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## CALCIUM PROMOTED NAPHTHA-STEAM REFORMING CATALYST : MAGNETIC STUDIES

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### Abstract

The beneficial role of calcium in alumina supported nickel catalyst producing less carbon deposition, sustained large active area, and increased longevity has been investigated by magnetic methods.

ESR spectra and Curie point depression indicate the formation of a nickel layer weakly bonded to  $\text{Ca}_3\text{Al}_2\text{O}_8$  covering the alumina surface. It is suggested that the bond retards the rate of migration of nickel over the surface, thus discouraging formation of large lumps with lower specific area. Magnetic saturation characteristics support the hypothesis of formation of nickel layer. Lower rate of carbon deposition may be the result of less area of alumina exposed for catalytic cracking of naphtha.

### Introduction

In previously reported studies from this laboratory<sup>1)</sup> it was found that catalytic activity of nickel for the reformation of naphtha varied markedly with the crystallite size of nickel. It was also shown that by incorporating calcium to nickel-alumina system for naphtha reforming was beneficial in two ways. Firstly, it reduced carbon deposition on the catalyst and secondly it inhibited the growth of nickel crystallites. But the mechanism of the processes could not be ascertained. The reducibility of nickel and the variation of crystallite size are considered to be responsible for the variation in the activity of nickel.<sup>2-5)</sup> Useful information on the factors affecting these parameters can be obtained from magnetic studies.<sup>6-9)</sup> Therefore, it was decided to obtain magnetic data on catalyst samples free from calcium as well as containing it to find whether the role of calcium in arresting the growth of the nickel crystallites could be understood from such studies.

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### Experimental

For this investigation the types of sample as in the previous study<sup>1)</sup> were taken. The samples are A, B and C with ten percent nickel incorporated in  $\alpha$ -alumina support were prepared following different techniques.

Sample A: Prepared by precipitating nickel by ammonium carbonate from a solution of nickel nitrate in which finely powdered alumina was kept in suspension. The dried mass was cured by heating at 800°C.

Sample B: Prepared by soaking alumina in nickel nitrate solution followed by drying and curing.

Sample C: Sample A was soaked in calcium nitrate solution and again dried and cured.

All the samples were reduced and were tested for activity for various lengths of time. The samples discharged at different time were taken for measurement of magnetic parameters, such as Curie temperature, relative magnetic susceptibilities and ESR spectra. For the former two investigations an automatic magnetic balance<sup>10)</sup> was used and for the latter, an X-band ESR spectrometer (Bruker-Physik, Model B-ER-402) operating at 9.5 GHz was employed.

### Results and Discussion

For phase composition and particle size, results of X-ray diffraction studies are reproduced from previous study<sup>1)</sup> in Table 1. It can be seen from Table 1 that all the samples are multicomponent systems containing several phases in varying concentrations. It would have been useless to measure the absolute magnetic susceptibility of such samples, and only relative measurement have been made to obtain the necessary information.

The ESR spectra of the series A and B exhibit a featureless broad line, typical of ferromagnetic substances, around  $g=2.20$ . In series C, however, a second line was found which developed with time. The spectra of the end members of this series (10 hrs and 30 hrs) after reforming reaction are presented in Fig. 1. The relative magnetic susceptibilities of samples from each series after 10 hrs and 30 hrs reforming reaction were plotted as a function of the applied magnetic field in Fig. 2.

The Curie temperatures for different samples obtained from thermomagnetic studies is tabulated in Table 2. From the Table 2 it is found that in samples free from calcium, the Curie temperature registers a slight

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TABLE 1. Phase composition and particle size.

Catalyst	Period of run (hrs)	Phase Composition	Ni Size Å
A	10	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , Ni, $\delta$ -Al <sub>2</sub> O <sub>3</sub> , $\kappa$ -Al <sub>2</sub> O <sub>3</sub>	250
	20	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , Ni, $\delta$ -Al <sub>2</sub> O <sub>3</sub> , $\kappa$ -Al <sub>2</sub> O <sub>3</sub>	350
	25	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , Ni, $\delta$ -Al <sub>2</sub> O <sub>3</sub> , $\kappa$ -Al <sub>2</sub> O <sub>3</sub>	442
	30	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , Ni, $\delta$ -Al <sub>2</sub> O <sub>3</sub> , $\kappa$ -Al <sub>2</sub> O <sub>3</sub>	720
B	10	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , $\delta$ -Al <sub>2</sub> O <sub>3</sub> , Ni, $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , $\kappa$ -Al <sub>2</sub> O <sub>3</sub>	164
	20	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , Ni, $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , $\delta$ -Al <sub>2</sub> O <sub>3</sub> , $\kappa$ -Al <sub>2</sub> O <sub>3</sub>	338
	25	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , Ni, $\delta$ -Al <sub>2</sub> O <sub>3</sub> , $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , $\kappa$ -Al <sub>2</sub> O <sub>3</sub>	523
	30	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , Ni, $\delta$ -Al <sub>2</sub> O <sub>3</sub> , $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , $\kappa$ -Al <sub>2</sub> O <sub>3</sub>	960
C	10	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , NiAl <sub>2</sub> O <sub>4</sub> , Ca <sub>3</sub> Al <sub>10</sub> O <sub>18</sub> , Ni, $\delta$ -Al <sub>2</sub> O <sub>3</sub>	261
	20	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , Ni, Ca <sub>3</sub> Al <sub>10</sub> O <sub>18</sub> , $\delta$ -Al <sub>2</sub> O <sub>3</sub>	274
	25	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , Ni, Ca <sub>3</sub> Al <sub>10</sub> O <sub>18</sub> , $\delta$ -Al <sub>2</sub> O <sub>3</sub>	269
	30	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , Ni, Ca <sub>3</sub> Al <sub>10</sub> O <sub>18</sub> , $\delta$ -Al <sub>2</sub> O <sub>3</sub>	285

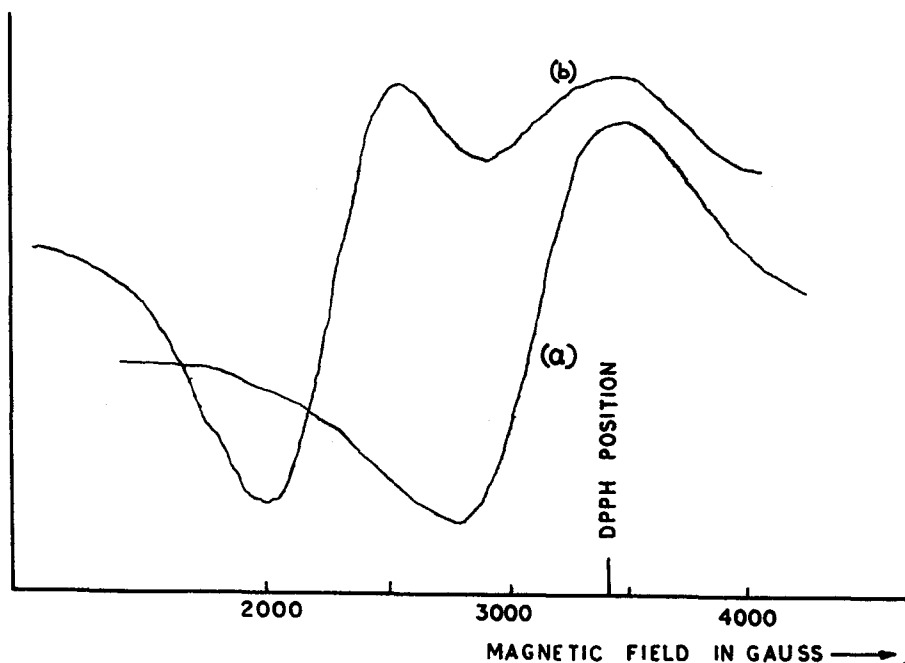
TABLE 2. Curie Temperatures.

Catalyst	Time of run (hrs)	Curie Temp. °C
A	10	340
	20	345
	25	355
	30	355
B	10	360
	20	360
	25	365
	30	365
C	10	400
	20	375
	25	365
	30	340

initial increase as may be expected as the crystallites grow in size indicating migration of nickel over the surface. The ESR spectra also are typical of ferromagnetic nickel, without any evidence of any other phase being present.

The calcium containing samples are distinct from the others in many respects. From X-ray data, the particle size of nickel crystallites appears

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**Fig. 1.** First derivative of absorption  $V_s$  Magnetic field in gauss.  
 Curve (a) is for C (10 hrs) and also represents A and B series.  
 Curve (b) is for C (30 hrs).

to remain more or less constant (Table 1). The Curie point also shows a steady downward drift with time of run (Table 2). The ESR spectrum of the sample taken out after 30 hrs run distinctly shows the existence of a different phase, which gives rise to an ESR line at a lower magnetic field as seen in Fig. 1. The apparent magnetic susceptibilities, plotted in Fig. 2 shows that in samples A and B free from calcium, the susceptibility shows the usual initial rise, corresponding to the early rapid movement of domain walls on application of magnetic field followed by a fall as saturation sets in. In sample C however the saturation effect is evident from the very lowest fields. The initial permeability is also large, showing that a component with large magnetisation value is present, which attains saturation at very low values of the magnetic field. This phase is seen to increase in amount with longer time of run.

To explain all the observed facts, the following mechanism is suggested.

After the initial curing, isolated nickel crystallites of an average size of about 250 Å form on the surface, leaving exposed alumina surface between them as shown in Fig. 3 (i). In sample C, the calcium treatment

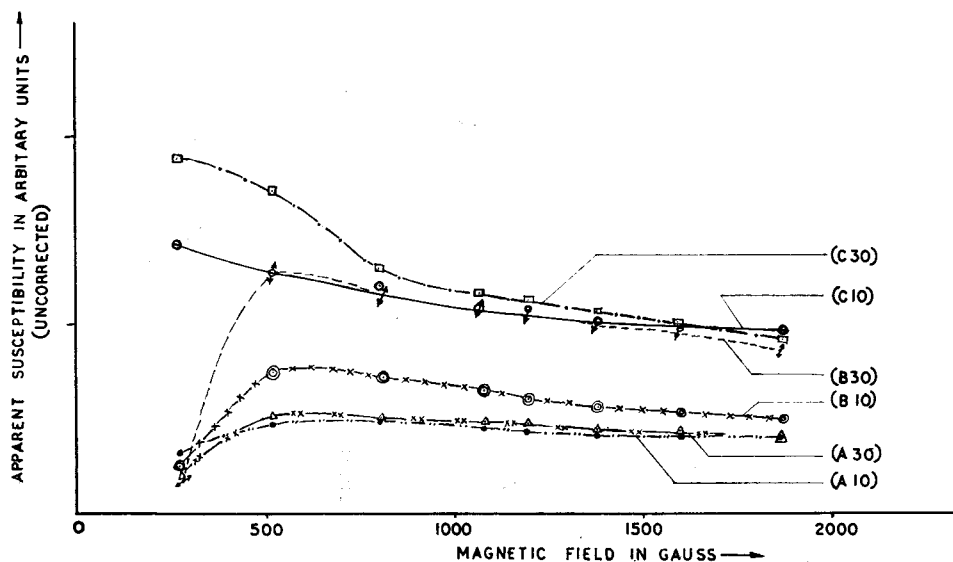


Fig. 2. Magnetic field  $V_s$  Apparent Susceptibilities.

- (a) A (10 hrs)      (c) B (10 hrs)      (e) C (hrs)  
 (b) A (30 hrs)    (d) B (30 hrs)      (f) C (hrs)

causes this exposed alumina surface to be at least partially covered with  $\text{Ca}_3\text{Al}_2\text{O}_8$ . This stage is depicted in Fig. 3 (ii). During the catalytic reaction, nickel tends to migrate over the surface, as seen in the case of samples A and B. But in sample C, this migration of nickel is probably arrested by the formation of a weak chemical bond between nickel and the  $\text{Ca}_3\text{Al}_2\text{O}_8$  phase, in contradistinction to the case of alumina substrate. Thus, a thin chemically bonded layer of nickel is formed in sample C, which slowly spreads with the time of run in the catalyst bed, as shown in Fig. 3 (iii). The evidence for this chemically bonded layer lies in the splitting of the ESR line, the new line appearing in the lower field side clearly indicates the effect of zero field splitting produced by ligands from  $\text{Ca}_3\text{Al}_2\text{O}_8$ . The gradual spreading of nickel in a thin layer at the cost of the crystallites originally present provides an adequate explanation for the downward shift of Curie point with reaction time, if the thickness of the layer is smaller than average domain dimensions. This spread is also likely to escape detection by X-ray line width determination.

The hypothesis of the spread layer explains the low magnetic hardness and easy saturation characteristics observed in sample C. The spread layer, if thinner than average domain dimensions, will behave as single domain

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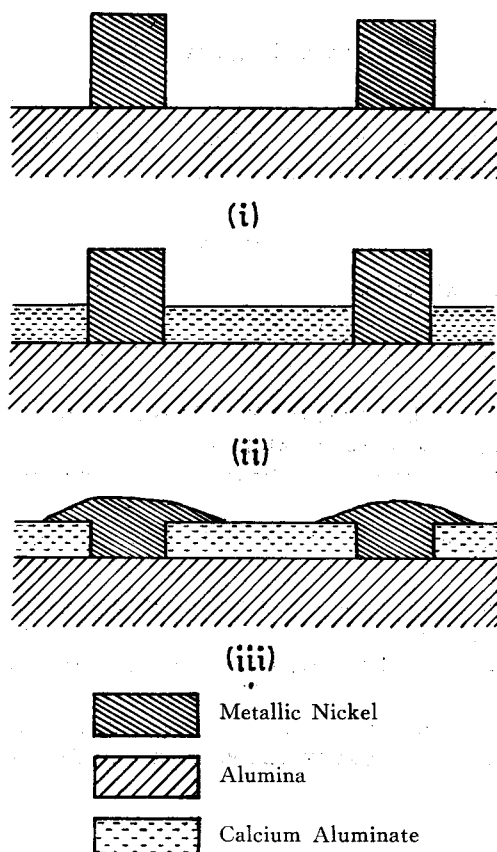


Fig. 3.

crystals, spontaneously magnetised, and a very small magnetic field strength will be adequate to orient all such single domains.

It may be argued that such spreading should result in enhancement of catalytic activity with time. It should be remembered however, that there is a competing process negating the effect, namely deposition of carbon on the surface, which reduces the active area. In sample C, thus, the activity is held more or less constant, while in the other two, it registers a steady decline. The rate of carbon deposition is also lower in sample C than in the others, because the exposed alumina surface, which acts as an efficient naphtha cracking catalyst, must be much lower than the other two. Therefore it is seen that all the features of distinction of the calcium treated catalyst can be satisfactorily explained by the above model of the catalyst surface.

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