catalyst, successive measurements yielded quite different ratios. Certainly, these results are more in agreement with those of Kubicka (*5*) than with those of Taylor (*4*). As can be seen in Fig. 2, O_2 titration on Ru is relatively fast process. The initial reaction

$$Ru(s)H + \tfrac{5}{4}\,O_2 \rightarrow Ru(s)O_2 + \tfrac{1}{2}H_2O$$

probably takes no more than 4 hr. This particular experiment shown in Fig., 2 yielded a value of O/Ru(s) = 2.14 after 4 hr. For O_2 chemisorption the initial reaction would be

$$Ru(s) + O_2 \rightarrow Ru(s)O_2$$

Once $Ru(s)O_2$ is formed additional O atoms can react with the highly dispersed Ru. This

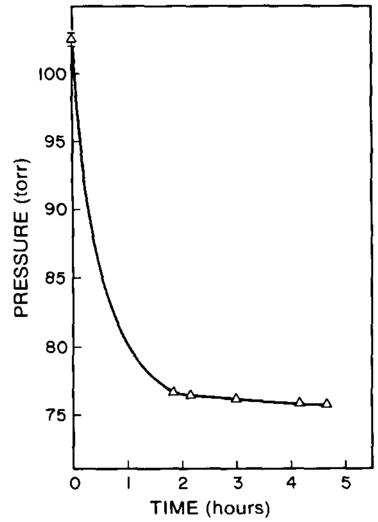

FIG. 2. O_2 titration on Ru/NaY (1.34 wt% Ru).

latter reaction would seem to be considerably slower than the initial reaction. Thus, the other measurements of O_2 titration/chemisorption which were allowed to span as much as several days resulted in much higher O/Ru(s) ratios. Since the process was occurring so slowly, the criterion for equilibrium, no significant pressure drop during a 2-hr period, would be met at any time beyond the initial 4-hr reaction period. Galvagno and Schwank (*18*), studying highly dispersed Ru/SiO_2, have also noted an additional consumption/adsorption of O_2 on a surface of Ru previously covered with oxygen. Taylor (*4*) has suggested that the slow adsorption of O_2 by Ru/Al_2O_3 following the rapid initial uptake may be due to adsorption on the support. If this is the case there is chemisorption of oxygen on the support since the reversible adsorption O_2 isotherm extrapolates to 0 at $P = 0$. Thus, regardless of the cause of O/Ru(s) being able to exceed 2 (oxygen spillover, bulk oxidation of large particles, or formation of surface stabilized RuO_3 (*19*) or RuO_4), these results indicate that O_2 chemisorption or titration is extremely difficult to use to determine accurately the Ru dispersion in highly dispersed systems.

H_2 titration of a Ru surface covered with oxygen was a slow process requiring as much as 2 days before equilibrium was attained (Fig. 3). The reaction, on the average, can be represented by

$$\mathrm{Ru(s)O}_x + \left(\frac{2X + 1.04}{2}\right) \mathrm{H_2} \rightarrow \mathrm{Ru(s)\ H_{1.04}} + X\ \mathrm{H_2O}$$

and was followed in nearly all cases regardless of the value of X. The usefulness of H_2 titration as a method of determining Ru dispersion is severely limited by (1) the reaction rate and (2) the variability of X (as discussed above).

CONCLUSIONS

Based on the results of this investigation H_2 chemisorption would seem to be the best method to determine the dispersion of highly dispersed Ru catalysts. While the ratio of H/Ru(s) is not perfectly determined, its value is probably between 1.0 and 1.15. Thus, an assumption of 1.0 does not result in too great an error, although 1.1 may be a better assumption.

H_2–O_2 titration seems to be capable of determining the dispersion of Ru. Compared to H_2 chemisorption, however, its advantage of greater sensitivity due to larger numbers of molecules taking part in the reaction is counterbalanced by the

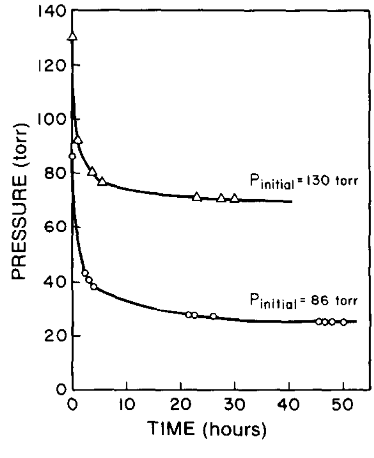

FIG. 3. H_2 titration on Ru/NaY (1.34 wt% Ru).

greater supervision required and the difficulty of knowing exactly the stoichiometry of the oxygen with the Ru surface atoms.

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JAMES G. GOODWIN, JR.

Chemical and Petroleum Engineering Department
University of Pittsburgh
Pittsburgh, Pennsylvania 15261

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