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Application of a Pulse Poisoning Technique in Catalytic Studies

Hydrogenation of Cyclopropane

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A pulse poisoning technique has been used to determine the specific activities and metal areas of a series of supported metal catalysts for the hydrogenation of cyclopropane. The areas and activities obtained by this technique agree well with values determined by conventional methods thus establishing the validity of the experimental method. Data are presented showing (i) the effect of pretreatment on the activity and selectivity of a supported Ni catalyst, (ii) a comparison between the activities of differently supported catalysts of Ni, Pt, Pd, Rh, (iii) the order of the specific hydrogenation and hydrocracking activities of a series of transition metals, compared under standard conditions.

INTRODUCTION

In order to interpret kinetic data for supported metal catalysts knowledge of the specific metal area is required as without such information it is not possible to make proper comparisons between the activities of different catalysts. The usual method for determining the specific activities of supported metal catalysts involves separate measurements of the reaction rate and the metal surface area (*1–3*). As an alternative to the conventional methods we have suggested a technique by which both the active metal area and the specific activity of the catalyst may be determined, under reaction conditions, in a single experiment (*4*). Apart from the advantages of speed and simplicity this technique therefore offers the great advantage that the specific activity and area are determined at a particular time so that difficulties arising from slow sintering or poisoning of the catalyst are avoided.

The method depends on introducing successive pulses of a strongly adsorbed poison into a flow reactor and following the decline in reaction rate. The present paper reports results obtained by the application of this technique to a study of the effect of pretreatment on catalyst activity and a comparison of the specific activities of a series of supported and unsupported transition metal catalysts for the hydrogenation of cyclopropane.

A basic assumption of the method is that the relationship between the catalyst activity (reaction rate) and the amount of poison adsorbed is linear. This was found to be true for the systems studied experimentally but this condition restricts to some extent the choice of poison since a linear relationship will not always be found (*5–10*).

If the catalytic surface is heterogeneous with sites of widely different activity then a linear relationship between activity and

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poison uptake cannot be expected. However, even if the sites are reasonably homogeneous it has been shown by Herington and Rideal (*11*) that certain conditions concerning the relative sizes of reactant and poison must be fulfilled for a linear relationship to hold. In order to simulate the effect of poisoning the catalyst surface we consider, after Herington and Rideal (*11*), an ideal surface with a fixed number of identical active sites. We simulate the effect of blocking the surface with a poison which requires one, two or three sites by randomly blocking a certain fraction of the total sites, subject to the restriction that, for a two or three site poison, the two (or three) sites required must be adjacent. The fraction of the surface which is available to the reactant can then be calculated subject to the restriction that for an n-site reactant *n adjacent sites* are required. A typical plot obtained by this method for a two site poison and 1–7 site reactants is shown in Fig. 1. It is evident that the relationship between the fraction of surface occupied by the reactant (proportional to the catalyst activity) and the fraction of surface occupied by the poison (proportional to the quantity of poison adsorbed) is essentially linear except when the number of sites required by the reactant molecule is much greater than the number of sites occupied by a molecule of poison. Although this analysis depends on a very simplified representation of the catalyst it is probably valid to conclude that a linear decline in catalyst activity with poison uptake is to be expected except when the reactant molecule is very large relative to the poison or when there is a wide distribution of site activity.

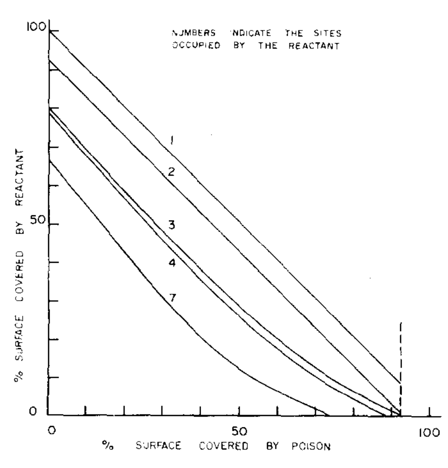

Fig. 1. Theoretical curves showing the decline in available surface with amount of poison adsorbed. (A poison molecule is assumed to occupy two sites.)

EXPERIMENTAL METHODS

Details of the apparatus are given in our earlier paper (*4*). The reaction was carried out in a differential flow reactor at 25°C and at a total pressure of 1 atm. The catalyst sample (0.3–1.0 g) was reduced initially under a flow of hydrogen (60 ml/min). Except in the study of the effect of pretreatment the temperature during reduction was maintained at 360°C for a period of 18 hr.

Reaction rates were measured at 25°C with a standard gas mixture containing 54% cyclopropane and 46% hydrogen at a flowrate of 60 ml/min. The reaction rate was calculated from chromatographic analyses of inlet and outlet composition and the known gas flowrate. Successive pulses of known quantity of poison (CO) were then introduced into the system and the decline in reaction rate was noted. In order to facilitate accurate measurement of the quantity of CO adsorbed on the catalyst the cyclopropane flow was shut off each time a pulse of CO was injected. The quantity of CO adsorbed was calculated from the difference in peak areas (obtained from the thermal conductivity detector) at the inlet and outlet of the catalyst bed.

The catalysts used are listed in Table 1. The Ni, Co and Mo catalysts were from Harshaw Chemical Co., U.S.A. while the Pt, Pd and Rh catalysts were from Matheson, Coleman and Bell, Canada. Over Ni, Co, Mo and Rh catalysts both hydrogenation and hydrocracking reactions occurred;

TABLE 1

Metal Areas of Catalysts

Catalyst	Clean metal surface area obtained by CO adsorption (m^2/g)	Metal surface area from deactivation plots (m^2/g)
Harshaw Ni-0707 (14% Ni-alumina)	2.75[a]	2.58–2.79
Harshaw Ni-1430 (40% alumina)	5.80	6.58
Harshaw Co-0101 (35% CO-kieselguhr)	3.95	3.68–3.9
Harshaw Mo-1201 (10% Mo-alumina)	0.70	0.66
Rh (5% Rh-alumina)	13.38	13.35
Rh (5% Rh-charcoal	15.50	14.63
Rh (0.5% Rh-alumina)	1.90	1.78
Pd (5% Pd-alumina)	5.06	5.32
Pd (5% Pd-charcoal)	6.0	5.12–5.92
Pd (10% Pd-charcoal)	12.0	9.93
Pd black —	3.90	3.19
Pt (5% Pt-alumina)	3.50	3.28
Pt (0.5% Pt-alumina)	0.34	0.24–0.28
Pt black —	11.9	11.43

[a] For this catalyst metal area was also determined by H_2 chemisorption (2.8 m^2/g).

$$\text{cyclo–}C_3H_6 + H_2 = C_3H_8,$$

$$\text{cyclo–}C_3H_6 + 2H_2 = C_2H_6 + CH_4,$$

whereas over Pt and Pd catalysts there was no hydrocracking.

Metal areas of samples of the clean catalysts, after reduction, were determined independently by the method of Brooks and Kehrer (*2*) or Gruber (*3*) (chemisorption of CO measured chromatographically under nonreacting conditions). The areas so determined are given in Table 1, based on the assumption that one CO molecule occupies 12.0 Å². The area of a sample of Ni-0707 was also determined by H_2 chemisorption and the value so obtained was very close to the value from CO chemisorption as well as to the value obtained from the poisoning plot.

RESULTS AND DISCUSSIONS

The Effect of Reduction Temperature

The effect of reduction conditions on the area, activity and selectivity of a supported nickel catalyst (Harshaw 0707, 14% Ni–Al_2O_3) was investigated by varying the temperature and period of initial reduction and then determining the specific activity and metal area of each sample by the method outlined above. The results are summarized in Table 2. Total catalyst areas determined by the BET method were found to be essentially independent of the reduction conditions (158–160 m^2/g), whereas the specific metal area increases

TABLE 2

The Effect of Pretreatment on a Ni–Al_2O_3 Catalyst[a]

Reduction temp. (°C)	Reduction period (hr)	Metal area (m^2/g)	r	Activity (molecules cyclopropane converted/ hr-Å² metal)
260	18	0.14	0.43	11.4
360	18	2.75	1.29	48.0
360	26	2.86	1.1	38.4
410	18	3.93	0.81	11.2
460	18	4.20	0.3	5.2

[a] BET area = 158–160 m^2/g; catalyst: Harshaw 0707; r = rate of cracking/hydrogenation.

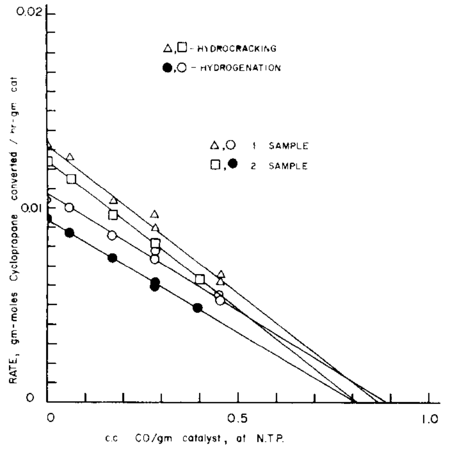

FIG. 2. Experimental deactivation plots for catalyst Ni-0707.

appreciably with increasing time and temperature. The most probable explanation for this effect is increasing reduction of the metal, although it is somewhat surprising that such a long period should be required to effect reduction even at these elevated temperatures. On prolonged exposure to high temperatures one might expect some crystal growth to occur with a corresponding reduction in metal area. The observed increase in metal area, however, suggests that any such effect is small in comparison with the increase in area arising from more complete reduction.

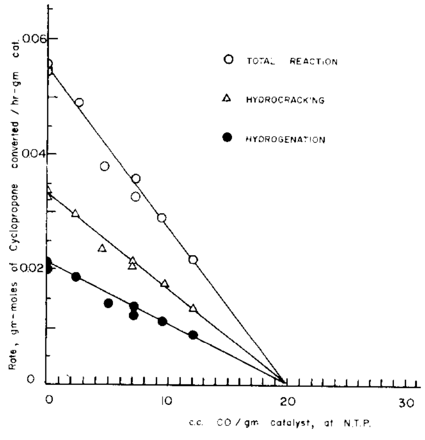

FIG. 3. Experimental deactivation plots for catalyst Ni-1430.

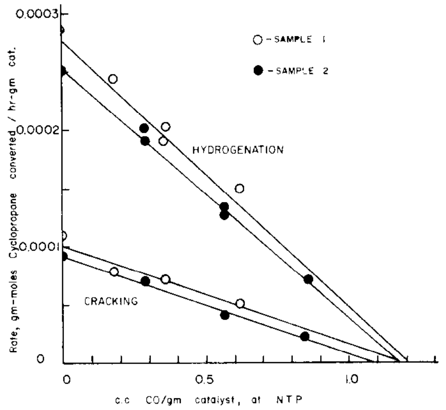

FIG. 4. Experimental deactivation plots for catalyst Co-0101.

The specific activity of the catalyst (defined as the total rate of conversion of cyclopropane per unit metal area) is highest for reduction at 360°C for 18 hr and is appreciably lower for either more or less severe reduction conditions. Associated with these changes in specific activity there is also a change in the ratio of the rate of hydrocracking to the rate of hydrogenation (the selectivity, r). The precise reason for this variation in activity is not clear although it is evident that if the active catalyst is in fact in a partially reduced form then changes in the extent of reduction may exert a considerable influence on the electronic and catalytic properties of the surface.

Alternatively it is possible that both the increase in area and the changes in activity arise from changes in the metal crystallite size. Significant variation in catalytic properties with extent of dispersion have been previously reported for several systems (*12–16*). However, the variation in metal crystallite diameter required to account for the change in specific area from 2.75 to 4.2 m^2/g is quite modest (a factor of 1.5) and it seems unlikely that such an effect could account for the observed 10-fold change in catalyst activity. Furthermore, for this explanation to hold it is necessary to assume that crystallite size decreases on

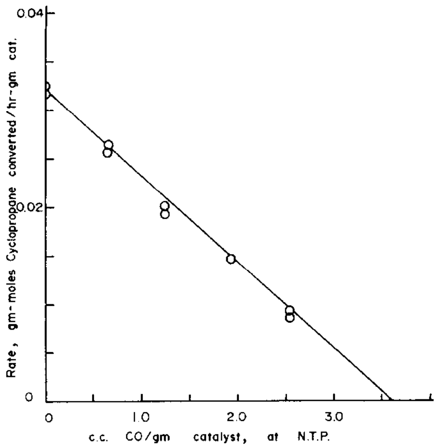

FIG. 5. Experimental deactivation plot for Pt black catalyst.

prolonged exposure at high temperatures, whereas under these conditions crystal growth is more likely.

Comparison of Activities of Various Metal Catalysts

As a further application of the chromatographic poisoning technique a series of different supported metal catalysts was studied. Typical deactivation plots are shown in Figs. 2–5 and in Table 1 the metal areas obtained from the deactivation plots are compared with the values determined directly from CO adsorption. For all catalysts the agreement is excellent confirming the validity of the experimental technique. It may be seen that in most cases the areas obtained from the deactivation plots are slightly smaller than the chromatographic values for the clean catalyst. This is probably because, under reaction conditions, the activity of the catalyst declines slowly presumably as a result of slow poisoning by trace impurities.

The specific activities of the various catalysts are compared in Table 3 in which the data reported by Dalla Betta *et al.* (*18*) are also included. These data have been corrected to the temperature of the present study (25 °C) using the reported activation energies but the difference in partial pressures has not been allowed for. The data for Pt, Pd and Rh are in order of magnitude agreement with the present results and show similar general trends.

For Ni, Co, Mo and Rh catalysts both hydrogenation and hydrocracking reactions were observed while with Pt and Pd there was no cracking. The observed order of total activity Rh > Ni > Pd > Pt > Mo > Co and the order of cracking activity Ni > Co > Mo > Rh ≫ Pt, Pd are in general agreement with the results of Sinfelt *et al.* (*17*), Dalla Betta *et al.* (*18*) and of Wallace and Hayes (*19*).

Both the activity and selectivity of the catalysts are to some extent affected by the support. Such effects are relatively minor for Rh, Ni and Pt but are more significant for Pd. The results for Pt catalysts agree well with the data of Boudart *et al.* (*20*) and Kahn *et al.* (*21*) which show no more than a twofold variation in activity between a single Pt crystal

TABLE 3

Comparison of Specific Activities of Catalysts

Catalyst	Rate		
	Total	Hydrogenation	Cracking
Ni-0707	48	21.0	27
Ni-1430	50	18.6	31
Co-0101	0.57–0.60	0.41–0.46	0.16–0.19
Mo-1201	0.82	0.68	0.41
Rh (5% on Al_2O_3)	135	135	0
Rh (5% on charcoal)	118	115	2.7
Rh (0.5% on Al_2O_3)	140	124	16.0
Pd black	0.72	0.72	0
Pd (5% on charcoal)	6.0–6.9	6.0–6.9	0
Pd (10% on charcoal)	14.5	14.5	0
Pd (5% on Al_2O_3)	35.4	35.4	0
Pt black	16.8	16.8	0
Pt (5% on Al_2O_3)	26.0	26.0	0
Pt (0.5% on Al_2O_3)	26–27	26–27	0
Pd (10% on SiO_2)[b]	21	21	0
Rh (0.3% on SiO_2)[b]	780	780	0
Ru (10% on SiO_2)[b]	1.2	0	0.22
Pt (0.6% on SiO_2)[b]	117	117	0
Ir (10% on SiO_2)[b]	3.0	3.0	0
Os (10% on SiO_2)[b]	1.91	1.67	0.24

[a] Reaction rate: molecules cyclopropane/hr-Å^2 metal surface.
[b] Data from Dalla-Betta *et al.* (*18*) corrected to 25°C.

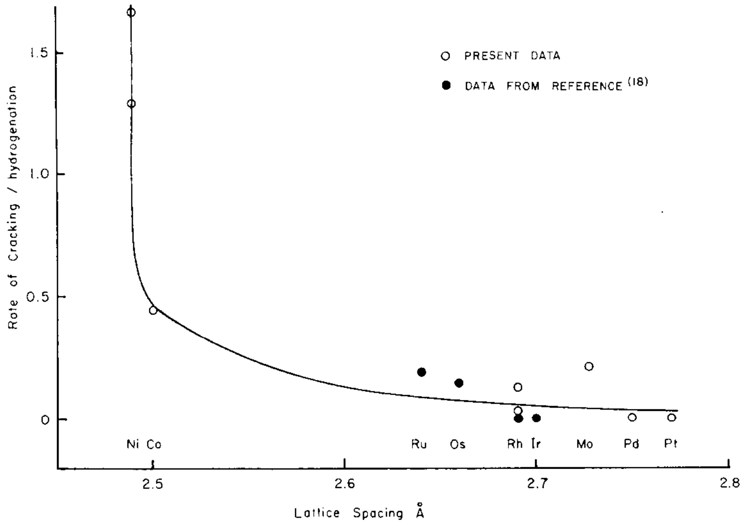

FIG. 6. Correlation of hydrocracking activity with lattice spacing (different metals).

and an alumina supported Pt catalyst. By contrast for Pd catalysts there is nearly a 50-fold difference in activity between Pd black, the least active catalyst, and Pd–Al_2O_3, the most active. The differences in activity between different metals are, however, even more pronounced so that in spite of the uncertainty arising from support effects it is possible to make a general comparison between the activities of the different metals.

For several hydrogenation reactions correlations between catalytic activity and lattice distance or "% *d* character" have been established (*22*). The present data show no such correlation although there appears to be a general increase in activity with work function. Such a correlation is to be expected if the rate controlling step in the reaction involves the transfer of electrons from sorbate to metal. This is consistent with the reaction mechanism proposed by Sridhar and Ruthven (*23*) although in view of the very larger uncertainty in the values of the work functions for these metals any such conclusion is speculative.

The cracking activity of the catalysts shows a fairly clear correlation with the lattice spacing as illustrated in Fig. 6. Ni and Co which have the smallest lattice spacing (2.49–2.50 Å) show pronounced cracking activity, whereas for Pt and Pd (lattice spacing 2.75–2.77 Å) there is no significant cracking. Furthermore, for the various nickel catalysts subjected to different reduction conditions the relative rates of cracking and hydrogenation show a clear correlation with the total activity (Fig. 7) again suggesting that the density of the surface sites (atoms) may be the important variable.

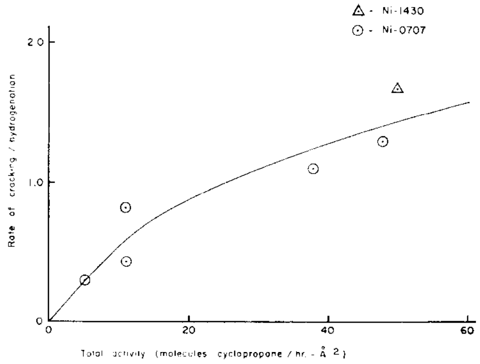

FIG. 7. Correlation of hydrocracking activity with total catalyst activity for Ni catalysts.

CONCLUSIONS

The potential advantages of the pulse poisoning technique were discussed briefly in our earlier paper (*4*). The present study shows that the technique provides a quick and efficient method of determining specific activities and metal areas and it should therefore be very useful for catalyst screening. The consistency and reproducibility of the results and the agreement with the data obtained by conventional methods establish clearly the validity of the technique.

Apart from speed and simplicity the technique offers a number of other advantages. Both specific activity and area are determined in a single experiment. Moreover these measurements do not require either a clean catalyst surface or a reproducible steady state activity since, provided that the rate at which the catalyst activity declines under reaction conditions is not too large, the slope of the plot of activity vs poison uptake will not be significantly affected. This should make the technique especially valuable for studying systems in which the activity of the catalysts declines continuously under reaction conditions.

Additional information concerning the details of a reaction may also be obtained by this technique. A comparison between the clean metal area, measured under nonreacting conditions, and the area under reaction conditions provides an estimate of the fraction of the total metal area on which the reaction occurs. For all systems studied here the Y-intercept of the deactivation plots was close to the CO monolayer volume for the clean catalyst. Taken in conjunction with the linearity of the deactivation plots this provides evidence that for these catalysts the entire metal surface is active and all surface sites are approximately equivalent.

Throughout the present study CO was used as the poison but there is in principle no reason why other strongly adsorbed species should not be employed. The only requirement is that there should be a linear decline of reaction rate with the quantity of poison adsorbed and that the poison should be adsorbed irreversibly so that it is not significantly desorbed during the time scale of an experiment.

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