

MECHANISM OF HYDRODESULPHURISATION OF THIOPHENE OVER ALKALISED IRON CATALYST

by P. K. GOUR, S. N. UPADHYAY, S. K. NATH, N. B. BHATTACHARYYA and S. P. SEN,
P & D Division, The FCI Ltd., Sindri, Dhanbad, Bihar

(Communicated by Prof. S. K. Bhattacharyya, F.N.A.)

(Received 1 August 1973; after revision 7 September 1976)

Effect of alkali content on hydrogenation activity of alkalised iron has been studied. Alkali content upto 35 per cent by weight has no effect on its efficiency. Removal of thiophene is of the order of 46-47 per cent in a single pass. However, catalyst with spinel structure obtained by heat treatment at 800°C exhibited higher activity and conversion of thiophene improved from 47 per cent to 62 per cent. Sulphur is preferentially picked up by alkali. Specific surface area and porosity drop with increase in alkali content of the sample. Sulphiding upto 30 per cent by weight has no effect on its hydrogenation efficiency. Thereafter it deteriorates slowly. A mechanism of hydrogenation for thiophene has been proposed.

INTRODUCTION

Normally in industry, comox or nimox is employed for hydrofining purposes. Since both the active ingredients cobalt and molybdenum are not available indigenously, the laboratory at the P & D Division of the FCI Ltd., is engaged in developing a substitute based on indigenous resources. Alkalisid iron appears to be a potential substitute which has been utilised earlier for purification of synthetic gas etc. It hydrogenates major fractions of sulphur compounds present in naphtha; however, non-reactive sulphur compounds are only partially hydrogenated. The present investigation is an extension of our earlier work. We have studied the effect of alkali content, as well as, progressive sulphiding of the mass on activity of the catalyst. Mechanism of hydrogenolysis has also been discussed.

EXPERIMENTAL

Catalyst samples were prepared by mixing requisite amounts of alkali with iron oxide. Alkali content was varied in the range of 0-35 per cent by weight. Sodium ferrite spinel sample was obtained by heat treatment of sample No. 6 containing 35 per cent alkali at 800°C for 4 hours. Samples containing 0, 5, 10, 15, 25 and 35 per cent alkali are termed as samples 1, 2, 3, 4, 5 and 6 respectively.

Straight run naphtha of the boiling range 60-160°C and sulphur content of 0.2 ppm. has been used as feed stock. Its sulphur content was raised from 0.2 ppm to 1200 ppm (wt/wt) by mixing calculated amount of L. R. Grade BDH Thiophene. Total sulphur content of the liquid hydrocarbon was estimated by Raney nickel method.

Effect of sulphiding of the catalyst on its hydrogenation efficiency has been

studied. Hydrogen sulphide of known purity and concentration was employed for progressive sulphiding of sample No. 6 and it was varied in the range of 5 to 50 per cent. Sulphur retained by alkali and iron oxide has been estimated separately. Hydrogen sulphide and mercaptan formed during hydrogenation of thiophene has been determined potentiometrically after retaining it in 10 per cent NaOH solution. Since mercaptan is easily removed by alkalised iron the experiment was conducted at a LHSV of 12 cc/cc/hr for 8 hours to ensure measurable slippage of mercaptan formed during hydrogenolysis.

Reduction studies were conducted in a Stanton mass flow thermobalance. Rate of heating employed for non-isothermal experiment was 6.5°C/minute. All the reduction studies were conducted at 400°C. Surface area was determined by BET low temperature nitrogen adsorption method. Pore size distribution was determined by a Aminco-Winslow mercury porosimeter having working pressure upto 15000 lbs/sq. inch. X-ray diffraction studies were conducted with Philips PW-1010 model diffractometer using FeK α radiation. Voltage employed was 30 KV with a current flow of 10 mA.

RESULTS AND DISCUSSION

Iron oxide is the main constituent of alkalised iron and is easily reduced by hydrogen at 175°C. Incorporation of alkali, as well as, sodium ferrite spinel only increased the reduction threshold temperature. Reduction commenced at 280°C in presence of alkali. However alkali content of the sample had no effect on its threshold temperature. In presence of sodium ferrite spinel the reduction commenced at 220°C. Although the presence of alkali, as well as, ferrite spinel advanced the threshold temperature, the overall reaction remained unaffected. Ferric oxide was finally reduced to metallic 'Fe' stage. Sodium ferrite remained unaffected upto 400°C in hydrogen atmosphere. Probably 'Fe' is the active species which is responsible for the hydrogenation of thiophene during hydrodesulphurisation.

Hydrogenation of thiophene over pure iron oxide was maximum and of the order of 61 per cent and desulphurisation over alkali was 43 per cent. In case of binary Fe $_2$ O $_3$ —Na $_2$ CO $_3$ system, it was 47–48 per cent and remained unaffected by change in alkali concentration in the range of 5–35 per cent. It was seen experimentally that thermal factor is also responsible to a considerable degree for hydrogenation of sulphur compounds. In the blank run, naphtha was stripped off its sulphur content to a tune of 33 per cent under similar conditions. Conversion in the homogeneous phase appears to proceed through hydrocracking of thiophene. Alkali and alkaline earth oxides have been found effective for desulphurisation (Wilfried *et al.* 1964). However, desulphurisation over these oxides was never quantitative. It was only partial as observed by us over pure alkali. Although best results were obtained over pure iron oxide but it cannot be utilized in the process as such because of extensive carbon lay down due to hydrocracking. Incorporation of alkali suppressed hydrocracking and carbon lay down was nominal. This was probably due to acceleration of gasification rate of carbon deposited or masking of acid centres which eventually will suppress hydrocracking. Alkalised iron is known to have hydrogenation efficiency. It chemisorbs H $_2$ over metallic iron and this brings about hydrogenation of sulphur and unsaturates.

TABLE I
Physical parameters of fresh alkalisied iron samples

Sl. No.	Details of sample	Surface area m ² /gm.	Total pore volume cc/g.	Pore size distribution (%)				
				4-175 Å	175-300 Å	300-400 Å	400-500 Å	500-75000 Å
1.	Fe ₂ O ₃ + 5% Na ₂ CO ₃	65.6	0.6064	26.8	4.5	2.1	1.9	64.4
2.	Fe ₂ O ₃ +10% Na ₂ CO ₃	54.6	0.5747	33.5	5.5	2.6	2.2	56.0
3.	Fe ₂ O ₃ +15% Na ₂ CO ₃	49.8	0.4968	36.7	4.9	2.3	1.4	54.5
4.	Fe ₂ O ₃ +25% Na ₂ CO ₃	34.6	0.4487	40.4	4.3	2.1	1.6	51.4
5.	Fe ₂ O ₃ +35% Na ₂ CO ₃	28.9	0.2891	38.3	4.4	2.8	1.2	53.2

It is evident from Table I that initial surface area of the catalyst has no relationship with the activity. Samples 2 and 6 with respective surface area of 65.6 and 28.9 m²/gm gave the same performance. Loss of surface area during operation was considerable. Most interesting aspect was that all the discharged samples practically had the same surface area i.e., in the range of 5.0 to 7.0 m²/gm. Practically all the pores in the range of 175-500 Å were eliminated and new wider pores in the range of 500-75000 Å appeared. Pores in the region of 4-175 Å also dwindled and constituted only 18 to 25 per cent of the total pores. Major part of the total pore volume is constituted due to wider pores in the range of 500 to 75000 Å (Table II).

TABLE II
Physical parameters of discharged alkalisied iron samples

Sl. No.	Details of sample	Surface area m ² /gm.	Pore volume cc/gm.	Pore size distribution (%)				
				4-175 Å	175-300 Å	300-400 Å	400-500 Å	500-75000 Å
1.	Fe ₂ O ₃ + 5% Na ₂ CO ₃	5.8	0.6590	18.0	0.0	0.0	0.0	81.9
2.	Fe ₂ O ₃ +10% Na ₂ CO ₃	4.8	0.6154	16.4	0.0	0.0	0.0	83.5
3.	Fe ₂ O ₃ +15% Na ₂ CO ₃	5.0	0.5420	19.7	0.0	0.0	0.0	80.3
4.	Fe ₂ O ₃ +25% Na ₂ CO ₃	6.3	0.5938	28.6	0.0	0.0	0.0	71.3
5.	Fe ₂ O ₃ +35% Na ₂ CO ₃	7.0	0.4260	12.5	0.7	0.3	0.5	86.0

From all these data mentioned above it is evident that only wider pores are effective and principally responsible for thiophene hydrogenation. Pores in the range of 4-175 Å are not so much important.

During hydrodesulphurisation operation, the catalyst is liable to pick up sulphur. Keeping this fact in view the effect of sulphiding on its hydrogenation efficiency has been investigated. Results obtained indicate clearly that sulphiding upto 30 per cent by weight has practically no effect on hydrogenation efficiency. Thereafter, it deteriorates slowly. Although sulphur retained by catalyst is picked up by both iron oxide, as well as, alkali but the major portion goes to alkali. Alkali has more affinity for sulphur than iron oxide. Only after virtually complete sulphiding of alkali, the sulphur is picked up by iron oxide fraction. An X-ray analysis of the 50% fouled discharged sample revealed the presence of (1) αFe, (2) FeS and (3) Na₂S. It appears

TABLE III

Physical parameters of fouled and discharged sample No. 6

Sl. No.	Percentage sulphided	Surface area m ² /gm	Pore volume cc/gm.	Pore size distribution (%)				
				4-175 Å	175-300 Å	300-400 Å	400-500 Å	500-75000 Å
1.	0.0	7.0	0.4260	12.5	0.7	0.3	0.5	86.9
2.	5.0	3.0	0.4415	19.2	0.0	0.3	0.3	80.1
3.	10.0	4.2	0.4972	8.1	0.8	0.0	0.8	90.3
4.	15.0	3.6	0.7179	23.3	3.1	1.5	1.3	70.5
5.	30.0	4.6	0.4961	13.6	1.4	0.3	0.6	84.0
6.	50.0	3.4	0.6095	31.6	0.0	0.0	0.0	68.3

that activity starts falling from 30-35 per cent fouling onwards. This observation shows that in the binary system of Fe₂O₃-Na₂CO₃ probably Fe is the catalyst. As iron is removed from the system as FeS, activity starts declining.

An examination of physical parameters of discharged fouled samples reveals the same trend as observed in the case of unfouled discharged samples. Nature of pore size distribution and order of total pore volume and residual surface area are almost same (Tables II and III). Practically all pores are confined to 4-175 Å and 500-75000 Å regions only out of which approximately 80 per cent lie in the range of 500-75000 Å. Residual surface area for all the system varied in the range of 4 to 6 m²/gm only. From these figures a hydrogenation efficiency of the same order as for fresh sample is expected theoretically which has been observed experimentally.

Results on hydrodesulphurisation of thiophene over sodium ferrite containing approximately 12 per cent Fe₂O₃ are presented in Table IV. Sample containing spinel exhibited the best performance and 65 per cent thiophene could be removed in a single stage operation. Another distinct advantage with this system was lesser carbon laydown. Discharged sample was practically free from carbon. Extent of

TABLE IV

Effect of LHSV on conversion of thiophene over sodium ferrite spinel and iron oxide

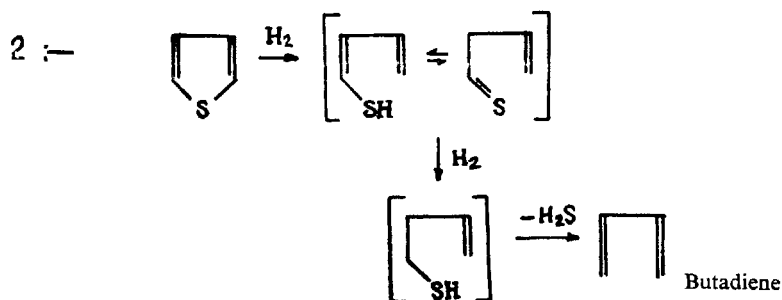
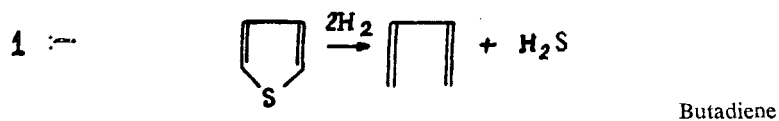
		Vapouriser temperature	— 250°C
		Reactor Temperature	— 400°C
		Partial pressure of Hydrogen	— 0.469
Sl. No.	LHSV cc/cc/hr.	Percentage conversion	
1.	1.0	65.0	
2.	2.0	63.0	
3.	3.0	62.0	
4.	4.0	60.0	
5.	5.0	57.0	
6.	6.0	50.0	

TABLE V
Physical parameter of sodium ferrite spinel

Sample	Surface area m ² /g.	Total pore volume cc/g.	Pore size distribution (%)				
			4-175 Å	175-300 Å	300-400 Å	400-500 Å	500-75000Å
Fresh	5.4	0.2115	31.9	5.7	1.4	2.5	58.4
Discharged	3.1	0.3182	15.1	1.3	0.0	7.9	82.7

hydrogenation decreased with increase in liquid hourly space velocity. But even at a LHSV of 4 cc/cc/hr. hydrogenation is 60 per cent. Although various ferrite spinel have been used as catalyst for dehydrogenation reaction (Hightower *et al.* 1973), there is no published information about hydrogenation efficiency of sodium ferrite spinel containing free iron oxide. However, similar studies have been made with Ni-Al₂O₃ spinel catalyst for naphtha steam reformation. Morita *et al.* (1968) observed higher activity with NiAl₂O₄ and they attributed it due to formation of fine Ni particles after reduction which in turn had a favourable effect on reformation properties of the catalyst. Sodium ferrite itself is amorphous in nature (Gour *et al.* 1973) and possibly is the factor responsible for its better performance. Physical parameters of the catalyst also play a vital role in its performance. An examination of its pore size distribution reveals a definite deviation from the pattern exhibited by the rest of the series (Table V). Discharged ferrite sample has developed new pores in the region of 400-500 Å which constitute 7.9 per cent of the total pores. This is probably another significant factor which is responsible for its better performance compared to the rest of the series and improved the efficiency by approx. 18 per cent.

Mechanism of hydrogenation of thiophene has been studied by various workers over different catalysts (Lipsch & Schuit 1969; Desikan & Amberg 1964; and Wells 1970). At present there are two established routes through which the hydrogenolysis proceeds i.e.,



and butadiene so formed in both the routes is hydrogenated to butane *via* butene. It is evident that the presence or absence of the mercaptan in the treated product can establish the route of the hydrogenolysis followed. Keeping this in view, the effluent gases after separation of naphtha and condensable gases were passed through two bubblers in series containing 10 per cent NaOH solution which was expected to retain H₂S, as well as, mercaptans if any. Presence of H₂S was confirmed by lead acetate paper test. Sulphur solution so obtained was titrated potentiometrically against N/100 silver nitrate solution. A plot of e.m.f. vs. volume of AgNO₃ shows two inflections indicating the presence of H₂S as well as, mercaptan in the effluent gas. This in turn confirms that hydrogenolysis of thiophene over alkalised iron proceeds as per scheme 2. Probably thiophene is held at catalyst surface due to a two point adsorption of C-S bond initially. Later on hydrogen adsorbed at the neighbouring site migrates and C-S bond is subsequently hydrogenated leading to mercaptan formation. Similar facts were observed by Desikan and Amberg (1964) also

REFERENCES

- Desikan, P., and Amberg, C. H. (1964). Catalytic hydrodesulphurisation of thiophene. V. Hydrothiophenes. Selective poisoning and acidity of the catalyst surface. *Can. J. Chem.*, **42**(4), pp. 843-850.
- Gour, P. K., Cursetji, R. M., Sengupta, G., Ahluwalia, H. S. and Bhattacharyya, N. B. (1973). Effect of heat treatment on physical parameters of alkalised iron. *Technology*, **10**(3 & 4), pp. 204-208.
- Lipsch, J. M. J. G., and Schuit, G. C. A. (1969). The CoO-MoO₃-Al₂O₃ catalyst-III. Catalytic properties. *J. Catal.*, **15**(2), pp. 179-189.
- Hightower, Joe W., and Cares, W. Ronald (1971). Ferrite spinels as catalyst in the oxidative dehydrogenation of butenes. *J. Catal.*, **23**(2), pp. 193-203.
- Morita, Y., Saito, M., Takemura, Y., and Yamamoto, K. (1968). Catalytic reaction between petroleum and steam XIV. Preparation of nickel-aluminium oxide catalysts and effect of calcination conditions on its activity. *Kogyo Kagaku Zasshi*, **71**, pp. 1453-1456.
- Wells, P. B. (1970). ESR Examination of untrammarines and their activities as catalysts in thiophene hydrodesulphurisation. *J. Catal.*, **19**(3), pp. 372-377.
- Wilfried, Rothe, Karl, Achenbach and Guenther, Bretschneider (1964). A new process for the desulphurisation of hydrocarbons and technical gases. *Erdöl Kohle*, **17**(5), pp. 352-356.