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Measurement of Surface Dispersion of Ruthenium on γ-Al_2O_3 Support by Low-Temperature Oxygen Chemisorption (LTOC) Technique[1]

Ruthenium can be employed as a catalyst in FT synthesis of paraffins, in the methanation of carbon monoxide, in the partial hydrogenation of benzene to cyclohexene (*1–4*), and in ammonia synthesis (*5, 6*). The activity of a supported ruthenium catalyst depends on dispersion (number of surface metal atoms/number of total metal atoms × 100) or on the specific metal surface area. The number of surface metal atoms is normally estimated by gas adsorption techniques. The number of strongly chemisorbed adsorbate molecules or atoms determines the number of surface metal atoms, taking into account the chemisorption stoichiometry of the adsorbate. For ruthenium, hydrogen chemisorption has been extensively studied for the determination of dispersion and metal area (*7–18*). Carbon monoxide was also used (*7, 19*) but has limitations because it forms multiple bonds with surface ruthenium atoms (*20, 21*). The hydrogen–oxygen titration technique, another method developed for the determination of active surface area of ruthenium, was considered to be more sensitive due to higher consumption of hydrogen (*8, 9*). Selective chemisorption of oxygen was also used for the characterization of ruthenium catalysts (*8, 19*).

In the determination of metal surface area by H_2–O_2 titration, Taylor (*8*) found a value of 0.5–1.0 for O/Ru_S if the Ru particle diameter was >4 nm and 0.86–2.25 for samples with particle size of <4 nm. The determination of Ru dispersion by H_2–O_2 titration requires greater supervision and by room temperature chemisorption it is difficult to know exactly the stoichiometry of the oxygen with the Ru surface atoms (*18*). In the hydrogen adsorption method, the rate of hydrogen chemisorption is slow on Ru catalysts (*7, 8*). However, the chemisorption stoichiometry of hydrogen on Ru catalysts is well established. The value for H/Ru_S was determined to be 1.17 by Dalla Betta (*7*), 1.1 by Taylor (*8*), and 1.0–1.15 by Goodwin (*18*). Good agreement was also reported between particle size calculated from hydrogen adsorption and the particle size observed by electron microscopy (*7, 18*). Very recently, the H/RU_S ratio determined by irreversible hydrogen chemisorption on Ru–SiO_2 catalysts was validated by PMR studies (*22*).

In the recent past low-temperature oxygen chemisorption (LTOC) technique has been applied quite successfully to provide quantitative information about the dispersion of molybdenum (*23–27*) and vanadium (*28–31*) in supported catalysts. However, literature on the application of LTOC for the determination of Ru dispersion is scanty. Taylor (*8*) has carried out oxygen adsorption measurements at −78°C on only two samples. In the present article we report the results of our work on the measurement of dispersion of Ru on γ-Al_2O_3 support by low-temperature oxygen chemisorption at −78°C. These values are compared with those obtained by hydrogen chemisorption at ambient temperature (25°C).

The Ru/γ-Al_2O_3 catalysts were prepared by the impregnation of γ-alumina

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(Harshaw, Al-111-61E, S.A. 204 $m^2 g^{-1}$, P.V. 0.65 ml g^{-1}) with aqueous solutions of $RuCl_3$, $3H_2O$ (Aldrich) by incipient wetness method. The catalysts were dried at 110°C overnight.

A conventional high-vacuum glass system was used for the low-temperature oxygen chemisorption and room temperature hydrogen adsorption measurements. About 2 g of the catalysts was taken for each experiment. Prior to the adsorption measurements, the catalyst samples were reduced at 400°C in flowing hydrogen (50 ml/min) for 12 h. Finally, the samples were evacuated at the same temperature for several hours at 10^{-6} Torr in order to clean the catalyst surface. Low-temperature oxygen chemisorption experiments at −78°C (solid carbon dioxide + acetone) were performed on these catalysts following the method of Parekh and Weller (*32*). The first adsorption isotherm representing the total of the reversibly adsorbed and irreversibly adsorbed oxygen was measured at −78°C. After evacuating the catalyst at 10^{-5} Torr for 1 h at the same temperature, a second isotherm representing only reversibly adsorbed oxygen was generated in an identical manner. An equilibration time of 10 min was found to be sufficient for each adsorption point in the pressure range up to 300 Torr. The total and reversible LTOC isotherms of all the catalysts are linear and parallel. The hydrogen adsorption measurements were done at room temperature (25°C). An equilibration time of 1 h was allowed for each adsorption point. The total and reversible hydrogen adsorption isotherms were generated in a manner identical to that done for LTOC. However, the pressure range for adsorption was extended up to 1 atm as the isotherms were parallel only above 500 Torr. The difference between the total and reversible hydrogen adsorption from the parallel part of the isotherms (at 740 Torr) was taken as a measure of strong chemisorption. Taylor (*8*) noted that hydrogen adsorption isotherms measured at 100°C were not parallel below 200 Torr.

Crystallite sizes (l) were calculated from the oxygen and hydrogen chemisorption data using the relation $l = 5/Sd$, where S is the metal surface area and d is the density of ruthenium (*33*).

Table 1 provides the chemisorption capacities and other data on Ru/γ-Al_2O_3 catalysts. On the basis of several findings, the H/Ru_S can be taken as unity for all practical purposes. From the results in Table 1, it is very clear that the O_2 uptakes are twice the H_2 uptakes with all the catalysts except the catalyst with 0.5% Ru. This suggests a surface stoichiometry of 2 : 1 for irreversibly adsorbed oxygen atoms or radicals on surface Ru atoms (Ru_S), compared to 1 : 1 stoichiometry for H and Ru_S atoms. It is interesting to note that the oxygen to surface

TABLE 1

Percentage Dispersions, Ru Crystallite Sizes, and Metal Areas of Ru/γ-Al_2O_3 Catalysts Obtained from Strong H_2 and O_2 Uptakes

Wt% Ru	BET surface area ($m^2 g^{-1}$)[a]	H_2 uptake (μmol g^{-1})	O_2 uptake (LTOC) (μmol g^{-1})	O_2 uptake / H_2 uptake	% Ru Dispersion		Metal area ($m^2 g^{-1}$)		Crystallite size (nm)	
					H_2 uptake	LTOC	H_2 uptake	LTOC	H_2 uptake	LTOC
0.50	183	7.0	6.8	0.97	28.3	27.4[b]	0.76	0.74[b]	2.65	2.72[b]
1.25	179	11.1	21.1	1.90	18.0	17.1	1.21	1.15	4.15	4.43
2.50	173	24.0	46.8	1.95	19.4	18.9	2.61	2.55	3.89	3.95
3.50	171	20.5	42.1	2.05	11.8	12.2	2.23	2.28	6.30	6.20
5.00	157	26.0	54.2	2.05	10.5	11.0	2.83	2.95	7.07	6.83

[a] Measured after reduction by N_2 adsorption at 77 K.

[b] Calculated by taking O/Ru_S = 1.

ruthenium stoichiometry corresponds to that of the most stable oxide, RuO_2:

$$Ru_S + O_2 \rightarrow Ru_SO_2.$$

Kubicka (*9*) has also found that oxygen chemisorption results in the formation of a surface oxide close to RuO_2. Values of 2.14–3.5 for O/Ru_S obtained by Goodwin from oxygen uptakes at room temperature may be attributed to oxygen spillover, bulk oxidation of large particles, or formation of surface-stabilized RuO_3 (*34*) or RuO_4. From our results it can be said that at −78°C the bulk oxidation of Ru or formation of higher oxide (RuO_3 or RuO_4) can be almost or completely ruled out and that the adsorption equilibrium is attained very fast (within 10 min). However, for 0.5% $Ru/\gamma\text{-}Al_2O_3$ the O/Ru_S was found to be 1. A similar value was also observed by Taylor *et al.* (*8*, *35*) for Ru loadings below 1% by room temperature (23°C) oxygen chemisorption. Lower oxygen uptake would be expected for metal surfaces which had not been completely reduced or which had been recontaminated with oxygen (*9*). However, at this moment it is not possible to explain why the O/Ru_S ratio is 1 for 0.5% Ru/Al_2O_3. The total and reversible isotherms for the low-temperature oxygen chemisorption are presented in Fig. 1 (1.25% Ru catalyst). The isotherms in the pressure range studied (150–300 Torr) are linear and parallel. The reproducibility of the results of LTOC for three different samples of the same catalyst was of the order of ±5%.

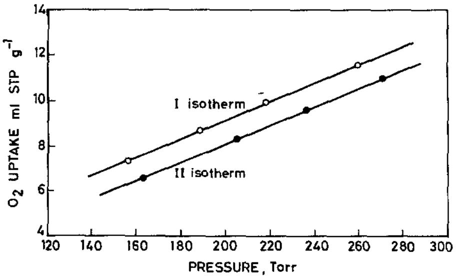

FIG. 1. Low-temperature oxygen chemisorption isotherms (at −78°C) of 1.25% $Ru/\gamma\text{-}Al_2O_3$ catalyst. (○) Total O_2 uptake; (●) reversible O_2 uptake.

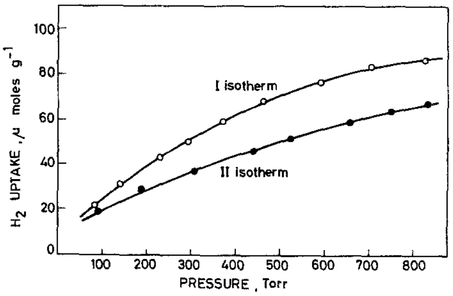

FIG. 2. Hydrogen chemisorption isotherms (at 25°C) of 3.5% $Ru/\gamma\text{-}Al_2O_3$ catalyst. (○) Total H_2 uptake; (●) reversible H_2 uptake.

Isotherms of hydrogen adsorption at ambient temperature (25°C) are presented in Fig. 2 (3.5% Ru catalyst). Since the irreversible and reversible adsorption isotherms are not linear and parallel below 500 Torr, extrapolation of the isotherms to zero pressure below 500 Torr would not give correct hydrogen uptakes. Instead, the difference of the parallel portions of the isotherms gives the correct chemisorption value. Don and co-workers (*15*) found, in accordance with Taylor's findings, that the equilibration with hydrogen is slow, especially at the lower pressures, needing 1 or 2 h for equilibration. Dalla Betta (*7*) has measured hydrogen desorption isotherms following overnight equilibration at ambient temperature (23°C). Since the adsorption equilibration was faster at higher temperature Taylor (*8*) has carried out hydrogen adsorption at 100°C rather than at 23°C. It is clear from the present study that reproducible hydrogen uptakes are obtained by equilibrating the $Ru/\gamma\text{-}Al_2O_3$ catalysts for 1 h at ambient temperature (25°C) with hydrogen pressure above 500 Torr. A point to be noted from Table 1 is that there is an excellent agreement between the values of ruthenium dispersion and crystallite sizes calculated from the low-temperature oxygen and ambient temperature hydrogen chemisorption data.

Low-temperature oxygen chemisorption (LTOC) technique has been successfully applied for the determination of metal areas of γ-Al_2O_3 supported ruthenium catalysts. Oxygen adsorption equilibration is faster at −78°C, needing only 10 min equilibration time for each measurement. This is an advantage over hydrogen adsorption, which requires 1 h equilibration. There is good agreement between LTOC results and the H_2 chemisorption data at ambient temperature and hydrogen pressure above 500 Torr. When the H/Ru_S value is taken as 1 (from the literature), the O/Ru_S was found to be 2 except with the catalyst having 0.5 wt% Ru.

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