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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 26(1), 25-35
Issue Date	1978-07
Doc URL	https://hdl.handle.net/2115/25040
Type	departmental bulletin paper
File Information	26(1)_P25-35.pdf

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J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 26 No. 1, pp. 25 to 36 (1978)

EFFECT OF IRON OXIDE AND ALKALI CONTENT ON ACTIVITY AND SELECTIVITY OF ZINC OXIDE

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(Received October 20, 1977; revised November 10, 1977)

Abstract

Chemical composition of naphtha changes after its treatment over ZnO, Fe_2O_3 and binary mixtures of ZnO-Fe_2O_3. An increase in olefinic and aromatic content is observed which is maximum over Fe_2O_3 and least over ZnO. In case of ZnO-Fe_2O_3 binary systems, it is proportional to Fe_2O_3 content. This has been ascribed due to cracking and subsequent dehydrocyclisation of feed stock. Acidic surfaces and higher operating temperatures are more favourable for these reactions. Additions of alkali to the systems investigated suppressed cracking, dehydrocyclisation and carbon deposition to a very marked extent.

Incorporation of iron oxide, as well as, alkali improved mechanical strength of ZnO globules appreciably. Attrition loss of finished globules came down from 40% for pure ZnO to 1.92% for sample containing 10% Fe_2O_3. It improved further to 1.04% after incorporation of 5% alkali in it. However, both the ingredients had an adverse effect on its sulphur absorption capacity. At 1000/hr space velocity, 1000 ppm H_2S concentration in feed stream and 400°C bed temperature, slippage of H_2S occured after 52% sulphiding of pure zinc oxide. Under similar conditions, H_2S was detected in treated gas after 30.2 and 22.5% sulphiding of samples containing 10% Fe_2O_3 and 10% Fe_2O_3+5% Na_2CO_3 respectively.

Introduction

Ni-Al_2O_3 catalyst employed in hydrocarbon steam reformation process is highly sensitive to sulphur poisoning and specified sulphur limit in processed naphtha is around 0.2 ppm only. This necessitates desulphurisation of feed prior to reformation which is generally achieved in two steps *viz.* (1) hydrogenation of organic sulphur compounds and (2) subsequent absorption of H_2S formed by suitable absorbant. Conventional catalysts employed in industry for the purpose are Comox or Nimox and ZnO for steps 1 and

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2 respectively.

Reformation of naphtha over Ni-catalyst is influenced by over all composition of feed. The feed stocks containing low concentration of olefins and aromatic contents are preferred, because high olefinic content leads to carbon deposition which in turn results into crumbling and dusting of catalyst hampering the process. On the other hand, increase in aromatic content may lead to oil see-page and will require higher operation temperature for gasification which is also not desirable. So the desulphurization catalyst employed should not favour cracking and aromatisation reactions over its surface.

Pure zinc oxide although has high activity but possess poor mechanical strength. Qualitatively it has been observed that incorporation of iron improves its mechanical strength, specific surface area and restricts crystal growth of ZnO during heat treatment. This has been attributed due to coverage of ZnO by Fe_2O_3 by Moorjani *et al.*[1] However, its effect on overall composition of liquid hydrocarbon treated over ZnO has not been reported in literature. Keeping these facts in view, present studies have been undertaken and influence of iron oxide and alkali on activity, selectivity and mechanical strength of ZnO catalyst has been investigated.

Experimental

Catalyst samples employed for the present investigation have been prepared as follows:

1. *Zinc Oxide*: Zinc carbonate was precipitated from zinc nitrate solution at room temperature by ammonium bicarbonate. Precipitated mass was filtered, washed free from NO_3^- and later on dried at 125°C. Dried mass was heat-treated at 350°C to obtain ZnO. The ZnO so obtained was milled to −100 mesh size and converted into globules. They were finally cured at 400°C for 4 hrs. Globules of −4+6 mesh size only were used for different experimental purposes.
2. *ZnO-Fe_2O_3*: Samples containing ZnO and 2.5, 5 and 10% Fe_2O_3 were prepared by coprecipitating zinc and iron as carbonate at room temperature from solution containing requisite amount of respective nitrates. Precipitated mass was filtered, washed free from NO_3^- and dried completely at 125°C. Remaining process was same as mentioned above.
3. *Fe_2O_3*: Ferric carbonate was precipitated from ferric nitrate solution. Rest of process was same as followed in the case of pure ZnO sample.

4. *Incorporation of alkali*: In order to investigate effect of alkali, all the above mentioned samples were blended with alkali. A portion of powdered mass obtained after milling of each sample was mixed with requisite amount of Na_2CO_3 in a mixer so as to give a product containing 5% Na_2CO_3. Mixed mass was dried at 125°C and powdered to −100 mesh size. Rest of process was same as mentioned earlier.

ZnO content of finished product was estimated volumetrically by EDTA using erichrome T as indicator after separation of iron. Iron and alkali content was also estimated volumetrically.

Straight run naphtha of boiling range 60～160°C was used as feed stock. Composition of feed naphtha was as follows: Olefins 0.12% v/v; Aromatics 15.38%, v/v; and saturates 84.5, v/v.

Experimental set up was same as described earlier[2]. During selectivity studies, partial pressure of hydrogen and LHSV of naphtha was kept constant and respective values were 0.469 atm and 4 cc/cc/hr. To investigate effect of temperature on cracking and aromatisation reaction, it was varied in the range of 200 to 500°C. Olefin and aromatic content of feed and treated product were estimated by ASTM methods.[3~5] Saturates were determined by difference.

Mechanical strength of samples were determined by measuring their attrition loss. A mini mill with mild steel balls was used for the purpose. 50 gms of sample and 250 gms of steel balls were charged in mini mill and it was operated for 2 hrs at 11 RPM. After milling was completed, globules were sieved through 6 and 50 mesh sieves. Globules retained by 6 mesh sieve were taken to be intact. The ones which passed through 6 mesh but were retained by 50 mesh were taken as broken one and fraction which passed through 50 mesh was taken as dust. Each portion was weighed separately. From these weights percentage of respective fractions were calculated. Percentage dust formation was taken as a measure of attrition loss and inversely proportional to mechanical strength.

Sulphur absorption capacity of catalyst was evaluated in all glass testing unit. Experimental set up was same as mentioned earlier.[6] Nitrogen was used as carrier gas. All tests were conducted at 400°C bed temperature, 1000/hr space velocity and 1000 ppm H_2S v/v in the stream. As soon as traces of H_2S appeared in exit, sample under investigation was discharged. Percentage zinc oxide sulphided was calculated from volume of H_2S adsorbed by it. Extent of sulphiding was taken as a measure of catalysts life.

Results and Discussion

It is apparent that many hydrocarbon reactions may occur simultaneously along with hydrogenation of organic sulphur compounds during hydrodesulphurisation. Paraffin and naphthene isomerisation reactions take place under all conditions and hydro-cracking increases as the temperature and pressure increases. At higher temperature and low pressure some naphthenes dehydrogenate and some paraffins dehydrocyclise. At lower temperature and high pressure aromatics are liable to be dehydrogenated. Paraffins are dehydrogenated to a small extent under more stringent conditions.[7] Nature of catalyst employed will play a significant role for all these reactions mentioned above. Normally an acidic catalyst favours hydrocracking and quite often it is followed by subsequent dehydrocyclisation.[8~11] However, these side reactions are undesirable from reformation point of view, because

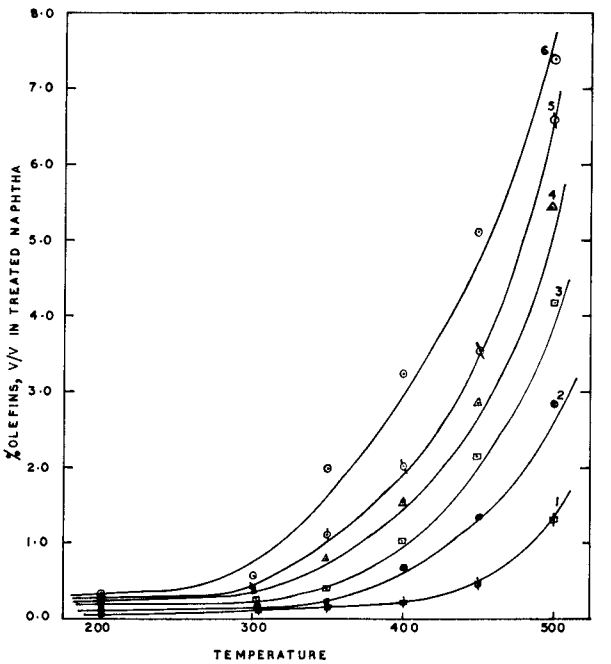

Fig. 1. Effect of temperature on cracking of naphtha over ZnO, Fe_2O_3 and ZnO–Fe_2O_3 systems.
LHSV of naphtha maintained=4 cc/cc/HR, and partial pressure of hydrogen=0.469 atm.

1. Blank, 2. ZnO, 3. ZnO+2.5% Fe_2O_3, 4. ZnO+5% Fe_2O_3, 5. ZnO 10% Fe_2O_3, 6. Fe_2O_3.

they will lead to an increase in olefinic and aromatic content of treated naphtha.

Iron oxide, incorporated in ZnO formulation basically for imparting desired mechanical strength, may aggravate these side reactions due to its acidic temperament. Its effect will be more pronounced at higher temperatures. Keeping above facts in view effect of iron oxide content and operating temperature on chemical composition of naphtha has been investigated. Its effect on sulphur absorption capacity and mechanical strength has also been evaluated in order to have an idea of the optimum values from activity and selectivity point of view.

Results on cracking of naphtha over ZnO, Fe_2O_3 and ZnO–Fe_2O_3 binary systems at different temperatures are shown in Fig. 1. Under the experimental conditions investigated, increase in olefinic content was least over pure ZnO and maximum over pure Fe_2O_3. In case of ZnO–Fe_2O_3 binary systems, it was proportional to its Fe_2O_3 content. Observed cracking over systems investigated is a cumulative effect of thermal and catalytic factors but contribution of thermal factor is very small. Thermal effect is practically

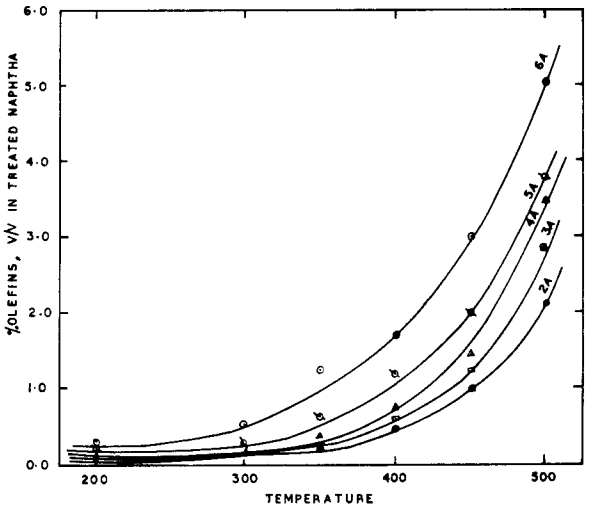

Fig. 2. Effect of alkali on suppression of cracking of naphtha over ZnO, Fe_2O_3 and ZnO–Fe_2O_3 systems.
LHSV of naphtha maintained = 4 cc/cc/HR, and partial pressure of hydrogen = 0.469 atm.

2 A. ZnO+5% Alkali, 3 A. ZnO+2.5% Fe_2O_3+5% alkali, 4 A. ZnO 5% Fe_2O_3+5% Alkali, 5 A. ZnO+10% Fe_2O_3+5% Alkali, 6 A. Fe_2O_3+5% Alkali.

nil upto 350°C and thereafter increases gradually (Fig. 1, Curve 1). Most of cracking is contributed due to catalyst surface itself (Fig. 1). This in turn suggested that surface acidity of systems investigated should have a significant role and extent of cracking over them should be proportional to their total acidity. Shibata *et al.*[12] measured total acidity of pure Fe_2O_3 and equimolar mixture of ZnO–Fe_2O_3 and respective values were 0.279 and 0.243 m moles/g. This indicates clearly that pure Fe_2O_3 will be more acidic in temperament than binary mixture of ZnO–Fe_2O_3 and its total acidity will increase with Fe_2O_3 content. Acidic surfaces are known to favour cracking over them. Fe_2O_3 being most acidic is expected to catalyse cracking to maximum extent and its magnitude should decrease with its blending with ZnO as has been observed experimentally.

Addition of Na_2CO_3 to various systems investigated suppressed cracking tendency to a very marked extent. Unsaturate content of treated product was reduced to almost half after alkali treatment. (Fig. 1 and 2). This was

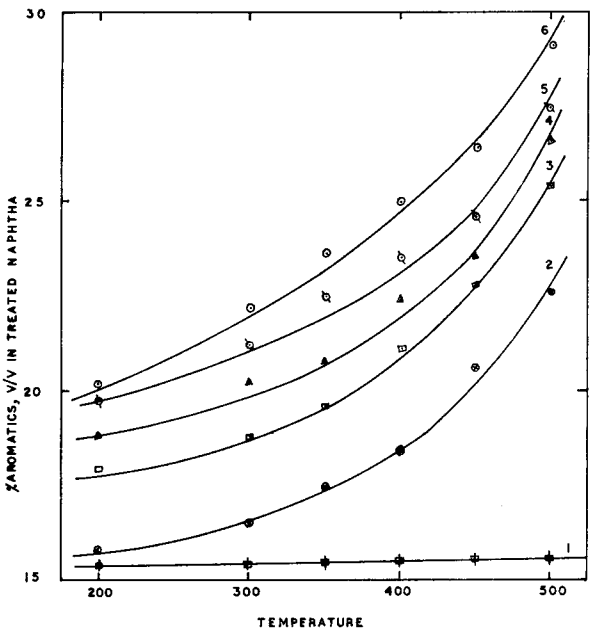

Fig. 3. Effect of temperature on aromatisation of naphtha over ZnO, Fe_2O_3 and ZnO–Fe_2O_3 system.
LHSV of naphtha maintained=4 cc/cc/HR, and partial pressure of hydrogen=0.469 atm.

1. Blank, 2. ZnO, 3. ZnO+2.5% Fe_2O_3, 4. ZnO+5% Fe_2O_3, 5. ZnO+10% Fe_2O_3, 6. Fe_2O_3.

probably due to masking of acid centres. Similar phenomenon was observed by Sugioka *et al.*[13] in case of cracking of organic sulphur compounds over silica-alumina catalyst. Initially, the extent of cracking was found to be directly proportional to number of acid centres which declined considerably after alkali treatment of catalyst employed.

Qualitatively it has been observed that incorporation of alkali minimised carbon laydown also. Very little carbon was deposited over catalyst surface during operation after alkali treatment. Probably, alkali affects process through following two routes *viz.* 1) By retarding cracking after masking of acid centres which in turn will control polymerisation of unsatureates over catalyst surface, and 2) by accelerating gasification rate of carbonaceous matter through hydrogenation.[14]

Results on aromatisation of naphtha over ZnO, Fe_2O_3 and ZnO–Fe_2O_3 systems are presented in Fig. 3. Increase in aromatic content was minimum

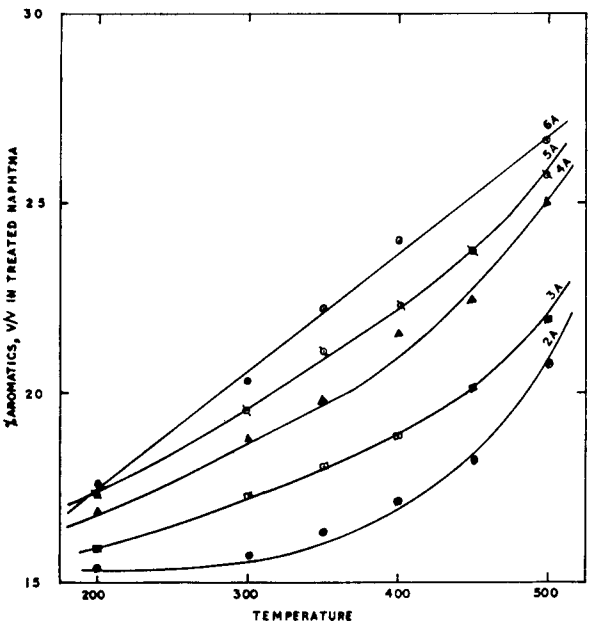

Fig. 4. Effect of alkali on suppression of aromatisation of naphtha over ZnO, Fe_2O_3 and ZnO–Fe_2O_3 systems.
LHSV of naphtha maintained =4 cc/cc/HR, and partial pressure of hydrogen=0.469 atm.

2 A. ZnO+5% Alkali, 3 A. ZnO+2.5% Fe_2O_3+5% Alkali, 4 A. ZnO+5% Fe_2O_3+5% Alkali, 5 A. ZnO+10% Fe_2O_3+5% alkali, 6 A. Fe_2O_3+5% Alkali.

over pure zinc oxide. In cases of ZnO-Fe_2O_3 mixtures, effect increased progressively with increase in Fe_2O_3 content. Operating temperature in general aggravated the effect but it was more pronounced at higher temperatures (Fig. 3). However, thermal factor as such had no role to play and its contribution towards aromatisation was practically nil (Curve 1, Fig. 3). This indicates clearly that aromatisation occurring at solid surface is basically catalytic one.

Dehydrogenation is most probable reaction which may occur under experimental conditions. It appears that observed increase in aromatic content of naphtha is due to dehydrogenation of naphthenes and dehydro-cyclisation of paraffins and olefins catalysed over solid surface. These reactions being endothermic in nature should be favoured at higher operating temperatures as has been observed, experimentally. Total acidity of system also played an important role. Maximum conversion was observed over most acidic pure Fe_2O_3 and least over pure ZnO (Fig. 3). Acidic surfaces were more favourable for these reactions. In addition to catalysing these reaction, such surfaces catalysed cracking also, which in turn provided intermediate olefins required for further cyclisation. Similar facts have been observed by other too.[15]

Incorporation of alkali affected process of aromatisation and decreased its intensity. Its effect was almost uniform for all systems investigated (Fig. 4). This was probably due to masking of acid centres which in turn retarded

TABLE 1. Effect of Fe_2O_3 and alkali on the attrition loss of ZnO catalyst

Sample No.	Details of sample	% Intact catalyst w/w	% Broken catalyst w/w	% Dust formation w/w
1.	ZnO	23.65	36.45	40.00
2.	ZnO+2.5% Fe_2O_3	42.75	33.90	23.35
3.	ZnO+5.0% Fe_2O_3	72.33	22.71	14.96
4.	ZnO+10% Fe_2O_3	86.94	11.14	1.92
5.	ZnO+5% Na_2CO_3	78.33	15.67	6.00
6.	ZnO+2.5% Fe_2O_3+5% Na_2CO_3	85.93	9.67	4.40
7.	ZnO+5% Fe_2O_3+5% Na_2CO_3	95.54	2.74	1.72
8.	ZnO+10% Fe_2O_3+5% Na_2CO_3	97.10	1.86	1.04

Weight of catalyst sample taken—50 gms
Weight of mild steel balls taken—250 gms
Duration of Ball milling — 1 hr.

TABLE 2. Effect of iron oxide and alkali on sulphur absorption capacity on ZnO catalyst

Sample No.	Details of sample	% ZnO sulphided at the time of slippage of H_2S
1.	ZnO	52.0
2.	ZnO+2.5% Fe_2O_3	43.5
3.	ZnO+5% Fe_2O_3	37.8
4.	ZnO+10% Fe_2O_3	30.2
5.	ZnO+5% Na_2CO_3	41.9
6.	ZnO+2.5% Fe_2O_3+5% Na_2CO_3	33.6
7.	ZnO+5.0% Fe_2O_3+5% Na_2CO_3	30.0
8.	ZnO+10% Fe_2O_3+5% Na_2CO_3	22.5
9.	Fe_2O_3	18.3
10.	Fe_2O_3+5% Na_2CO_3	17.9

Space velocity maintained—1000/hr, ppm of H_2S at inlet—1000, Carrier gas used—nitrogen, catalyst bed temperature maintained—400°C, and ppm H_2S in exit at the time of discharge—traces.

cracking, as well as, aromatisation.

Incorporation of iron oxide and alkali influences properties, as well as, life of zinc oxide catalyst. It can be seen from Table 1 that attrition loss for finished globules came down from 40% for pure zinc oxide to 1.92% for sample containing 10% Fe_2O_3. Addition of alkali to this binary system reduced it further. Minimum attrition loss observed was for sample 7 containing 10% Fe_2O_3 and 5% alkali (Table 1).

Zinc oxide is basically used for H_2S absorption. It is expected to remove H_2S completely and specified limit for treated product is less than 0.2 ppm. Extent of zinc oxide sulphided, when slippage of H_2S starts under experimental conditions has been taken as a measure of its life. Both the ingredients, Fe_2O_3 and Na_2CO_3 have an adverse effect on its life (Table 2). At 1000/hr space velocity, 1000 ppm H_2S concentration in feed stream and 400°C bed temperature, slippage of H_2S occurred after 52% sulphiding in case of sample 1. Under similar conditions H_2S was detected in treated gas after 43.5, 37.8 and 30.2% sulphiding in case of sample 2, 3 and 4 respectively (Table 2). Life of ZnO deteriorated progressively with increase in iron oxide content. Addition of alkali further deteriorated its reactivity (Table 2).

Zinc oxide has much higher sulphur adsorption capacity than iron oxide at 400°C (Table 2). Its affinity for sulphur too is higher than that of iron.[16] So, it is expected that performance of Fe_2O_3-ZnO systems will be poorer

than that of pure ZnO and deterioration will be directly proportional to its Fe_2O_3 content. Results obtained experimentally have shown that Fe_2O_3 and Na_2CO_3 have failed to act as a promoter and their incorporation though improved physical characteristics but reduced its life. Moorjani *et al.*[1] observed that incorporation of Fe_2O_3 improved specific surface area but formed protective layer around ZnO which restricted its rate of crystal growth. Normally with increase in specific surface, sulphur absorption capacity should increase but on the contrary it is deteriorated. Probably protective layer formed, offers resistance and obstructs access of H_2S to ZnO layer. This is probably responsible for poor performance of ZnO catalyst containing Fe_2O_3. Deterioration by alkali might have been caused by similar unfavourable distribution of ZnO in the system.

It is evident from above mentioned studies that although pure zinc oxide has higher sulphur absorption capacity and least cracking and aromatisation tendency, it finds difficulty in use due to its poor mechanical strength. Incorporation of alkali and Fe_2O_3 is necessary from mechanical strength, as well as, suppression of cracking and dehydrocyclisation point of view. Keeping these facts in view a compromise in formulation is necessary to achieve adequate activity, selectivity and mechanical strength.

A comparative study of typical data presented in Table 3 shows that at 500°C thermal cracking is about 1.32%. Under similar conditions with ZnO+10.0% Fe_2O_3 and pure Fe_2O_3, olefins in treated product were 6.6 and 7.4% respectively. It may be seen that addition of 5% alkali to both the samples has suppressed cracking to almost same extent. However, on the

TABLE 3. Effect of temperature on hydrocracking of naphtha over ZnO, Fe_2O_3 and ZnO–Fe_2O_3 systems

Sl. No.	Details of samples	% Olefins v/v at 400°C	% Olefins v/v at 450°C	% Olefins v/v at 500°C
1.	Fe_2O_3	3.25	5.1	7.4
2.	Fe_2O_3+5% Na_2CO_3	1.71	3.0	5.0
3.	ZnO	0.70	1.35	2.8
4.	ZnO+5% Na_2CO_3	0.50	1.0	2.12
5.	ZnO+2.5% Fe_2O_3	1.00	1.35	—
6.	ZnO+2.5% Fe_2O_3+5% Na_2CO_3	0.60	1.25	—
7	ZnO+10% Fe_2O_3	2.0	3.6	6.6
8.	ZnO+10% Fe_2O_3+5% Na_2CO_3	1.2	2.0	3.75
9.	Blank	0.24	0.45	1.32

other hand, olefin contents of product treated at 400 to 450°C over ZnO is between 0.7~1.35%. Addition of alkali improved selectivity for hydrogenation marginally. At the same time presence of Fe_2O_3 to the extent of 2.5% deteriorated it to almost same extent.

Keeping in view allowable olefins limit of 0.5% in processed naphtha at operating temperature of 400 to 450°C, it is clear that ZnO formulation should not contain Fe_2O_3 more than 2.5%. For safer operation and to control unsaturate content in treated naphtha below specified limit, incorporation of alkali seems advisable. A detailed study for optimum formulation of ZnO catalyst is under progress.

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