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Heats of Chemisorption on Promoted Iron Surfaces and the Role of Alkali in Fischer-Tropsch Synthesis

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The heats of adsorption of CO, CO_2 and H_2 on unpromoted, on singly and on doubly promoted reduced magnetite were determined calorimetrically. The heats of CO adsorption are similar to those reported on evaporated iron films. The heats of hydrogen adsorption are lower than on iron films but nevertheless similar to those reported on reduced iron oxide samples. Promotion with only MgO does not markedly influence the heats of adsorption of any of the above gases. Promotion with K_2O increases the heat of CO adsorption at low coverages while it decreases the initial heats of hydrogen adsorption. The K_2O markedly increases the heat of adsorption of CO_2 at all coverages. The CO_2 appears to chemisorb not only on the surface alkali but also on the metallic iron. The known influence of K_2O promotion on both the activity and selectivity of the Fischer-Tropsch synthesis is explained in terms of the observed influence of K_2O on the heats of adsorption of CO and of hydrogen on iron catalysts. The postulates are also applied to the case of the ammonia synthesis.

In the Fischer-Tropsch synthesis over iron catalysts it is well known that the catalyst must be promoted with a certain amount of basic potassium salt (*1*), e.g., the carbonate or the silicate. The alkali enhances the rate of synthesis and also shifts the selectivity towards the more desired heavier hydrocarbons. In the synthesis of ammonia over iron catalysts alkali promotion also increases the rate of synthesis. As alkali does not increase the total iron area available [in fact it lowers it (*2, 3*)] the promotion is no doubt chemical in nature and it has been postulated that the potassium influences the electronic state of the surface iron atoms (*4, 5*). If this were the case it would be reasonable to assume that alkali should influence the bonding strength of adsorbed molecules, i.e., the calorimetric heats of adsorption on iron catalysts should be affected by the presence of alkali on the surface.

Some work in this direction has been carried out by Kölbel and Haubold (*6*) on reduced precipitated Fe_2O_3. Their reduced samples, however, contained relatively large amounts of carbon and also of residual unreduced iron oxide, which casts some doubt on the cleanliness of the surfaces. On their unpromoted sample for instance the observed heat of adsorption of CO was only 10 kcal/mole which is very low compared to the 32 kcal/mole found on evaporated iron films (*7*). Kölbel reduced his catalysts at 270°C presumably because higher temperatures would have resulted in excessive loss of surface area of the unsupported iron. It was considered worthwhile to repeat this investigation but using promoted iron catalysts which would be more resistant to sintering, thus allowing higher reduction temperatures which should yield cleaner iron surfaces. Fused promoted magnetite was considered a suitable form of iron catalyst for this kind of study. It was also decided to extend the adsorption studies to hydrogen and carbon dioxide as well as to carbon monoxide and

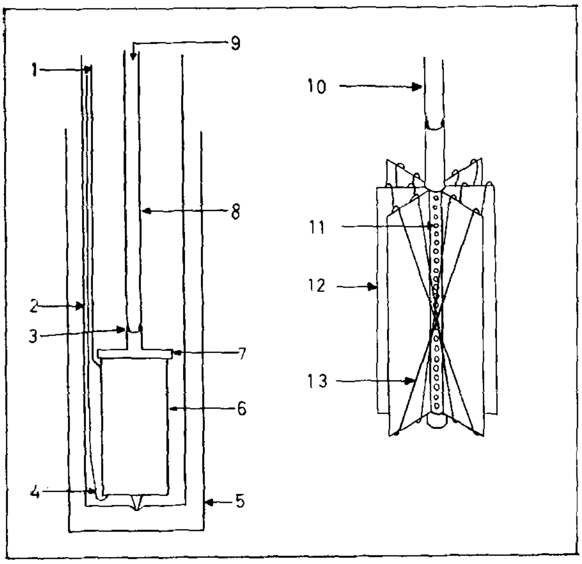


FIG. 1. Calorimeter and center piece: (1), heater wire leads; (2), glass jacket; (3), ground fitting; (4), thermocouple; (5), vacuum jacket; (6), perforated copper cylinder; (7), stainless steel screwcap; (8), spring loaded glass tube; (9), gas inlet; (10), spring loaded glass tube; (11), perforation; (12), copper fins; (13), heater wires.

also to the effect of one presorbed gas on the subsequent adsorption of another.

EXPERIMENTAL METHODS

Sample Preparation

The pure and magnesium promoted magnetite samples were prepared from Merck α-Fe_2O_3 (pro analysi) by the sintering technique described elsewhere (*8*). The particle size used in the calorimeter was 35 to 60 mesh. The alkali was added by soaking the samples in water solutions of the alkali carbonates, draining off the excess liquid and drying the samples at 110°C. The promoter contents of the five samples investigated are given in Table 1.

Calorimeter

The design of the calorimeter was, except for several modifications, essentially similar to the type used by Beebe (*9*). A diagram of the calorimeter is given in Fig. 1. The catalyst container consisted of a perforated copper cylinder into which a copper center piece fitted tightly. The center piece consisted of a perforated hollow cylinder with six fins. The heater wires were wound over the fins in a crisscross fashion as shown in Fig. 1. (For clarity, only a few windings are actually shown.) The catalyst particles were packed between the fins and the outside cylinder. The heater wires hence were completely embedded in the sample thus ensuring a fairly uniform heat release throughout the entire catalyst chamber during heat calibrations. The top of the catalyst chamber was closed with a stainless steel screw-cap.

The gas dosing system was arranged so that when an aliquot of gas was introduced into the calorimeter the gas arrived at the catalyst bed from both the outside and inside of the perforated copper container. The object was to minimize the possibility of progressive layerwise adsorption through

TABLE 1

Sample no.	MgO (g/100 g of Fe)	Alkali oxide (g/100 g of Fe)
1	0	0
2	1.6	0
3	1.6	0.38 (K_2O)
4	1.6	1.06 (K_2O)
5	1.6	0.10 (Li_2O)

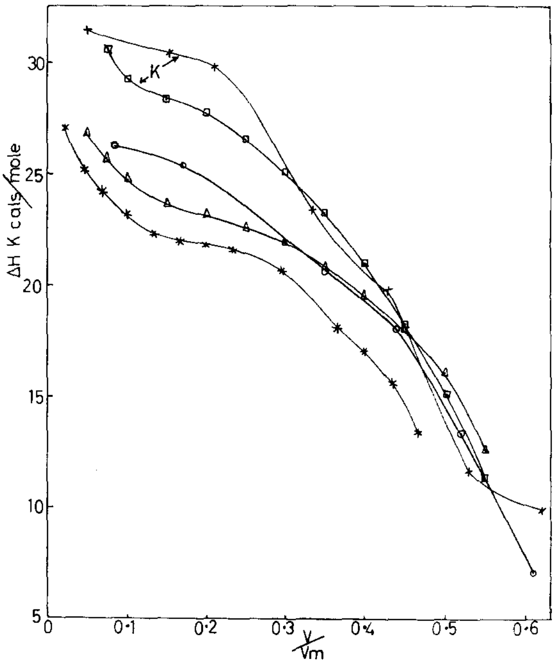


FIG. 2. Carbon monoxide heats of adsorption: (⊙), Sample 1, Fe_3O_4; (△), Sample 2, $Fe_3O_4/1.6$ MgO; (⊡), Sample 3, $Fe_3O_4/1.6$ MgO/0.38 K_2O; (+), Sample 4, $Fe_3O_4/1.6$ MgO/1.06 K_2O; (*), Sample 5, $Fe_3O_4/$1.6 MgO/0.1 Li_2O.

the bed, a phenomenon which is very likely in the case of strong chemisorption. At the start of an adsorption series a small aliquot of helium was introduced into the calorimeter chamber (0.01 torr) to further facilitate the distribution of heat within the catalyst bed.

One junction of an iron–constantan thermocouple was attached to the outer copper cylinder and the other was on the outside of the calorimeter. The signal from the thermocouple was amplified a thousandfold and fed to a 10 mV recorder. Calibrations were carried out at regular intervals during each experiment by passing a known electrical current through the heater wires for a set time. The recorder traces (i.e., emf–time curves) for the calibrations were identical in shape to those obtained when an aliquot of gas was chemisorbed on the catalyst. The curves reached their peaks in ca. 1.5 min after which Newtonian cooling took place, ca. 60 min. The peak heights were obtained by either simply reading off the maximum on the trace or by correcting for Newtonian cooling over the entire length of the trace. As the thermal insulation of the system was good (due to the vacuum jacket surrounding the calorimeter and to the low pressure inside the calorimeter) the difference between the peak heights as obtained by these two methods differed by only ca. 8%. Due to the similarity in the shape of the adsorption and calibration traces, however, the calculated heats of adsorption came to the same value irrespective of the method used for the peak evaluation.

Reduction and Adsorption Techniques

The capacity of the calorimeter was ca. it successively through hot copper turnings, 25 g of magnetite. The samples were reduced at 400°C for 50 hr with 800 ml of hydrogen flowing through the bed per minute. The hydrogen was purified by passing traps chilled to −197°C and finally through a charcoal trap immersed in liquid nitrogen. The direction of flow through the calorimeter was from the perforated center piece to the perforated outer cylinder. Although the expected amount of reduction

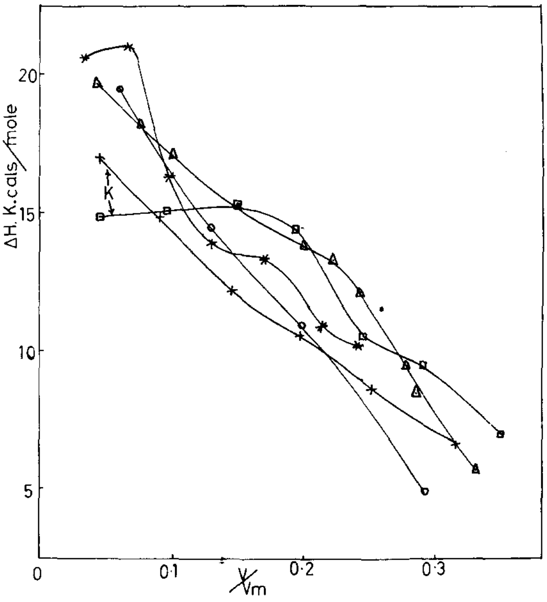


FIG. 3. Hydrogen heats of adsorption. (⊙), Sample 1, Fe_3O_4; (△), Sample 2, Fe_3O_4/1.6 MgO; (⊡), Sample 3, Fe_3O_4/1.6 MgO/0.38 K_2O; (+), Sample 4, Fe_3O_4/1.6 MgO/1.06 K_2O; (*), Sample 5, Fe_3O_4/1.6 MgO/0.1 Li_2O.

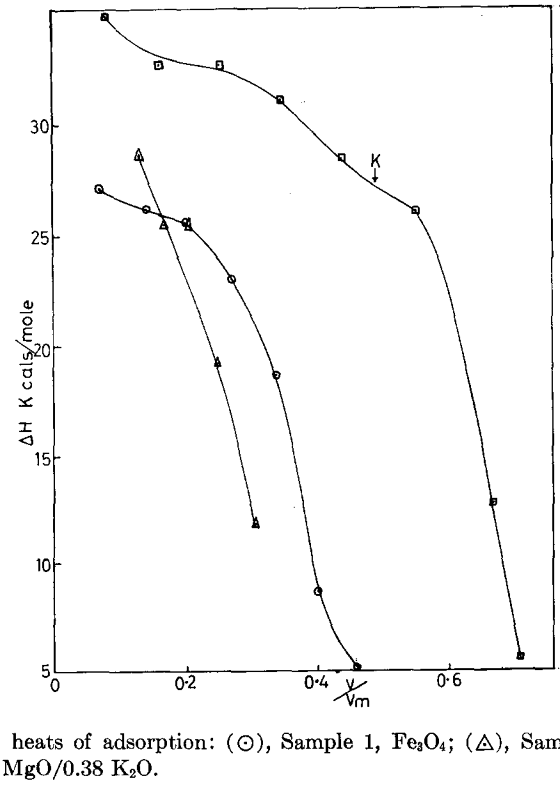


FIG. 4. Carbon dioxide heats of adsorption: (⊙), Sample 1, Fe_3O_4; (△), Sample 2, Fe_3O_4/1.6 MgO; (⊡), Sample 3, Fe_3O_4/1.6 MgO/0.38 K_2O.

water was obtained in ca. 16 hr preliminary investigations showed that the heats of adsorption of CO on the reduced iron increased with increasing time of reduction but that after 50 hr very little further change occurred. After reduction the samples were degassed at 400°C to less than 1×10^{-5} torr.

Gas adsorptions were carried out at ca. 20°C, the calorimeter being immersed in water contained in a large Dewar flask. Adsorptions were carried out stepwise by adding successive doses of gas until a residual pressure (ca. 0.2 torr) was obtained. Further adsorptions beyond the pressure breakthrough point were not carried out mainly because the rate of heat loss from the calorimeter became very high at this stage resulting in insufficiently accurate evaluation of the peak heights.

After each experiment the samples were re-reduced for 18 hr. The total BET surface area was also determined at each stage using argon at liquid oxygen temperatures.

RESULTS

The Figs. 2–4 give the plots of the heats of chemisorption of CO, H_2 and of CO_2 respectively as a function of surface coverage, the latter being expressed as the ratio of ml STP chemisorbed gas to the argon monolayer volume at liquid oxygen temperature. It is realized that each experimental heat in fact represents an integrated value for the increment of gas adsorbed and therefore that the presentation of the heats on the graphs as points strictly is incorrect. The data have nevertheless been plotted as points for the sake of better presentation.

Table 2 lists the initial heats of adsorption on an alkali-free reduced sample of different gases after some other gas had been presorbed onto the surface, followed by an evacuation for a set time at the same temperature. Table 3 gives the results of a similar series of experiments on the same type of reduced iron sample. In this case the amount of a gas that could be adsorbed onto the surface after the presorption of another gas was determined volumetrically. The surface coverages listed (ml/Vm) refer to the amount of gas adsorbed at the stage when a residual pressure (ca. 0.2 torr) was first observed in the sample chamber. (Small increments of gas were added consecutively until a residual pressure was observed.)

TABLE 2

Pre-adsorbed gas	Degassing time	Gas ads. on top.	Initial heats kcal/mole On top	On clean Fe
H_2	30 sec	CO_2	28	28
CO_2	1 min	H_2	12	20
CO	1 min	H_2	0	20
H_2	1 hr	H_2	15	20
CO	1 hr	CO	13	27

DISCUSSION

Carbon Monoxide Adsorption

Figure 2 shows that the heat of adsorptions fall from values of 32 to 27 kcal at low coverages ($\theta < 0.1$) to ca. 10 kcal/mole at $\theta = 0.6$ at which coverage a residual pressure is observed. The magnitude of the heats is in agreement with the results of other investigators. Bagg and Tompkins (*7*) working on evaporated iron films reported heats of adsorption of 32 kcal at low coverage falling to 15 kcal/mole at high coverage. Beeck (*10*) reported values of 35 kcal/mole on evaporated Ni films. The highest heat observed by Kölbel and Haubold (*6*) was 30 kcal/mole on a K_2CO_3 promoted reduced iron catalyst.

The experimental heats on the unpromoted iron sample and on the sample promoted only with MgO are sufficiently

TABLE 3

Pre-adsorbed gas	Coverage before degassing (ml/Vm)	Degassing	Gas ads. on top.	Coverage (ml/Vm)
H_2	0.31	1 min	CO_2	0.24
		1 hr	CO_2	0.32
CO_2	0.32	1 hr	H_2	0.13
CO	0.63	1 min	H_2	0
H_2	0.31	1 min	CO	0.06
		3 hr	CO	0.24

similar to suggest that the MgO promoter has apparently not changed the "chemical state" of the iron surface. Under the conditions of the experiment MgO itself does not adsorb any CO (*11*). This supports the general assumption that MgO acts purely as a structural promoter in these catalysts.

For those samples containing K_2O in addition to MgO the heats of adsorption at low coverage are clearly higher than on those samples not containing K_2O. At higher coverages the heats on the former samples are similar to those on the latter. For the sample promoted with Li_2O, however, the heats, if anything, are lower than those on the alkali-free samples. This is considered to be of significance as it is known that while K_2O strongly promotes the Fischer-Tropsch reaction, Li_2O is a relatively feeble promoter (*1*).

Hydrogen Adsorption

Figure 3 shows that the heats of adsorption at low coverages vary between 15 and 21 kcal/mole and fall to ca. 7 kcal/mole at higher coverages. These values are in good agreement with published work carried out on similar iron samples (*9, 12*), namely those obtained by hydrogen reduction of promoted oxides. On evaporated iron films, however, initial heats of adsorption are found to be in the region 32 to 36 kcal/mole (*7, 10*) which is about the same as the heats of adsorption of CO on such films. It appears therefore that while for CO the measured heat of adsorption on an iron surface obtained from the reduction of the oxide is not too different from the value obtained on evaporated iron film, the heat of adsorption of hydrogen is considerably lower on the former type of iron surface.

Because of the lower adsorption capacity as well as the lower heats of adsorption of hydrogen relative to carbon monoxide, the experimental accuracy in determining the calorimetric heat of adsorption of hydrogen is less than in the case of carbon monoxide. Superficial inspection of the experimental data plotted in Fig. 3 may therefore lead to the conclusion that different promoters have no marked influence on the heats of adsorption of hydrogen on iron surfaces. Closer inspection of the heat curves, however, indicates that at low coverages both the K_2O-containing samples have lower heats than those not containing K_2O. Furthermore, while the Li_2O promoted sample gave the lowest heat for CO it gave the highest heat for H_2 at low coverages. At low coverages therefore there appears to be an inverse relation between the curves of Fig. 2 and those of Fig. 3. Indirect evidence which supports the contention that K_2O lowers the heat of hydrogen adsorption is the following: Table 3 shows that when H_2 was presorbed onto a reduced iron sample (not promoted with K_2O) and the sample was then evacuated at the same temperature, subsequent CO chemisorption was less than half of its normal coverage on a clean surface ($\theta = 0.24$ as against 0.63 on the clean surface). In marked contrast to this when the same kind of experiment was carried out on a K_2O promoted iron surface neither the heat of adsorption nor the amount of CO adsorbed was lowered. Assuming that the hydrogen and carbon monoxide adsorb at similar surface sites these results imply that in the former case not all the preadsorbed hydrogen was removed during the evacuation step while in the latter case all the hydrogen was removed. This then would mean that in the case of the K_2O promoted iron the hydrogen is less tightly bound than on the K_2O-free iron. Further supporting evidence is the fact that when an iron surface was first saturated with hydrogen and then degassed for 1 hr the first increment of hydrogen subsequently reintroduced adsorbed with a heat of 15 kcal/mole (see the next to last line in Table 2). The same experiment with CO incidentally gives a similar "cut off" value; see last line of Table 2. This means that a gas adsorbed with more than 15 kcal/mole will not be removed by degassing at room temperature while one adsorbed with 15 or less will be removed. As not all the hydrogen could be removed by degassing a K_2O free sample, while apparently it could be from a K_2O promoted one, the initial heats of adsorption on the former should be greater than 15 kcal/mole while on the latter it should be less than 15 kcal/mole. This is in keeping with the experimental data plotted in Fig. 3.

Comparison of the relative amounts of CO and of H_2 adsorbed on clean surfaces at low pressure shows that the ratio of the amounts taken up is very close to 2. If, as is commonly assumed, hydrogen is dissociatively adsorbed and that the hydrogen atoms adsorb at the same kind of site as do the CO molecules then the ratio of 2 is to be expected. If the actual number of sites involved in the two adsorptions are the same then the results imply that the CO must be bound in the linear rather than in the bridged structure (*13*) on these iron surfaces.

Carbon Dioxide Adsorption

The adsorption heat curves are plotted in Fig. 4. It is well known that K_2O enhances the amount of CO_2 chemisorbed on reduced iron catalysts (*3, 14*) and therefore it is no surprise to find that the actual heats of adsorption on such samples are higher than on K_2O free samples. Even though it is known (*11*) that MgO also enhances the amount of CO_2 adsorbed on iron catalysts it appears from Fig. 4 that there is no big differences between the heats of adsorption on pure and on MgO promoted iron samples. The reason for this might be that the heat of adsorption of CO_2 on pure iron is not very different from that on pure MgO.

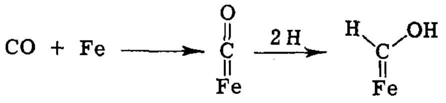
The influence of preadsorbed hydrogen on subsequent CO_2 adsorption and vice versa on MgO promoted, alkali-free, samples (Tables 2 and 3) are of interest as the results give some support to the contention (*3*) that CO_2 chemisorbs not only on the promoters but also on the iron surface itself. While the initial heat of adsorption of CO_2 is not influenced by the presence of preadsorbed hydrogen the actual amount of CO_2 adsorbed is less on top of hydrogen after a short degassing but the same after a long degassing. A plausible explanation is that the CO_2 initially adsorbs on the basic MgO on which the hydrogen does not in any event adsorb. Presorbed hydrogen therefore cannot have any influence on the initial heats of CO_2 adsorption. As CO_2 also adsorbs on iron sites, however, the amount of CO_2 adsorption on these sites will be diminished by preadsorbed hydrogen. Longer degassing removes most of the hydrogen and the CO_2 adsorption is then normal again. In any event, since hydrogen is generally assumed to adsorb on the metal, the fact that preadsorbed hydrogen does lower the total amount of CO_2 adsorbed does strongly suggest that CO_2, at least in part, does adsorb on the metal. When the reverse is carried out, namely adsorbing hydrogen on a surface containing preadsorbed CO_2, the initial heat of adsorption as well as the amount of hydrogen adsorbed is lower. While simple overlapping effects might account for the lower capacity (*14*) it does not readily account for the lower heat.

The Role of K_2O in Synthesis

Suhrmann (*15*) working on nickel; Sugita, on platinum (*16*) and Kölbel (*5*) on iron films observed that the electrical resistance of the film increased with increasing carbon monoxide adsorption and also that the work function of the metal rose. In the case of hydrogen chemisorption the resistance and work function first increased and then decreased with increasing coverage. More recently Ponec and Knor (*17*) working on iron films obtained results for hydrogen adsorption which were similar to those reported by Kölbel, while their results for nitrogen adsorption was again similar to that found for CO by Kölbel. These results are interpreted as meaning that when CO (or N_2) adsorbs onto an iron surface the molecule tends to draw electrons from the iron, whereas when hydrogen adsorbs (at not too low coverages) the atoms tend to donate electrons to the metal. Now K_2O is a very strong base and as in the broad sense, bases are electron donors the alkali will tend to donate electrons to neighboring iron atoms. In fact, photoelectric studies (*18*) have shown that K_2O on iron catalysts enhances electron emission. As CO tends to accept electrons from iron on adsorption the presence of K_2O on the surface should therefore facilitate the adsorption and this could result in a strengthening of the iron to carbon bond. This concept is in keeping with the observed increase in the initial heats of adsorption of CO on K_2O promoted iron. The reverse argument could be applied in the case of hydrogen adsorption: if hydrogen donates electrons to iron on adsorption the presence of the electron-donating alkali would be expected to discourage hydrogen adsorption, i.e., weaken the iron–hydrogen bond. In the case of hydrogen the actually observed effect on the heat of adsorption is small but the direction of the effect is opposite to that seen in the case of CO adsorption. With regard to the magnitudes of the observed changes in heats of adsorption it is of interest to point out that both Kölbel (*5*) and Ponec and Knor (*17*) found that the measured changes in electronic properties on their iron films were much larger in the case of CO than in the case of hydrogen adsorption. Detection of changes resulting from alkali promotion could therefore be expected to be more easily observed for CO than for H_2 adsorption.

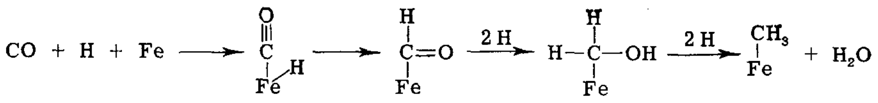
In infrared adsorption studies of CO on metals it is commonly observed, e.g., (*13*), that the carbon–oxygen stretching frequency progressively shifts to higher wave numbers as the coverage by CO increases. If the frequency can be taken as an indication of bond strength then it means that as the CO chemisorption coverage increases the carbon–oxygen bond strength increases. In heats of adsorption studies it is commonly found, as in this paper, that the heat of adsorption decreases with increasing coverage. If this in turn can be taken to mean that the iron–carbon bond strength decreases with coverage, then it appears that there is an inverse relation between the strengths of the iron–carbon and the carbon–oxygen bond: as the one increases the other decreases. Blyholder's (*19*) molecular orbital treatment of CO adsorption on metals supports the concept that an increase in the metal–carbon bond strength is accompanied by a decrease in the strength of the carbon–oxygen bond.

Now as the calorimetric results of this paper have shown that K_2O strengthens the bond between carbon and iron, the bond between carbon and oxygen should therefore be further weakened, making this latter bond more prone to attack by hydrogen. Consider for instance Anderson's (*1*) proposed mechanism for the Fischer-Tropsch reaction

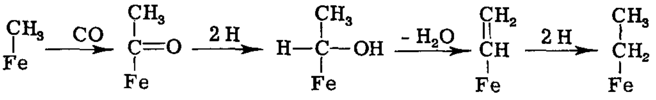


$$\mathrm{CO + Fe \longrightarrow \underset{\underset{Fe}{\|}}{\overset{\overset{O}{\|}}{C}} \xrightarrow{2\,H} \underset{\underset{Fe}{\|}}{\overset{H\diagdown\ \diagup OH}{C}}}$$

The surface hydroxyl complexes are the building blocks which link up by condensation reaction, chain termination occurring by hydrogenation and desorption. If, as proposed above, the presence of alkali on the iron surface facilitates the attack of the carbon–oxygen bond by hydrogen, then the rate of formation of the intermediate hydroxyl surface complexes will be increased, thus explaining why alkali increases the rate of Fischer-Tropsch synthesis. Furthermore, due to the increased strength of the carbon–iron bond the surface coverage as well as the residence time of the complexes on the surface should be increased and hence the statistical probability of chain growth by reac-



$$\mathrm{CO + H + Fe \longrightarrow \underset{\underset{Fe}{|}}{\overset{\overset{O}{\|\!|}}{C}}\!\diagup H \longrightarrow \underset{\underset{Fe}{|}}{\overset{\overset{H}{|}}{C}}{=}O \xrightarrow{2\,H} H{-}\underset{\underset{Fe}{|}}{\overset{\overset{H}{|}}{C}}{-}OH \xrightarrow{2\,H} \underset{Fe}{\overset{CH_3}{|}} + H_2O}$$



$$\mathrm{\underset{Fe}{\overset{CH_3}{|}} \xrightarrow{CO} \underset{\underset{Fe}{|}}{\overset{\overset{CH_3}{|}}{C}}{=}O \xrightarrow{2\,H} H{-}\underset{\underset{Fe}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH \xrightarrow{-\,H_2O} \underset{\underset{Fe}{|}}{\overset{\overset{CH_2}{\|}}{CH}} \xrightarrow{2\,H} \underset{\underset{Fe}{|}}{\overset{\overset{CH_3}{|}}{CH_2}}}$$

tion with neighboring complexes increased. This explains why alkali promotion results in the production of heavier hydrocarbons.

Contrary to Anderson, Sternberg and Wender (*20*) have proposed a one-site mechanism of chain initiation and growth. This mechanism still involves the formation of surface hydroxyl groups as initial surface complexes and hence chain initiation is still dependent on the attack of the carbon–oxygen bond of the adsorbed carbon monoxide by hydrogen. Continued chain growth would still be more probable the stronger the iron–carbon bond. Thus the explanation of the influence of alkali on activity and selectivity is unchanged.

As alkali lowers the heat of hydrogen adsorption the coverage of the surface by hydrogen would be expected to be lowered. (The increased surface coverage by carbon monoxide would in itself also result in a relative lowering of the hydrogen coverage.) Alkali should therefore depress the hydrogenation propensity of the surface and, as chain termination results from the hydrogenation of the iron–carbon bond, alkali should therefore enhance the statistical probability of continued chain growth. It is well known that the olefin content of the hydrocarbon product increases with alkali promotion. This is in keeping with the above postulate that alkali depresses the hydrogenation propensity of the iron.

Throughout this paper the potassium has been presented as K_2O. It is not known, however, in exactly what form the potassium is present on the surface. In commercial catalysts it is most probably present as the silicate while in the samples studied in the above work it could be there as KOH. The important point is, however, that the potassium is basic in character and therefore can behave as an electron donor.

In the Haber process promotion of the iron catalyst with alkali is known to increase the rate of the ammonia synthesis. It is of interest to postulate whether the role of alkali could also be explained in terms of the above concepts. From the electronic effects observed by Kölbel and by Ponec it appears that nitrogen behaves similarly to carbon monoxide on adsorption. The initial adsorption of nitrogen is presumably in the molecular form:

$$2\,Fe + N_2 \longrightarrow \begin{array}{c} N{=\!=}N \\ |\quad\;\; | \\ Fe\;\;Fe \end{array}$$

If alkali strengthens the iron–nitrogen bond, the nitrogen–nitrogen bond would be weakened, thus either facilitating the dissociation of the molecule into atoms (which are subsequently hydrogenated) and/or making the nitrogen–nitrogen bond more susceptible to direct attack by hydrogen, thus resulting in higher synthesis activity.

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