

EFFECT OF NICKEL CONCENTRATIONS ON ACTIVITY AND SELECTIVITY OF REFORMING CATALYST

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Nickel is the active component in a steam hydrocarbon reforming catalyst. In industrial catalysts concentration of nickel range from 10.0 to 30 per cent as nickel for identical service. The present paper deals with the investigation on the effect of nickel concentration on activity and selectivity of a reforming catalyst. The object was to arrive at the optimum concentration of nickel for formulating an active catalyst with minimum carbon laydown and also to understand the reaction steps involved in the reforming process.

For the investigation a two component system comprising of α -alumina and nickel oxide has been studied for activity, selectivity at a fixed steam/carbon ratio, feed rate and varying reaction temperature. Concentration of nickel in the catalyst has been varied from 5 to 20 per cent. Metal surface area and crystallite size of the reduced catalyst have been measured.

It has been observed both activity and selectivity improves with increasing nickel concentration in the catalyst. Temperature effect on activity and selectivity is identical irrespective of nickel concentration under the experimental conditions studied. The limiting concentration of nickel appears to be around 20 per cent for a alumina nickel system to achieve nearly theoretical gas composition. Crystallite size and metal surface area do not appear to have any linearity with nickel concentration. But activity is more, higher the nickel concentration and metal surface area. Carbon deposition decreased at higher bed temperature and with larger concentration of nickel in the catalyst. For complete elimination of carbon deposition 15 per cent and 10 per cent nickel is optimum for operation at 700°C and 800°C bed temperature.

INTRODUCTION

Application of steam reforming process in industry dates back as early as 1930 but light petroleum feedstocks could be used as raw material only after 1960. Use of light distillate became possible after the development of a suitable catalyst which could effectively reform hydrocarbons avoiding carbon deposition.

Nickel is invariably the active ingredient in all commercial reforming catalysts and its concentration ranged from 20 per cent to 40 per cent as NiO depending on make. But activity and selectivity of a catalyst may depend on various other factors like composition, concentration of active components, physical and structural parameters. The effect of these parameters on catalyst behaviour has been studied by many workers (Arnold *et al.* 1952; Sen *et al.* 1972; and Chowdhury *et al.* 1971). For arresting carbon deposition, incorporation of a promoter may be essential (Sen *et al.* 1972; Andrew 1969; Nicklin *et al.*, 1968; and Patai *et al.* 1952). Addition of potash and alkaline earth metal has been found to be effective for improved selectivity.

In recent years there is an attempt to bring down nickel concentration without curtailment of the effectiveness of a catalyst. It is interesting to note that nickel content of most commercial catalysts has a downward trend and today the upper limit hardly exceeds 25 per cent. It is worthwhile to study the effect of nickel concentration on overall catalyst performance and establish optimum nickel content. With this objective the present work was undertaken to investigate the effect of nickel concentration on activity and selectivity of reforming catalyst.

Kinetics of steam hydrocarbon reaction has been extensively studied (Phillips *et al.* 1969, 1970; Bhatta & Dixon 1967; Davies *et al.* 1967; Haensel & Ipatieff 1946; Schnell 1970; Bridger & Wyrewas 1967; and Bridger 1972). It is known that hydrogenolysis and catalytic cracking may be predominant phenomena in the initial stages of reforming process whereas in the later part steam-reforming is probably the only reaction. The function of the catalysts in the top and bottom zones is different and there may be necessity for a zoned scheme with two types of catalysts or a dual functional catalyst for satisfactory reformer performance. In this connection a study on the product distribution pattern in the catalyst bed as a function of nickel concentration may be pertinent to examine the necessity of a zonal packing in the reformer tube. In view of this a study of the composition of the reaction products as a function of nickel concentration has also been included in the programme of work.

EXPERIMENTAL

Five samples of catalysts were prepared by soaking alumina support in nickel salt solution. The concentration of nickel in the catalysts was varied. About 7.1 to 8.2 per cent calcium was incorporated in all the samples. The samples were finally heated to 500-550°C to decompose salts.

For measuring activity a specially designed reformer tube suitable for tapping gas samples and temperature measurement at different lengths of the reformer tube was mounted vertically in an electrically heated furnace (Fig. 1). The flow of reactants was down through the tube. Catalyst samples supported on a perforated alloy disc within the tube were used. Thermo-couples placed in the catalyst bed were used to measure the temperature. Naphtha and water were pumped through a preheating section and metered by separate rotameters. The naphtha vapour and steam were mixed in the preheater before passing on to the catalyst bed. Product gas was measured with a wet gasmeter after the excess steam condensed in a cooler.

Initially the reactor was packed with 70 gms catalyst in each experiment, assembled and pressure tested. After the reactor was brought to a temperature of 500°C in a stream of nitrogen the reduction of the catalyst was started in a current of steam and hydrogen. After 8 hours from the start of reduction the temperature of the bed was allowed to increase at predetermined level. After reduction is complete naphtha vapour along with hydrogen (hydrogen to naphtha molar ratio 0.3 to 0.35) was allowed to flow through the catalyst tube maintaining inlet catalyst bed temperature fixed at 500°C but outlet at 600°C, 700°C and 800°C according to requirement. Steam/carbon ratio equal to 4 (moles per carbon atom) and LHSV of

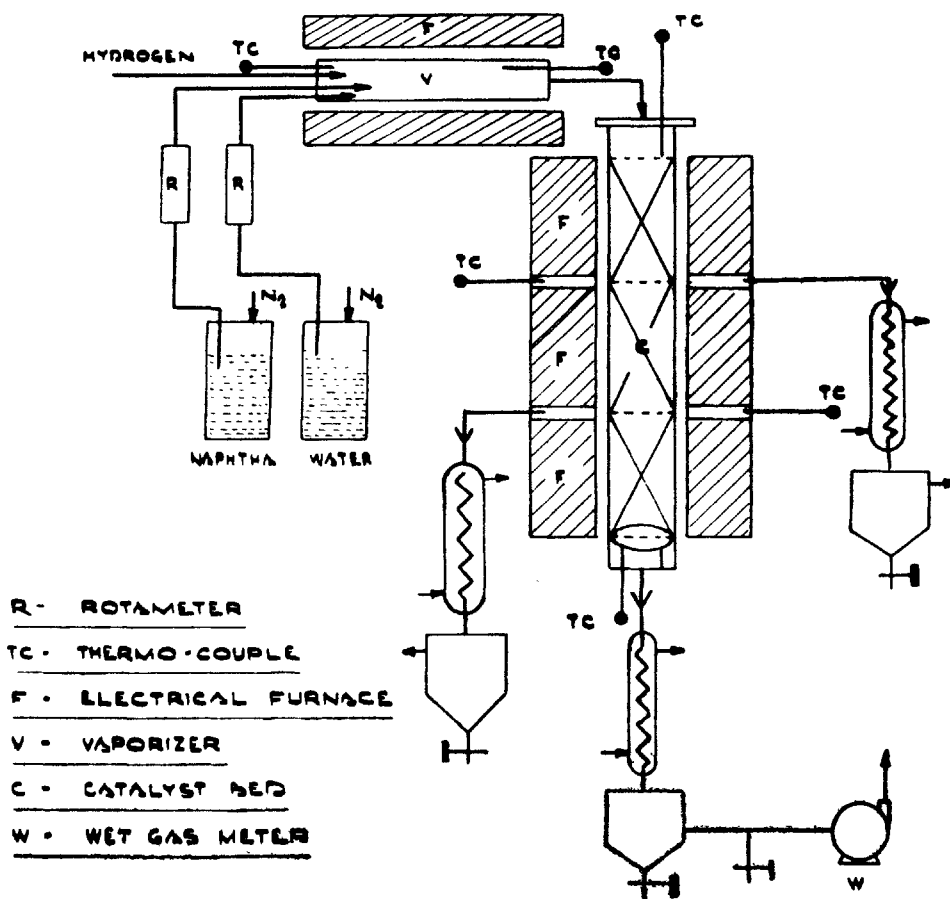


FIG. 1. Flow diagram of hydrocarbon steam reforming unit.

0.5 (gms of naphtha per gm of catalyst per hour) for a full bed charge were maintained. Composition of the products at 600°, 700° and 800°C exit temperature when the catalysts are packed to 1/3, 2/3 and full reactor volume respectively were determined. Under steady state gas samples were collected for analysis. At the end of 8 hours run the unit was cooled in nitrogen stream and the quantity of carbon deposited on the catalyst determined gravimetrically.

RESULTS

Chemical composition : Analysis of the samples are given in Table I. All the samples are prepared with α -alumina support, concentration of nickel varies from 2.83 per cent to 21.42 per cent. Calcia concentration was kept between 7.1–8.2 per cent as CaO.

Surface area : Total surface and metal surface (calculated from quantity of chemisorbed hydrogen) are presented in Table I. From chemisorption data, fraction

TABLE I
Physico-chemical analysis of samples

Sample No.	Chemical analysis		Specific surface area m ² /g	Metal surface area m ² /g	Available Ni on surface in gms'100 gms. cat.	Average crystallite size Å
	Ni	CaO				
1.	Nil	7.52	57.1	Nil	Nil	Nil
2.	2.83	7.89	47.1	0.174	0.026 × 10 ⁻²	701
3.	4.79	8.18	45.6	0.384	0.057 × 10 ⁻²	538
4.	11.13	8.23	42.2	0.763	0.112 × 10 ⁻²	628
5.	15.04	7.79	40.1	1.547	0.231 × 10 ⁻²	419
6.	21.42	7.09	38.8	1.880	0.280 × 10 ⁻²	491

of nickel on the surface has also been calculated and presented in Table I. It may be observed that metal surface is very small compared to total surface. But metal area increases with increase of nickel content. Minimum surface of 0.174 m²/gm is associated with the catalyst having 2.83 per cent nickel and maximum surface of 1.88 m²/gm. is possessed by the catalyst with the highest nickel content of 21.42 per cent. Amount of nickel calculated from the chemisorption data shows that only a small fraction of nickel varying from 0.9—3 per cent nickel is present on the surface for the lowest and the highest nickel content catalysts respectively. Increased availability of nickel in the surface at higher Ni/Al₂O₃ ratio may be due to its massive form where the interaction between Ni and Al₂O₃ is less. At lower concentration greater interaction makes larger fraction of nickel unavailable.

Crystallite size : Average crystallite sizes are given in Table I. Assuming hemispherical crystallites attached to the support with their equatorial plane, crystallite size was calculated from nickel area per gram of nickel in the catalyst sample.

Activity : Activity of the samples have been determined at 600°C, 700°C, and 800°C exit temperature and atmospheric pressure keeping steam/carbon ratio fixed at 4.0, naphtha flow 37–38 gms/hour and hydrogen partial pressure 0.3—0.35 atm. on dry basis. Reactor was designed to tap gas samples from one third and two third reactor length from top and also from reactor exit. In all, six samples were subjected to activity test. Sample 1 constitutes only the support of α-alumina.

The catalyst sample containing 15.04 per cent nickel were tested for varying exit temperature 600°C, 650°C, 700°C, 750°C and 800°C, inlet temperature was kept fixed at 500°C. Steam/carbon ratio, system pressure, hydrogen/naphtha ratio were same as in case of other tests. Percentage conversion x was calculated as—

$$x = \frac{P_{CO} + P_{CO_2}}{P_{CO} + P_{CO_2} + P_{CH_4}} \times 100$$

Small fraction of hydrocarbon cracked and deposited as carbon is ignored for percentage conversion calculation. Results on conversion, carbon deposition, product distribution in the bed as a function of nickel concentration in the catalyst are presented in Figs. 2, 3, and 4.

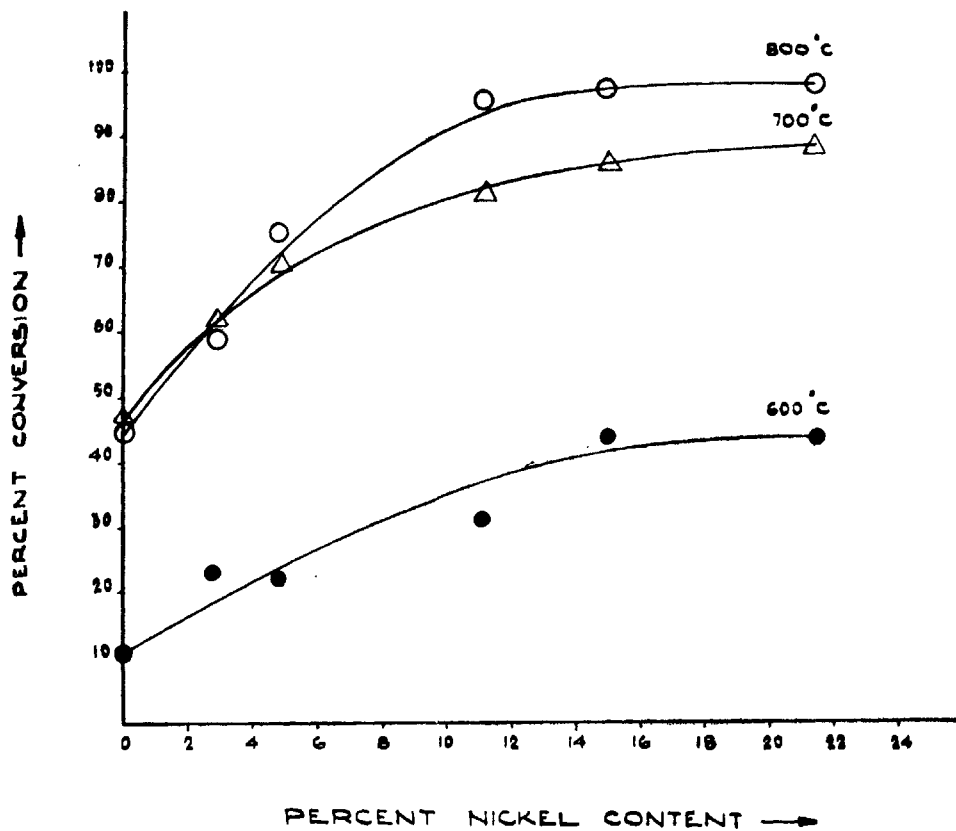


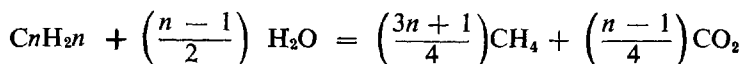
FIG. 2. Effect of nickel content on catalyst activity at different temperature.

TABLE II

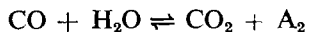
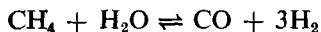
Theoretical Gas Composition at different temperatures

Temperature °C	CO	CO ₂	H ₂	CH ₄	% Conversion
600	7.07	18.69	72.04	2.20	90.00
650	9.42	16.95	73.00	0.63	97.00
700	11.34	15.65	72.80	0.21	99.00
750	12.63	14.55	72.76	0.06	99.75
800	16.08	11.93	71.97	0.02	99.99

Theoretical gas composition at various temperatures was calculated and presented in Table II. The theoretical conversion was calculated on the basis of equation given by Lihue (1965).



where n is usually taken as 7 for light naphtha. Methane formed by the above reaction then undergoes reversible reactions with steam in the following way.



DISCUSSION

The precise mechanism involved in the reaction is not clear. In the present investigation we have studied the overall composition of the products as a function of nickel concentration at selected bed temperatures under fixed flow and steam/carbon ratio. Whatever may be the initial products from reaction of naphtha and steam, finally a composition of CO, CO₂, H₂ and residual methane present in the product approach thermodynamic equilibrium under exit conditions.

We have observed that approach to equilibrium is not only a function of temperature it is also a function of nickel concentration. The product composition at various percentage conversion was estimated from analysis of the gas samples at 1/3 and 2/3rd of the packed bed, corresponding bed outlet temperatures fixed at 600°C and 700°C respectively. At 1/3rd, 2/3rd and full bed catalyst packing, respective space velocities are 1.5, 0.75 and 0.50. The experimental data at 600°C and 700°C exit temperature may not exactly correspond to the composition at the same bed length where the tube is fully packed. Because with fully packed bed, actual temp. profile may be different from our assumed condition at intermediate bed lengths.

It may be observed that the alumina support itself is not inert. Naphtha is appreciably cracked on the support and intensity of cracking increases as the temperature is increased. At 600°C more than 40 per cent of naphtha is cracked of which 11.5 per cent of the gas gets reformed (Fig. 4). At 700°C and 800°C corresponding value of cracking are 60 and 85 per cent respectively. Extent of reformation on the free alumina surface is practically identical at 700°C and 800°C. But it is known that above 600°C the reaction in the reformer is not entirely heterogenous. Homogenous phase reaction also will be considerable at 700°C and above. Bridger and Wyrwas (1967) observed that below 650°C reactions between hydrocarbon and steam are mostly catalytic but above 700—750°C reforming is a combination of homogenous and heterogenous reaction. It is likely that when the reaction temperature is increased cracking in the homogenous phase increases and above 700°C combined effect of catalytic and non-catalytic cracking decomposes naphtha completely.

Effect of nickel concentration on cracking and reforming activity is very significant. As nickel concentration is increased, extent of cracking and reforming increases and composition of the gas approaches faster towards equilibrium. (Table III and Fig. 4, a, b, c). On 15 per cent nickel at 700°C naphtha is completely decomposed to gaseous hydrocarbons and oxides of carbon but with lower concentration of nickel in the catalyst naphtha slip is observed in the exit of the reactor

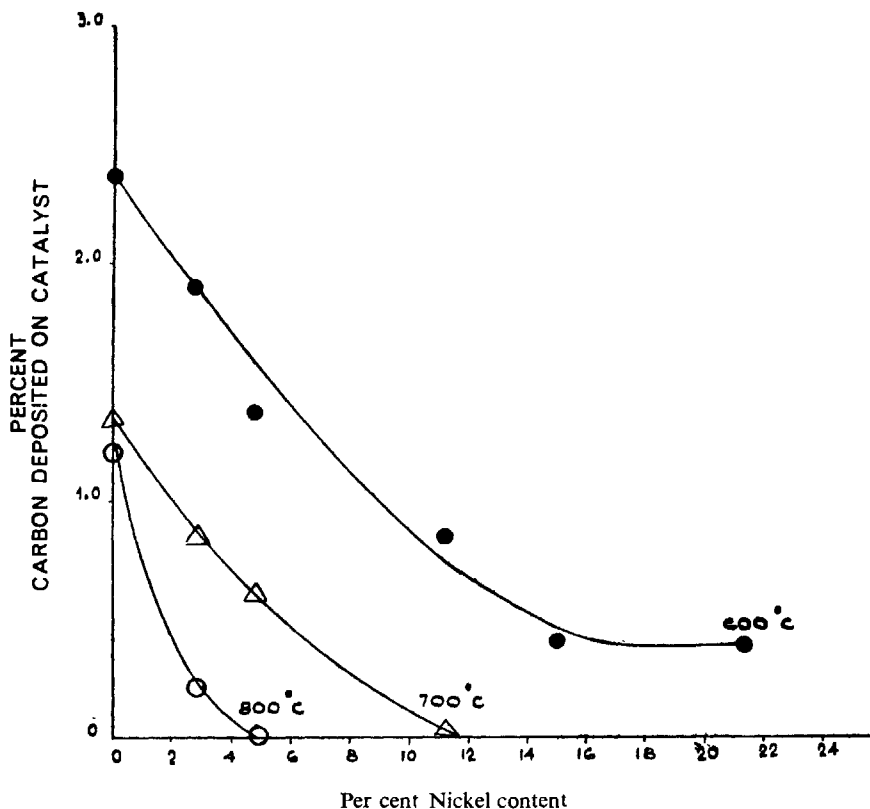


FIG. 3. Effect of nickel content on carbon deposition intensity.

and the extent of naphtha decomposition with 2.83, 4.79 and 11.13 nickel is 73.1 per cent, 78.3 per cent and 98.0 per cent respectively. With 21.4 per cent nickel conversion is 88.4 per cent at 700°C and at 800°C it is 97–98 per cent. Results show that when the reformer exit temperature is 800°C, catalyst containing 15 per cent nickel is adequate to bring the gaseous products to equilibrium composition. Our observations are identical qualitatively with earlier published work. Arnold *et al.* (1952) studied the effect of nickel concentration on activity but incorporated nickel on a multi-component support made interpretation of data difficult. The authors observed that in general catalyst with higher nickel content has higher activity. Exceptions were considered as an indication about the importance of other factors. It was also observed by the authors that increased nickel reduced carbon deposition. The results of the present investigation corroborates this earlier findings.

Regarding composition of the gas at various bed lengths and attainment of equilibrium, different authors have different observation and conclusions. Bhatta and Dixon (1967) observed that equilibrium was achieved with 15 per cent nickel-alumina system at all stages of decomposition whereas Rogers and Crooks (1966) using 25 per cent Nickel-alumina found the gas composition is away from equilibrium.

TABLE III

Gas composition with sample No. 5 LHSV=0.5; S/C=4. Inlet temp. 500°C

Catalyst bed exit °C	CO ₂	CnHm	CO	H ₂	CH ₄	% Conversion
						$\frac{P_{CO} + P_{CO_2}}{P_{CO} + P_{CO_2} + P_{CH_4}} \times 100$
600	7.4	4.6	3.8	69.8	14.4	43.7
650	9.0	3.0	5.4	70.0	12.6	53.0
700	17.0	nil	8.8	70.2	4.0	86.5
750	18.0	—	8.4	71.0	2.6	89.0
800	18.0	—	9.6	71.6	0.8	97.1

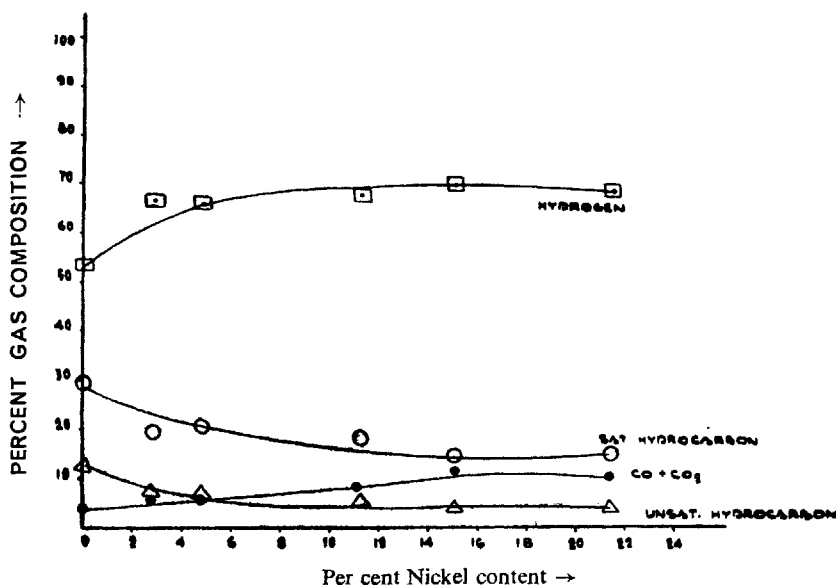


FIG. 4 a. Product distribution as a function of nickel content at 600°C

Philips *et al.* (1970) again obtained a satisfactory correlation between bed temperature and gas composition using a catalyst similar to that of Rogers. When the hydrocarbons are reacted with steam over a nickel catalyst to give a mixture of CO, CO₂, H₂ and CH₄ it has been found that the product gas composition satisfies water-gas and methanation equilibria at reaction outlet temperature, pressure and steam/carbon ratio. On this basis it is assumed that the same equilibria holds in other parts of the reactor also to explain the phenomena in the industrial reformer. Gas composition observed in the present investigation at 600°C, 700°C and 800°C exit temperature and the equilibrium compositions are presented in Fig. 4 and Table III respectively. Results clearly reflect the increasing catalytic effect of nickel on the reforming activity of the catalysts at all reaction temperature. A catalyst with higher

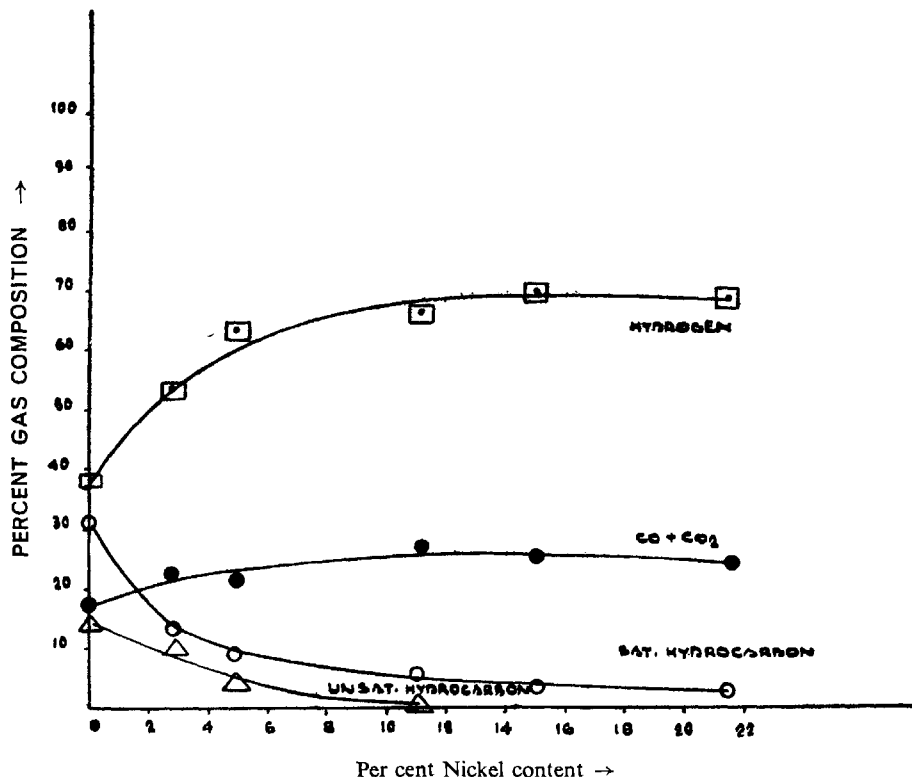


Fig. 4 b. Product distribution as a function of nickel content at 700°C.

nickel is equally effective in cracking, reforming and carbon gasification in the upper as well as in lower part of the bed. Extent of carbon deposition as estimated from the discharged catalysts are presented in Fig. 3. Suppression of carbon laydown by higher nickel catalyst may be explained in two ways. Firstly if carbon formation takes place by catalytic cracking on a site the same site may catalyse gasification of this deposited carbon. Secondly it is also possible that a—OH· group may migrate (Phillips *et al.* 1969) from alumina site and oxidise the deposited carbon. In such a case intensity of carbon laydown would have been less on catalysts with lower nickel content. Contrary to this, extent of carbon deposition is found more on low nickel catalyst. Deposition of carbon may occur by thermal cracking also but in the upper part of the bed where the temperature is around 600°C thermal cracking is unlikely. From earlier study (Schnell 1970) it may be assumed that CH_x radicals formed on nickel may further polymerise and undergo progressive dehydrogenation to give coke. Coke laydown on high nickel catalyst may be suppressed in two ways. Firstly the acidic sites may become inaccessible to the reactants and secondly proximity of nickel-nickel sites may create conditions favourable for gasification of deposited carbon.

Composition of the products at 600°C, 700°C and 800°C as presented in Fig. 4, a, b & c correspond to conditions at 1/3, 2/3 and full bed length respectively. It

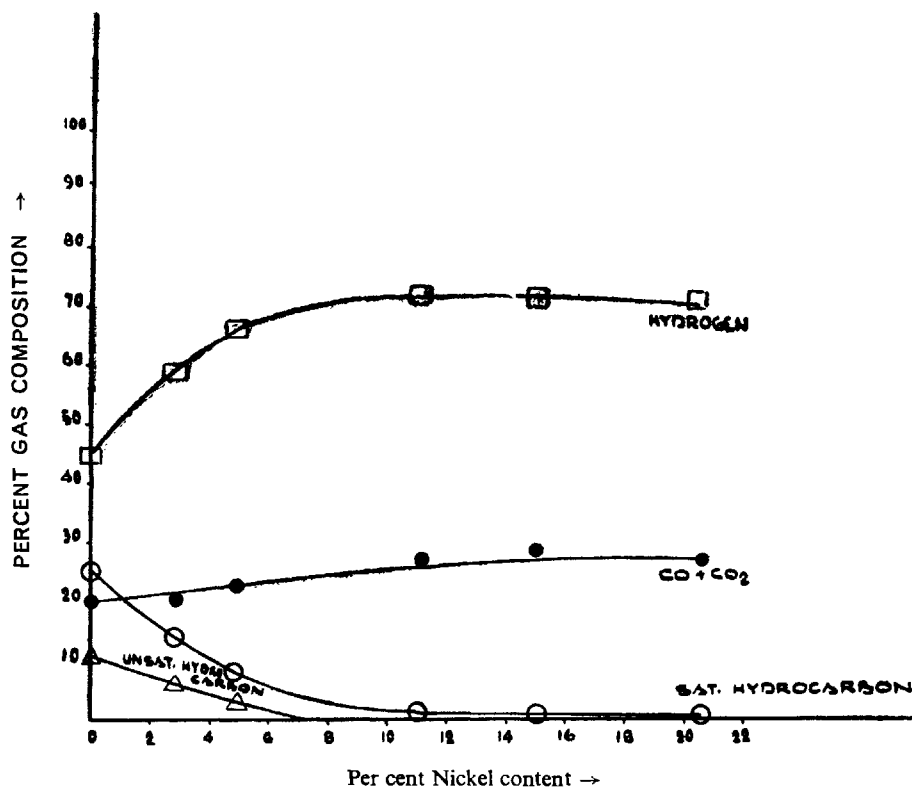


Fig. 4 c. Product distribution as a function of nickel content at 800°C.

may be seen that the composition of the gas is away from equilibrium when the concentration of nickel in this catalyst is low (Fig. 4 and Table II) but it approaches faster towards equilibrium with increasing concentration of nickel in the catalyst. Temperature has a favourable influence in general on reaction rate. When the nickel content of the catalyst is 15 per cent and above the conversion is almost near to equilibrium at 800°C and carbon laydown is nil (Fig. 3). In the product gas, concentration of the unsaturates appear to fall continuously with increasing temperature. When the temperature is 700°C and above unsaturates in the product gas completely disappear with a catalyst containing 15 per cent nickel. Concentration of CO and CO₂ in the gas increases with increasing temperature but it remains below the equilibrium value even at 800°C. Increasing percentage of CO and CO₂ in the bed along the downward flow may be accounted by assuming increased methane steam reaction and therefore greater approach to equilibrium at higher reaction temperature.

Crystallite size data do not throw any significant information about its influence on activity or carbon deposition. For correlation of such data it is essential to compare the data on catalysts having identical chemical composition and preparation but differing only in crystallite size.

From the experimental results it appears that the minimum requirement of nickel in Ni-Al₂O₃ system is 15.0 per cent for complete decomposition of the hydrocarbon, good reforming activity and selectivity. This catalyst has been investigated at exit temperature from 600 to 800°C with an interval of 50°C. It is observed that the conversions of hydrocarbon on this catalyst are 53 per cent and 97 per cent at 650°C and 800°C respectively. Carbon decomposition takes place upto 650°C but it is negligible above 700°C and product gases attain near equilibrium composition.

CONCLUSION

We conclude that optimum nickel concentration in a Ni-Al₂O₃ catalyst is around 15 per cent as nickel for operation of the reforming system at 800°C or above. At this temperature 15 per cent nickel in the catalyst is adequate to achieve nearly theoretical gas composition without significant carbon laydown. Decomposition of the hydrocarbon on the catalyst is complete at 700°C but carbon deposition is reduced to minimum with maximum approach to equilibrium at 800°C only. But if the system operates at lower exit temperature and 4–5 per cent methane in the product gas is desirable optimum nickel content is around 20 per cent. In the tubular catalytic reforming process it has been observed that major problem of carbon deposition occurs in upper part of the tube near the feed end. Since this region is at a comparatively lower temperature it is desirable that the catalyst in this portion should be selective and adequately resistant to undesirable side reactions. Therefore zoned packing may be advantageous for better performance of a steam-naphtha reformer.

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