

DISPERSION OF ACTIVE COMPONENT, PORE SIZE DISTRIBUTION AND ACTIVITY OF NAPHTHA STEAM REFORMING CATALYST

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The chemisorption of hydrogen has been used to find out the nickel metal area, specific adsorption capacity, surface nickel content, specific nickel area per gram of nickel and crystallite size of five different nickel alumina, naphtha steam reforming catalysts.

It has been found that the activity of the Catalyst increases with specific nickel area per gram of nickel. The growth of crystallite size results in lowering of activity.

It has been shown that pores in the range 4–300Å Angstrom radius of the reduced catalyst play an important role in the activity for steam naphtha reforming reaction.

INTRODUCTION

In a multi-component system the catalytic activity does not depend solely on the components present in the bulk, but on the types and distribution of the crystal phases on the surface, the size and dispersion of active component, pore size distribution, etc. In a steam-naphtha reforming catalyst where nickel is the active component, carriers like alumina, silica, magnesia, etc. are used to retain the finely dispersed state of metallic nickel. A knowledge of dispersion of this active component gives valuable information about the relationship between activity and active surface. Besides, for any catalyst the pore size distribution has a remarkable effect on the extent of reaction and nature of products (cf. Satterfield 1969; and Topchieva *et al.* 1960).

Different authors (Sinfelt *et al.* 1965; Brooks & Christophen 1968; and Nath *et al. unpublished*) have reported on the determination of nickel metal area on various supports. However, less information (Nielsen 1970; and Narayanan & Yeddanapalli 1970) is available as regards to the correlation between the activity and the nickel metal area.

Hence the present work was undertaken to see the bearing of activity on the nickel metal area and its dispersion in different steam-naphtha reforming catalysts. Physical properties like surface area, pore volume and pore size distribution with the fresh as well as the reduced catalysts, have also been studied to see their effect on the activity.

EXPERIMENTAL

The investigation was carried out with five different industrial naphtha-steam reforming catalysts. The samples were chosen on the basis of their varied nickel content and BET surface area as shown in Table I.

TABLE I
Chemical Composition and Surface Area

Sample No.	Chemical Composition (% by Weight)							BET Surface area m ² /g		Percentage reduction in Surface
	NiO	Al ₂ O ₃	SiO ₂	MgO	CaO	K ₂ O	IOI	Fresh	Reduced	
1	2							3	4	5
A	15.3	83.3	—	—	—	—	1.4	53.5	28.8	46.1
B	42.9	5.2	19.4	9.8	—	—	22.7	45.3	26.4	41.7
C	15.0	74.7	—	—	8.1	—	2.2	27.4	14.3	47.8
D	15.3	84.1	—	—	—	—	0.6	12.5	9.0	28.0
E	19.0	64.4	—	—	3.9	1.6	11.1	13.4	11.8	13.5

The surface areas were found out by the conventional BET method. The pore size distribution was determined using a mercury pressure porosimeter by the method described in Mahapatra *et al.* (1971). The apparent and true volumes of the samples were measured by mercury and helium displacements respectively.

The nickel metal area in the reduced samples was determined by chemisorption of hydrogen at room temperature (25–27°C) in a manner suggested by Sinfelt *et al.* (1965). The hydrogen used for this purpose was purified by the method as described earlier (cf. Sengupta *et al.* 1971). The catalyst was separately reduced in a tubular quartz furnace in a stream of purified hydrogen at 650°C, which was subsequently raised to 850°C. To ensure complete reduction and stabilization, the flow of hydrogen was maintained for 24 hours. Then the sample was cooled down to room temperature in hydrogen atmosphere. Finally the reduced sample was transferred to a specially designed glass reactor tube, which was connected to the adsorption apparatus. To avoid any possible aerial oxidation the sample was again reduced, *in situ*, at 400°C by purified hydrogen. The sample tube was carefully sealed and degassed at 450°C for 8 hours. A steady pressure of less than 5×10^{-3} mm. of Hg for 15 minutes after the pumps were cut off, was taken as the test for a clean surface. Then the sample tube was cooled to room temperature and chemisorption experiments were carried out.

The activity of the samples was determined in an apparatus as described in Mukherjee *et al.* (1971). After reduction of the catalyst at 650°C in hydrogen the bed temperature was raised to 850°C. Desulphurized straight run naphtha was used as the feed. The steam to carbon molar ratio was maintained at 4.0 and the LHSV was kept at 0.6. The activity of all the samples was determined at 850°C.

RESULTS AND DISCUSSION

The chemical composition and surface area of the fresh and reduced samples are shown in Table I. For the fresh samples the nickel content varies from 12 to 34 per cent and the surface area varies from 12.5 to 53.5 m²/g of catalyst. After

reduction there is a decrease in surface area for each sample. But the percentage reduction in surface area for different samples are found to be different. This change in surface area may be due to the difference in the rearrangement of particles which is dependent on the method of preparation.

From the chemical composition of the different catalysts it can be seen that in addition to the alumina carrier, some catalysts contain small percentage of CaO, SiO₂, MgO and K₂O. A survey of literature (Brooks & Christophen 1968; Nath *et al. unpublished*; Viswanathan & Yeddanapalli 1969; and Alder & Keavney 1960) indicates that there is little or no chemisorption of hydrogen on these oxides. Hence in the present study the chemisorption of hydrogen on these oxides have been neglected. From hydrogen chemisorption, the nickel metal area was determined. It was calculated on the basis that each nickel atom on the surface adsorbs one hydrogen atom and that each hydrogen atom occupies 6.5 Å (Topchieva *et al.* 1960) on the surface (Klemperer & Stone 1958). The specific adsorption capacity, surface nickel content, specific nickel area and nickel crystallite size have been calculated following Brook's method (Brooks & Christophen 1968), and are shown in columns 4, 6, 7 and 8 of Table II respectively. The activity of the samples for steam naphtha reforming reaction in terms of methane leakage is presented in column 9 of Table II.

TABLE II
Nickel Surface and Activity

Sample No.	Nickel content g/g. of cat.	Hydrogen chemisorbed ml./g. of Cat.	Specific adsorption capacity ml./g. of Ni.	Nickel metal area m ² /g of Cat.	Surface Ni g/g. of cat. × 10 ⁴	Specific Nickel area m ² /g of Ni.	Nickel crystallite size Å	Activity CH ₄ leakage (% Vol. dry basis)
1	2	3	4	5	6	7	8	9
A	0.1202	0.62	5.16	2.17	32.49	18.05	373.2	0.6
B	0.3371	1.03	3.05	3.60	53.98	10.68	630.8	1.2
C	0.1179	0.30	2.54	1.05	15.72	8.90	757.0	1.6
D	0.1202	0.17	1.41	0.59	8.91	4.91	1372.0	2.1
E	0.1493	0.09	0.60	0.31	4.72	2.08	3238.9	2.4

From a comparison of column 5 (Table II) and column 4 (Table I) it can be seen that the nickel metal area is in the range of 0.3 to 3.6 m²/g as against a BET surface area of 9 to 29 m²/g. This indicates that out of the total surface only a very small fraction is responsible for reaction and this clearly shows the importance of determining the area of active component.

From a comparison of column 2 and 6 of the Table II it is interesting to note that out of the total nickel content in the bulk only a small fraction ranging from 2.7 per cent to as low as 0.32 per cent is only present on the surface. A better method of

catalyst preparation aims at retaining higher percentage of nickel distribution on the surface. However, often a higher nickel content is required to compensate for the loss of nickel area due to interaction between the carrier and metal in the form of spinel (Nielsen 1970).

From columns 2 and 7 of Table II it can be seen that there is no definite relationship between nickel content and specific nickel area. Nielsen (1970) in his studies on naphtha reformation catalyst has reported that for catalysts prepared by impregnation of some carrier a higher concentration of nickel results in the lowering of specific nickel area. However, in our case due to varied method of preparation no such relationship occurs.

Nielsen (1970) reported that the activity of the catalyst increases with the size of the nickel area per gram of catalyst. In our case also, the activity increases with the increase of nickel area per gram of catalyst (columns 9 and 5 of Table II) except for sample B. This anomaly for sample B can be explained when the specific nickel area per gram of nickel, is taken into consideration. From columns 7 and 9 of Table II it can be seen that the activity increases with the increase of specific nickel area. At first instance it appears that the sample B having the maximum nickel metal area, should be the most active catalyst. On the contrary, the activity of sample B falls in between that of A and C. It can be seen that sample B fits well between A and C. An increase in crystallite size is accompanied by decrease in activity. This fall in activity is very sharp in the beginning which later on becomes almost asymptotic. This indicates that smaller the crystallite size, the better the activity. Sample A which shows the maximum activity has the smallest crystallite size or in other words has most favourable dispersion of nickel. Hence it is evident that the activity of the sample depends not only on the nickel metal area but also on its dispersion on the surface. In their studies on the catalytic dehydrogenation of cyclohexane over nickel alumina catalyst Narayanan and Yeddanapalli (1970) have reported that the catalytic activity depends on the specific adsorption capacity per gram of nickel and have explained the

TABLE III

Pore volume and Pore size distribution

Sample No.	Fresh Samples					Reduced Samples				
	Hg dis- place- ment cc/g.	He dis- place- ment cc/g.	Pore volume cc/g.	Pore Size Distribution (% by volume)		Hg dis- place- ment cc/g.	He dis- place- ment cc/g.	Pore volume cc/g.	Pore size distribution (% by volume)	
				4-300 Å	300- 75000 Å				4-300 Å	300- 75000 Å
A	0.4896	0.2583	0.2313	82.0	18.0	0.5122	0.2459	0.2663	74.4	25.6
B	0.3971	0.2867	0.1104	92.6	7.4	0.4547	0.2450	0.2117	66.5	33.5
C	0.4573	0.2723	0.1850	78.7	21.3	0.4786	0.2778	0.2008	62.5	37.5
D	0.4845	0.2428	0.2417	55.2	44.8	0.5032	0.2531	0.2501	31.0	69.0
E	0.5613	0.2962	0.2651	26.8	73.2	0.6627	0.2558	0.4069	23.8	76.2

activity on the basis of differences in crystallite size. Our observations are also similar to that of these workers.

Table III gives the pore volume and pore size distribution (percentage by volume) of the fresh and reduced samples. For any catalyst the pore size distribution depends on the method of preparation. In the present case the varied distribution of pores may be due to their difference in the method of preparation. The irregularity in the pore size distribution is also reflected in the surface area as shown in column 3 of Table I.

The pore size distribution data for the reduced catalysts reveal some interesting facts. The catalytic activity for any catalyst is influenced by the nature of its surface when it is in the activated state. As indicated earlier it is the pore geometry which decides the accessibility of the surface. In the present case, with the reduced samples A, B and C, the pores are more concentrated in the micro region i.e., below 300 Å; whereas in case of D and E the pores are more concentrated in the higher range. Heinrich (1969) has reported that when nickel catalysts are reduced, the change in the original pore size distribution takes place which manifests itself in its catalytic activity. According to him the micro pores in the range 10 to 300 Å, whose contribution exceeds 60 per cent are of particular importance for its activity. Bhattacharyya *et al.* (1972) during their study on the ageing of nickel catalyst have reported that activity of the catalyst appears to be related with finer pores. Our observation is also similar to that of both Heinrich (1969) and Bhattacharyya *et al.* (1972). Out of the five catalysts the first three having more than 60 per cent of micropores in the range 4–300 Å (Table III column 10) show good activity whereas the last two having only 31.0 and 23.8 per cent micro pores, are comparatively less active.

From a comparison of column 5 and 10 (Table III) it is to be seen that the percentage of micropores in each sample is lowered after reduction. The total pore volume in each sample also increases after reduction as is evident from column 4 and 9 (Table III). This indicates that the process of reduction of NiO to Ni is accompanied by creation of intragranular voidage which is reflected in an increase in pore volume.

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