

## STUDIES ON HYDROCARBON STEAM REFORMING CATALYST— EFFECT OF CALCIUM AND GAMMA ALUMINA

by D. K. MUKHERJEE, J. MISRA, R. L. CHOWDHURY and S. P. SEN, *Planning and Development Division, The Fertilizer Corporation of India Ltd., Sindri, Bihar*

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Two series of nickel catalysts—one supported on pure  $\alpha$ -alumina and the other supported on mixtures of  $\alpha$ - and  $\gamma$ -alumina having nickel content around 10 per cent and CaO content varying between 0 and 16 per cent have been investigated. The studies include assessments of activity, carbon liberation, mechanical stability, compressive strength and specific surface area of altogether 9 samples of catalyst. The results show that within the limits of the present investigation the increase in CaO content in a pure  $\alpha$ -alumina supported nickel catalyst increases the resistance to both carbon liberation and dusting but decreases the activity. Whereas, increase in CaO content alongwith proportional increase of  $\gamma$ -alumina in the catalyst improves the activity in addition to improvement of resistance to carbon liberation and dusting.

### INTRODUCTION

Catalytic steam reformation of naphtha is a widely adopted industrial process for the production of hydrogen. A supported nickel catalyst is almost invariably used for that purpose. While high orders of activity of supported nickel catalysts can be achieved by incorporating a finely divided nickel oxide on suitable refractory carriers, other qualities like resistance to carbon liberation and erosion, desirable for commercial use of such a catalyst are relatively difficult to achieve and require suitable modification of the structure and composition of the catalyst.

Although  $\alpha$ -alumina is believed to be suitable as a carrier for reformation catalysts due to its stable structure (Nicklin & Whittaker 1968) and several patents (Shmorgunenko *et al.* 1968; Taylor & Sinfelt 1966; Esso 1967; and Gas Council 1967) have claimed efficient nickel catalysts for hydrocarbon reformation prepared by co-precipitation of nickel and aluminium compounds, in which the alumina will be predominantly in  $\gamma$ -phase. Previous investigations by some of the authors (Misra *et al.* 1970; and Mukherjee *et al.* 1971a) have revealed that replacement of  $\alpha$ -alumina with  $\gamma$ -alumina in the carrier improves mechanical strength, stability and reforming activity to a certain extent but causes increase in carbon liberation. This appears to be due to the fact that  $\gamma$ -alumina possesses more of acid sites which are responsible for carbon liberation (Nicklin & Whittaker 1968). It has been reported that addition of alkali and alkaline earth metal oxides can suppress carbon liberation (Phineas 1967; Bridger & Redpath 1968; Hayes 1968; Morgan 1968; Andrews 1969; ICI Ltd. 1964; Power Gas Corpn. 1967; and Cockerham *et al.* 1969) by neutralizing the acid sites as well as by enhancing the rate of steam carbon reaction. But these oxides are also believed to reduce the reforming activity

of nickel catalysts (Andrews 1969; Ogura & Huzimura 1939). So it appears that incorporation of an alkali or alkaline earth metal oxide along with  $\gamma$ -alumina in a nickel catalyst may result in a suitable compromise between activity and resistance to carbon liberation.

In view of the above, two series of nickel catalysts corresponding to pure  $\alpha$ -alumina and mixtures of  $\alpha$ - and  $\gamma$ -alumina as carriers, having a fixed concentration of 10 per cent nickel and varying concentrations of CaO between 0 and 16 per cent, have been studied in the present investigation. The studies on the different catalyst samples comprise of activity, carbon liberation, mechanical stability, compressive strength and specific surface area.

#### EXPERIMENTAL

*Catalyst preparation:* Experiments were carried out with altogether 9 samples of nickel catalysts prepared by the co-precipitation method, having a nickel content around 10 per cent. The catalyst samples are of two distinct series. One series consisting of 5 samples (C-1 to C-5), was prepared by incorporating nickel on  $\alpha$ -alumina containing 0 to 16 per cent of CaO. The other series consisting of 4 samples (CA-1 to CA-4), was prepared by incorporating nickel on carriers composed of  $\alpha$ -alumina (Calcined  $\text{Al}_2\text{O}_3$ ) and  $\gamma$ -alumina obtained from its nitrate by precipitation with ammonium carbonate and containing 4 to 16 per cent of CaO in which the molar ratio of precipitated alumina and CaO was maintained constant at 1:3. All the catalyst samples were made into 6 mm  $\times$  6 mm solid cylindrical tablets and finally cured at 750°C. Brief method of preparation and chemical composition of the catalyst samples are shown in Table I.

TABLE I  
*Description of Catalyst Samples*

Sample No.	History of preparation	Percentage by wt. of		
		$\text{Al}_2\text{O}_3$ (coprecipitated)	CaO	Ni
C—1	Nickel incorporated by precipitation of nickel carbonate from its nitrate solution with ammonium carbonate keeping $\alpha$ - $\text{Al}_2\text{O}_3$ in suspension.	Nil	Nil	9.7
C—2	Same as above excepting that $\text{CaCO}_3$ was coprecipitated along with $\text{NiCO}_3$ , keeping $\alpha$ -alumina in suspension.	Nil	4.1	9.3
C—3	—do—	Nil	8.2	9.8
C—4	—do—	Nil	11.8	9.4
C—5	—do—	Nil	15.9	9.2
CA—1	Pure $\alpha$ -alumina kept in suspension in a solution containing nitrates of Nickel, Calcium and Aluminum. Ni, Ca and Al coprecipitated by adding ammonium carbonate.	3.2	4.1	9.4
CA—2	—do—	6.3	8.0	9.6
CA—3	—do—	9.4	12.4	9.9
CA—4	—do—	12.6	16.2	9.4

*Activity and stability tests:* Activity and mechanical stability of the catalyst samples under reforming conditions were tested in a bench scale unit which has been described elsewhere (Mukherjee *et al.* 1971 *a*). 25 gms of catalyst in the form of 6 mm  $\times$  6 mm solid cylindrical tablets was charged in the reactor in each case. Pure n-heptane was used as feed and steam to carbon molar ratio in the feed stream was maintained constant at 4.0 (moles H<sub>2</sub>O/atom of C). The unit was run under atmospheric pressure maintaining the reactor inlet and outlet temperatures at 500°C and 750°C respectively and liquid hourly space velocity (LHSV) with respect to heptane at 1.0. After 4 hours of run under the above condition, outlet gas samples were collected and analysed in a precision orsat apparatus with double action pipettes to determine the activity. The unit was continued to run for a total period of 65 hours under the same condition. After 65 hours of run the catalyst bed was subjected to steaming at 750°C for 2 hours passing steam at the rate of 5 gms/gm of catalyst per hour. Finally the reactor was cooled down in a stream of nitrogen and the catalyst was discharged. Weight of the discharged catalyst tablets after removing adhered dust, was noted.

*Surface area and compressive strength:* Specific surface area (BET) and compressive strength of both fresh and spent (after activity tests) catalyst samples were determined by the methods described elsewhere (Mukherjee *et al.* 1971 *b*). For compressive strength mean value of the results obtained with ten tablets of a catalyst sample, was taken into consideration.

## RESULTS AND DISCUSSION

X-ray investigations with the catalyst samples show that the fresh samples C-1 to C-5 contain NiO, CaCO<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> whereas samples CA-1 to CA-4 contain  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in addition to NiO, CaCO<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and minor amounts of NiAl<sub>2</sub>O<sub>4</sub> and Ca(AlO<sub>2</sub>)<sub>2</sub>. It is also observed that the extent of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> increases continuously from CA-1 to CA-4 so that CA-1 contains minimum  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CA-4 the maximum.

*Activity:* The product gas analysis and carbon in the inlet and outlet on hourly basis are shown in Table II. The activity of each catalyst sample has been computed in terms of percentage of input carbon reformed into CO and CO<sub>2</sub> and the same has also been shown in Table II. Activity has been plotted against corresponding CaO content of the catalysts in Figure 1. Curves A and B of figure 1 show that there is a decreasing trend of activity of a nickel catalyst with increasing CaO content when the carrier is pure  $\alpha$ -alumina whereas increasing CaO content with corresponding increase of  $\gamma$ -alumina in the carrier results in increase of activity. Thus, it appears that the effect of CaO on the reforming activity of a nickel catalyst can be favourably modified by incorporating a suitable quantity of  $\gamma$ -alumina in the carrier.

*Carbon liberation:* The extent of carbon liberation on the catalyst has been calculated from the carbon entering the reactor as heptane and the carbon coming out of the reactor as product gas in a given time. Although this is an approximate method of calculating carbon liberation, it gives a fairly good comparative idea. Curves C and D of Figure 1 show the relationships between carbon liberation and

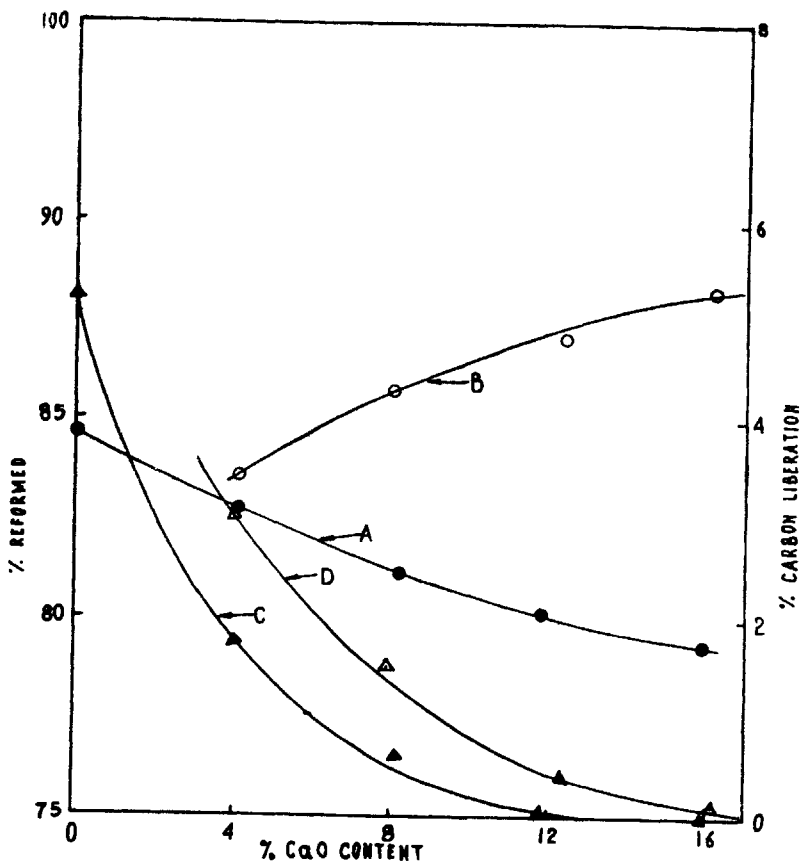


FIG. 1. Effect of CaO content on activity and carbon liberation. Curve A — Activities of catalyst without  $\gamma\text{-Al}_2\text{O}_3$ ; Curve B — Activities of catalyst with  $\gamma\text{-Al}_2\text{O}_3$  ( $\gamma\text{-Al}_2\text{O}_3$  increases with CaO content); Curve C — Carbon liberation on catalysts without  $\gamma\text{-Al}_2\text{O}_3$ ; Curve D — Carbon liberation on catalysts with  $\gamma\text{-Al}_2\text{O}_3$  ( $\gamma\text{-Al}_2\text{O}_3$  increases with CaO content).

CaO content of catalysts having pure  $\alpha$ -alumina and mixtures of  $\alpha$ - and  $\gamma$ -alumina as carriers respectively. It is obvious from these curves that the presence of CaO reduces carbon liberation on catalyst both in absence and in presence of  $\gamma$ -alumina. That CaO inhibits carbon liberation on nickel catalyst has also been observed by other workers (ICI Ltd. 1964; and Cockerham *et al.* 1969). However, the catalysts containing  $\gamma$ -alumina show comparatively higher carbon liberation particularly when CaO content is below 12 per cent.

*Mechanical stability:* Mechanical stability of the catalysts has been assessed from the loss of catalyst due to dusting during the period of bench scale test. The losses due to dusting for different catalysts are shown in Table III and also illustrated in Figure 2 as a function of CaO content. It follows that increase in CaO content decreases catalyst dusting both in the absence and in the presence of  $\gamma$ -alumina in the catalyst. But for same CaO content catalyst dusting is much less

TABLE II

*Results of Activity Tests*

Operating conditions: Pressure—Atmospheric, LHSV—1.0 g., Heptane/g. Catal./hr., Steam/Carbon—4.0 moles/atom, Temperature—inlet/Outlet—500/750°C

Catalyst sample	Product gas volume at NTP Litres/hr.	Product gas composition (% by vol.)					Carbon g/hr.		Percentage carbon reformed into CO & CO <sub>2</sub>	Percentage carbon liberated on Catalyst
		CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	Feed	Exit		
C—1	107.1	12.7	0.3	18.3	65.6	3.1	21.0	19.90	84.7	5.24
C—2	104.2	11.1	1.0	20.1	64.0	3.8	21.0	20.63	82.8	1.76
C—3	101.6	11.0	1.1	20.4	62.7	4.8	21.0	20.87	81.2	0.62
C—4	100.1	10.8	1.2	20.8	62.0	5.2	21.0	20.99	80.2	0.05
C—5	98.5	10.9	1.2	20.9	61.4	5.6	21.0	21.00	79.4	0.00
CA—1	105.1	13.0	0.8	18.2	64.6	3.4	21.0	20.36	83.6	3.05
CA—2	109.2	12.5	0.8	18.3	65.4	3.0	21.0	20.68	85.7	1.52
CA—3	111.7	12.5	0.8	18.1	65.8	2.8	21.0	20.91	87.1	0.43
CA—4	113.2	12.4	0.7	18.2	66.1	2.6	21.0	20.97	88.3	0.14

TABLE III

*Dusting of Catalyst*

Catalyst sample	Weight of Catalyst charged (g)	Weight of catalyst discharged (g)	Percentage loss due to dusting
C—1	25.0	20.5	18.0
C—2	25.0	22.4	10.4
C—3	25.0	23.6	5.6
C—4	25.0	24.2	3.2
C—5	25.0	24.6	1.6
CA—1	25.0	24.1	3.6
CA—2	25.0	24.6	1.6
CA—3	25.0	24.8	0.8
CA—4	25.0	24.9	0.4

in presence of  $\gamma$ -alumina than what is observed in absence of the same. This appears to be reasonable from the fact that  $\gamma$ -alumina alone can also reduce the dusting of catalyst as reported earlier (Mukherjee *et al.* 1971a).

*Surface area and compressive strength:* Table IV includes the specific surface area of both fresh and spent catalyst samples. It is observed that while with increase of CaO in the catalyst containing no  $\gamma$ -alumina the surface area decreases considerably,

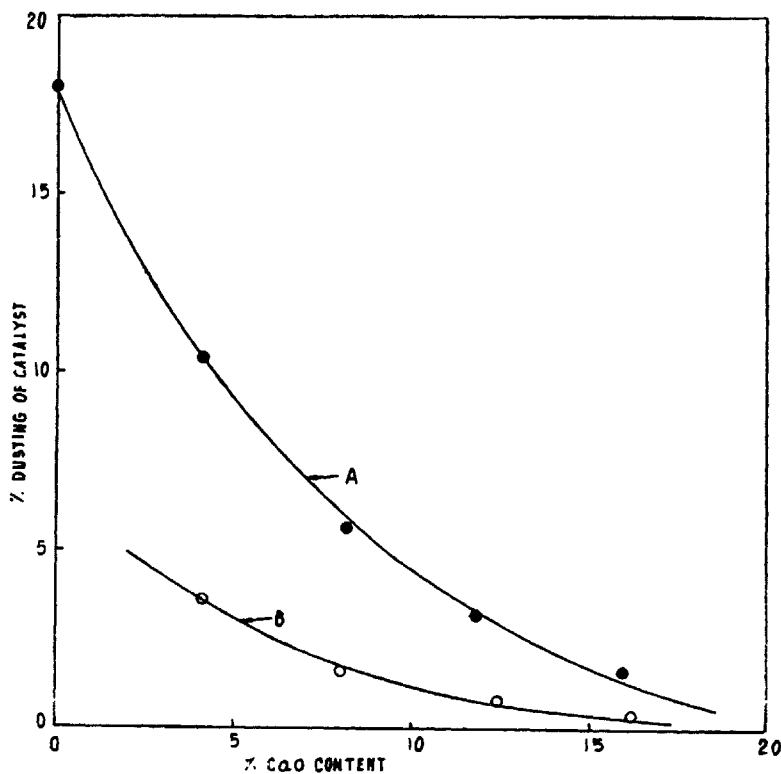


FIG. 2. Effect of CaO content on catalyst dusting. Curve A — Catalyst without  $\gamma$ -alumina ; Curve B — Catalyst with  $\gamma$ -alumina.

TABLE IV

*Compressive strength and specific surface area*

Catalyst sample	Compressive strength Kg/cm <sup>2</sup>		Specific surface area m <sup>2</sup> /gm.	
	Fresh	Spent	Fresh	Spent
C-1	418	531	31.9	9.8
C-2	566	650	30.8	9.2
C-3	636	714	29.0	8.6
C-4	704	806	27.4	8.2
C-5	741	861	24.0	7.5
CA-1	488	392	33.2	8.5
CA-2	642	535	40.6	9.8
CA-3	777	604	44.8	10.5
CA-4	863	688	46.5	11.2

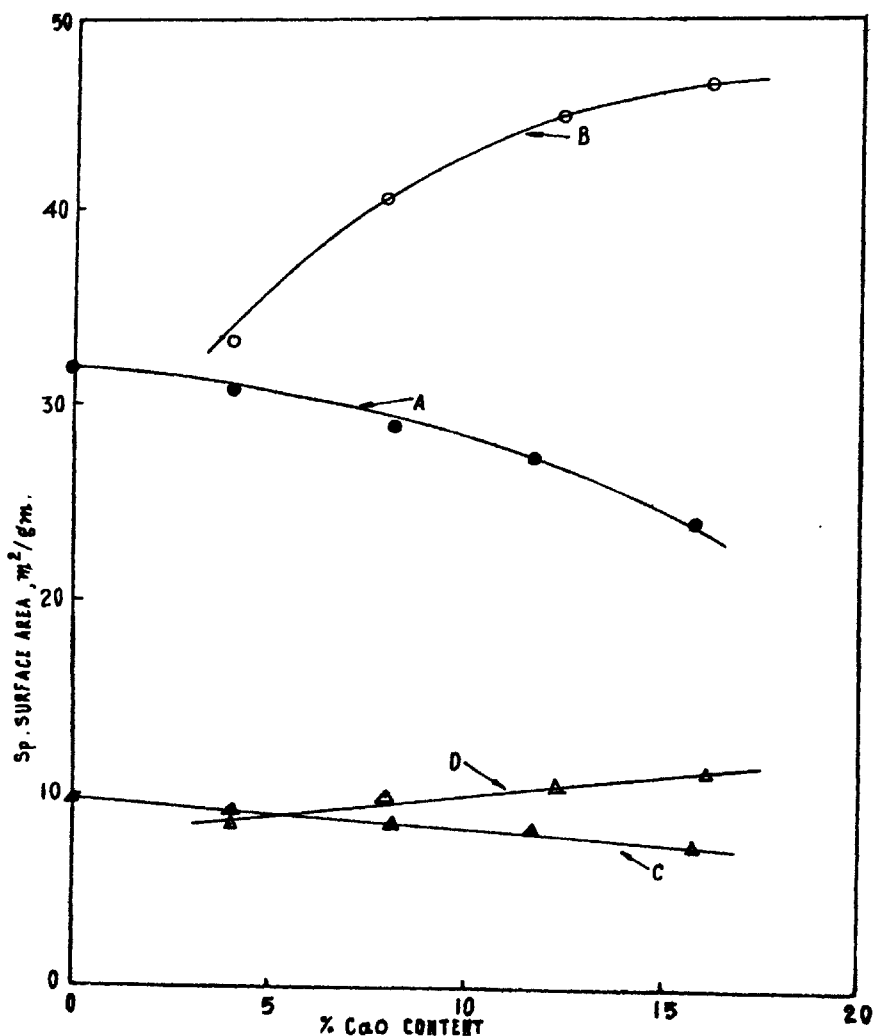


FIG. 3. Effect of CaO content on specific surface area. Curve A — Fresh catalyst without  $\gamma$ -Alumina ; Curve B — Fresh catalyst with  $\gamma$ -Alumina ; Curve C — Spent catalyst without  $\gamma$ -Alumina ; Curve D — Spent catalyst with  $\gamma$ -Alumina.

there is increase in surface area when  $\gamma$ -alumina content is increased along with CaO content. This is clearly illustrated in Figure 3 where specific surface area of both fresh and spent catalysts have been plotted against CaO content. Comparison of specific surface area of fresh catalyst with that of the corresponding spent sample shows that there is a sharp fall in surface area during reformation reaction in case of all the catalyst samples. However, the extent of fall is observed to be more in case of the catalysts containing  $\gamma$ -alumina.

Compressive strengths of the catalyst samples before and after use are shown in Table IV. Dependence of compressive strength of both fresh and spent catalyst tablets on CaO content has also been illustrated in Figure 4. It is observed that

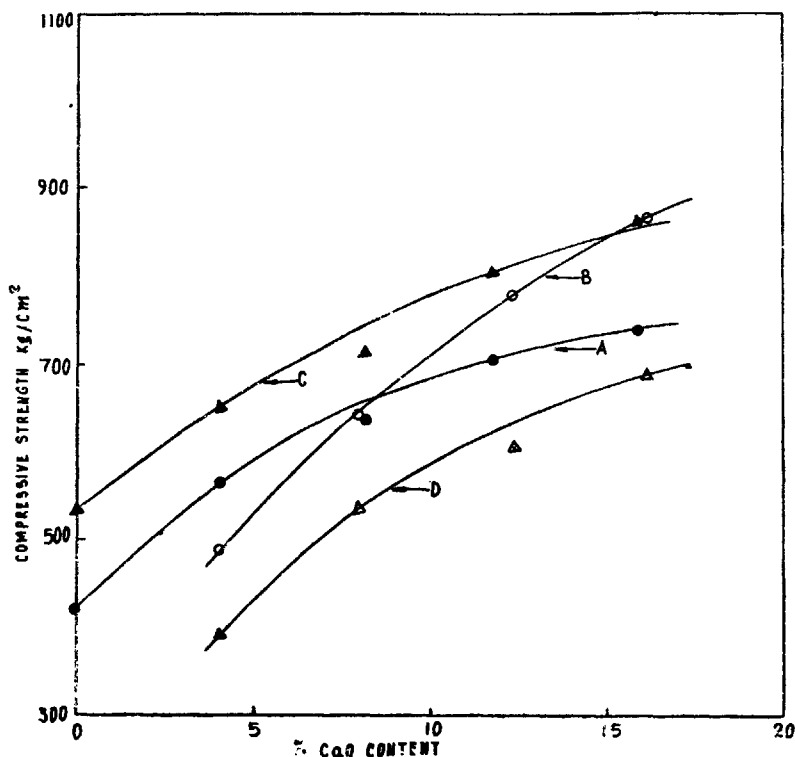


FIG. 4. Effect of CaO content on compressive strength. Curve A — Fresh catalyst without  $\gamma$ -Alumina ; Curve B — Fresh catalysts with  $\gamma$ -Alumina ; Curve C — Spent catalyst without  $\gamma$ -Alumina ; Curve D — Spent catalysts with  $\gamma$ -Alumina.

compressive strength of a catalyst increases with increase of CaO content both in the absence and in the presence of  $\gamma$ -alumina. But it is interesting to note that while in the case of catalysts without  $\gamma$ -alumina there is considerable increase in compressive strength during reformation reaction the catalysts possessing  $\gamma$ -alumina show decrease in strength. This is probably due to the fact that presence of  $\gamma$ -alumina favours the formation of aluminates spinels which are responsible for lowering of compressive strength (Mukherjee *et al.* 1971 b). But it is reported that the presence of spinel compound makes a catalyst more resistant to dusting (Mukherjee *et al.* 1972). This can explain why in spite of fall in compressive strength, in use  $\gamma$ -alumina containing catalysts have exhibited higher resistance to dusting.

#### CONCLUSION

From the results and observations of the present investigation it follows that within the limits of experiments increase in CaO content in  $\alpha$ -alumina based nickel catalyst not only increases resistance to carbon liberation but also its mechanical stability although activity decreases to some extent. However, increase in CaO



content along with proportional increase of  $\gamma$ -alumina in a nickel catalyst results in improvement of activity in addition to carbon liberation and mechanical stability.

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