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Rapid Measurement of Hydrogen Chemisorption by Supported Catalytic Metals

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Surface areas of supported catalytic metals (e.g., platinum on silica gel) can be rapidly determined by measuring evolution of chemisorbed hydrogen in a flowing hydrogen–argon mixture that contains 1 mole % hydrogen. The freshly reduced sample is first equilibrated at 0°C, then heated to 500°C to desorb the hydrogen. In examining a variety of platinum–silica-gel catalysts, chemisorption values obtained by means of this flow technique are in good agreement with those obtained by a static technique.

INTRODUCTION

The surface area and dispersion of a supported catalytic metal can be conveniently determined from the measurement of a chemisorbed monolayer of an appropriate adsorbate such as hydrogen at conditions under which little or no adsorption occurs on the support. Such measurements can be carried out by means of conventional high-vacuum-adsorption apparatus (*1–4*), but more rapid flow methods of measuring chemisorption are often found useful (*5–8*). This is especially true when the need arises to characterize the multitude of catalyst samples generated by varying preparation, pretreatment, and use of a given series of supported metals.

A rapid method for the measurement of hydrogen chemisorption has been in use in this laboratory for several years. It consists of three steps: (1) reduction of the sample in flowing hydrogen; (2) equilibration of the reduced sample at 0°C with a stream of argon that contains a low—but finite—concentration of hydrogen; and (3) heating the sample in the same argon–hydrogen stream to drive off adsorbed hydrogen—measured by means of a thermal conductivity detector. The above technique has been used to characterize Group VIII metals on a variety of supports. Its application for the determination of the dispersion of platinum on silica gel is described below.

EXPERIMENTAL DETAILS

The procedure is as follows. The sample is reduced in hydrogen (20 ml/min) at 500°C for 30 min. It is then cooled to 0°C in an argon stream containing 1 mole % hydrogen (20 ml/min) while the composition of the exit gas can be monitored by means of a Perkin-Elmer–Shell Sorptometer of the type used for physical adsorption measurements (*9*). After the exit composition attains a constant value, the sample is heated to 500°C (by raising a preheated furnace to the appropriate position), and the hydrogen thus desorbed gives rise to a peak in the composition-time curve. By comparing the area of this peak with that corresponding to the addition of a known amount of hydrogen to the argon–hydrogen stream, the amount of chemisorbed hydrogen can be calculated. The cooling and heating procedure can be repeated to yield subsequent adsorption and

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desorption peaks, which are reproducible unless sintering of the catalytic metal has occurred during the previous desorption step.

The sample cell consisted of a glass U tube that fit inside a tube furnace (150 mm long, 32 mm i.d.). The bottom portion of the U tube was large enough (6–12 mm o.d.) to allow gas to pass over the sample. Hydrogen and argon were obtained from Linde Division, Union Carbide Company. The hydrogen–argon mixture (1 mole % hydrogen) was prepared by adding hydrogen to an evacuated cylinder to a pressure of 620 Torr, then adding argon to a pressure of 1200 psig. The hydrogen had been manufactured by electrolysis of water, then passed over supported palladium catalyst to remove traces of oxygen. The amount of catalyst sample used was estimated to take up 10 to 50 μmoles of chemisorbed hydrogen. Water evolved from the sample was removed by means of a U tube (kept at −78°C) placed between the sample tube and the thermal conductivity detector. Calibration was carried out by injecting known amounts of hydrogen (0.1–2 ml) into the argon–hydrogen stream by means of gas-tight syringes.

DISCUSSION

The choice of a hydrogen–argon mixture that contained 1 mole % hydrogen was based on previous adsorption studies (*10*) which showed that the surface of platinum is saturated at 0°C, but bare at 500°C, at hydrogen pressures in the range 1–10 Torr. Adsorption of hydrogen by supports such as silica gel, alumina, silica–alumina, and crystalline zeolites is negligible under these conditions.

Table 1 lists chemisorption values obtained by the present method and the conventional static method for a series of catalysts consisting of platinum supported on silica gel. Agreement is good despite the variation in platinum content and dispersion (given by the atomic ratios of chemisorbed hydrogen to platinum content listed in the last column). The high dispersion of supported platinum was obtained by ion exchange of $Pt(NH_3)_4^{2+}$ with hydrogen ions in the silica gel support (*11*); low dispersions were obtained by impregnation of silica gel with chloroplatinic acid (*10*).

TABLE 1
HYDROGEN CHEMISORPTION BY PLATINUM ON SILICA GEL

% wt Pt	Hydrogen chemisorption (μmoles/g-cat.) Static method	Present method	Hydrogen/platinum ratio[b]
2.6[a]	20	24	0.33
4.1[a]	14	14	0.13
4.6[a]	30	38	0.29
4.5	110	105	0.93

[a] Prepared by impregnation with chloroplatinic acid (*10*).

[b] From average of the two chemisorption values.

The above results demonstrate that the flow technique can give reliable chemisorption values—values that were obtained in roughly one-third the time required in the case of the static technique. However, caution should be exercised in accepting all such values as gospel, especially when a completely new supported metal is to be examined. Under the latter circumstances, a thorough adsorption study of at least one representative sample should be made in order to establish the conditions (argon–hydrogen composition, equilibration and desorption temperatures) under which the flow technique will give meaningful chemisorption values. Completeness of outgassing and of attainment of equilibrium of hydrogen adsorption or desorption are more reliably determined by means of high-vacuum equipment because of the sensitivity and accuracy that is possible in measuring low residual pressures in such systems.

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