A Pulse Chromatographic Method of Determining the Specific Activity of Supported Metal Catalysts

The problem of characterizing supported metal catalysts has recently attracted considerable attention since, without knowledge of the metal surface area, it is not possible to express kinetic data for such systems on a meaningful basis (*1*). Metal areas are usually determined from chemisorption measurements using an adsorbate gas, such as carbon monoxide or hydrogen, which is specifically chemisorbed on the metal but not to a significant extent on the support. The conditions under which reliable measurements of metal areas may be obtained have been discussed in some detail by Innes (*2*). As an alternative to the conventional gravimetric or volumetric methods a pulse chromatographic technique has been developed (*3*, *4*) and shown to have a number of advantages. The method which is proposed here is essentially an extension of this chromatographic method and is dependent on the availability of a suitable adsorbate which, under reaction conditions, is strongly and specifically chemisorbed on the metal and not displaced by the reactants. If such an adsorbate is available both the metal area and the specific catalyst activity may be determined in a single experiment by injecting successive pulses of adsorbate into the reactant stream and measuring the decline in reaction rate. Although the phenomenon of catalyst poisoning has been extensively studied, this method of determining specific activities does not appear to have been previously suggested. This communication describes the successful application of the method in a study of the hydrogenation of cyclopropane over supported nickel catalysts, using carbon monoxide as the adsorbate. The experiments were carried out at 25°C using a commercial alumina supported nickel catalyst (Harshaw 0707). Both hydrogenation and hydrocracking occur:

$$C_3H_6 + H_2 = C_3H_8,$$

$$C_3H_6 + 2H_2 = C_2H_6 + CH_4,$$

and the values obtained for both the specific catalyst activity and the metal surface area agree well with the values previously obtained by conventional methods (*5*).

EXPERIMENTAL METHODS

The apparatus, which is shown diagrammatically in Fig. 1, consists of a standard flow reactor coupled directly to a sorptometer. Gas sampling valves before and after the reactor facilitate chromatographic analysis of the inlet and outlet gas streams. A third gas sampling valve (Perkin-Elmer) was used to inject pulses of carbon monoxide, which were measured before and after passing through the catalyst bed, using the thermal conductivity detector of the sorptometer (Perkin-Elmer model 154-D). The detector was calibrated in the normal way (*6*) so that the difference in peak area gave the quantity of carbon monoxide adsorbed by the catalyst. A small difference in the calibration constants of the two detector cells, due presumably to the pressure difference, was corrected for.

The gases used were obtained from the Matheson Company. Hydrogen (pre-purified grade, min. purity 99.5%) was further purified by passing through a deoxo unit and a molecular sieve drying bed. Carbon monoxide (min. purity 99.5%) was passed through a bed of activated charcoal to remove any iron carbonyl. Helium (ultra high purity 99.999%) and cyclopropane (99%) were used without further purification.

In order to check the system the metal area of the catalyst was measured using the pulse chromatographic method. The catalyst sample ($\simeq$0.3 g) was reduced in hy-

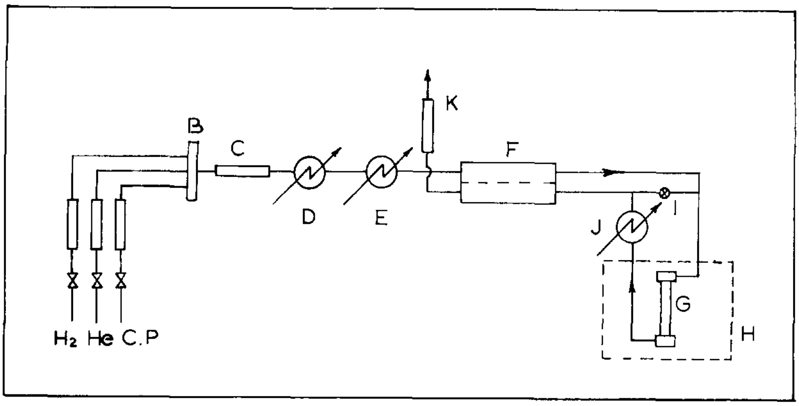

FIG. 1. Schematic diagram of the apparatus: (A) flow rotameters; (B) mixing manifold; (C) Cartesian manostat; (D) gas sampling valve; (E) carbon monoxide injection valve; (F) thermal conductivity cell of sorptometer; (G) flow reactor; (H) thermostat; (I) by-pass valve; (J) product sampling valve; (K) bubble flowmeter.

drogen for 18 hr at 360°C and then cooled to 25°C in a stream of helium, (100 ml/min). Successive pulses of carbon monoxide ($\simeq$0.1 ml) were then introduced into the helium stream with the result shown in Fig. 2. After 3 pulses the surface was completely saturated and no further uptake of carbon monoxide occurred. The experiment was then repeated in a stream of hydrogen. The rate at which carbon monoxide was adsorbed from the hydrogen stream was considerably slower due, presumably, to competiton for the adsorption sites. Approximately 8–9 pulses were required to saturate the surface but the total volume of carbon monoxide adsorbed was found to be precisely the same [0.850 ml (NTP)/g of catalyst]. The area occupied by a chemisorbed carbon monoxide molecule is generally taken as 12–13 Å^2 (*7*, *8*) and on this basis the specific metal area of the catalyst is calculated to be 2.75–3.0 m^2/g. This

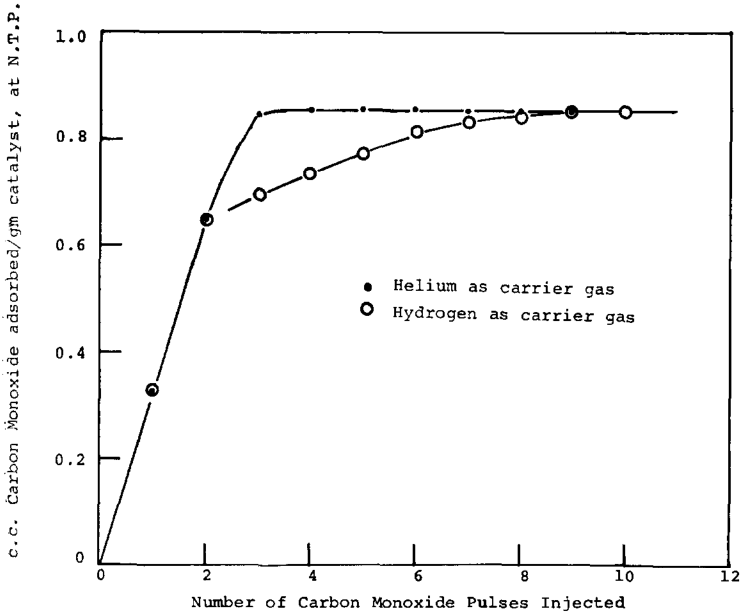

FIG. 2. Chemisorption of carbon monoxide on nickel surface by chromatographic procedure at 25°C.

agrees well with the value (2.8 m^2/g) previously obtained by conventional hydrogen chemisorption measurements with a Cahn microbalance (*5*).

After saturation with carbon monoxide, the catalyst was purged with hydrogen for a period of 2 hr and further pulses of carbon monoxide were then introduced. Only a very small additional amount of carbon monoxide (~5% of saturation) was adsorbed indicating that the rate at which hydrogen displaces carbon monoxide from the surface is quite low and therefore, provided measurements are carried out reasonably rapidly, little error will result from the use of a hydrogen carrier. This suggests that measurements of this type may be carried out in a reacting system in order to determine the specific activity of the catalyst.

For the activity studies the catalyst was preconditioned in the standard manner and then exposed to a steady flow (60 ml/min) of hydrogen and cyclopropane (46% H_2, 54% C_3H_6) at 25°C. The rate of reaction under steady state conditions was calculated from chromatographic analyses of the inlet and outlet gas streams. Successive pulses of carbon monoxide were introduced into the system and the decline in the rate of reaction was observed. In order to facilitate measurement of the quantity of carbon monoxide adsorbed the cyclopropane flow was shut off each time a pulse of carbon monoxide was introduced and sufficient time (~10 min) was allowed, as determined from the chromatographic analyses, to reestablish steady state reaction conditions. The results of experiments of this type, carried out with two different samples of catalyst, are shown in Fig. 3. The decline in the reaction rate is evidently directly proportional to the quantity of carbon monoxide adsorbed: this is consistent with the simple picture of the blocking of surface sites. A similar result was recently reported by Clay and Peterson for a platinum catalyst (*9*). On this basis both the specific catalyst activity and the metal area may be determined from the slope and intercept of these plots. The values so obtained are summarized in Table 1. The slope of both

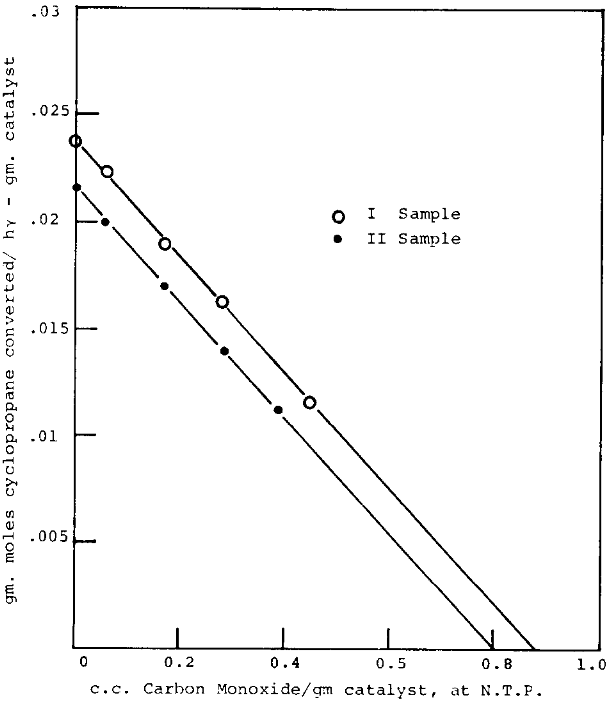

FIG. 3. Deactivation plots (Harshaw Ni-0707).

TABLE 1
NICKEL AREAS AND SPECIFIC REACTION RATES FOR HARSHAW Ni-0707[a]

Nickel area by H_2 chemisorption	2.8 m^2/g
Nickel area by CO chemisorption (pulse)	2.75 m^2/g
Nickel area by catalyst deactivation	2.58–2.79 m^2/g
Specific reaction rate calculated from slope of deactivation plots	48 molecules/Å^{2}hr

[a] The area occupied by a chemisorbed molecule is taken as 12.0 Å^2 for both CO and H_2.

plots is essentially the same and corresponds to a specific reaction rate of 576 molecules of cyclopropane/hr/carbon monoxide site or, taking the area occupied by a carbon monoxide molecule as 12.0 Å^2, 48 molecules/hr Å^2 nickel area. The quantity of carbon monoxide required for complete deactivation of the catalyst is calculated from the intercepts as 0.80 and 0.865 ml NTP/g of catalyst. These values correspond to specific nickel areas of 2.58 and 2.79 m^2/g in satisfactory agreement with the values determined by hydrogen chemisorption and carbon monoxide adsorption under nonreacting conditions. The reproducibility between successive experiments is evidently good and the small difference in the values obtained for the saturation volume (the intercept) arises because, under reaction conditions, the activity of the catalyst declines slowly, presumably due to a slow poisoning of the surface sites by trace impurities in the reactants. The initial level of activity therefore depends to some extent on the time on stream.

CONCLUSION

As an experimental technique this method appears to have many advantages. It is simpler, faster, and probably more accurate than conventional methods in which the specific activity is calculated from independent measurements of reaction rate and specific metal area carried out on different samples of catalyst. The method is especially useful for systems in which the catalyst activity declines continuously under reaction conditions. For such systems it is difficult, if not impossible to obtain a reproducible steady state catalyst activity and the effective area of the catalyst at any time is uncertain. The conventional method of measurement in which the specific activity is calculated from area measurements carried out on a clean surface can therefore lead to large errors. The present method does not however depend on obtaining either a clean surface or a reproducible steady state activity since, provided the rate at which the catalyst activity declines under reaction conditions is not too large, the slope of the plot of activity versus carbon monoxide adsorbed will not be significantly affected.

The present method also yields additional information. By comparing the saturation volume of adsorbate required to deactivate the catalyst measured under reaction conditions, with the saturation volume for a clean surface measured in a nonreacting system, it is possible to estimate the fraction of the total surface on which reaction occurs. For the present system, the relationship between reaction rate and volume of carbon monoxide adsorbed is approximately linear and the intercept of this plot corresponds closely with the monolayer volume for the catalyst. This suggests that the entire nickel surface is catalytically active and that all surface sites have approximately the same activity. Such simple behavior should not, however, be regarded as universal since it is well established that, for some systems, the relationship between reaction rate and poison adsorbed is nonlinear *(10, 11)*. In such cases the interpretation of the poisoning plots is necessarily less straightforward *(12)*. The results of a more extensive current study which includes examples of both linear and nonlinear behavior will be discussed in a future publication.

The principal disadvantage of this technique is the difficulty of obtaining a suitable adsorbate since this severely restricts both the type of reaction which may be studied and the range of conditions which may be employed. Carbon monoxide can only be used satisfactorily as an adsorbate at or near room temperature since at low temperatures physical adsorption on the support becomes significant and at high temperatures volatile metal carbonyls are formed. There are, however, many hydrogenation reactions which can be conveniently studied at room temperature and the technique described should be directly applicable to such systems. The value of the technique is not, however, limited to hydrogenation reactions and it would appear that with a judicious choice of adsorbate and reaction conditions the technique should be valuable for studying a great variety of different catalytic reactions.

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Catalytic Oxidation over Molecular Sieves Ion-Exchanged with Transition Metal Ions

II. Selective Oxidation of Propylene over Cu(II)–Y in the Presence of Steam

In a previous paper (*1*), it was reported that Y-molecular sieve ion-exchanged with cupric ions [Cu(II)–Y] had a very high catalytic activity for deep (i.e., total) oxidation of propylene. In addition, some ion-exchanged molecular sieves are reportedly highly active solid acid catalysts for various acid-catalyzed reactions (*2*). These two characteristics have suggested to us that a molecular sieve might be developed as a bifunctional catalyst which is acidic and oxidative at the same time. Recently, Ohki and Ozaki (*3*) and Ogasawara *et al.* (*4*) reported a ketone synthesis using some binary catalysts containing molybdena. This reaction was thought to proceed via a hydration of olefin followed by an oxidation of alcohol formed. In the present work, selective oxidation of propylene over Cu(II)–Y catalyst has been tried in the presence of steam, and some results are reported.

EXPERIMENTAL METHODS

The Cu(II)–Y molecular sieve used was described in a previous paper (*1*). The oxidation reaction was studied by an ordinary flow method, with a fixed catalyst bed diluted by carborundum. Composition of the feed and reacted gases were analyzed with gas chromatography using a Porapak Q column (Water Associated Inc.) for car-