# The Correlation between Catalyst Surface Basicity and Hydrocarbon Selectivity in the Fischer-Tropsch Synthesis

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Carbon dioxide chemisorption studies at 0°C were used to determine the relative basicities of alkali-promoted reduced magnetite catalysts. Catalysts promoted with oxides of Li, Na, K, Ca, and Ba were studied. For the equivalent amounts of alkali present the basicity of the reduced catalysts increased in the order Ba, Li, Ca, Na, and K. Data are given which show that a higher surface basicity correlates with a lower methane selectivity in the Fischer-Tropsch synthesis. Impregnating the catalyst with alkali after fusion rather than addition of the alkali at the fusion stage of preparation, results in catalysts with higher surface basicities and consequently lower methane selectivities. Silica depresses surface basicity and results in increased methane production. $CO_2$ appears to chemisorb on the oxide promoters present on the surface of the reduced catalyst and possibly also on the metallic iron surface. The BET surface areas of the catalysts decrease with increasing basicity of the alkali promoters.

## INTRODUCTION

In the hydrogenation of carbon monoxide over iron catalysts (Fischer-Tropsch process) it is essential that a certain amount of potassium salt be present on the catalyst (1). Not only does this promoter increase the CO conversion but it also shifts the selectivity towards the more useful long-chain hydrocarbons. In the absence of potassium the main hydrocarbon product is methane when the catalyst is run under normal commercial synthesis conditions.

It has been demonstrated (2) that the effectiveness of the alkali promoter decreases in the order Rb, K, Na, Li. High-pressure pilot plant synthesis tests (3) have shown that promotion with CaO or $Li_2O$ is quite ineffective in comparison to promotion with $K_2O$. Clearly then a strongly basic alkaline promoter is required. Pilot plant studies (3) have provided ample evidence which showed that it is not only the actual amount of $K_2O$ which is important but also the surface area of the catalyst as well as

the chemical nature of the other additives or impurities present. The higher the area the more $K_2O$ was required to obtain the desired selectivity spectrum. When acidic compounds, e.g., silica, were present more $K_2O$ was also required. This indicates that there appear to be two surface basicity factors which must be met. The intrinsic basicity of the alkali promoter must be above a certain strength and the promoter must also cover a certain fraction of the catalyst surface. Viewed in the above manner a measure of the surface basicity should be of use in selecting suitable Fischer-Tropsch catalysts. The determination of the amount of $CO_2$ adsorbed at 0°C by the surface of the freshly reduced catalyst has proved to be a suitable means of estimating surface basicity (4). The technique employed in the adsorption experiments involves an intermediate degassing step at 0°C when all physically and weakly chemisorbed $CO_2$ is removed, leaving only the relatively strongly bound $CO_2$ on the sur-

face. The technique thus to some extent provides a combined measure of both the strength and extent of the surface basicity. The results presented in this paper show that there is indeed a correlation between $CO_2$ chemisorption coverage and hydrocarbon selectivity in the Fischer-Tropsch process. As it is known that promoters other than alkali also have a marked influence on the $CO_2$ chemisorption on reduced catalysts (5), the series of catalysts were, except for the alkali contents, of identical chemical composition. Only the type, quantity, and mode of addition of the alkali promoter was varied.

## EXPERIMENTAL

The preparation of the fused magnetite samples, the conditions of reduction with hydrogen, and the subsequent determination of the amounts of $CO_2$ and CO chemisorbed by, as well as the surface areas of the reduced samples, have all been previously described (5). In several series of samples the alkali was added not at the fusion stage but later by impregnation. The 100- to 200-mesh fused magnetite was soaked in water solutions of the alkali carbonates of suitable concentrations. The excess liquid was then drained off by suction and the samples were dried in air at 110°C. All samples were chemically analyzed for their promoter contents.

The laboratory synthesis tests were carried out at atmospheric pressure at 290°C with a gas having a $H_2/CO$ ratio of 3.2. The input volume space velocity was maintained at 600 hr$^{-1}$. Tail gas was analyzed mass spectrometrically. Pilot plant synthesis tests were carried out at 250 psig and 320°C.

All samples used in the chemisorption studies were reduced for 16 hr at 400°C. These apparently mild reduction conditions justify some discussion. For the type of sample studied the reduction is about 95% complete after 10 hr. At this stage the surface area of the sample is at a maximum and continued reduction results in a progressive decrease in area. At 16 hr the reduction is 99% or higher and further reduction proceeds only very slowly. At

this stage the volume of $CO_2$ chemisorbed by the sample is at a maximum and on further reduction it declines steadily as does the total surface area. The ratio of chemisorbed $CO_2$ to the argon BET monolayer volume ($V_{CO_2}/V_m$), however, continues to increase until about 40 hr of reduction and then appears to level off. The change of $V_{CO_2}/V_m$ with time of reduction for three differently promoted samples is illustrated in Fig. 1. It is not clear
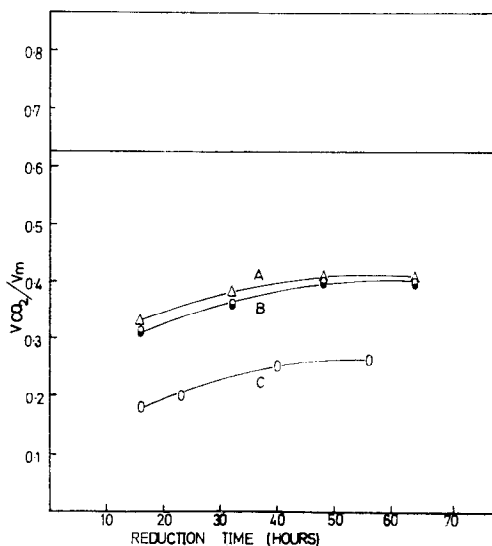


FIG. 1. The change in the value of $V_{CO_2}/V_m$ with increasing reduction time. The promoter contents of the samples in g/100 g Fe were as follows: A, 1.4 MgO, 1.2 $SiO_2$, and 0.24 $Na_2O$; B, 1.4 MgO, 1.3 $SiO_2$, and 0.37 $K_2O$; C, 0.8 $Al_2O_3$, 1.3 $SiO_2$, and 0.41 $K_2O$.

whether this change does indicate the slow removal of the last traces of oxide from the surface or whether it is the result of a slow rearrangement of the promoters which are present on the iron surface. It has been repeatedly found in this laboratory that slight reoxidation of the catalyst with either oxygen or water vapor results in an *increase* in $CO_2$ chemisorption. This observation argues against the idea that the slow increase in $V_{CO_2}/V_m$ is due to the further removal of surface oxide. Higher reduction temperatures (500°C) lead to lower $V_{CO_2}/V_m$ values and so does not improve the situation. It can be argued that

the reduced catalyst can in any event never be free of surface oxygen ions as these ions are associated with the promoter cations as oxides (MgO, $K_2O$, etc.) which are finely dispersed on the surface of the reduced iron crystallites. In view of the above uncertainties it is felt that reductions of 16-hr duration are adequate for comparison purposes at least. Note from Fig. 1 that the differences between samples remain constant even though the actual values of $V_{CO_2}/V_m$ change with continued reduction. The reproducibility of the technique was found to be quite satisfactory.

### RESULTS

Figures 2 and 3 illustrate the influence of the alkaline promoters Li, Na, K, Ca, and Ba on the $CO_2$ chemisorption capacity of the reduced catalysts. $V_{CO_2}/V_m$ is the ratio of the STP volume of $CO_2$ strongly chemisorbed to the argon BET monolayer volume. The ratio gives a measure of the coverage of the reduced catalyst by chemisorbed $CO_2$. For the samples presented in
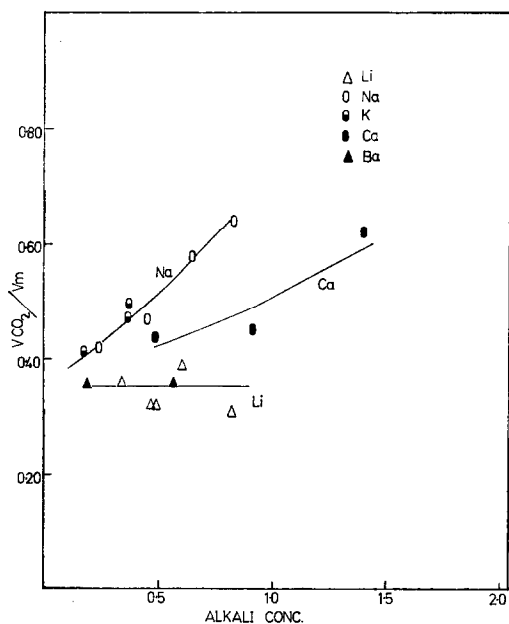


FIG. 3. The chemisorption coverage of the reduced samples by $CO_2$ as a function of alkali concentration. Concentrations and symbols as in Fig. 2. The alkali was added by impregnation after fusion.



FIG. 2. The chemisorption coverage of the reduced samples by $CO_2$ ($V_{CO_2}/V_m$) as a function of alkali concentration expressed as g atom of promoter cation per 100 g atom of Fe. The alkali was added to the catalyst at the fusion stage of preparation.
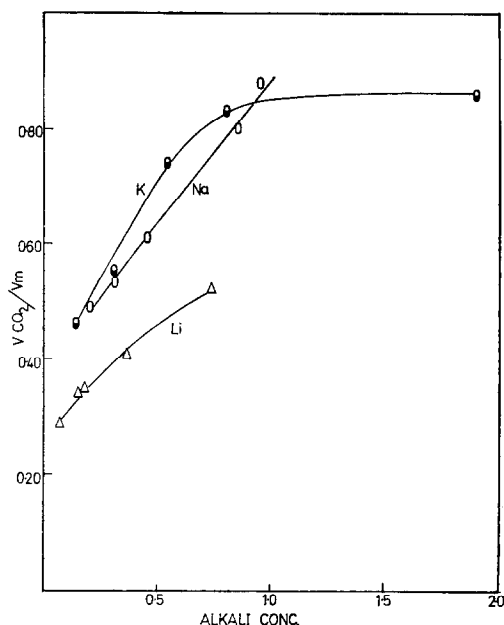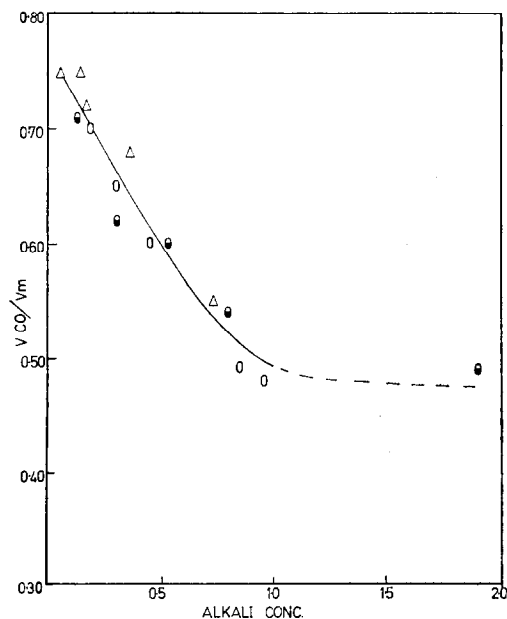


FIG. 4. The chemisorption coverage of the reduced samples by CO ($V_{CO}/V_m$) as a function of alkali concentration for the impregnated series of catalysts. Symbols and concentrations as in Fig. 2.
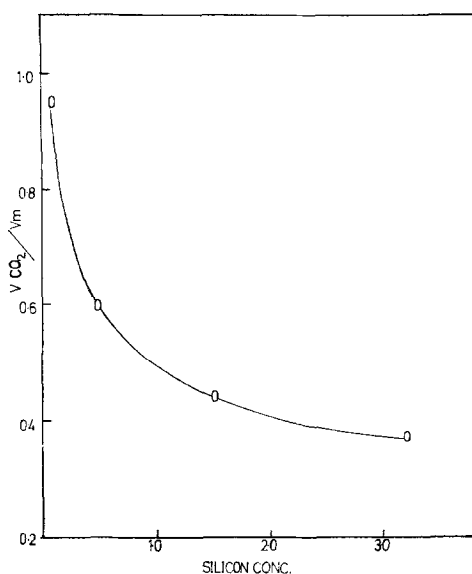
FIG. 5. The influence of silica on the surface coverage by $CO_2$ of a $K_2O$-promoted iron catalyst. The potassium content of each sample was fixed at 0.64 g atom/100 g atom Fe while the silica content was progressively increased.



FIG. 6. The influence of alkali on the BET areas of the reduced catalysts (in $m^2/g$ unreduced catalyst). Symbols and concentrations as in Fig. 2.

Fig. 2 the alkali promoter was added to the catalyst at the fusion stage. For those in Fig. 3 the samples were all prepared from a single master batch of previously fused material and the alkali was added by impregnation as described in the experimental section. Figure 4 gives the results of the carbon monoxide chemisorption coverages $(V_{CO}/V_m)$ obtained on the samples of the impregnation series. All the samples represented in Figs. 2, 3, 4, and 6 also contained 1.5 g MgO/100 g Fe. The MgO was added at the fusion step in the sample preparations and served as a surface area promoter. Figure 5 illustrates the change in the value of $V_{CO_2}/V_n$ for a series of re-
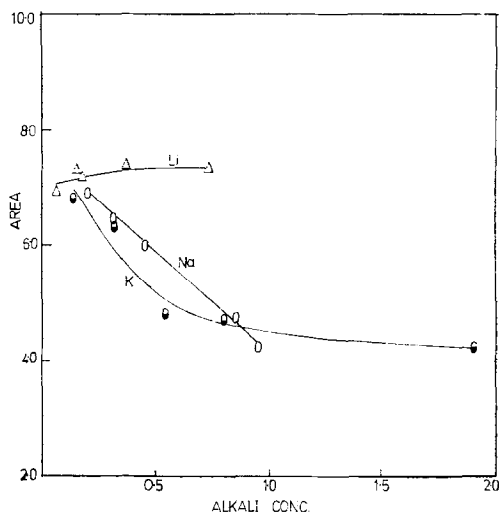
duced catalysts in which the $K_2O$ content was fixed but the amount of $SiO_2$ was progressively increased. Both promoters were added at fusion. Figure 6 shows how the promoters Li, Na, and K influence the BET surface areas of the reduced catalysts. In all the figures the promoter concentrations are given as gram atom promoter cation per 100 gram atom metallic iron. The effects of the promoters are therefore directly comparable on an atomic basis.

Tables 1 and 2 show the correlation that exists between the $CH_4$ selectivity and the ratio $V_{CO_2}/V_m$ of the catalysts. All the samples listed in Table 1 were prepared from the same batch of fused alumina-promoted magnetite. The samples in Table 2 contain different structural promoters. For each pair of the latter catalysts the amount of structural promoter as well as

TABLE 1

CORRELATION BETWEEN $CO_2$ COVERAGE AND $CH_4$ SELECTIVITY—LABORATORY ATMOSPHERIC PRESSURE TESTS

| Sample No. | Method of alkali addition | $K_2O$ content (g/100 g Fe) | $V_{CO_2}/V_m$ | $CH_4$ selectivity (%) |
|---|---|---|---|---|
| 1 | Fused | 0.04 | 0.19 | 16 |
| 2 | Fused | 0.46 | 0.25 | 13 |
| 3 | Impregnated | 0.35 | 0.36 | 8 |
| 4 | Impregnated | 0.54 | 0.45 | 5 |

TABLE 2

THE INFLUENCE OF SILICA ON THE $CO_2$ COVERAGE AND ON THE
METHANE SELECTIVITY—HIGH-PRESSURE SYNTHESIS TESTS

| Structural promoter | Chemical promoter | $V_{CO_2}/V_m$ | $CH_4$ selectivity (%) |
|---|---|---|---|
| None | $K_2CO_3$ | 0.71 | 9 |
| | $1K_2CO_3 + 4SiO_2$ | 0.18 | 16 |
| MgO | $K_2CO_3$ | 0.62 | 10 |
| | $1K_2CO_3 + 4SiO_2$ | 0.39 | 27 |
| $Al_2O_3$ | $K_2CO_3$ | 0.36 | 11 |
| | $1K_2CO_3 + 4SiO_2$ | 0.25 | 20 |

the amount of $K_2O$ was fixed, the only difference being that the one was promoted with potassium carbonate while the other was promoted with potassium carbonate and silica.

## DISCUSSION

### Surface Basicity and Hydrocarbon Selectivity

Although the experimental points in Fig. 2 are somewhat scattered it is clear that $K^+$ and $Na^+$ ions have a much more marked influence on the $V_{CO_2}/V_m$ values that do $Ca^{2+}$, $Ba^{2+}$, and $Li^+$ ions. The promoters $Li^+$ and $Ba^{2+}$ appear to have little or no influence. Taking the $V_{CO_2}/V_m$ ratio as a measure of surface basicity, it is apparent that $K^+$ and $Na^+$ will be better promoters than $Ca^{2+}$, $Ba^{2+}$, or $Li^+$ as far as the production of long-chain hydrocarbons is concerned. This tallies with experimental findings, as has already been discussed in the introduction to this paper.

As can be seen in Fig. 3 the experimental results are much less scattered when the alkali is added to the catalyst by the impregnation technique. This is no doubt due to the fact that all the impregnated samples were prepared from a single batch of fused material whereas each sample in the series illustrated in Fig. 2 represents a separate fusion. The fusion operations as well as the exact impurity contents of the material were difficult to control with the relatively crude fusion apparatus used and some experimental scatter in the results was therefore not surprising. In the case of the impregnation series, $Li^+$ clearly had a positive influence on the value of the

$V_{CO_2}/V_m$ ratios. This was not the case for the samples in which $Li^+$ was added during fusion (see Fig. 2). The influence of $Li^+$ was nevertheless still very much less pronounced than that of $K^+$ or $Na^+$.

Comparison of the curves of Figs. 2 and 3 shows that for the same alkali content the impregnation series have higher $V_{CO_2}/V_m$ values. This means that a higher surface basicity was attained by the impregnation technique, which in turn should mean that for the same alkali content a catalyst which was promoted by impregnation should have a higher heavier hydrocarbon selectivity than one in which the alkali was added during the fusion of the starting material. The results of the atmospheric pressure tests confirm this. Sample 3 in Table 1, in spite of its lower alkali content, has a higher surface basicity and, in agreement with this, a lower methane selectivity than Sample 2. (The lower the methane selectivity the higher the long-chain hydrocarbon selectivity.) From Table 1 it can be seen that there is a clear relationship between surface basicity $(V_{CO_2}/V_m)$ and methane selectivity, whereas there is no such obvious relationship between the actual $K_2O$ content of the catalyst and its selectivity. The surface basicity and hence the hydrocarbon selectivity therefore depends not only on the amount of $K_2O$ present but also on how well it is distributed over the catalyst surface.

Silica is a common impurity in the iron oxide ores which are used in the preparation of the catalyst. During the fusion of the promoted catalyst it can be expected that the acidic silica will combine with

the basic potassium promoter. These silicates are less basic in character than pure $K_2O$ and therefore the surface basicity of the final reduced catalyst would be expected to be lowered by the presence of silica. This effect is clearly indicated by the results given in Fig. 5. At a fixed $K_2O$ content the $V_{CO_2}/V_m$ value of the reduced catalyst markedly drops with increasing silica content. This decrease in surface basicity should result in an increase in methane selectivity in the Fischer-Tropsch synthesis. The results listed in Table 2 illustrate that there is a correlation between the surface basicity as determined by $CO_2$ chemisorption and the methane selectivity of the catalyst. For each pair of catalysts in Table 2 the one which contains silica in addition to the fixed amounts of other promoters has a lower surface basicity and also has a higher methane selectivity in the Fischer-Tropsch synthesis. The silica content of the iron ores used in catalyst manufacture is therefore of considerable importance and must be borne in mind when deciding on the amount of $K_2O$ which is to be added to the catalyst.

*Surface Coverage by Alkali Promoter*

In Brunauer and Emmett's (6) original chemisorption studies on reduced magnetite catalysts it was assumed that $CO_2$ was exclusively adsorbed by the surface alkali molecules, while CO adsorbed only on the exposed metallic iron surface. The results in Fig. 3, which show a smooth increase in $CO_2$ coverage with increasing alkali content, conform to this concept. In one of the samples in Fig. 3 an excessive amount of $K_2O$ was put onto the catalyst. The $V_{CO_2}/V_m$ for this sample was nevertheless still about 0.86, which appears to represent surface saturation. The adsorbed $CO_2$ molecule is presumably larger than the physically adsorbed argon atom and hence even at saturation the value of $V_{CO_2}/V_m$ will be less than 1.0. This result confirms the assumption that the $CO_2$ adsorption is a purely surface phenomenon. If it did react with the bulk phase of the surface alkali, i.e., reaction beyond the surface layer, the amount of $CO_2$ adsorbed

would have to be higher than that experimentally observed.

The higher the coverage of the surface by alkali the lower should be the amount of metallic iron surface exposed. Figure 4 shows that this is so: $V_{CO}/V_m$ decreases as the alkali content increases. Closer comparison of Figs. 3 and 4, however, reveals that there is at least one aspect which indicates that the concept that $CO_2$ only chemisorbs on the surface alkali is an oversimplification. While there is an obvious difference in $CO_2$ coverage between the Li- and K-promoted samples there is very little corresponding difference in CO chemisorption. Present indications are that under the current experimental conditions CO does only chemisorb on the iron surface while $CO_2$ chemisorbs on oxides, other than those of the Group I metals, which happen to be present in the surface of the reduced catalyst (5). It is also known that $CO_2$ chemisorbs on clean iron surfaces (7). It is suggested therefore that $CO_2$ chemisorbs not only on the oxides but to some extent on the free iron surface as well. As the percentage of the surface consisting of metallic iron is the same for the Li- and the K-promoted samples, the large difference in the $CO_2$ chemisorption capacities of these two series must be due to differences in the adsorption capacity of the alkalis themselves and/or differences in adsorption capacity of the exposed iron due to the presence of the alkali on the iron surface, e.g., by altering the chemical potential of the neighboring surface iron atoms. Carbon dioxide chemisorption studies cannot therefore be expected to give any absolute measure of the extent of coverage of the surface by alkali promoter. The adsorption studies nevertheless remain useful as a means of gauging surface basicity.

*Influence of Alkali Promoters*
*on Surface Area*

The BET surface areas of the reduced alkali-impregnated catalysts are illustrated in Fig. 6. While Li has little or no effect, Na and K clearly influence the surface area, the area decreasing with increasing alkali

content up to at least 1.0 g atom alkali cation per 100 g atom iron. In the catalyst series in which the alkali was added before the fusion of the magnetite, results similar to those depicted in Fig. 6 were obtained, Li and Ba having little effect while Na and K markedly lowered surface area. Although it was known (8) that $K_2O$ did lower surface area it is of interest to record that the more basic the alkali added the greater the loss in area of the reduced catalyst appears to be.

It was repeatedly found in the present studies that when silica was present in alkali-promoted catalysts, the surface areas were always higher than when silica was absent. As silica itself is an ineffectual structural promoter (5) it is postulated that the influence of silica is due to the fact that it combines with the alkali to form silicates, thus lowering the basicity of the alkali. This in turn results in a smaller loss in surface area. X-ray line-broadening studies carried out in this laboratory on reduced $K_2O$-promoted catalyst (9) have shown that those samples containing $K_2O$ have larger crystallites than those without $K_2O$. The loss of surface area is hence due to crystal growth and not due to other reasons such as pore blocking. While the authors have no satisfactory explanation of this fluxing action of the alkalis it does appear that the more basic the alkali the larger the iron crystallites are after reduction and hence the lower the surface area.

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