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# A Study of Relationships between Pore Size Distribution, Hydrogen Chemisorption, and Activity of Hydrodesulphurisation Catalysts

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A series of commercial catalysts was tested for hydrodesulphurisation (HDS) activity using an atmospheric gas oil. The pore volume distribution in the radius range 10–300 Å and the hydrogen uptake at 350°C were measured for each catalyst. A correlation was found between relative HDS activity and the pore volume contained in the radius range 37.5–55 Å. The hydrogen uptake was also found to correlate with the same pore volume. The significance of the correlation between hydrogen uptake, a chemical property, and pore volume distribution, a physical property, is discussed.

## INTRODUCTION

Steam reforming catalysts used to process liquid hydrocarbons in the gas industry are extremely sensitive to poisoning by sulphur compounds in the feedstock and consequently purification of the feedstock to a sulphur level of $<0.2$ ppm is required (*1*). For lighter feedstocks, such as naphtha fractions, the purification or hydrodesulphurisation (HDS) process presents little difficulty. However, for heavier feedstocks, such as gas oil, the achievement of the high level of purity required becomes more arduous, mainly because their initial sulphur content is higher and because the complex sulphur-containing molecules found in these materials are more difficult to rupture than the simpler compounds found in the lighter fractions. For the heavier materials, an initial conventional hydrotreatment is followed by a stage of fine purification incorporating zinc oxide for hydrogen sulphide removal.

Many advanced HDS catalysts are now commercially available, but in order to establish which is the best for the particularly arduous degree of purification required, further screening is necessary. During the course of screening tests in a laboratory scale reactor, the relative activities of a number of commercial catalysts were established. In addition, two other properties, namely, hydrogen adsorption and pore volume distribution, were measured and correlation was attempted to see if any time-consuming activity tests could be replaced with other tests of shorter duration. The results were rather surprising, in that an unexpected correlation was found between hydrogen adsorption and the pore volume distribution, as well as between activity and these properties.

## EXPERIMENTAL

### *Activity Tests*

The relative order of activity for a range of readily available commercial catalysts was determined by carrying out a series of 100-h tests.

The feedstock used for the activity-ranking tests was an atmospheric gas oil which after a preliminary hydrofining treatment had the physical properties shown in Table 1. The catalysts were all alumina-supported molybdenum oxide promoted either by cobalt or nickel and presulphided before use.

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TABLE 1

Activity Test Details and Feedstock Properties

| | |
|---|---|
| Catalyst bed temperature | 360°C |
| Pressure | 4.2 MPa |
| Liquid hourly space velocity (LHSV) | $9.5 \times 10^{-1}$ h$^{-1}$ |
| $H_2$ (STP): feedstock (liquid) volume ratio | 260 |
| Feedstock | |
| Initial boiling point | 208°C |
| Final boiling point | 360°C |
| API gravity | 36.8 |
| Average molecular weight | 210 |
| Type analysis (wt%) | |
| Aliphatics | 70.0 |
| Aromatics | 30.0 |
| Sulphur ppm | 116 |
| Nitrogen ppm | 95 |

The relevant properties of each of the catalysts are shown in Table 2.

The activity tests were carried out in a laboratory scale apparatus. The evaporated oil and hydrogen were passed through a preheater into a 26.6-mm-i.d. reactor which contained the catalyst being tested. The catalyst was loaded as a 0.305-m bed supported and surmounted by 6.4-mm alumina balls. The process fluid then passed onto an absorber stage containing heated zinc oxide to remove $H_2S$ formed in the process. Facilities were available for taking liquid samples at the outlet of the reactor stage and the samples were analysed for total sulphur content by a microcoulometric technique (*2*).

Since all the catalysts tested are "advanced" HDS catalysts, under normally recommended operation conditions even the worst catalysts would give >90% conversion of the sulphur compounds to $H_2S$. In order to magnify any differences in activity, therefore, the tests were performed under conditions which were more severe for the catalysts than those used in commercial practice. Table 1 shows these conditions. HDS plants in general tend to operate at higher temperatures and pressures. Under these conditions, the different catalysts showed differences of conversion varying over the range 70–95%.

For each of the tests, the charged catalyst was subjected to a standard presulphiding procedure. In this, a naphtha feedstock (FBP 170°C) doped to a level of 0.65% sulphur by the addition of $CS_2$ was passed over the catalyst at 360°C at a liquid hourly space velocity (LHSV) of 2.0 h$^{-1}$ with a hydrogen (STP)/feedstock (liquid) volume ratio of 90. After 24 h the catalyst had been exposed to sulphur which corresponded to two to four times the amount necessary to

TABLE 2

Details of Catalysts Examined

| Catalyst | Size/shape | Metal content (% w/w) | | | BET surface area (m$^2$ g$^{-1}$) | Bulk density (g cm$^{-3}$) |
|---|---|---|---|---|---|---|
| | | Mo | Ni | Co | | |
| A | $\frac{1}{16}$-in. extrudate | 12.6 | 2.6 | | 184 | 0.82 |
| B | $\frac{1}{16}$-in. extrudate | 9.4 | 2.1 | | 143 | 0.85 |
| C | $\frac{3}{32}$-in. extrudate | 11.1 | | 4.0 | 222 | 0.65 |
| D | $\frac{1}{8}$-in. pellet | 9.4 | 2.1 | | 156 | 0.95 |
| E | $\frac{1}{16}$-in. extrudate | 7.8 | | 2.1 | 231 | 0.76 |
| F | $\frac{1}{16}$-in. extrudate | 8.6 | | 2.1 | 252 | 0.86 |
| G | $\frac{1}{8}$-in. extrudate | 6.2 | 2.2 | | 112 | 0.55 |
| H | $\frac{1}{16}$-in. extrudate | 9.6 | | 3.5 | 207 | 0.77 |
| I | $\frac{1}{8}$-in. extrudate | 5.7 | | 1.7 | 182 | 0.57 |
| J | $\frac{1}{16}$-in. extrudate | 6.7 | | 2.7 | 210 | 0.82 |

allow for complete conversion of the oxides of the active metals to their stoichiometric sulphides. The actual sulphur contents of the catalysts were not measured, since there would in any case be a reequilibration of the sulphur content during subsequent operations.

After sulphiding, the test feed was introduced into the reactor without interruption of flow and the run was continued for a period of about 100 h under the conditions shown in Table 1. During the run, samples of product on exit from the reactor were taken at regular intervals and analysed for sulphur content after the removal of dissolved $H_2S$. For each catalyst the outlet sulphur concentration was taken as the mean value for the sulphur content of at least four samples.

### *Pore Volume Distribution Measurements*

Pore size distributions for the catalysts were measured using a Micromeritics Digisorb 2500 instrument. This uses nitrogen porosimetry to measure pore size distributions in the radius range 10–300 Å. The measurements, for convenience, were performed on the oxide form of the catalysts. Sample weights of 0.5 to 0.7 g were used and prior to BET surface area and desorption pore volume determinations, the samples were each outgassed for 4 h at 300°C. Pore volume and pore size distributions were calculated using a method developed by Roberts (*3*), following that of Barrett, Joyner, and Halenda.

### *Hydrogen Adsorption*

The hydrogen uptake during isothermal reduction was measured using the catalysts in the oxide form. The experiments were carried out using a grease-free, high-vacuum volumetric glass apparatus and the amount of hydrogen uptake equalled that consumed by reduction processes together with any adsorbed by chemisorption. In order to avoid inconsistencies, a small cold finger trap was incorporated into the system to remove any water which might desorb from the catalyst during the reduction process.

The procedure for an experimental run was as follows. A weighed sample of catalyst (0.6 g) in the form of extrudates or pellets was dehydrated by heating *in vacuo* (to 1.33 mPa) for 16 h at 350°C. The catalyst was then exposed to $H_2$ (at a pressure of 13.3–26.6 kPa) at 350°C and the hydrogen uptake was followed by observing the pressure change with time. An initial rapid removal of hydrogen from the gas phase was followed by a slower continuous adsorption which made it difficult to judge the final uptake accurately. For comparison purposes uptakes were measured after a 45-min period and an identical $H_2$ pressure (20 kPa) was used for each of the catalysts.

## RESULTS AND DISCUSSION

The conversion achieved in a particular activity test is given by

$$C = \frac{[S_{\text{in}}] - [S_{\text{out}}]}{[S_{\text{in}}]}, \tag{1}$$

where $[S_{\text{in}}]$ and $[S_{\text{out}}]$ are the experimentally measured inlet and outlet sulphur concentrations. Over the 100-h period of all the tests the conversion, and hence catalyst activity, was maintained at a fairly constant level. Indeed, further tests showed that the activity was maintained over a much longer period than 100 h.

For a particular catalyst the pseudo-first-order rate constant for the hydrodesulphurisation, $k_1'$, is related to the conversion by

$$k_1'\left(\frac{V}{F}\right) = \ln\left(\frac{1}{1-C}\right) = \ln\left(\frac{[S_{\text{in}}]}{[S_{\text{out}}]}\right), \tag{2}$$

where $V$ is the volume of the catalyst space and $F$ is the volume rate of flow of feedstock. Since the contact time, $V/F$, was the same in all the activity tests a relative HDS activity value, $R$, for each catalyst relative to the standard catalyst, B, can be simply defined as a ratio of pseudo-first-order rate constants:

TABLE 3

Pore Size Distribution and Hydrogen Adsorption Data

| | Activity ranking (relative activity value, $R$) | Pore size distribution | | | $H_2$ adsorption | | |
|---|---|---|---|---|---|---|---|
| | | $V_p$[a] ($cm^3\ g^{-1}$) | $\bar{r}_p$ for $\Delta V_p/\Delta r_p$ maximum (Å) | $\Delta V'$ (37.5–55)[b] ($cm^3\ cm^{-3}$) | $H_2$ uptake, 350°C (μmole $cm^{-3}$) | Specific reduction (×$10^2$) 350°C | Percentage surface coverage of Mo |
| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) |
| A | 1.05 | 0.560 | 43 | 0.243 | 218.5 | 15.3 | 86.0 |
| B | 1.0 | 0.492 | 29, 49 | 0.222 | 191.6 | 15.9 | 82.3 |
| C | 0.91 | 0.617 | 33 | 0.126 | 125.0 | 9.3 | 62.4 |
| D | 0.83 | 0.419 | 29, 44 | 0.180 | 219.5 | 17.1 | 75.4 |
| E | 0.82 | 0.611 | 34 | 0.166 | 141.4 | 14.3 | 42.2 |
| F | (1) 0.69[c]<br>(2) 0.65 | 0.542 | 25, 37 | 0.101 | 144.8 | 12.2 | 42.7 |
| G | 0.59 | 0.639 | 23, 43 | 0.162 | 121.2 | 21.7 | 69.6 |
| H | 0.50 | 0.542 | 35 | 0.133 | 125.0 | 9.0 | 58.5 |
| I | 0.50 | 0.340 | 22 | 0.017 | 47.9 | 8.6 | 39.5 |
| J | 0.41 | 0.207 | ND[d] | 0.005 | 46.0 | 4.3 | 39.9 |

[a] Total volume of pores contained in pores of radii 10–300 Å.

[b] Volume of pores in $cm^3/(cm^3$ catalyst space) in radius range 37.5–55 Å.

[c] Values from two different activity tests.

[d] Not discernible.

$$R = k_1'/k_1'(\mathrm{B}). \qquad (3)$$

Relative activity values for the ten catalysts calculated from experimentally measured inlet and outlet sulphur concentrations are shown in Table 3 (column 2). The two values for catalyst F were derived from two different 100-h tests and demonstrate the repeatability of the tests.

The results of pore size distribution measurements are shown in Table 3, columns 3–5. From these, the following general comments can be made. The total volume of pores contained in the radius range 10–300 Å $V_p$, has a value between 0.4 and 0.65 $cm^3\ g^{-1}$ for all but two of the catalysts; the exceptions are catalysts I and J which are at the bottom of the ranking order. It is also apparent that the maxima in the PSD curves of all but two catalysts lie in the radius range 25–50 Å; the two exceptions are again catalysts I and J.

To investigate a possible correlation between pore size distribution and HDS activity, a detailed histogram breakdown of the pore volume distribution in the radius range 10–75 Å was compiled for all the catalysts. The initial stage of correlation involved the use of pore volume data for ten selected 20-Å-radius intervals in the radius range 10–75 Å. The pore volume $\Delta V(r_1 - r_2)$ in each selected radius interval $r_1 - r_2$ is tabulated for each of the catalysts A to J in Table 4. The derived HDS activity values relate to the same fixed volume of catalyst space, whereas the $\Delta V(r_1 - r_2)$ values are weight specific. Hence, before any attempted correlation, $\Delta V(r_1 - r_2)$ values are converted to $\Delta V'(r_1 - r_2)$ values in cubic centimeters per cubic centimeter catalyst space by multiplying by the appropriate catalyst bulk densities in Table 3.

For each pore radius interval a linear regression was performed using appropriate $\Delta V'$ values as abscissae and $R$ values as ordinates. After each linear regression curve.was determined the associated correlation coefficient, $r$, was calculated. The "degree of fit" of the points to the least-squares line was measured by the correla-

TABLE 4

Pore Volume Distribution Data for 20-Å Intervals in the Radius Range 10–75 Å

| Catalyst | Pore radius range (Å) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 10–30[a] | 15–35 | 20–40 | 25–45 | 30–50 | 35–55 | 40–60 | 45–65 | 50–70 | 55–75 |
| A | 0.076 | 0.145 | 0.221 | 0.312 | 0.358 | 0.342 | 0.279 | 0.178 | 0.097 | 0.041 |
| B | 0.078 | 0.014 | 0.159 | 0.198 | 0.236 | 0.285 | 0.285 | 0.242 | 0.164 | 0.080 |
| C | 0.176 | 0.284 | 0.362 | 0.392 | 0.340 | 0.247 | 0.157 | 0.086 | 0.059 | 0.036 |
| D | 0.096 | 0.140 | 0.197 | 0.244 | 0.248 | 0.231 | 0.168 | 0.101 | 0.046 | 0.018 |
| E | 0.157 | 0.276 | 0.378 | 0.431 | 0.388 | 0.283 | 0.169 | 0.074 | 0.036 | 0.015 |
| F | 0.300 | 0.340 | 0.373 | 0.321 | 0.225 | 0.160 | 0.079 | 0.018 | 0.008 | 0.004 |
| G | 0.061 | 0.144 | 0.180 | 0.249 | 0.328 | 0.343 | 0.323 | 0.263 | 0.180 | 0.117 |
| H | 0.159 | 0.269 | 0.362 | 0.393 | 0.346 | 0.232 | 0.118 | 0.044 | 0.018 | 0.011 |
| I | 0.200 | 0.217 | 0.191 | 0.125 | 0.067 | 0.040 | 0.024 | 0.019 | 0.017 | 0.013 |
| J | 0.136 | 0.063 | 0.034 | 0.012 | 0.009 | 0.008 | 0.007 | 0.006 | 0.006 | 0.005 |

[a] Pore volume (cm$^3$ g$^{-1}$) contained in pore radius range 10–30 Å, $\Delta V(r_{10} - r_{30})$.

tion coefficient. When $r = \pm 1$, the correlation is said to be exact; when $r = 0$, the variables are said to be uncorrelated with a linear equation. The best correlations with activity were obtained using $\Delta V'(35\text{–}55)$ and $\Delta V'(40\text{–}60)$. The correlation coefficients were 0.81 and 0.80, respectively; the correlation coefficients for the other eight selected intervals were in the range $-0.24 < r < 0.68$.

The second stage of the correlation involved the use of pore volume data for ten selected radius intervals in the radius range 35–60 Å; these comprised five $r_1 - 55$ and five $r_1 - 60$ intervals where $r_1$ was increased from 35 to 45 Å in 2.5-Å steps. A second set of linear regressions was carried out as before; the calculated correlation coefficients ranged from 0.75 to 0.83. The maximum value of $r$ was obtained for the radius range 37.5–55 Å. Figure 1 shows the plot of relative HDS activity, $R$, vs pore volume in the radius range 37.5–55 Å, $\Delta V'$.

The conclusion is that the relative HDS activities of the catalysts in general give a good correlation with the pore volume contained in pores of 37.5 to 55-Å radius.

However, the correlation between HDS activity and pore size distribution derived in this study relates only to the particular operating conditions and feedstock used. For different operating conditions and/or different feedstocks different pore size distribution requirements for optimum activity will probably exist. Nevertheless, the importance of pore size distribution in relation to HDS activity is clearly demonstrated.

The results for hydrogen uptake on the different NiMo and CoMo catalysts are shown in Fig. 2 and Table 3 (column 6) in which hydrogen uptake (per cm$^3$ catalyst space) at 350°C is plotted against the relative HDS activity. It can be seen that in general the trend is for the hydrogen uptake

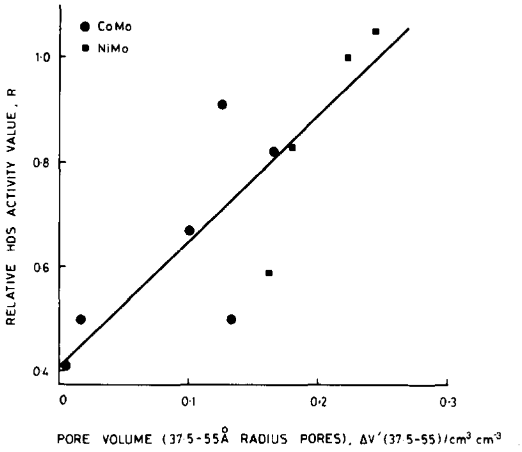


FIG. 1. Correlation of HDS activity and pore volume in 37.5 to 55-Å pores.

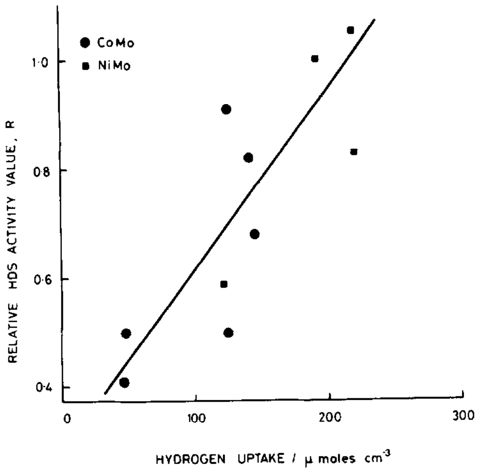


FIG. 2. Correlation of HDS activity and $H_2$ uptake.

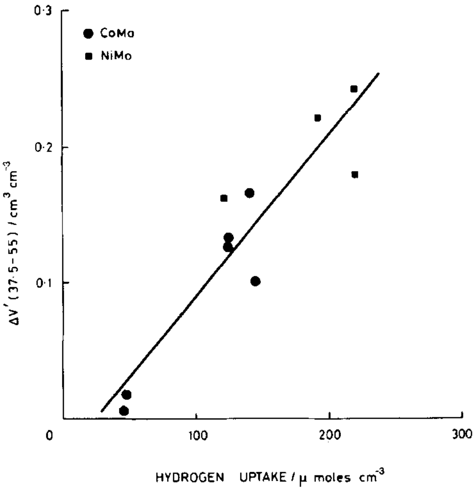


FIG. 3. Correlation of pore volume in 37.5 to 55-Å pores and $H_2$ uptake.

to increase with increasing catalytic activity. It is interesting to note that the NiMo catalysts take up more hydrogen than the CoMo catalysts. The line was again derived by linear regression and the value for the correlation coefficient is in this case 0.83.

This plot is similar to the one derived from the pore volume distribution results and if $H_2$ uptake is plotted against $\Delta V'$ for the range 37.5–55 Å a good correlation is obtained (Fig. 3).

We consider this correlation between hydrogen uptake, a chemical property, and pore size distribution, a physical property, to be of great significance. It is tempting to hypothesise that the form of the catalytic species found in pores of this size range is particularly active for HDS and that under the conditions of our measurements it is also capable of being titrated with hydrogen. The recent work of Pollack *et al.* (*4*) suggests that the form of the molybdenum could be that which on sulphiding gives rise to two-dimensional platelets of the sulphide and can be formed in pores of less than 60-Å radius, in very good agreement with our own findings. However, this could be an oversimplification since the catalysts tested in this work contain different amounts of active metals and if this is taken into account a rather different view may emerge.

In a study of the kinetics of reduction of similar catalysts, Ratnasamy *et al.* have found a correlation between desulphurisation activity and the fractional reduction of the catalyst under specified conditions (*5*). Hall and Massoth (*6*) have shown that hydrogen consumption which occurs when heating molybdena/alumina catalysts in hydrogen involves three processes, namely, oxygen removal, irreversible hydrogen adsorption, and reversible hydrogen adsorption (*6*). They also showed that the contribution each of these makes to the total consumption varies with the extent of hydrogen consumption. If one relates hydro-

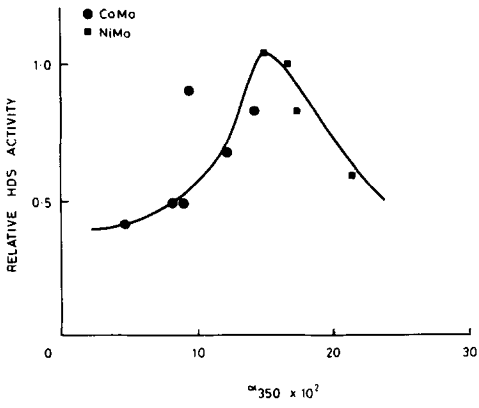


FIG. 4. Plot of relative HDS activity vs fractional hydrogen consumption.

gen consumption to the maximum amount which can be associated with oxygen removal during the reduction processes

$$MoO_3 + H_2 \rightleftharpoons MoO_2 + H_2O,$$
$$Co_3O_4 + 4H_2 \rightleftharpoons 3Co + 4H_2O,$$
$$NiO + H_2 \rightleftharpoons Ni + H_2O,$$

it is possible to calculate values for the fractional hydrogen consumption, $\alpha$, where

$$\alpha = \frac{[H_2]}{[Mo] + 1.33\,[Co]} \quad \text{or} \quad \frac{[H_2]}{[Mo] + [Ni]},$$

where

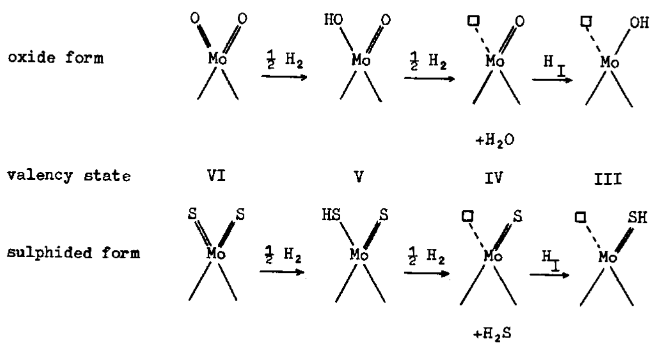
$[H_2]$ = g moles $H_2$ uptake/g of catalyst,

$[Mo]$ = g atoms Mo/g of catalyst,

$[Co]$ = g atoms Co/g of catalyst.

The results of these calculations (Table 3, column 7) when plotted against catalyst activity are shown in Fig. 4. It can be seen that catalysts containing cobalt have increased HDS activity as $\alpha$ increases, whilst nickel catalysts show the reverse trend. However, it is possible to say that for NiMo and CoMo catalysts high activity for HDS will be given when $\alpha$ measured at 350°C lies between 14 and 18%.

Using the data in Ref. (*6*) which were derived for an 8% Mo on alumina catalyst, one can estimate the amounts of reversibly adsorbed hydrogen ($H_R$), irreversibly adsorbed hydrogen ($H_I$) and the amount of oxygen removed to form anion vacancies ($H_\square$). As is shown in Fig. 5, it is found that the amount of irreversibly adsorbed hydrogen passes through a maximum. Data in a paper by Lo Jacono and Hall (*7*) suggest that the hydrogenolysis of cyclopropane is primarily related to the introduction of Brønsted acid sites onto the surface during reduction. It is often accepted that HDS activity is likewise related to the presence of vacancy sites and adsorbed hydrogen on the surface of HDS catalysts. By analogy with the model of Hall and Massoth (*6*), the sulphided forms of the catalyst could result in the required active configuration as shown below:



Thus the activity expressed as a function of $\alpha$ might be expected to show a maximum value, though the value of $\alpha$ might vary considerably from that in Ref. (*6*) because of the influence of promoter ions.

## CONCLUSIONS

The activity tests were successful in showing differences between the commercial HDS catalysts. Pore size distribution

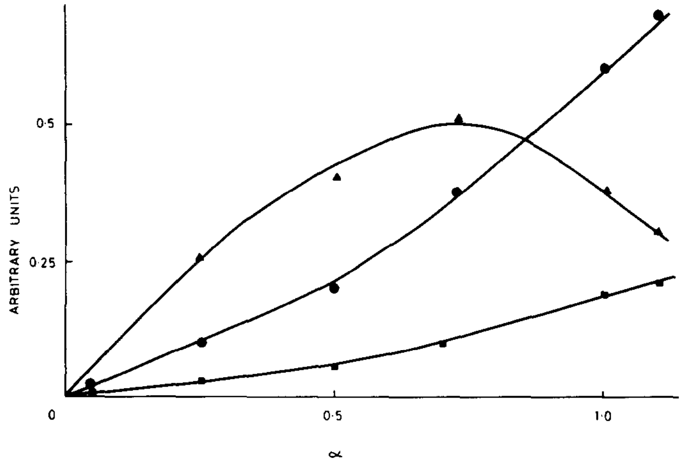


FIG. 5. Hydrogen uptake per Mo atom, α vs (●) $O_2$ removed per Mo atom, (▲) $H_2$ irreversibly adsorbed per Mo atom, (■) $H_2$ reversibly adsorbed per Mo atom (data derived from Ref. (*6*)).

and hydrogen uptake showed fair correlation with HDS activity and these techniques may offer ways of predicting HDS activity of newly available commercial catalysts.

## ACKNOWLEDGMENT

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## REFERENCES

*1.* Davies, H. S., Templeman, J. J., and Wragg, D., Institute of Gas Engineers Communication 979, 41st Autumn Research Meeting, London, 1975.
*2.* White, D. C., *Anal. Chem.* **49**, 1615 (1977).
*3.* Roberts, B. F., *J. Colloid Interface Sci.* **23**, 266 (1957).
*4.* Pollack, S. S., Makovsky, L. E., and Brown, F. R., *J. Catal.* **59**, 452 (1979).
*5.* Ratnasamy, P., Ramaswamy, A. G., Banerjee, K., Sharma, D. K., and Ray, N., *J. Catal.* **38**, 19 (1975).
*6.* Hall, W. K., and Massoth, F. E., *J. Catal.* **34**, 41 (1974).
*7.* Lo Jacono, M., and Hall, W. K., *J. Colloid Interface Sci.* **58**, 76 (1977).