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# Kinetic Studies for Elucidation of the Promoter Effect of Alkali in Fischer–Tropsch Iron Catalysts

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The kinetics of the formation of hydrocarbons in Fischer–Tropsch synthesis and of consecutive reactions, i.e., hydrogenation and double bond isomerization of primarily formed 1-alkenes, were studied in a slurry-phase reactor using alkalized and nonalkalized precipitated iron catalysts. Both consecutive reactions have an order of about $-2$ with respect to carbon monoxide and an order of about 1 with respect to 1-alkenes. The order with respect to hydrogen is 1 for the hydrocarbon formation and also 1 for the consecutive hydrogenation, but 0 for the consecutive isomerization. The reaction orders are not changed by addition of $K_2CO_3$ to the catalyst. The kinetics of consecutive reactions can be interpreted by competitive adsorption of 1-alkene and carbon monoxide. Alkali addition causes an increase in the strength of carbon monoxide adsorption and consequently a decrease in 1-alkene adsorption so that the rates of the consecutive reactions are reduced. This hypothesis could be proved by studies of 1-hexene hydrogenation in the presence and absence of carbon monoxide for alkalized and nonalkalized iron catalysts. The kinetics were studied in the ranges $1.3 < P_{CO}(10^5 \text{ Pa}) < 7$, $1.6 < P_{H_2}(10^5 \text{ Pa}) < 9$, and $490 \text{ K} < T < 530 \text{ K}$. © 1989 Academic Press, Inc.

## INTRODUCTION

The selectivity of the Fischer–Tropsch synthesis is strongly influenced by addition of alkali compounds, for example, $K_2CO_3$, to iron catalysts. Alkali causes an increase in both the 1-alkene selectivity and the average carbon number of hydrocarbons produced (*1–6*).

In order to elucidate the promoter effect of alkali the adsorption of carbon monoxide and hydrogen on promoted and unpromoted iron catalysts has been intensively studied. The most important result was that addition of alkali to iron catalysts increases the heat of adsorption of carbon monoxide. This was found by Kölbel and Haubold (*7*) and later confirmed by Dry *et al.* (*8*). In the case of hydrogen the observed effect on the heat of adsorption is small but the direction of the effect is opposite that of carbon monoxide adsorption. Desorption experiments carried out by Arakowa and Bell (*6*) confirmed the result of Kölbel and Haubold that with an increase in the K/Fe ratio the strength of carbon monoxide adsorption on reduced iron is increased markedly. However, the strength of hydrogen chemisorption is decreased slightly. From these results Dry *et al.* (*8*) and Arakowa and Bell (*6*) have drawn the conclusion that alkali depresses the hydrogenation propensity of the iron surface, which would explain the increase in 1-alkene selectivity by alkali promotion. The same interpretation has been given recently by van der Lee and Ponec (*9*) in a comprehensive review dealing with problems of selectivity in syngas reactions.

Experiments carried out by Anderson *et al.* (*10*) and Weitkamp *et al.* (*11*) have shown that 1-alkenes constitute the primary products of the synthesis, which, however, gradually isomerize to 2-alkenes and can be hydrogenated to alkanes in consecutive reactions (*12–14*). A small proportion of alkanes is also formed in the primary reaction

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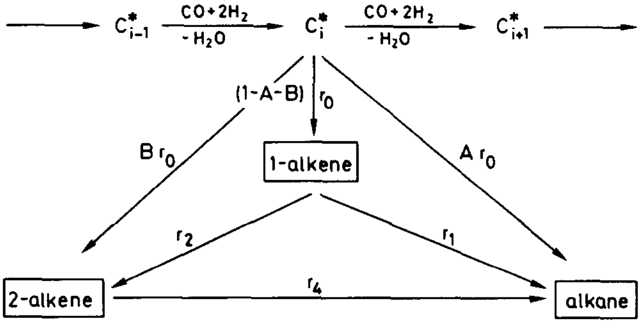

FIG. 1. Reaction scheme of Fischer–Tropsch synthesis.

(*15, 16*). The reaction scheme is shown in Fig. 1. $C^*_i$ symbolizes a chemisorbed species of carbon number *i*, which can either be built up to a species $C^*_{i+1}$ or be detached as hydrocarbons of carbon number *i* from the catalyst surface.

Sudheimer and one of us (*17*) have studied the kinetics of these primary and consecutive reactions using an alkalized precipitated iron catalyst in a slurry reactor. Hydrocarbon formation and consecutive hydrogenation of 1-alkenes to alkanes are approximately of first order with respect to hydrogen. The consecutive reactions, hydrogenation and double-bond isomerization, are of first order with respect to 1-alkene. On the basis of kinetic studies for which the total pressure was varied, a negative order of reaction with respect to carbon monoxide was estimated for both consecutive reactions. This explains the well-known effect that the 1-alkene selectivity increases with increasing carbon monoxide pressure. The kinetics of consecutive reactions can be interpreted by competing adsorption of 1-alkene and carbon monoxide. Therefore, the promoter effect of increased 1-alkene selectivity can also be explained by an enhanced desorption of 1-alkene caused by an increased strength of carbon monoxide adsorption on alkali promotion. The rates of consecutive hydrogenation and isomerization are reduced as a consequence of decreased 1-alkene adsorption.

The experiments of Arakowa and Bell (*6*) have shown that the ratio of hydrogen to carbon monoxide chemisorption at total surface coverage is close to unity and independent of the degree of potassium promotion. The adsorption of hydrogen can be regarded as independent of the strength of carbon monoxide adsorption.

The present study was undertaken in order to come to a decision between the two different interpretations of the promoter effect of increased 1-alkene selectivity, viz., decreased hydrogenation activity of the catalyst surface or enhanced desorption of 1-alkenes by carbon monoxide.

## NOMENCLATURE

*Symbols*

| | |
|---|---|
| $A$ | fraction of alkane directly formed by parallel reactions |
| $a$ ($g^{-1}$ $h^{-1}$) | coefficient to convert relative values of GC analysis into molar flow rates |
| $B$ | fraction of 2-alkene directly formed by parallel reaction |
| $C_{ji}$ (mol $m^{-3}$) | concentration of substance *ji* |
| $f_{ji}$ | factor of FID gas chromatography |
| $F_{ji}$ | relative peak area of FID gas chromatogram |

| | |
|---|---|
| $k_1$ | reaction rate constant of reaction 1 (unit according to applied equation) |
| $k_{1(ad)}$, $k_{CO(ad)}$ | adsorption constants (unit according to applied equation) |
| $m_K$ (g) | mass of catalyst (Fe) |
| $m$ ($cm^3$ $h^{-1}$ $g^{-1}$) | $m = k_1' P_{CO}^1 m_K$ |
| $M_{ji}$ (g $mol^{-1}$) | molecular mass of substance $ji$ |
| $\dot{n}_{ji}$ (mol $h^{-1}$) | flow rate of substance $ji$ at reactor outlet |
| $P$ (Pa) | total pressure |
| $P_{H_2}$, $P_{CO}$ (Pa) | partial pressure |
| $P_{ji}^0$ (Pa) | vapor pressure of substance $ji$ |
| $r$ (mol $h^{-1}$ $g^{-1}$ (Fe)) | reaction rate |
| $T$ (K) | temperature |
| $\overline{V}$ ($m^3$ $mol^{-1}$) | molar volume of liquid mixture |
| $y_{ji}$ | mole fraction of substance $ji$ analyzed by Janak gas chromatograph |
| $\beta$ | reaction order with respect to hydrogen |
| $\gamma$ | reaction order with respect to carbon monoxide |
| $\theta_{1\text{-en}}$ | coverage of catalyst surface by 1-alkene |

*Indices*

$i$ carbon number
$j$ class of material
  $j = 0$, all unbranched hydrocarbons
  $j = 1$, 1-alkene
  $j = 2$, 2-alkene
  $j = 4$, alkane
$k$ reaction, indicated in Fig. 1

## EXPERIMENTAL

### *Apparatus and Product Analysis*

The Fischer–Tropsch synthesis was studied in a slurry reactor. This type of reactor was chosen for the kinetic investigations on account of the strong back mixing which results in the equalization of 1-alkene concentration throughout the liquid phase. The slurry reactor can be regarded as an ideal CSTR (*17, 18*).

The flow diagram of the experimental unit is shown in Fig. 2. The feed was measured and controlled by thermal sensors and magnetic valves. In some experiments 1-hexene was continuously fed into the reactor by a metering pump. The reactor had a height of 90 cm and a diameter of 6 cm. The gas feed was preheated and sparged by a sintered metal plate with an average pore diameter of 80 $\mu$m. Oligomers of ethylene with an average C number of $\approx C_{50}$ and a melting temperature of about 360 K were used as liquid phase. The gas flow leaving the reactor passes through two cooling traps. The first trap was maintained at about 423 K in order to separate components which would form solid deposits in the second trap in which the product stream was cooled to 273 K. After expansion to atmospheric pressure the gas flow was measured and its content of carbon dioxide were determined continuously. For on-line gas chromatography, a small gas flow was withdrawn from the main flow, downstream from the hot trap, and was passed through a heated capillary to the heated sample valve of the on-line gas chromatograph for analysis of hydrocarbons with carbon numbers $C_1$–$C_9$. Another part of this small gas flow was cooled to room temperature and was passed to a Janak gas chromatograph for analysis of CO, $H_2$, and $C_1$–$C_4$ hydrocarbons. In contrast to a gas chromatographic analysis using an FID detector, the results of Janak gas chromatography represent the actual volume fractions of the analyzed components. The flow rate of $C_1$–$C_4$ hydrocarbons can be calculated from these volume fractions and the gas flow leaving the second cooling trap.

The flow of substance $\dot{n}_{ji}$ ($i$ = carbon number; $j$ = class of substance, with $j = 0$ for all unbranched hydrocarbons, $j = 1$ for

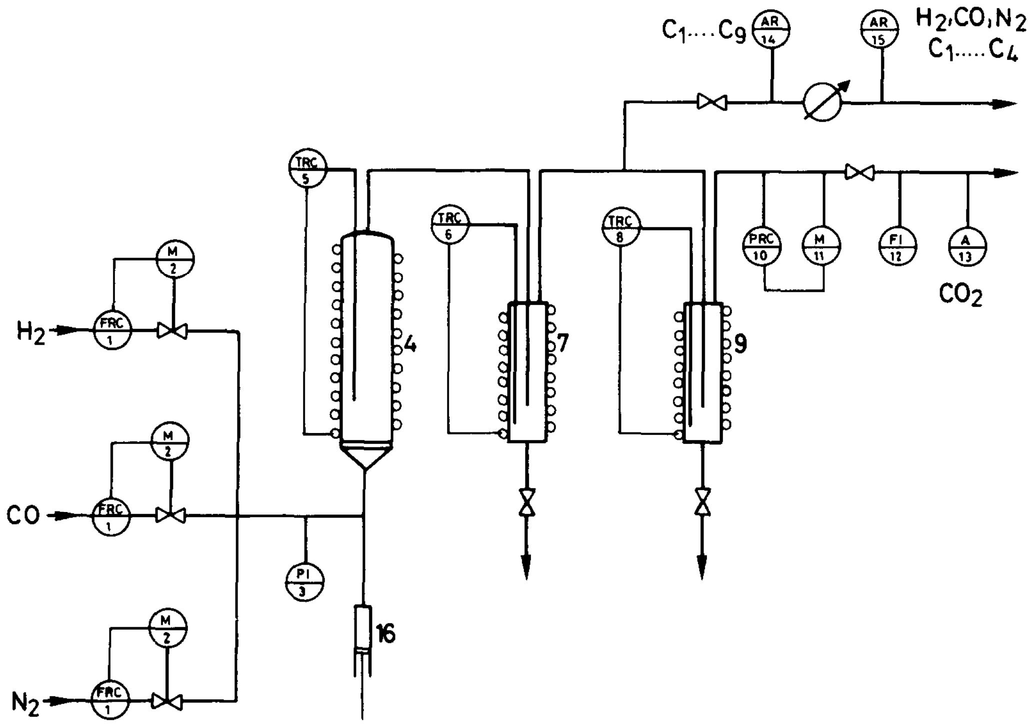

FIG. 2. Schematic drawing of the experimental unit: 1, flow meter; 2, 11, magnetic valves; 3, 10, pressure gauges; 4, slurry reactor; 5, 6, 8, temperature controllers; 7, hot condenser; 9, cold condenser; 12, gas meter; 13, $CO_2$ analysis; 14, on-line gas chromatograph; 15, Janak gas chromatograph; 16, 1-hexene feed.

1-alkene, $j = 2$ for 2-alkene, $j = 4$ for alkane) at the reactor outlet can be calculated by use of the equations

| Carbon number range | |
|---|---|
| 1–4 | $\dot{n}_{ji} = \dot{n}_R y_{ji}$ |
| 1–8 | $\dot{n}_{ji} = a f_{ji} F_{ji} / M_{ji}.$ |

Relative values of GC (FID) analysis were converted into molar flow rates by the coefficient $a$. For evaluation of $a$ relative values of GC analysis were fitted to absolute values of Janak-GC analysis in the overlapping range $C_1$–$C_4$ by linear regression of the pairs of data

$(\dot{n}_R y_{ji})$ : $(f_{ji} F_{ji} / M_{ji})$.
Janak-GC on-line GC (FID)

Details of product analysis are given in Ref. (*18*).

### *Behavior of the Slurry Reactor*

For the present kinetic studies the flow of products must be in a steady state. Calculations have shown that up to $C_8$ it takes about 3–4 h after a change of reaction conditions to achieve a steady state of the product flow. This delay is due to the large volume of the liquid phase in the slurry reactor and the low formation rate of the high boiling hydrocarbons. Therefore, the determination of the rate of hydrocarbon formation was limited to components up to $C_8$.

It could be shown that for the reaction conditions applied the conversion of carbon monoxide is governed by the chemical reaction and not by mass transfer from gas bubbles into the liquid and from there to the catalyst particles (*17, 18*), a precondition for kinetic studies.

At the gas inlet, hydrocarbons are transferred from the liquid to the gas phase. This causes a fall in the hydrocarbon concentration of the liquid near the gas inlet. However, calculations of concentration profiles indicate that in the case of hydrocarbons with more than four carbon atoms backmixing produces a nearly complete equalization of concentration.

Reaction rates are represented by functions of the concentration of hydrocarbons (1-alkene, 2-alkene) and the partial pressures of hydrogen and carbon monoxide. The concentrations of hydrocarbons are calculated by Raoult's law assuming that the gas leaving the reactor with mole fraction $y_{ji}$ is in phase equilibrium with the liquid phase in which the concentrations are equalized by backmixing. This assumption has been proved by analysis of the liquid and gas phases (*17*),

$$C_{ji} = \frac{P}{P_{ji}^{0}\bar{V}} y_{ji}.$$

### *Catalyst*

A detailed description of catalyst preparation has been given by Rähse (*19*). A solution of ammonia (10 wt%) is poured under vigorous stirring into a boiling solution of $Fe(NO_3)_3$ (500 g/liter $H_2O$) until the pH value amounts to 6.8 to 7.2. The precipitate is filtered, washed with hot distilled water, and resuspended in an aqueous solution, containing a calculated amount of $K_2CO_3$ or $Cs_2CO_3$. The resulting paste-like gel is dried at 383 K under a pressure of $2 \times 10^3$ Pa for 36 h.

For the preparation of the catalyst without alkali, polyethylene and stainless-steel vessels have been used in order to avoid contamination by alkali. Thus, the alkali content of the catalyst could be kept below 0.04 g ($K_2CO_3 + Na_2CO_3$)/100 g Fe. Fifty to seventy grams of the oxidic catalyst was ground to an average grain diameter of 16 $\mu$m. Subsequently the catalyst powder was suspended in 1.5 liters of an alkane fraction with an average C number of 50. The catalyst was first reduced with carbon monoxide and subsequently with hydrogen at 543 K and $10^5$ Pa for 24 h.

### *Procedure of Kinetic Study*

At the beginning of each new synthesis run the temperature was slowly increased to 493 K. After 1 week on stream the catalyst had reached a nearly constant activity and the kinetic investigations were started.

The degrees of hydrogen and carbon monoxide conversion were kept below $U_{CO+H_2} = 0.3$ in all the experiments by a high gas flow rate in order to exclude any effects of carbon dioxide and water on selectivity. For low partial pressures of carbon dioxide and water the influence of these reaction products on the reaction rate is assumed to be negligible.

In the kinetic experiments for the determination of reaction orders the temperature and the partial pressures were varied within the ranges

$$\begin{array}{lll} 493\ \mathrm{K} < T & & < 528\ \mathrm{K} \\ 1.6 & < P_{H_2}\ (10^5\ \mathrm{Pa}) < & 9 \\ 1.3 & < P_{CO}\ (10^5\ \mathrm{Pa}) < & 7 \\ 0.6 & < P_{H_2}/P_{CO} \quad < & 7.8. \end{array}$$

For evaluation of reaction orders of carbon monoxide the hydrogen pressure has been kept at a constant level and vice versa.

## RESULTS

The rate of hydrocarbon formation is expressed as a function of hydrogen and carbon monoxide pressure,

$$r_{0i} = k_{0i} P_{H_2}^{\beta_0} P_{CO}^{\gamma_0} \quad \mathrm{mol/h\ g\ (Fe)}$$
$$r_{0i} = \dot{n}_{0i}/m_K.$$

The rates of consecutive reactions are expressed as functions of 1-alkene or 2-alkene concentration and of hydrogen and carbon monoxide pressure,

$$r_{1i} = k_{ki} C_{ji} P_{H_2}^{\beta_1} P_{CO}^{\gamma_1} \quad \mathrm{mol/h\ g\ (Fe)}.$$

The gas-phase partial pressures of $H_2$ and CO can be converted into concentrations using Henry's law, a linear relationship between $P$ and $C$.

The index $k$ signifies the reaction which is denoted in Fig. 1. It has previously been shown that the reaction order with respect to alkenes is in every case close to unity (*17*).

For evaluation of orders only the unbranched hydrocarbons 1-alkene, 2-alkene, and alkane are considered. The formation of 3-alkene is negligible. The reaction rates $r_{ki}$ can be calculated using the set of balance equations

$$\dot{n}_{0i} = m_K r_{0i}$$

$$\dot{n}_{1i} = m_K((1 - A - B)r_{0i} - r_{1i} - r_{2i})$$

$$\dot{n}_{2i} = m_K(\mathrm{B} r_{0i} + r_{2i} - r_{4i})$$

$$\dot{n}_{4i} = m_K(\mathrm{A} r_{0i} + r_{1i} + r_{4i}).$$

Values of the flow rates of products $\dot{n}_{ji}$ are obtained from experiments. Note that in $\dot{n}_{ji}$ the index $j$ indicates the class of material and in $r_{ki}$ the index $k$ indicates the number of reaction given in Fig. 1.

As an example the evaluation of the reaction order with respect to carbon monoxide of the consecutive hydrogenation of 1-alkenes (to be referred to as Reaction 1) will be explained in detail. The evaluation of all other reaction orders and the numerous experimental results are described in full in Ref. (*18*).

For a carbon monoxide pressure $P_{CO} > 3 \times 10^5$ Pa the formation of alkane by hydrogenation of 2-alkene, $r_{4i}$, could be neglected (*18*). Then the alkane fraction at the reactor outlet is given by

$$\frac{\dot{n}_{4i}}{\dot{n}_{0i}} = A + \frac{m_K r_{1i}}{\dot{n}_{0i}}.$$

For $P_{CO} < 3 \times 10^5$ the hydrogenation of 2-alkene had to be taken into account. This more complicated procedure is described in detail in Ref. (*18*).

Since for evaluation of the carbon monoxide order the hydrogen pressure was kept constant, the rate of Reaction 1 is given by

$$r_{1i} = k_{1i} C_{1i} P_{H_2}^{\beta_1} P_{CO}^{\gamma_1} = k'_{1i} C_{1i} P_{CO}^{\gamma_1}.$$

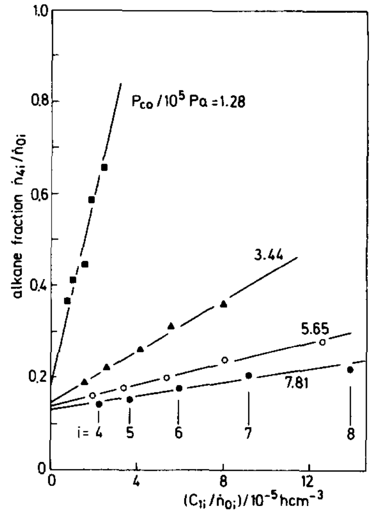

FIG. 3. Plot for evaluation of reaction rate constants; unpromoted catalyst $m_K$ = 28 g Fe, $T$ = 523 K, $P_{H_2}$ = 2 × $10^5$ Pa; $i$ = carbon number of alkane.

Then the alkane fraction is

$$\frac{\dot{n}_{4i}}{\dot{n}_{0i}} = A + k'_{1i} P_{CO}^{\gamma_1} \frac{C_{1i}}{\dot{n}_{0i}} m_K.$$

In Fig. 3 these fractions for alkanes with carbon number $i$ = 4–8 are plotted versus the ratio $C_{1i}/\dot{n}_{0i}$ for an unpromoted catalyst.

Previous studies (*18*) have shown that the alkane fraction of Fischer–Tropsch products formed in a slurry reactor can be generally described as a function of the mean residence time of 1-alkenes. This indicates that the reaction rate constant of the consecutive hydrogenation can be regarded as independent of the carbon number. In Fig. 3 for constant carbon monoxide pressures the data points which are attributed to alkanes of different carbon number can be represented by straight lines with the slope $k'_1 P_{CO}^{\gamma_1} m_K$. This linear relationship is expected because the consecutive hydrogenation is of first order with respect to 1-alkene and the reaction rate constant is independent of the carbon number (see Ref. (*16*, Fig. 8)).

The fraction $A \approx 0.15$ which represents the primarily formed alkanes was found to be independent of the carbon monoxide

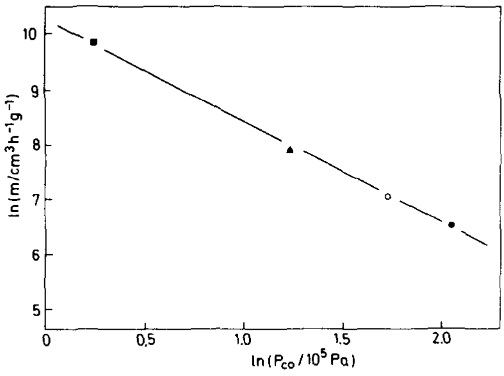

FIG. 4. Plot for evaluation of reaction order with respect to carbon monoxide; for reaction conditions and symbols, see Fig. 3.

pressure. The carbon monoxide order $\gamma_1$ of the consecutive hydrogenation of 1-alkenes was evaluated from the slope of the logarithmic plot $m = k'P_{\mathrm{CO}}^{\gamma_1}m_{\mathrm{K}}$ versus $P_{\mathrm{CO}}$ (see Fig. 4).

Table 1 lists the orders of the studied primary and consecutive reactions with respect to hydrogen and Table 2 those with respect to carbon monoxide. Taking into account the reproducibility of Fischer–Tropsch experiments and the accuracy of product analysis the standard deviation of the various reaction orders is about ±0.2.

There is no indication that the reaction orders of the primary and the consecutive reactions are affected by addition of alkali promoter. Differences are in the range of variations of reaction order evaluation. It is remarkable that the orders with respect to carbon monoxide of both consecutive reactions are about −2.

The reaction rate equation for the consecutive hydrogenation obtained from experiments

$$r_1 = k_1'P_{\mathrm{H_2}}\frac{C_{\text{1-en}}}{P_{\mathrm{CO}}^2}$$

may be interpreted by Langmuir–Hinshelwood kinetics writing

$$r_1 = k_1'P_{\mathrm{H_2}}\theta_{\text{1-en}},$$

where $\theta_{\text{1-en}}$ is the degree of 1-alkene coverage. Considering only competing adsorption of 1-alkene and carbon monoxide gives

$$\theta_{\text{1-en}} = \frac{k_{1(\mathrm{ad})}C_{\text{1-en}}}{1 + k_{1(\mathrm{ad})}C_{\text{1-en}} + k_{\mathrm{CO(ad)}}P_{\mathrm{CO}}}$$

and for strong carbon monoxide adsorption and weak 1-alkene adsorption

$$\theta_{\text{1-en}} = \frac{k_{1(\mathrm{ad})}C_{\text{1-en}}}{k_{\mathrm{CO(ad)}}P_{\mathrm{CO}}}.$$

The exponent 2 of carbon monoxide pressure obtained from experiments may be explained by different space requirements of carbon monoxide and of 1-alkenes. On the basis of the results of Arakowa and Bell (*6*)

TABLE 1

Orders of Reactions with Respect to Hydrogen

| Reaction | Alkali addition (g $K_2CO_3$/100 g Fe) | |
|---|---|---|
| | 0 | 2.0 |
| Synthesis of hydrocarbons; $\beta_0$ | +1.0 | +0.8 |
| Consecutive hydrogenation; $\beta_1$ | +0.9 | +0.8 |
| Consecutive isomerization; $\beta_2$ | 0 | 0 |

TABLE 2

Orders of Reactions with Respect to Carbon Monoxide

| Reaction | Alkali addition (g $K_2CO_3$/100 g Fe) | | | |
|---|---|---|---|---|
| | 0 | 0.1 | 0.2 | 0.6 |
| Synthesis of hydrocarbons; $\gamma_0$ | +0.2 | +0.2 | +0.1 | +0.1 |
| Consecutive hydrogenation; $\gamma_1$ | −1.9 | −1.6 | −2.1 | −1.7 |
| Consecutive isomerization; $\gamma_2$ | −1.7 | −2.0 | −1.9 | −2.1 |

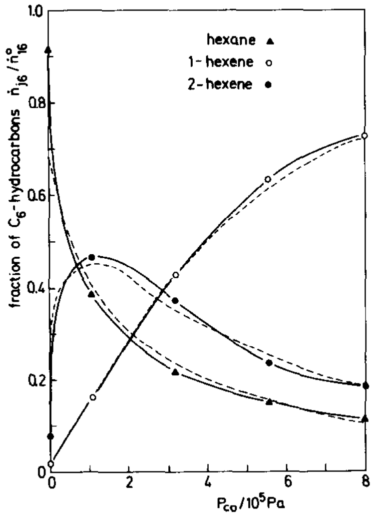

FIG. 5. Dependence of 1-hexene hydrogenation on carbon monoxide pressure: unpromoted catalyst $m_K$ = 28 g Fe; $T$ = 513 K; $P_{H_2} = 2 \times 10^5$ Pa; $\dot{n}^0_{1\text{-hexene}} = 0.02$ mol $h^{-1}$; $\dot{n}^0 = 3.2$ mol $h^{-1}$. The dashed curves are calculated by the kinetic model.

the adsorptions of hydrogen and of carbon monoxide are regarded as independent of each other so that the denominator does not contain a term due to hydrogen adsorption.

In this model the promoter effect of alkali would be manifested either in an increase in the adsorption constant $k_{CO(ad)}$ which causes a reversible deactivation of the catalyst or in a decrease in $k_1'$ due to a reduction of hydrogenation activity of the alkalized catalyst.

In order to decide between these two methods of interpretation, the hydrogenation of 1-hexene on alkalized and nonalkalized iron catalysts has been studied in the presence and in the absence of carbon monoxide. In every case the rate of 1-hexene formation by the synthesis is small compared to the flow rate of 1-hexene fed into the slurry reactor. In Fig. 5 the fractions of $C_6$ hydrocarbons leaving the reactor are plotted versus the carbon monoxide pressure for the unpromoted catalyst. In the absence of carbon monoxide more than 90% of the 1-hexene is hydrogenated to hexane. With increasing carbon monoxide pressure the hydrogenation of 1-hexene decreases. The fraction of 2-hexene passes through a maximum with increasing carbon monoxide pressure indicating that 1-hexene is isomerized in a first step to 2-hexene and subsequently hydrogenated. These curves can be well represented by the model of competitive adsorption,

$$r_1 = k_1' P_{H_2} C_{1\text{-en}} P_{CO}^{\delta}$$

hydrogenation of 1-alkene

$$r_2 = k_2' C_{1\text{-en}} P_{CO}^{\delta}$$

isomerization of 1-alkene

$$r_4 = k_4' P_{H_2} C_{2\text{-en}} P_{CO}^{\delta}$$

hydrogenation of 2-alkene.

The carbon monoxide order $\delta$ and the reaction rate constants were evaluated by fitting this kinetic model by use of the Nelder–Mead method to the experimental data. The obtained value $\delta \approx -1.5$ agrees reasonably well with the carbon monoxide orders between $-1.7$ and $-1.9$ obtained from the Fischer–Tropsch experiments (Table 2).

In Fig. 6 the fractions of $C_6$ hydrocarbons are plotted versus the carbon monoxide pressure for a catalyst promoted with 4.7 g $Cs_2CO_3$/100 g Fe. This catalyst has been

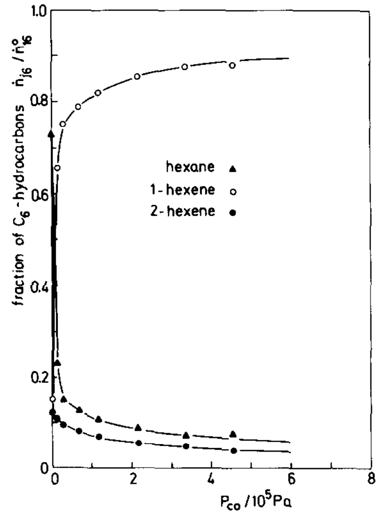

FIG. 6. Dependence of 1-hexene hydrogenation on carbon monoxide pressure: catalyst promoted with 4.7 g $Cs_2CO_3$/100 g Fe; $m_K$ = 31 g Fe; $T$ = 513 K; $P_{H_2}$ = 2 × $10^5$ Pa; $\dot{n}^0_{1\text{-hexene}} = 0.02$ mol $h^{-1}$; $\dot{n}^0 = 4.0$ mol $h^{-1}$.

chosen because $Cs_2CO_3$ shows the strongest promoter effect of all alkali carbonates (*20*). In the absence of carbon monoxide 75% of the 1-hexene is hydrogenated to hexane. It should be noted that the BET surface area of the alkalized catalyst ($\approx$22 $m^2$/g Fe) is smaller than that of the unpromoted catalyst ($\approx$35 $m^2$/g Fe) (*22*). Referring to the surface of the unpromoted catalyst and to the gas flow of that experiment a conversion of 1-hexene to hexane of 86% is calculated for the alkalized catalyst. Since for the unpromoted catalyst a conversion of 90% is observed the conclusion can be drawn that the promoter effect on the hydrogenation activity of the iron catalyst is negligible. However, in the presence of small amounts of carbon monoxide the hydrogenation activity abruptly decreases. Alkalization of the iron catalyst also causes the isomerization of 1-alkenes to 2-alkenes and to other alkanes with internal double bonds to be suppressed.

## DISCUSSION

In the absence of carbon monoxide both the unpromoted and the promoted catalyst show strong hydrogenation activity. However, in the presence of carbon monoxide a large difference between the hydrogenation activity of these two catalysts appears. From these results the conclusion can be drawn that the alkali promoter takes effect by an increase in the strength of carbon monoxide adsorption which causes an enhanced 1-alkene desorption and finally a decrease in the rate of consecutive hydrogenation.

Since both consecutive reactions show the same reaction orders with respect to carbon monoxide ($\gamma \approx -2$) and also with respect to 1-alkene ($\alpha \approx 1$) the given interpretation is also valid for the consecutive isomerization.

Recently Dictor and Bell (*21*) have interpreted the effect of alkali on 1-alkene selectivity by a reduction of the hydrogenation activity. On the basis of the experimental finding that for an unpromoted iron catalyst the ratio of alkenes with internal double bonds and total alkenes increases with increasing hydrogen pressure, the rate of isomerization has been assumed to be dependent on the hydrogen pressure similar to the response of the consecutive hydrogenation to hydrogen pressure. Therefore, they considered an adsorbed alkyl species formed by hydrogenation of 1-alkene as a common intermediate of both consecutive reactions. Then the decrease in the rates of both consecutive reactions can be interpreted by a reduced hydrogenation activity of the catalyst surface caused by alkali addition. However, a more detailed study of selectivity shows that this interpretation is not conclusive.

The present kinetic study has shown that the fractions of 2-alkene, $\dot{n}_{2i}/\dot{n}_{0i}$, and of 3-alkene, $\dot{n}_{3i}/\dot{n}_{0i}$, are independent of hydrogen pressure whereas the alkane fraction $\dot{n}_{4i}/\dot{n}_{0i}$ increases with increasing hydrogen pressure (*18*). Therefore, the experimental finding of Dictor and Bell that the ratio (2-alkene + 3-alkene)/total alkene,

$$\frac{\dot{n}_{2i} + \dot{n}_{3i}}{\dot{n}_{0i} - \dot{n}_{4i}} = \frac{\dot{n}_{2i}/\dot{n}_{0i} + \dot{n}_{3i}/\dot{n}_{0i}}{1 - \dot{n}_{4i}/\dot{n}_{0i}},$$

increases with increasing hydrogen pressure is the consequence of the positive hydrogen order of the consecutive hydrogenation of 1-alkenes. Accordingly, the kinetic model given in the present study is also consistent with the experimental results of Dictor and Bell (*21*).

## ACKNOWLEDGMENTS

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