CHAPTER VIII

PROMOTERS FOR IRON CATALYSTS

"General"

Few metal or metal oxide catalysts are able to be utilized as a commercial catalyst unless they are promoted by the incorporation small amount of one or more additional components. The initial commercial synthetic ammonia catalyst was a success because, by trial and error, effective promoters were discovered (VIII-1). In this instance two promoters were utilized: a nonreducible metal oxide improved both the initial activity and the resistance to aging, primarily through the production and retention of surface area and an alkali metal that increases activity, presumably by altering the electronic characteristic (basicity) of the metal (VIII-2).

In general, promotion of iron catalysts supported on a high area material is vastly different from the case where the nonreducible metal oxide is present in small quantities. The primary reason for this difference is that the added promoter, present in minor amounts, distributes between the active metal component and the high area support. This means that the amount of promoter associated with the active component is seldom known with accuracy whenever a significant amount of high area support is present.

The products from synthesis gas reactions can be grouped into three principal classes: (i) hydrocarbons, (ii) methanol and (iii) higher oxygen containing molecules (oxygenates). According to Nonneman and Ponec (VIII-3), there is no unambiguous evidence that methanol or higher molecular weight oxygenates have ever been produced without the use of promoters.

Activity of Precipitated Iron Fischer-Tropsch Catalysts

Effect of Alkali Promoters on Fischer-Tropsch Synthesis

An early report by Fischer and Tropsch (VIII-4) described the effect of alkali promoters on Fischer-Tropsch synthesis (FTS) activity of a Fe-Cu (4:1) catalysts. The results are summarized in Figure VIII-1 where the % contraction (a measure of conversion) is plotted against run time for catalysts promoted by various amount of K_2CO_3 (VIII-5).

The activity of potassium promoted catalysts increases with potassium loading, then attains a maximum activity at an optimum potassium concentration. For those catalysts having $K_2CO_3 \geq 0.08\%$, severe aging was observed, high loadings of K_2CO_3 can cause fast catalyst deactivation. Kodama and Fujimura (VIII-6) have also reported that an Fe-Cu (1:1) catalyst promoted by 0.5% of K was active for a considerably longer time than those containing more alkali. Fischer and Tropsch (VIII-4) also compared the promotion effect of various alkali and alkali earth carbonates (0.5 wt%) on FTS activity for the Fe-Cu (4:1) catalyst. The data in Figure VIII-2, indicate that all of the alkali that is included in the tests promote FT activity, some more than others. Potassium and rubidium carbonate show an exceptionally high promotion effect, but the catalysts containing them also exhibit a rapid deactivation. Lithium carbonate produces only a slight increase in FTS activity.

For precipitated Fe-Cu-Mn-Kieselguhr (100:25:2:125) catalysts, Murata et al. (VIII-7) reported that addition of K_2CO_3 led to a sharp increase in C_5^+ yield. The optimum loading of K_2CO_3 was 2.0 wt%. A further increase in K_2CO_3 content caused a decrease in the FTS activity. The promotional effects of various alkali elements were

evaluated for the same Fe-Cu-Mn-Kieselguhr base catalyst system at 250 °C; however, these studies were at 1 atm. The C_5^+ yields were plotted against gram-mole of alkali oxide as M_2O and these data are shown in Figure VIII-3 (ref. VIII-8). $KMnO_4$ and KNO_3 effected the greatest increase in C_5^+ yield, followed by Na_2CO_3 and NaOH. Li_2CO_3 promotion shows the lowest C_5^+ yield. The data in Figure VIII-3 also indicate that there is an optimum alkali loading for the production of C_5^+ compounds.

The effect of potassium loading on FT activity has also been studied as a function of reaction pressure (VIII-9). The CO conversions as a function of K_2CO_3 loading are shown in Figure VIII-4 for several pressures (VIII-8). The results indicate that in all cases an optimum potassium loading is about 1 K_2O/100 Fe, and this is not affected significantly by the system pressure. The promotion of activity, however, seems to be more pronounced at high reaction pressure. At low K loading, the promotion effect is low; in contrast, increasing K concentrations above the maximum caused a sharp decrease in CO conversion.

For a precipitated Fe-Cu catalyst (100:10) Anderson *et al.* (VIII-8) also reported a linear increase in FTS activity with potassium loading. With the addition of 0.8 wt% K_2O, a 50% increase in FTS activity was observed (VIII-10). In this respect, promotion of the precipitated catalyst differed from that of the sintered, fused or cemented catalysts which attained a leveling of activity or a maximum followed by a decrease in activity with increasing K_2O loading (Figure VIII-5; ref. VIII-10). The increase in activity for the precipitated catalyst was much less than that for a sintered catalyst; a 50% increase was observed for 0.8% K_2O/100Fe precipitated catalyst verses about a 1000% increase for the sintered catalyst. This sintered catalyst was

prepared by sintering a commercial sample of hematite at 1200°C. The cemented catalyst was prepared from the same hematite sample as used for the sintered sample except it was mixed with 30% aqueous aluminum nitrate prior to drying and calcining at 500°C. The precipitated, but not the other catalysts, contained Cu.

Recently, the effect of potassium promotion on FTS activity has been studied for Fe-Mn (21:79) catalysts using a continuous slurry tank reactor (CSTR) (VIII-11). At a low potassium loading (0.1 wt%), no promotion was observed. Significant increases in CO and $CO+H_2$ conversion were observed for catalysts containing 0.5 or 1.3 wt% K. However, a severe deactivation was observed for these two active catalysts with 0.5 or 1.3 wt.% K. For 1.3 wt% K promoted catalyst, $CO+H_2$ conversion was lower than the unpromoted catalyst following only 120 hrs. of reaction.

Bukur *et al.* (VIII-12) also studied the effect of potassium on FTS activity for precipitated Fe and Fe-Cu (100:3) catalysts. They reported that FTS activity increased with increasing potassium loading for both catalyst types. The activity for both series of catalysts levels off at potassium loadings greater than 0.2 wt%. These catalysts were very stable toward aging; no deactivation was observed after 150 h on stream. Itoh, *et al.* (VIII-13) reported that the catalyst prepared by precipitation of a $FeCl_2/CuCl_2$ solution with K_2HBO_3 and containing 3 wt% K has hydrocarbon and CO_2 formation rates that are 2 and 12 times, respectively, those of a similar catalyst without K.

The above studies show that activity can be increased by the addition of K; however, not all of the data in the literature agree with these observations. Pichler and Merkel (VIII-14) reported that there was no significant impact on FTS activity for

precipitated Fe catalysts containing 0.25 to 10 wt% of K_2CO_3. Dictor and Bell (VIII-15) reported that there is a decrease in the FTS activity for a potassium promoted Fe_2O_3 (hematite). A monotonous decrease in FTS activity with increasing Na content has been reported for Fe-Mn catalyst (VIII-16).

Activity

Dry (VIII-2) reports that the most important promoters for fused iron catalysts are undoubtedly the stronger basic alkali metals of Group I of the Periodic Table. In particular, the most commonly employed promoter is potassium oxide. In fact, Dry reports that potassium oxide is the only promoter essential for industrial iron catalysts. The main function of structural promoters (e.g., alumina, chromia, silica, MgO, etc.) is to increase and/or stabilize surface area to the levels required for high conversion. Dry also makes the important observation that if the catalysts are utilized at high temperatures the reaction rate appears to be diffusion controlled. This means that beyond a certain surface area, the internal surface area of the catalyst produces little or no benefit.

Diffenbach and Fauth (VIII-17) prepared a series of precipitated iron catalysts using various pH levels with a Kölbel in-line mixing unit (Figure VIII-6; ref. VIII-17). Either sodium carbonate or ammonium hydroxide was used as the precipitant. The surface area appears to show a maximum at a pH of about 6 when sodium carbonate was the base used to effect the precipitation; however, the sample prepared at pH 7.6 did not fit the pattern defined by the other catalysts. The base used in the precipitation did not appear to cause a significant difference in the surface area of the

air-dried sample nor of the sample following carbiding at 250°C (Table VIII-1). For two catalysts prepared by precipitation using sodium carbonate, it was demonstrated

Table VIII-1
BET Surface Area and Pore Volume of Precipitated Iron Samples [from reference VIII-17]

pH	Air-Dried at 383K for 24 Hours		Carbided at 523 K for 2 Hours	
	S.A. (m^2/g)	P.V. (mL/g)	S.A. (m^2/g)	P.V. (mL/g)
3.7 SC[a]	160	0.21	24	0.12
4.7 SC[a]	244	0.25	21	0.10
5.8 SC[a]	267	0.34	63	0.19
7.6 SC[a]	148	0.20	45	0.18
9.8 SC[a]	225	0.28	54	0.18
6.2 AH[b]	229	0.31	46	0.16
7.6 AH[b]	264	0.30	62	0.18
8.9 AH[b]	238	0.33	39	0.16

a. The number is the pH for the catalyst preparation using sodium carbonate to effect precipitation.
b. The number is the pH for the catalyst preparation using ammonium hydroxide to effect precipitation.

that the air-dried sample (110°C) had essentially the same surface area and pore volume as the sample after heating at 250°C in nitrogen. Upon reduction in hydrogen at 250°C the surface area declined by 15 to 30%; treatment at this same temperature in synthesis gas produced essentially the same surface area as the hydrogen reduced sample (Table VIII-2). These workers reported that the catalysts precipitated with sodium carbonate at low pH (3.7 and 4.7) showed unusually high olefin selectivity (C_2-C_4) and an activity maintenance that was superior to the ones prepared at higher pHs. Thermogravimetric studies showed that graphitic carbon deposited to a greater

degree on the samples precipitated at the higher pHs with sodium carbonate; supposedly this carbon deposition is responsible, at least in part, for the poorer activity characteristics of the catalysts prepared at the higher pHs.

Table VIII-2

BET Surface Area and Pore Volume after Pretreatment in Various Gases at 523 K for 2 hrs [from reference VIII-17]

Gas	Surface Area (m^2/g)		Pore Volume (mL/g)	
	5.8 SC[a]	7.6 SC[a]	5.8 SC[a]	7.6 SC[a]
Air (383 K)	267	148	0.34	0.20
N_2	234	143	0.34	0.19
H_2	46	41	0.18	0.17
50% H_2 - 50% CO	53	45	0.19	0.18

a. The number is the pH for the catalyst preparation using sodium carbonate to effect precipitation.

In the preparation of the Rührchemie catalyst, it appears that the base used in the preparation has a significant influence upon the surface area and pore volume of the catalyst. Dry (VIII-2) has recently summarized the details of the preparation and promotion of the catalyst developed by Rührchemie and used in fixed bed reactors at Sasol for several years; this catalyst is described more fully by Frohning (VIII-18).

Dry (VIII-2) wrote: "The early precipitated iron catalysts were promoted only with potassium salts. To improve the stability of these catalysts towards thermal sintering many supports such as zinc oxide, dolomite, kieselguhr and alumina were investigated. Silica supports appeared to be the most effective. Rührchemie used an alkali-waterglass solution as the source of the silica instead of Kieselguhr. To recap

briefly, the successive preparation steps were as follows. A near boiling solution of iron and copper nitrate (40 g Fe and 2 g Cu per dm^3) was poured into a hot solution of sodium carbonate with vigorous stirring over a period of several minutes until the pH reached 7 to 8. The precipitate was washed with hot distilled water in a filter press until the Na content in the effluent was very low. The washed precipitate was re-slurried with water and impregnated with a potassium waterglass solution to give 25 g SiO_2 per 100 g Fe. Sufficient nitric acid was added to remove some of the excess potassium so that after filtration the K_2O content was 5 g per 100 g Fe. The filter cake was pre-dried, extruded and finally dried to a water content of less than 10 wt. percent. In the preparation technique currently employed at Sasol several changes have been made in both the preparation process and in the type and contents of promoters which have improved the economics of the catalyst production as well as its performance in the Fischer-Tropsch synthesis."

"When the solution of potassium waterglass is added to the slurry of precipitated iron oxide, the silica is effectively precipitated. It presumably adsorbs onto or reacts with the high area Fe_2O_3, up to about 300 m^2g^{-1}, since on thorough washing and filtering all of the potassium but none of the SiO_2 is removed. Thus the addition of HNO_3 to the Fe_2O_3/waterglass slurry is to control the K_2O content of the catalyst, and not to precipitate the silica. The presence of the intimately mixed silica phase stabilizes the high area of the Fe_2O_3 by preventing crystal growth, i.e. sintering, of neighboring Fe_2O_3 crystallites. In Table VIII-3 the influence of the SiO_2 on the total area and pore structure is illustrated. As can be seen SiO_2 increases the area and stabilizes the presence of larger pores. The increase in area with increasing SiO_2 content has also been reported elsewhere (VIII-19). The pore structure of the

catalyst is largely determined in the very first stage of the catalyst preparation, i.e., the precipitation of the Fe_2O_3. Thus if the precipitation conditions are such that the Fe_2O_3

Table VIII-3

Influence of SiO_2 on Precipitated Fe_2O_3 [from reference VIII-2]

SiO_2/g (100g Fe)$^{-1}$	Unreduced			H_2 Reduced			
	Pore Vol/ cm^3g^{-1}	Area/ m^2g^{-1}	Area in Pores >4.5 nm/ m^2g^{-1}	Pore Vol/ cm^3g^{-1}	Area/ m^2g^{-1}	Area in Pores > 4.5 nm/ m^2g^{-1}	Reduction/%[a]
0	0.37	275	41	0.22	35	35	100
8	0.47	345	59	0.43	190	68	80
19	0.74	375	90	0.48	250	80	46
25	0.71	390	94	0.61	270	84	58
29	0.75	370	96	0.65	265	85	57
50	N.A.	405	N.A.	N.A.	280	N.A.	N.A.

a. Percentage of total Fe present in metallic state after a fixed time at a fixed temperature.
N.A.: Not available.

has narrow pores then the final catalyst will also have this feature. The nature of the pore size distribution has been found to be influenced by the concentrations of the solutions used, the time over which the precipitation occurs, the precipitating temperature and the pH during precipitation. Figure VIII-7 for instance illustrates the influence of the environment in which the Fe_2O_3 precipitate is formed. Figure VIII-7a is for Fe_2O_3 prepared by adding the iron solution to the carbonate solution while Figure VIII-7b is for the reverse procedure, all other conditions being identical. The two cases have very similar total pore volumes and surface areas but as can be seen from the shapes of the N_2 adsorption isotherms there is a marked difference in the

distribution of pore sizes. Figure VIII-8 illustrates the result if an excess of Fe^{3+} ions is added to the carbonate solution resulting in a low final pH. The final pH is obviously a critical factor in determining the pore size and distribution. The chemical nature of the precipitating agent also has an influence on the pore structure. This influence could partly be a pH effect. Table VIII-6 shows that using carbonates results in catalysts with more big pores. The SiO_2 content for the four cases in Table VIII-4 is all the same." The pore size and pore volume must be independent of the surface area; otherwise, the results in references VIII-2 and VIII-19 are in disagreement.

Table VIII-4

Influence of Precipitating Agent (from ref. VIII-2)

Precipitant	Average Pore Size/nm	Pore Volume in Pores > 12.5 nm/%
NaOH	2.9	1
Na_2CO_3	4.0	40
NH_4OH	2.6	1
$(NH_4)_2CO_3$	3.1	18

"The total porosity of precipitated catalysis is largely determined by the amount of shrinkage that occurs during the drying process. The presence of water appears to enhance the degree of shrinkage. When the precipitate is re-slurried in an excess of a low surface tension liquid such as acetone, and the catalyst is then dried, the pore volume is increased more than two fold. In practice it is necessary to strike a balance between physical strength and pore volume as large pore volume catalysts are usually weaker."

Dry contends that the major impact of promoters other than K_2O (or presumably other Group I metal oxides) is to determine the amount of alkali influencing the iron. For example, silica forms sodium silicate in the fused iron catalysts when it is present; this lowers the effective potassium content on the iron surface and this influences catalytic activity (VIII-19). In general, it is claimed that the more acidic the other promoter (e.g. $A/_2O_3$,TiO_2), the more it will decrease the effectiveness of the added K_2O. The total surface area of iron will also be a factor in determining the effectiveness of the K_2O; the higher the surface area the larger the amount of K_2O needed to obtain the same change in activity.

The influence of increasing the K_2O content of catalysts is not always consistent and it depends on the type of catalyst and on the conditions under which it is being tested. In Table VIII-5 it can be seen that when a fused catalyst is used at low

Table VIII-5

Synthesis Performance of Fused Magnetite Promoted with a Fixed Amount of Al_2O_3 and Varying Amounts of K_2O. Fixed Bed Operation at about 473 K [from reference VIII-2]

K_2O Content/Relative Units	Activity/Relative Units	CH_3OH^a Selectivity
0	64	6.6
0.4	60	4.8
0.8	55	4.9
1.1	50	3.6
2.6	29	2.7

a. % C atom basis.

temperatures in a fixed bed reactor, both the activity and the alcohol selectivity decrease as the K_2O content is increased. When fused catalysts are employed at

higher temperatures in a fluidized bed, the activity at first increases as the K_2O content is raised and then attains a constant value at high conversion levels (Table VIII-6). The CH_4 selectivity progressively decreases. The acid and alcohol selectivity increase as does the olefins in the hydrocarbons. Thus the activity can either increase or decrease with K_2O promotion depending on the reaction conditions (Figure VIII-9, plotted from data in ref. VIII-2). It has been observed in other studies that the activity passes through a maximum as the K_2O content is increased (VIII-8).

Table VIII-6

Synthesis Performance of Promoted Fused Catalysts. SiO_2 Varied with Alkali Content Fixed. Fluidized Bed at 593 K [from reference VIII-2]

Alkali Type	SiO_2/Alkali Molar Ratio	$CO + CO_2$ Conversion/%	CH_4 Selectivity/% Carbon Atom	$\frac{C_3H_6}{C_3H_8}$ Ratio
Na_2O	0.6	86	13	2.8
	2.1	83	13	2.4
	4.2	81	13	3.1
K_2O	0.8	85	10	6.1
	4.2	78	27	0.9

Dry reports data (Table VIII-6) to compare the influence of the amount of SiO_2 incorporated together with Na_2O or K_2O promoted catalysts. When NaO_2 is present, the addition of SiO_2 has no effect on selectivity whereas for K_2O containing catalyst the addition of SiO_2 markedly effects both the selectivity and the activity of the catalyst. This effect has also been observed by other workers (reference VIII-8).

Dry also points out that it has been observed (VIII-20) that the manner in which the K_2O was added to the iron catalyst (i.e. whether by impregnation or simply

by adding the loose powder) used in a fluidized bed reactor had relatively little effect on the catalyst's performance. Investigations at Sasol have shown similar effects. When finely ground potassium silicate was simply added to the pre-reduced powdered iron catalyst the overall performance was not markedly inferior to that of a catalyst in which the potassium silicate was fused together with the iron oxide and then milled and reduced. It was also found that the performance of a catalyst prepared by fusing pure Fe_3O_4 with only Na_2O is little different from that of a Na_2O promoted catalyst prepared from iron oxide containing silica. In the former case the Na_2O goes into solid solution and is automatically distributed throughout the fused catalyst mass while in the latter case separate sodium silicate occlusions are present in the catalyst and so the distribution of the Na_2O is relatively poor. A possible explanation of these observations is that under synthesis conditions the alkali is capable of diffusing over the catalyst surface. Given time it will distribute itself evenly over all the catalyst particles in the reactor and so be able to exert its influence on the majority of the active iron sites. It must be deduced that maldistribution of the K_2O promoter is of some consequence since it results in some differences in performance.

Dry and Ferreira (VIII-21) made the important observation that the oxides of Ca, Mn, Ti, Al, Li, and Na readily go into solid solution with Fe_3O_4. They concluded that it should be possible to prepare magnetite catalysts in which there is a true homogeneous distribution of these promoters. Silica does not dissolve in Fe_3O_4 so that it is an ineffective structural promoter; moreover, it does inhibit the solution of the more basic promoters. Potassium and barium ions could not be induced to enter into solution in magnetite. The size of the unit cell determined from X-ray diffraction was used to judge the solid solution (Figure VIII-10; ref. VIII-2). The size of the iron

crystallites of the reduced magnetite samples decreases with increasing promoter content, and some promoters are more effective than others. The longer the reduction time the more the iron crystals already formed could be expected to grow. The effectiveness to produce small crystallites increases in the order MnO, MgO, TiO_2, and Al_2O_3. This corresponds exactly to the order deduced from BET surface area measurements on reduced fused magnetite promoted with the above oxides (VIII-14).

The above literature review indicates that potassium is the best promoter whenever promotion effects are observed, and in those cases the initial source of potassium is not important. When promotional effects are observed, an optimum potassium loading is generally observed. A summary of the effect of potassium on FTS activity for the systems mentioned above are compiled in Table VIII-7. In most cases, the catalysts surface area before or after pretreatment was not specified. Due the difference in the catalyst compositions, pretreatments, reaction conditions and deactivation profile of catalysts, it is difficult to make comparison among these systems. In order to make valid comparisons among catalyst systems, the performance of the base catalyst (unpromoted) as well as the catalyst surface area and composition following pretreatment should be specified. This is needed because the effect of the other alkali is sensitive loading levels and this is probably related more to the surface than to the bulk concentration of alkali. It is also likely to be dependent on the extent of sintering of the catalyst after pretreatment. Expressing the effect of alkali on the FTS activity as a function of surface concentration of alkali after pretreatment and the time dependent behavior of the catalytic activity are the two key factors that are still needed to make valid comparisons among the data for various catalytic systems and from various research groups.

Table VIII-7

Summary of Studies in the Effect of Potassium on FTS Activity

Catalyst	Method for Alkali Addition	Activation Conditions	Reaction Conditions	Effect on Activity	Ref.
Ppt. Fe	Impregnation of K_2CO_3 (abs. loading unspec.)	Unspecified	T, P Unspecified H_2CO = 1.9	Volcano type	VIII-17
Ppt Fe	Impregnation of K_2CO_3 (0-10 wt.%)	Unspecified	250°C, 15 atm., H_2CO = 2/3	No effect	VIII-14
Fe_2O_3 9 m^2/g	Impregnation of K_2CO_3 K/Fe = 0.011	250°C, 8 atm. H_2/CO = 1	250°C, 8 atm., H_2CO = 1	10 fold decrease	VIII-15
Ppt. Fe and Ppt Fe-Cu	Impregnation of $KHCO_3$ 0-1 wt.%	220°C, 1 atm., H_2, 500 cc/min.	220°C, 14.8 Mpa, H_2/CO = 1, SV = 2, nl/g-h	Increase with K loading and levels off at K = 0.2 wt.%	VIII-12
Fe:Cu, 4/1 from decomposition of metal nitrate	Impregnation of $KHCO_3$ (0-1.28 wt.%)	T.P. unspecified, H_2/Co = 1	250°C, 1 atm., H_2/CO = 1	Increase with K	VIII-4
Fe:Cu	Coppt. with Fe, Cu 0.0.8% K_2O	Unspecified	T unspecified, 7.8 atm., H_2/CO = 1	Slightly increase with K loading	VIII-10
Fe:Cu:Kieselghur, 100:25:125	Unspec. K_2CO_3 (2-8 wt.%)	250°C, 1 atm., 24 hrs., H_2/CO = 1	210°C, 2.4-19.4 atm., H_2/CO = 1	Volcano type, max at 6 wt.%	VIII-10
Fe-Cu-B	Coppt. with Fe, Cu, B 3 wt.%	300°C, 30 atm., H_2/CO = 1, w/f = 50	300°C, 30 atm., H_2/CO = 1, g/min./CO	Two time increase in HC and 12 times increase in CO_2	VIII-13
Ppt. Fe:Mn 1:1	Coppt. with Fe-Mn, Wt.% controlled by washing (0.1-15 wt.%)	350°C, 1 atm., H_2	280°C, 1 atm., H_2/CO = 1, % Conv. < 10	Decrease with Na loading	VIII-16
Ppt. Fe:Mn 21:79	Impregnation of K_2CO_3 0-1.3 wt.%	275°C, 0 psig, CO, WHSV = 2.25	275°C, 200 psig, H_2/CO = 1, WHSV = 1.21	Significant increase for 1.3 wt.% K-promoted cat. decrease for 0.1 and 0.4 wt.% K-promoted cat.	VIII-11

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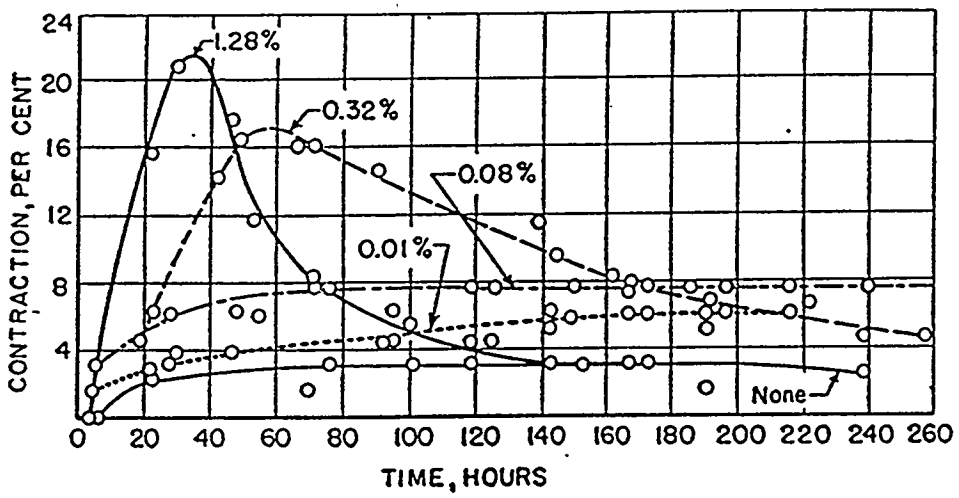

Figure VIII-1. Effect of amount of added K_2CO_3 on activity of 4 g of Fe-Cu (4:1) catalyst. Reproduced from reference VIII-5.

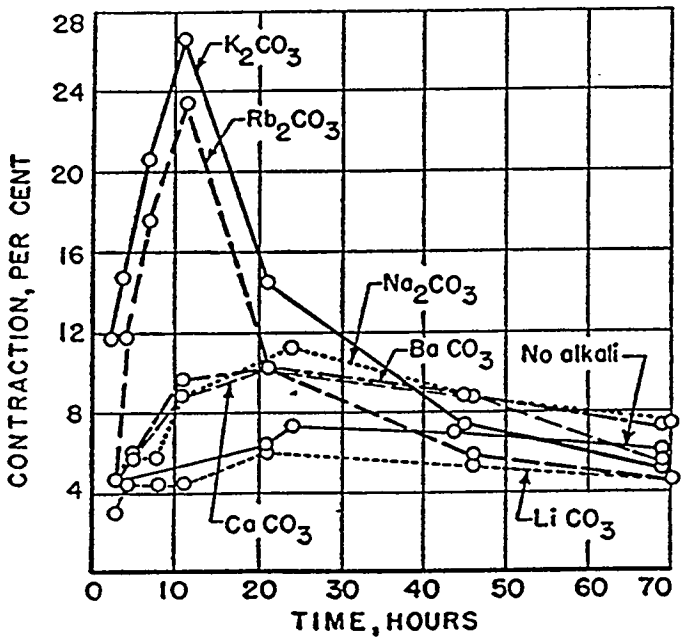

Figure VIII-2. Effect of amount of added K_2CO_3 on activity of 4 g of Fe-Cu (4:1) catalyst. Reproduced from reference VIII-5.

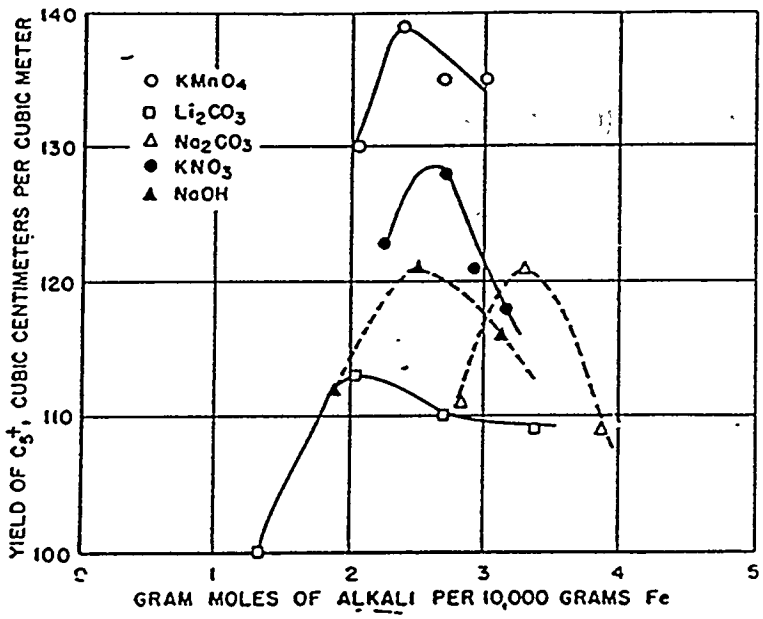

Figure VIII-3. Influence of type and concentration of alkali on productivity of a precipitated iron catalyst. $1H_2 + 1CO$ gas at atmospheric pressure (from data of Reference VIII-8).

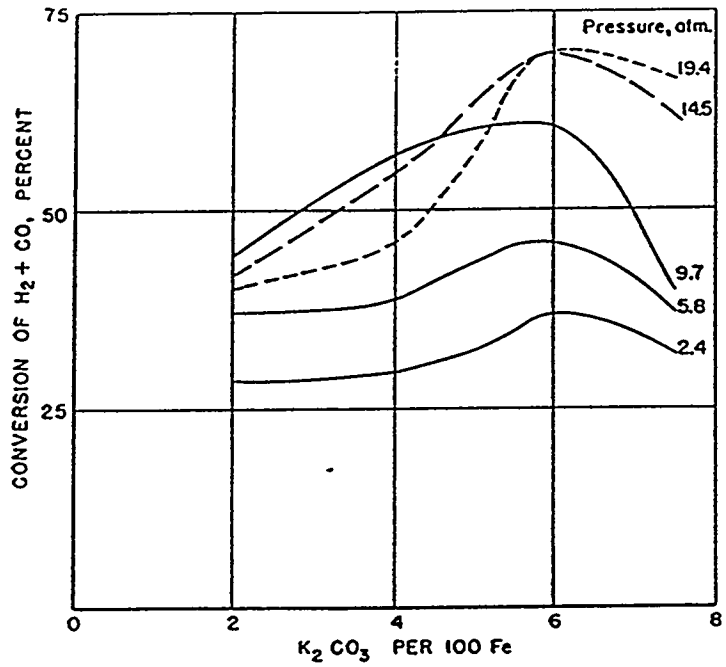

Figure VIII-4. Conversion as a function of alkali content for Fe-Cu-kieselguhr catalysts at 210°C (from data of Reference VIII-8).

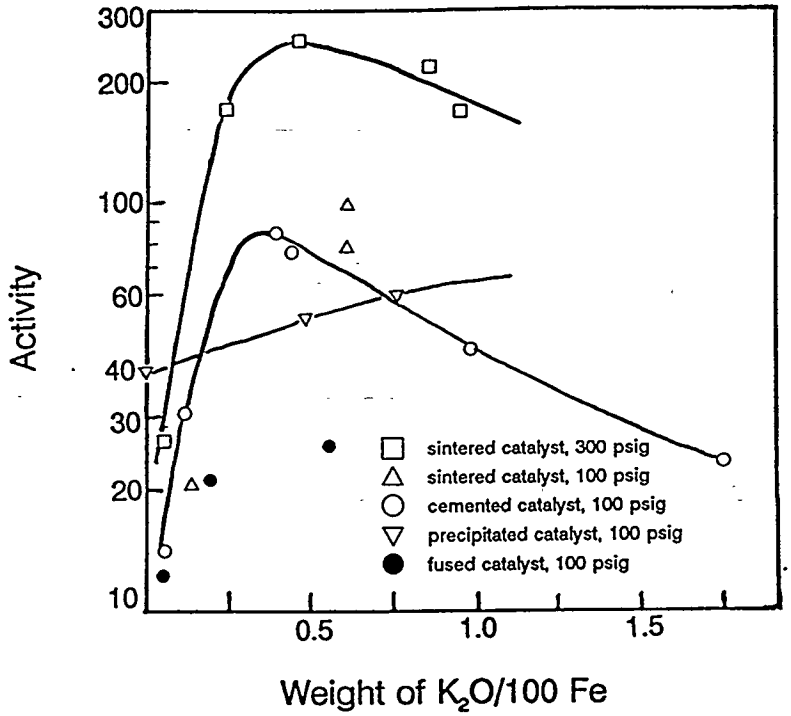

Figure VIII-5. Variation of activity of iron catalysts with alkali content (from ref. VIII-10).

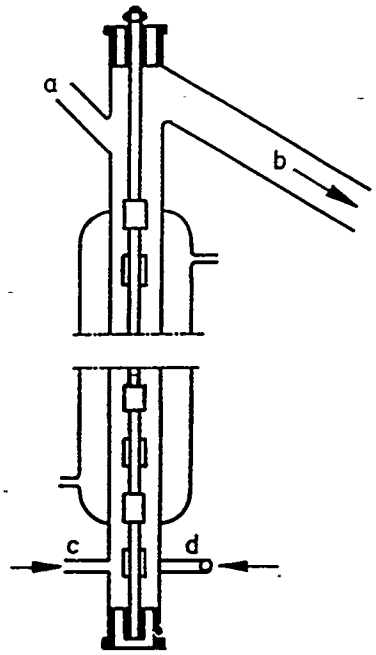

Figure VIII-6. Kolbel precipitator (from ref. VIII-17).

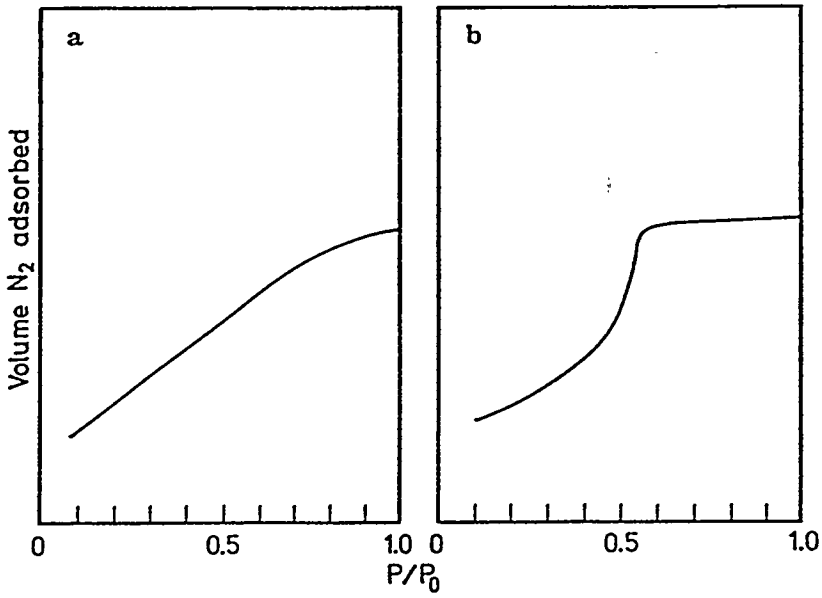

Figure VIII-7. Plots of N_2 adsorption isotherms at liquid N_2 temperature against relative saturation pressure. Curve 6A is for the Fe_2O_3 sample prepared by adding the iron solution to the carbonate solution. 6B is for a Fe_2O_3 sample prepared by adding the carbonate solution to the iron solution (from ref. VIII-19).

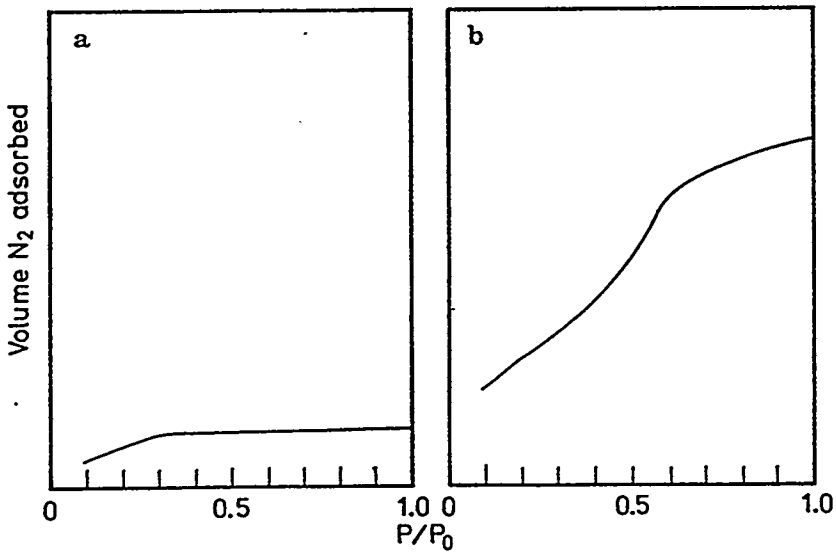

Figure VIII-8. Plots of N_2 adsorption isotherms at liquid N_2 temperature against relative saturation pressure. Both Fe_2O_3 samples were prepared by adding the iron solution to the carbonate solution. For case A the final pH was 2.0 (i.e., an excess of Fe^{3+} ions was added). For case B the final pH was 6.9 (from ref. VIII-19).

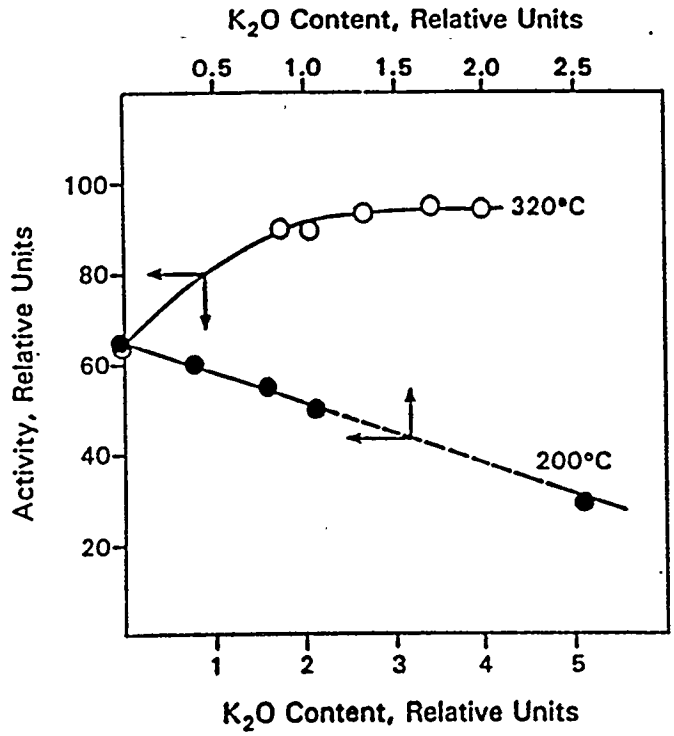

Figure VIII-9. Dependence of conversion on the alkali content for different catalyst batches (drawn from data in ref. VIII-2).

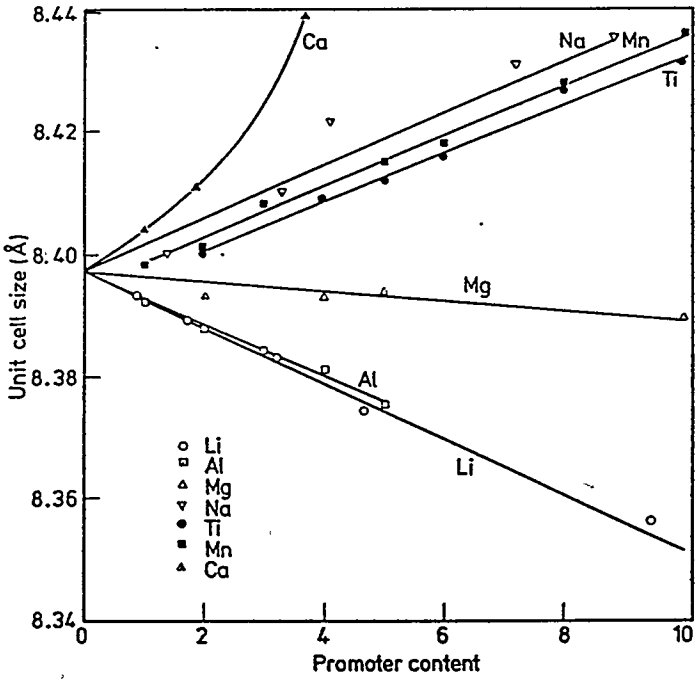

Figure VIII-10. The influence on the unit cell size of magnetite (in Å) of various promoters which go into solid solution with magnetite. Promoter content is in g atom cation per 100 g atom Fe (from ref. VIII-2).