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The Influence of Structural Promoters on the Surface Properties of Reduced Magnetite Catalysts

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Several series of fused magnetite samples promoted with, respectively, Al_2O_3, TiO_2, Cr_2O_3, MgO, MnO, CaO, SiO_2, and BeO were prepared, reduced with hydrogen, and the surface area, CO, and CO_2 chemisorptive capacity of each reduced sample determined. The effectiveness of the additives as BET area promoters decreased in the order given above. For each individual promoter the area increased with promoter content. The amount of free iron area (CO chemisorption) in general paralleled the total BET area except in the case of TiO_2-promoted samples, where an actual loss of total iron area occurred with increasing TiO_2 content. On a percentage basis MgO is the best iron surface promoter. CO_2 chemisorptions are clearly influenced by the structural promoters, the more basic the latter the higher the CO_2 chemisorption coverages obtained. This was confirmed by studying the CO_2 chemisorptive capacity of some of the above promoters by themselves.

INTRODUCTION

In the preparation of fused magnetite catalysts for use in the ammonia or Fischer-Tropsch hydrocarbon synthesis it is common practice to add metal oxides which are not reduced by hydrogen to the fused magnetite. These oxides form solid solutions with the magnetite and are therefore well distributed in the magnetite phase. Upon subsequent hydrogen reduction of the catalyst these oxides are, as it were, precipitated between the metallic iron crystallites, so preventing to a large degree the sintering of neighboring iron crystallites. This stabilization results in high surface area catalysts. As the surfaces of the reduced catalysts are partially covered with promoter molecules, the BET surface areas do not necessarily reflect the total metallic iron surfaces available and an independent estimation of the iron area is therefore also desirable. In the present studies the amount of carbon monoxide chemisorbed by the catalyst at −80°C has been taken as a measure of the exposed iron area.

In order to attain the desired product selectivity pattern in the Fischer-Tropsch synthesis over iron catalysts it is essential that the correct amount of alkali, normally potassium carbonate or silicate, be present on the catalyst (*1*). This implies that the iron surface needs to be "basified" to some extent and if this is the case the basicity of the other promoters such as the structural promoters which are added primarily to boost the surface area, also needs to be taken into consideration when choosing suitable promoters. The basicity of surfaces can be conveniently estimated by comparing the extent to which they adsorb an acidic gas such as carbon dioxide.

In order to help compare and evaluate the effectiveness of different possible structural promoters, several series of fused magnetite samples were prepared, each series containing increasing amounts of the promoter under consideration. After hydrogen reduction the BET area and the carbon monoxide and carbon dioxide chemisorption coverage of each sample were determined. To aid in the interpretation of the chemisorption results, chemisorption studies were carried out on several of the pure promoter oxides themselves under experimental conditions identical to those used for the promoted iron samples.

EXPERIMENTAL

The magnetite used in the sample preparations was a commercially available oxide containing 1.0 g atom of foreign cations per 100 g atoms of iron, the main impurities being Al, 0.1; Si, 0.25; and Mn, 0.4. The magnetite, mixed with the desired amount of promoter, was fused in a resistance furnace with water-cooled electrodes. After cooling and crushing the ingots, the 100 to 200 mesh size fraction, which was used throughout in these studies, was isolated and analyzed.

The adsorption studies were carried out in standard all-glass adsorption apparatuses. The samples were reduced *in situ* at 400°C with the hydrogen flow, 400 ml/min, passing through 12.0-g sample beds. Cylinder hydrogen was purified by passage through hot copper (400°C), cold traps chilled to liquid nitrogen temperatures, and finally a charcoal trap (previously degassed at 400°C) at −197°C. The latter trap removed traces of nitrogen which previous investigations had shown to influence the CO_2 chemisorption on the reduced catalysts (*2*).

BET surface areas were determined by argon adsorption at liquid oxygen temperatures. The cross-sectional area of the adsorbed argon atom was taken as $18.0 Å^2$, as the use of this figure gave surface areas in agreement with those obtained with nitrogen cross-sectional area taken as $16.2\ Å^2$, at liquid nitrogen temperatures. CO and CO_2 chemisorptions were determined at −80° and 0°C, respectively. For both gases the technique was to measure the total adsorption at 30 cm Hg pressure, degas the sample at the adsorption temperature for 20 min, and then repeat the adsorption measurement. The difference in the volumes adsorbed was taken as a measure of the amount of chemisorbed gas. Twenty minutes was found to be sufficient time for the establishment of equilibrium at 30 cm Hg pressure. Preadsorbed CO was found to result in approximately a 60% decrease in CO_2 chemisorption while preadsorbed CO_2 lowered the CO adsorption by ~25%. Rereduction of the catalyst at 400°C for 1 to 2 hr, which was found to remove all chemisorbed gas, was therefore always carried out when more than one chemisorption determination on the same sample was carried out. Preadsorbed hydrogen was found to have little or no effect on the adsorptive capacity of the samples for either CO or CO_2. The experimental technique has been discussed more fully elsewhere (*2*, *3*).

The catalyst series promoted with Cr_2O_3 was reduced for 41 hr, those promoted with Al_2O_3, MgO, TiO_2, or with SiO_2 were reduced for 23 hr, and those containing MnO, CaO, or BeO were reduced for 16 hr. All the samples were more than 95% reduced. It should be mentioned here that the influence of extended reduction times on the adsorption measurements has been investigated in this laboratory. It was found that up to about 95% reduction, the BET surface area as well as the volume of CO chemisorbed increased linearly with the extent of reduction. After this the rate of reduction was very slow and both the BET area and the amount of CO chemisorbed slowly decreased but with the ratio between these latter two measurements remaining constant. The bulk of the remaining unreduced oxide therefore is presumably not on the surface of the reduced samples. Reductions were carried out at 400°C as this is the temperature at which commercial fused Fischer-Tropsch catalysts are being reduced. Although the reduction rate at 500°C is higher, both the surface area and the ratio of CO chemisorbed to BET area are lower than when the reduction is carried out at 400°C.

RESULTS

Table 1 gives the results of the CO_2 and CO chemisorption determinations on the pure promoter samples. V_m is the argon BET monolayer volume and V_{CO_2} is the CO_2 chemisorbed volume. The ratio V_{CO_2}/V_m is a measure of the chemisorption coverage attained. In Figs. 1 to 4 are plotted, respectively, the surface areas of the reduced samples in square meters per gram of unreduced material, the volume (STP ml) of CO chemisorbed per gram of unreduced

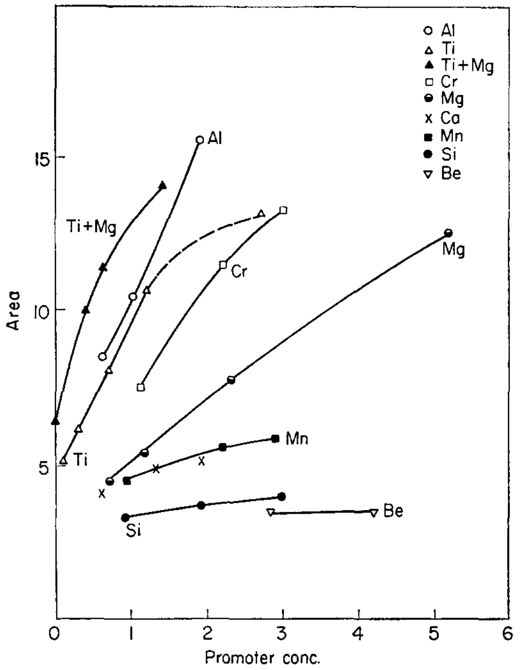

FIG. 1. The surface area in m^2/g of unreduced sample as a function of amount of promoter added expressed as g atom of promoter cation per 100 g atom of Fe.

catalyst, and the coverages attained by chemisorbed CO and by CO_2 on the reduced samples. In all the figures the abscissa gives the amount of promoter added as gram atoms of promoter cation per 100 gram atoms of iron.

TABLE 1
CO_2 AND CO CHEMISORPTION ON PROMOTER OXIDES

Oxide	V_{CO_2}/V_m	V_{CO}/V_m
MgO	0.43	0.0
Cr_2O_3	0.35	0.05
Al_2O_3	0.29	0.0
SiO_2	0.01	0.0

Table 2 lists the ratios of ionic charge (valence) to ionic radius (in Å) of the promoter cations.

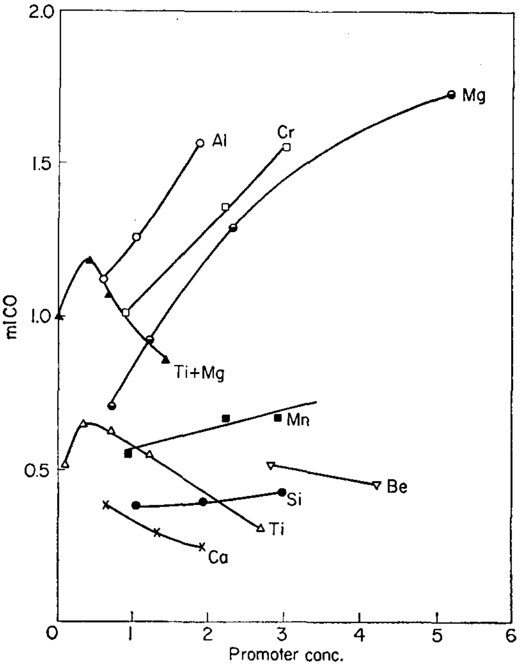

FIG. 2. The volume of CO chemisorbed by the reduced catalysts (STP ml per gram unreduced sample) as a function of g atom of promoter cation added per 100 g atom of Fe. Symbols as used in Fig. 1.

TABLE 2
CHARGE/RADIUS RATIOS OF PROMOTER CATIONS

Cation	Ratio
Al^{3+}	6.0
Ti^{4+}	5.9
Cr^{3+}	4.3
Mg^{2+}	3.1
Mn^{2+}	2.5
Ca^{2+}	2.0

DISCUSSION

Total Surface Area

As can be seen from Fig. 1 the effectiveness of the promoters to yield high area reduced catalysts decreased in the order Al_2O_3, TiO_2,Cr_2O_3, MgO, MnO, CaO, SiO_2, and BeO, the last two having little or no effect. Unpromoted samples yielded areas of 3 to 3.5 m^2/g.

The ineffectiveness of SiO_2 and BeO may be due to the fact that they do not enter into solid solution with the magnetite to any appreciable extent under the experimental conditions employed in the preparation of the catalysts. No silica ferrite with

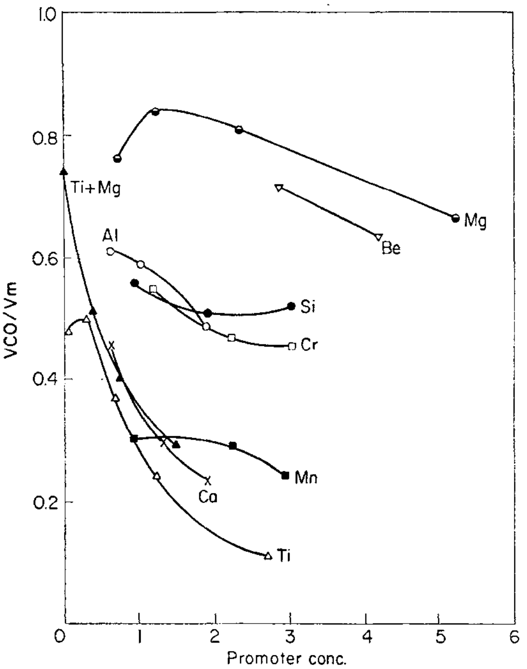

FIG. 3. The chemisorption coverage of the reduced samples by CO (V_{CO}/V_m) as a function of promoter concentration expressed as in previous figures. Symbols as in Fig. 1.

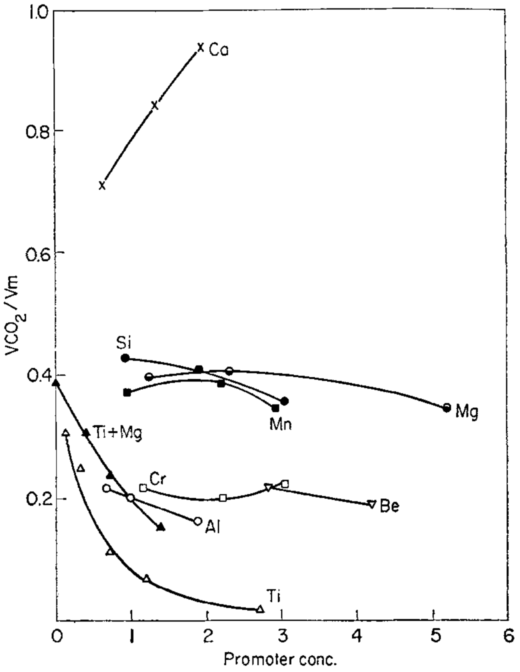

FIG. 4. The chemisorption coverage of the reduced samples by CO_2 as a function of promoter content. Concentrations and symbols as in Fig. 1.

a spinel structure is known to the authors. Unpublished X-ray diffraction studies carried out recently in this laboratory have shown that there is only a small initial shift in the lattice parameter of magnetite when doped with silica, which indicates that either no or very limited solid solution occurred. The ferrite $BeO \cdot Fe_2O_3$ is unstable and decomposes at about 360°C. The beryllium ion is probably too small (*4*) to form a stable ferrite having the spinel structure.

The oxides Al_2O_3, TiO_2, Cr_2O_3, and MnO are known to form stable compounds having the spinel structure, with iron oxides (*4*) and therefore these promoters should readily go into solid solution with magnetite. There is some doubt whether small amounts of CaO will go into solid solution as $CaFe_2O_4$ has no spinel structure (*4*). It will be seen, however, that as far as surface area promotion is concerned, CaO is very much on a par with MnO and the latter definitely does go into solid solution. A further study of magnetite doped with CaO is at present under way in this laboratory. With regard to the oxides which do form solid solutions with magnetite (CaO is provisionally included) it is of interest to note from Table 2 that the ratio of ionic charge to ionic radius of the promoter cation decreases in the same order as the effectiveness of the cation as structural promoter. The force of attraction between a cation and an adjacent oxygen anion in the oxide lattice will be proportional to $q^+q^-/(r^+ + r^-)^2$ where q and r represent ionic charge and radius, respectively. The smaller r^+ and the larger q^+, that is the higher the charge/radius ratio, the stronger the attraction, and hence the less mobile the cation is likely to be in the spinel lattice. The more immobile the cations in the magnetite the less likely they are to agglomerate during the reduction of the magnetite, and so they remain well dispersed throughout the catalyst, resulting in more effective surface area promoting by preventing the sintering of neighboring iron crystallites. Lack of mobility in the magnetite phase would also be expected to slow up the rate of reduction. It is an observed fact that high-area catalysts are associated with slow reduction and low-area catalysts with rapid reduction under the same conditions (*3*).

One series of doubly promoted catalysts in which the TiO_2 content was varied and the MgO content kept constant (1.4 g atom Mg per 100 g atom Fe) was also studied and the plot is included in Fig. 1. The effects of the TiO_2 and the MgO appear to be roughly additive.

Metallic Iron Area (CO Chemisorption)

Comparing Figs. 1 and 2 it can be seen that in general, as could be expected, the accessible metallic iron area increased with promoter content as did the total BET area. There are, however, two exceptions: CaO and TiO_2. The case of CaO is not very surprising in that since CaO is a relatively poor total surface area promoter, it could be expected that the surface would be progressively cluttered up by further additions of CaO. The case of TiO_2 is more surprising in that TiO_2 is an excellent BET area promoter. In order to confirm this effect another series of TiO_2-promoted samples in which each sample contained in addition a fixed amount of MgO, was prepared and studied. As can be seen from Fig. 2 the general features of the two TiO_2-promoted series are similar in that there is an initial increase of iron area up to ~0.5 g atom Ti per 100 *g* atom Fe, after which the actual iron area decreases with increasing Ti content in spite of a continued increase in BET area. In view of this effective blanketing of the reduced iron crystallites by TiO_2, it would be expected that TiO_2-promoted catalysts would be less active in synthesis than say Al_2O_3- or MgO-promoted catalysts. Unpublished pilot plant results confirm this for the case of the Fischer-Tropsch synthesis process.

Figure 3 shows how the proportion of the surface that consists of metallic iron (V_{CO}/V_m) varies with promoter concentration. Of the more effective structural promoters MgO clearly yields the highest percentage of free iron reduced catalyst, followed by Cr_2O_3 and Al_2O_3, while TiO_2 is markedly inferior in this respect. On the whole the percentage of free iron surface decreases with promoter content.

The assumption that under the present experimental conditions CO chemisorbed only on the iron surface is supported by the results of the CO chemisorption experiments carried out on several of the promoters themselves. Of those investigated (see Table 1) only Cr_2O_3 showed a small affinity for CO.

CO_2 Chemisorption

Figure 4 illustrates the results obtained in the CO_2 chemisorption determinations. V_{CO_2}/V_m gives a measure of the CO_2 chemisorption coverage attained at 0°C and so can be taken to reflect the overall "basicity" of the reduced catalyst surfaces. Of the good structural promoters MgO yields reduced surfaces with the highest CO_2 coverages followed by Cr_2O_3, Al_2O_3, and finally TiO_2. This trend is as would be expected from the basicities of the structural promoters themselves. In Table 1 the CO_2 chemisorption coverage on basic MgO is compared with that obtained on the amphoteric oxides Al_2O_3 and Cr_2O_3 and on the acidic oxide SiO_2. Clearly the more basic the oxide the higher the CO_2 coverage attained.

Although the CO_2 coverage does decrease with increasing SiO_2 content, as would be expected for such an acidic oxide, the actual coverage level appears to be too high when compared with the other promoters. Contrary to the other promoters, however, SiO_2 does not go into solid solution with magnetite and therefore it will not be as well distributed in the final reduced catalyst, so that its influence on the CO_2 coverage will be less marked. The very high coverages attained with CaO-promoted samples are no doubt due to both the relatively high basicity of CaO as well as the low final surface areas of the reduced catalysts which result in high coverages of the surface by CaO. Higher CO_2 coverages are obtained on the TiO_2-promoted samples containing MgO in addition than on the samples promoted with TiO_2

only, as could be expected from the higher basicity of MgO relative to TiO_2.

It is common practice (*5*) to employ the CO_2 chemisorption on reduced doubly promoted iron catalysts as a measure of the proportion of the surface covered by alkali. It is clear from the above results, however, that it is not only the oxides of Group I alkali metals that influence the CO_2 chemisorption but also the other (structural) promoters present. Taken further this means that although the potassium promoter has the predominant effect on the chemical nature of the surface and hence on the performance of the catalyst in synthesis, the other promoters present must also exert a contributing chemical influence and this should be taken into consideration when selecting suitable promoters.

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