Sintering of Nickel–Alumina Catalysts

Nickel–alumina catalysts are widely used in the C.R.G. process (*1*, *2*) to catalyse the reaction between steam and hydrocarbons to form methane-rich gas. They perform satisfactorily as regards life and conversion, but there is a gradual loss of activity due to chemical poisoning (*3*) and to sintering. The principal cause of sintering is the thermal instability of the alumina base. This note shows how surface areas and pore-size distributions of a C.R.G. catalyst change with time, and particularly how the presence of steam affects the sintering.

The catalyst was prepared by co-precipitation from mixed nickel and aluminum nitrates with potassium carbonate. It was pelleted as ⅛ inch diameter cylinders after calcination in air at 450°C. The reduced form contained about 25% of alumina, and X-ray investigations indicated that this was predominantly present in a poorly crystalline γ form.

The specific surface area and pore-size distributions in the range 20–10 000 Å were calculated from the nitrogen adsorption isotherm at −196°C and mercury porosimetric measurements by standard methods. The specific nickel area, i.e. the nickel area per gram of catalyst, was estimated from the amount of hydrogen adsorbed by the catalyst at 20°C according to the method of Yates *et al.* (*4*). Calcined batches of the catalyst were reduced in a stream of hydrogen at 450°C and 25 atm pressure for 17 hr.

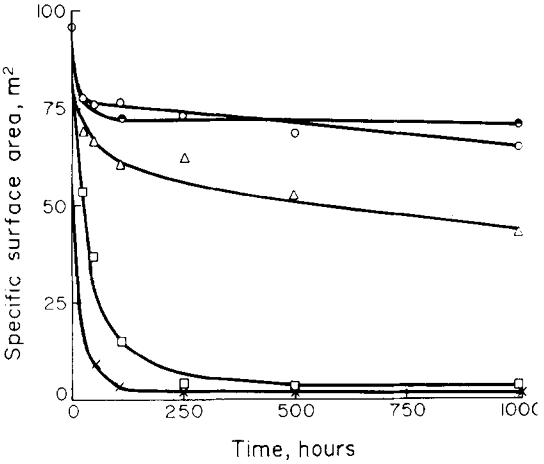

FIG. 1. Decrease in specific total area with time in the temperature range 400–800°C. ○ total area at 400°C; △ total area at 500°C; □ total area at 600°C; × total area at 800°C; ◓ total area at 800°C (in hydrogen only).

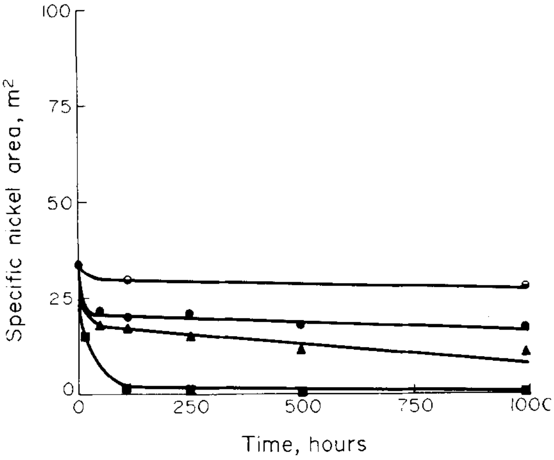

FIG. 2. Decrease in specific nickel area with time in the temperature range 400–800°C. ● nickel area at 400°C; ▲ nickel area at 500°C; ■ nickel area at 600°C nickel area at 800°C (not measureable); ◒ nickel area at 800°C (in hydrogen only).

The effects on the specific surface and nickel areas of the temperature and the duration of treatment in a steam and hydrogen mixture (9:1 by volume) at 25 atm pressure and in hydrogen at 1 atm pressure are shown in Figs. 1 and 2. The areas decrease rapidly during the initial hours of treatment and then more slowly as the time at temperature is further extended. The treatment temperature has a considerable influence on the magnitude of the initial decrease in area but its effect on the subsequent slow change is much less marked. Specific surface areas of samples treated in the steam and hydrogen

TABLE 1
EFFECT OF STEAM/HYDROGEN RATIO

Steam/hydrogen ratio	v/v	untreated	1/2	1/1	2/1	9/1
Specific surface area	m^2	95	79	76	65	52
Specific nickel area	m^2	27	22	22	15	13

mixture fell to about 5 m^2 after several thousand hours of treatment.

Results given in Table 1 show that the extent of sintering during 250 hr at 25 atm pressure and 500°C increases with increase of the steam content of the treatment atmosphere. Table 2 shows that the total pressure of the treatment atmosphere has little effect on the sintering during 250 hr in a 9:1 by volume steam and hydrogen mixture at 500°C. It is also apparent from Fig. 1 that the nature of the atmosphere in which the catalyst is treated has a much greater effect on sintering than the pressure and temperature of this atmosphere. Indeed, the area loss in hydrogen at 800°C and 1 atm pressure is no greater than that in the steam and hydrogen mixture at 400°C and 25 atm pressure.

One sample of the ⅛ inch diameter cylinders of catalyst was ground to different particle sizes and heat treated for 250 hr in the 9:1 by volume steam and hydrogen mixture at 500°C and 25 atm pressure. Table 3 shows that particle size has no appreciable effect on the area loss.

Other work showed that the areas of catalyst samples after reduction for 17 hr decreased as the size of the calcined batches increased. Reduced catalysts with specific surface areas of 130 m^2 and 95 m^2 and specific nickel areas of 35 m^2 and 27 m^2 were obtained by reducing 1 and 50 g calcined batches. The reasons for this effect were not ascertained but it is thought possible that sintering caused by steam produced during the reduction may have been responsible. Unfortunately, other considerations not connected with the present work determined the size of the calcined batches used in each series of experiments. Thus, it is probable that the differences in the areas after identical treatments which can be discovered by examination of Figs. 1 and 2 and Tables 1–3 were due to differences in calcination batch sizes.

TABLE 2
EFFECT OF PRESSURE OF STEAM AND HYDROGEN MIXTURE

Period of treatment hr	Pressure atm	Specific surface area m^2	Specific nickel area m^2
250	23.8	47	14.5
	68	44	16
1000	23.8	36	16
	68	38	13

TABLE 3
EFFECT OF PARTICLE SIZE

Particle size	Specific surface area m^2	Specific nickel area m^2
⅛ inch cylindrical pellets	70	16
8–10 B.S.S.	71	15.5
10–14 B.S.S.	68	18.5
10–30 B.S.S.	72	18

Electron microscopy showed that the nickel was evenly distributed as small particles of <100 Å diameter on the alumina in a freshly reduced catalyst, and that on heat treatment the average size of the particles increased, due to coalescence, whilst they remained fairly evenly distributed on the catalyst surface. Particles measuring between 300 and 3000 Å diameter were present after 1000 hr treatment in the steam and hydrogen mixture (9:1 by volume) at 500°C and 25 atm.

Table 4 gives details of the interplanar spacings calculated from the electron diffraction patterns of a freshly reduced sample and a sample treated in the steam and hydrogen mixture (9:1 by volume) at 500°C and 25 atm for 1000 hr. Comparison of these spacings with those given in the

TABLE 4
ELECTRON DIFFRACTION RESULTS

Sample	Interplanar spacing Å
Freshly reduced	2.390, 2.032, 1.758, 1.443, 1.239, 1.149, 1.059
After 1,000 hr in steam and hydrogen mixtures at 25 atm and 500°C	3.482, 2.798, 2.571, 2.431, 2.375, 2.087, 2.048, 1.773, 1.756, 1.602, 1.492, 1.409, 1.363, 1.249, 1.063, 1.057, 1.014.

A.S.T.M. index (*5*) shows that both samples contained nickel and either γ-alumina or a mixture of γ- and η-alumina, and that the treated sample also contained α-alumina.

X-Ray examination of the catalyst confirmed the production of α-alumina and the growth in the average nickel particle size on heat treatment. Table 5 gives some results for samples treated in the steam and hydrogen mixture (9:1 by volume) at 25 atm pressure.

The pore size distribution of the freshly reduced catalyst shows two peaks, at approximately 20 Å and 800 Å radius. Figure 3 shows that heat treatment in the 9:1 by volume steam and hydrogen mixture reduces the numbers of small radius pores without affecting their average radius and increases the average radius of the large pores. The tendency of small pores to disappear is particularly marked at 600°C, even after only a few hours of treatment.

The results clearly show that steam plays an important part in the sintering of nickel–alumina catalyst. This is perhaps not surprising since the transformation of γ- and other forms of alumina to the α-form is known to be accelerated under hydrothermal conditions (*6, 7*); for example, the minimum temperature at which α-alumina is formed is lowered from 1000° to 400°C (*8*).

The roughly parallel losses of nickel and total surface areas and the results of the X-ray and electron microscope investigations indicate that the nickel area decrease is probably caused by a coalescence of the nickel particles when they are brought together by the sintering of the alumina. Table 5 compares the average nickel particle size determined by X-ray methods with those calculated from the specific nickel area assuming that the nickel is present as cubes and that one side is in contact with the alumina. Considering the assumptions made in the calculations and the accuracy of X-ray measurements there is reasonable agreement. It seems reasonable to suppose that the nickel particles do not become buried in the alumina as its structure collapses.

Comparison of the area and pore-size distribution results indicates that the dis-

TABLE 5
RESULTS OF X-RAY EXAMINATION

			Nickel crystallite size, Å		
Treatment temp., °C	Treatment time, h	α-alumina % by wt.	1.1.1	2.0.0	Calculated from area measurements
400	0	0	100	100	150
	110	4.5	275	180	238
	500	7.4	290	365	301
	1000	8.4	310	390	319
500	0	0	100	100	150
	110	4.9	275	215	301
	500	7.7	345	275	465

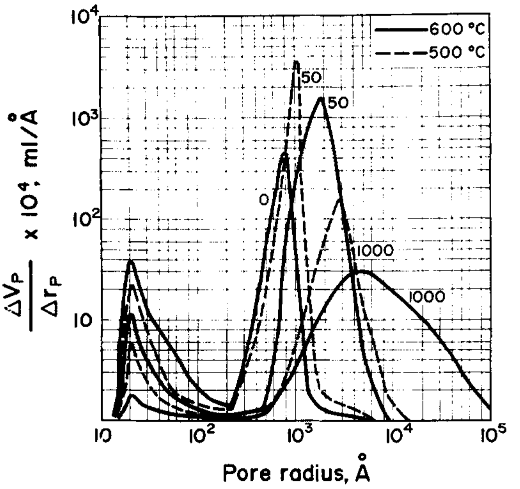

FIG. 3. Pore size distributions after 50 and 1000 hr at 500 and 600°C.

appearance of the fine pore structure is the direct cause of the loss of total area. The loss of fine pore structure is most probably associated with the transformation of γ-alumina into α-alumina under the hydrothermal treatment conditions. It would also appear that the nickel area loss is closely associated with the collapse of the fine pore structure of the γ-alumina.

The reaction between steam and hydrocarbons over a similar catalyst has been extensively investigated (*2*, *3*). These investigations have shown that the most important contribution to loss of catalyst activity is poisoning by a constituent or constituents of the hydrocarbon feedstock. Sintering also makes a contribution but fortunately only a small one. The sharp early drops in nickel and total surface areas with time in the presence of steam, typified by the results shown in Figs. 1 and 2 lead to rapid initial activity loss, but the C.R.G. catalyst as prepared is so active that the residual surface areas after the initial loss are still adequate at all but the highest temperatures to promote fast gasification. Generally the subsequent slow sintering is at too small a rate to have a significant effect on catalyst performance.

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REFERENCES

1. COCKERHAM, R. G., PERCIVAL, G., AND YARWOOD, T. A., *Inst. Gas. Engrs. J.* **5**, 109 (1965).
2. PHILLIPS, T. R., YARWOOD, T. A., MULHALL, J., AND TURNER, G. E., *J. Catalysis* **17**, **28** (1970).
3. MOSELEY, F., STEPHENS, R. W., STEWART, K. D., AND WOOD, J. A., unpublished.
4. YATES, D. J. C., TAYLOR, W. F., AND SINFELT, J. H., *J. Am. Chem. Soc.* **86**, 2996, (1964).
5. X-ray Powder File and Index to X-ray powder file A.S.T.M. (1960).
6. YAMAGUCHI, G., AND YANAGIDA, H., *Bull. Chem. Soc. Japan* **36**, 1155 (1963).
7. MURRAY, R. F., AND RHODES, D. L., *U. S. At. Energy Comm. Report No.* IDO14581 (1962).
8. COOKE, P. W., AND HARESNAPE, J. W., *Trans. Faraday Soc.* **43**, 395 (1947).

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