Effects of manganese oxide and sulphate on the olefin selectivity of iron catalysts in the Fischer Tropsch reaction

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EFFECTS OF MANGANESE OXIDE AND SULPHATE ON THE OLEFIN SELECTIVITY OF IRON CATALYSTS IN THE FISCHER TROPSCH REACTION

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ABSTRACT

Although it has been claimed by various authors that the addition of manganese oxide, MnO, to an iron catalyst gives a marked increase in the olefin selectivity of iron catalysts, we have been unable to confirm these claims in Fischer Tropsch experiments at 513 K for an iron manganese oxide catalyst made from P.A. chemicals. After the initial very low activity of the catalyst, the increase in activity is associated with an increase of the ethane to ethene ratio. This increase is explained in terms of the formation of special hydrogenation ensembles. The iron manganese oxide catalyst was also studied during Fischer Tropsch synthesis with Mössbauer spectroscopy and X-ray diffraction. These investigations also failed to find differences between a pure iron catalyst, on which we have reported previously, and an iron manganese oxide catalyst. The latter catalyst forms in the course of a Fischer Tropsch synthesis experiment at 513 K about the same quantities of the carbides X-Fe₅C₂, c'-Fe₂₂C and FeₓC as a pure iron catalyst.

At 623 K the iron manganese catalyst deactivates quickly and selectively produces methane. However, when small quantities of a sulphate salt are added to an iron manganese oxide catalyst it remains rather stable at 623 K and produces light olefins very selectively. The production of methane as well as the deposition of carbon are hindered by this sulphate treatment.

INTRODUCTION

An intensive research effort is at present directed towards the development of iron catalysts which are selective for the production of light olefins.

Köbel et al. [1] prepared olefin selective catalysts with a low iron to manganese atomic ratio (1:9). Before the start of the Fischer Tropsch synthesis, their catalysts were activated with carbon monoxide at 513 K. Büssemeier et al. [2] developed an olefin selective catalyst by fusing iron catalysts with an iron: manganese atomic ratio of (1:1). They observed a low methane production, deviating very greatly from the Schulz-Flory distribution. Compared to a pure iron catalyst,
Yang and Oblad [3] observed in their iron manganese oxide catalysts an increased olefin selectivity even at a high iron to manganese atomic ratio (20:1).

In a previous publication [4], we described the behaviour of a pure iron catalyst during the Fischer Tropsch synthesis at 513 K and 100 kPa. The composition of the catalysts was investigated by Mössbauer spectroscopy and X-ray diffraction analysis. When carburized, that catalyst showed an ethane/ethene ratio of about 0.2 in the steady state, while the product distribution agreed well with the Schulz-Flory prediction.

In the present investigation we have studied the promotor effect of manganese oxide on Fischer Tropsch catalysts. Since it has been long known from the patent literature [5,6,7] and more recently from the work of Dalla Betta et al. [8], that the addition of small quantities of a sulphur containing compound resulted in an enhanced olefin content of the products, we have investigated that effect also. A review of the effect of sulphur is given by Madon and Shaw [9].

EXPERIMENTAL

Catalyst preparation

The iron manganese oxide catalysts were prepared by slowly adding ammonium hydroxide (12 wt % ammonia, Merck P.A., 45 mm$^3$ s$^{-1}$) to 3 dm$^3$ of a solution containing 0.25 kmol m$^{-3}$ iron(III) nitrate (Fe(NO$_3$)$_3$.9H$_2$O, Merck P.A.) and 0.16 kmol m$^{-3}$ manganese(II) nitrate (Mn(NO$_3$)$_2$.4H$_2$O, Riedel P.A.), which was heated to 365 K. An atomic ratio of Fe:Mn of 1.54 was used. The ammonia addition was stopped when a pH of 8 was reached. The precipitate was filtered off and washed with 200 cm$^3$ distilled water. The catalyst was dried at 395 K for 24 h and calcined at 675 K for one h. In all experiments a sieve fraction of 0.2 - 0.6 mm was used.

In the same way, manganese oxide was obtained starting from only manganese(II) nitrate.

A sulphated catalyst was prepared by suspending sufficient iron manganese oxide catalyst in an ammonium sulphate solution (0.01 kmol m$^{-3}$ (NH$_4$)$_2$SO$_4$, Merck P.A.) to give an Fe/S atomic ratio of 200:1. The water was evaporated at 368 K while the catalyst mass was stirred continuously. Thereafter, the same procedure was followed as is described in the unsulphated catalyst preparation after the filtration. After reduction with H$_2$ the catalyst had atomic ratios of Fe:Mn:S of 1.54:1:0.008. According to electron microprobe results, the sulphur containing groups were present as large clusters on the catalyst surface.

The experimental methods and analytical procedures have been described in a previous paper [4]. From carbon monoxide and hydrogen adsorption measurements, we estimate the sulphated and unsulphated catalysts to have an exposed iron surface of about 1.2 m$^2$ g$^{-1}$. 
**Nomenclature**

The hydrocarbon reaction rate $r$ is defined as the number of µmoles of CO converted into $C_1$ through $C_3$ hydrocarbons per kg of iron per second. The selectivity $S_j$ is defined as the ratio of the rate $r_j$ of formation of the product $j$ to the overall reaction rate:

$$S_j = \frac{r_j}{r} \quad (1)$$

The following further abbreviations will be used in this paper: I.S., isomer shift; $\Delta E_Q$, electric quadrupole splitting of a doublet; $H_{\text{eff}}$, magnetic hyperfine fields; $\varepsilon'$, line shift due to the interaction of the nuclear quadrupole moment with the electric field gradient in a magnetically split spectrum; $A$, total absorption of a spectrum.

**Catalyst testing**

Mössbauer spectra of the catalysts before and after reduction were analysed by fitting sets of Lorentzian line shapes to the observed spectra with the aid of a least squares method. In order to obtain results of physical significance, a number of constraints was imposed on the final fits to the spectra:

(i) Peaks belonging to the same subspectrum should have equal widths,
(ii) In the case of a doublet peak, intensities should be equal,
(iii) For a magnetically split spectrum or sextuplet, the intensities of the first and the sixth, of the second and the fifth and of the third and the fourth peaks should be pairwise equal,
(iv) Distances between peaks in the same sextuplet should satisfy the ratios following from the different g-factors for the ground and excited level of the $^{57}$Fe nucleus. In the presence of an electric field gradient (EFG) these ratios must be corrected for the interaction of the nuclear quadrupole moment with the EFG.

The more complex Mössbauer spectra of catalysts after Fischer Tropsch synthesis were analysed by fitting a linear combination of single-phase spectra of the constituents.

**RESULTS**

The iron manganese oxide catalyst before and after reduction

Figure 1 shows the Mössbauer spectra of the unreduced catalyst recorded at 4.2 K, 77 K and 259 K. The spectra obtained at room temperature have been analysed with the 'Lorentzian fitting procedure'; the results are listed in Table 1. The spectra show two components, labelled I and II.

Component I has the I.S. and $\varepsilon'$ of $\alpha$-Fe$_2$O$_3$, but $H_{\text{eff}}$ (507±2 kOe) is significantly lower than the 515 kOe field of bulk $\alpha$-Fe$_2$O$_3$. The subspectrum of component I at
FIGURE 1 Mössbauer spectra of the manganese oxide promoted iron catalyst recorded at the indicated temperatures before reduction.

TABLE 1
Mössbauer parameters at T = 295 K of catalysts before and after reduction.

<table>
<thead>
<tr>
<th>Component</th>
<th>I.S. *</th>
<th>$\Delta E_Q$</th>
<th>$\epsilon'$</th>
<th>$H_{eff}$</th>
<th>Relative area /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before reduction</td>
<td>I</td>
<td>0.64±0.03</td>
<td>-</td>
<td>0.09±0.03</td>
<td>50±2</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.59±0.02</td>
<td>0.67±0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>After reduction</td>
<td>I</td>
<td>0.26±0.03</td>
<td>-</td>
<td>0.00±0.01</td>
<td>332±2</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.48±0.06</td>
<td>0.55±0.06</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>1.35±0.06</td>
<td>0.63±0.06</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Relative to the standard NBS Standard SNP.

295 K is slightly asymmetrically broadened towards the lower hyperfine splittings. This broadening and the reduced value of $H_{eff}$ indicate that $\alpha$-$Fe_2O_3$ is present in small particles, with a distribution of particle diameters. Following Van der Kraan [10] an average diameter of 23±2 nm can be estimated for these $\alpha$-$Fe_2O_3$ particles.

Component II shows a doublet at 295 K, but is magnetically split at 77K and 4.2 K, with a broad distribution in $H_{eff}$. The average value of $H_{eff}$ at 77K and 4.2 K, and also the I.S. and $\Delta E_Q$ at 295 K, are characteristic of small particles of $\alpha$-FeOOH,
with a distribution in particle diameters. Based on the average hyperfine field and on the fact that the superparamagnetic transition temperature is lower than 295 K, it can be concluded [10] that the crystallite diameter is smaller than 8.5 nm.

It should be noted that estimates of particle diameters are presented under the assumption that Van der Kraan's results, obtained with samples of small particles of α-Fe₂O₃ or α-FeOOH, apply also to our samples in which Mn₂O₃ is also present.

According to X-ray diffraction data, the unreduced catalyst consists of α-Fe₂O₃, α-FeOOH and also Mn₂O₃. The relevant part of the X-ray diffraction pattern of the reduced pure manganese oxide is shown in Figure 2A. These data agree with the pattern of MnO, as is seen from Table 2.

TABLE 2
X-ray diffraction data of reduced Mn₂O₃ samples for angles 2θ between 40° and 80°.

<table>
<thead>
<tr>
<th></th>
<th>This study</th>
<th>Swanston et al. [11]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (°)</td>
<td>I (%)</td>
<td>2θ (°)</td>
</tr>
<tr>
<td>44.4±0.1</td>
<td>45</td>
<td>44.52</td>
</tr>
<tr>
<td>51.6±0.1</td>
<td>100</td>
<td>51.66</td>
</tr>
<tr>
<td>76.2±0.1</td>
<td>50</td>
<td>76.26</td>
</tr>
</tbody>
</table>

FIGURE 2 X-ray diffraction patterns of A) manganese oxide, MnO, B) a reduced manganese oxide promoted iron catalyst and C) as B after 16 h of Fischer Tropsch reaction at 513 K.
Mössbauer spectra of the iron manganese oxide catalyst after reduction are shown in Figure 3. The spectrum obtained at room temperature was analysed with the 'Lorentzian fitting procedure' as a combination of a sextuplet, labelled I, and two doublets, labelled II and III respectively. See Table 1 for the numerical results.

**TABLE 3**

<table>
<thead>
<tr>
<th>Component</th>
<th>295 K</th>
<th>77 K</th>
<th>4.2 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before reduction I</td>
<td>507±2</td>
<td>503±2</td>
<td>537±2</td>
</tr>
<tr>
<td>II</td>
<td>-</td>
<td>470±5*</td>
<td>502±5*</td>
</tr>
<tr>
<td>After reduction I</td>
<td>332±2</td>
<td>339±2</td>
<td>341±2</td>
</tr>
<tr>
<td>II</td>
<td>-</td>
<td>495±5*</td>
<td>513±5*</td>
</tr>
</tbody>
</table>

*Average value

**FIGURE 3** Mössbauer spectra of the manganese oxide promoted iron catalyst recorded at the indicated temperature after the reduction.

Component I is easily identified as α-Fe. The parameters of component II are those of a paramagnetic Fe$^{3+}$ compound, while the parameters of component III are more indicative of Fe$^{2+}$, although $\Delta E_Q$ is rather small for a Fe$^{2+}$ compound.
At temperatures of 77 K and 4.2 K, components II and III are magnetically split, each with a distribution in hyperfine fields. Estimated averages of $H_{\text{eff}}$ for component II are given in Table 3; these values support the conclusion that II is a Fe$^{3+}$ compound. The subspectrum of component III is very broad and difficult to observe at these low temperatures, so that even a rough estimation of its Mössbauer parameters seems hardly warranted.

The contribution of α-Fe to the Mössbauer spectrum obtained at 295 K is (80±3)%, so it can be concluded that the main part of the iron oxide that was present in the precipitated catalyst has been reduced.

![Diagram of reaction rate and selectivities](image)

**FIGURE 4** A) Reaction rate during Fischer Tropsch synthesis on a Fe/MnO catalyst at 513 K, B) the corresponding methane, ethane and ethene selectivities.

The X-ray diffraction pattern (see Figure 2D) showed clearly the diffraction line of reduced iron (at $2\theta = 57^\circ$), while the compounds containing Fe$^{2+}$ and Fe$^{3+}$ were not observed, probably because of their small dimensions. A remarkable shift of the MnO diffraction lines occurred in the direction of the α-Fe diffraction line, which cannot be explained by the spinel structures of iron and manganese oxide. It is likely that this shifted MnO pattern and the presence of the unreduced iron compounds containing Fe$^{2+}$ and Fe$^{3+}$ reflects the interaction between the iron...
compounds and the promotor MnO.

**Fischer Tropsch synthesis on an iron manganese oxide catalyst**

The composition of the catalyst during the synthesis at 513 K was studied by Mössbauer spectroscopy and X-ray diffraction analysis; for this a number of catalysts after increasing periods of reaction was investigated. For each experiment a fresh catalyst sample was used, taken from the same batch of unreduced material.

With the promoted catalyst we found differences of about 10% in the reaction rate between the various experiments after the same period of Fischer Tropsch synthesis. The accuracy of the product analysis itself was better than 1%. Probably the differences observed were due to poor reproducibility of the reduction of these promoted catalysts. Because the product distributions did not differ and the general shape of the curves of the reaction rate were comparable, we believe that these experiments still give a good qualitative picture of the catalyst behaviour during the Fischer Tropsch reaction. The reaction rate and the selectivities for methane, ethane and ethene are shown in Figure 4.

This catalyst needed about 5 ks before the maximum activity was reached; in that period the ethane to ethene ratio increased drastically, as is shown in Figure 5. During the deactivation of the catalyst the ethane to ethene ratio decreased again. The ethene selectivities of the MnO promoted and pure iron catalysts were about equal at corresponding reaction periods.

![Figure 5 Ethane to ethene ratio during Fischer Tropsch synthesis over an unsulphated (solid line) and a sulphated (broken line) Fe/MnO catalyst at 513 K.](image)

Fischer Tropsch synthesis at 513 K on several iron manganese oxide catalysts with differing manganese oxide contents showed no relation between the olefin selectivity of the catalyst and the amount of manganese oxide added.

Mössbauer spectra of the catalyst after various periods of Fischer Tropsch synthesis at 513 K are shown in Figure 6. The spectra were analysed by fitting a
FIGURE 6 Mössbauer spectra of the reduced Fe/MnO catalyst after different periods of Fischer Tropsch synthesis at 513 K. Spectra were recorded at room temperature.

linear combination of base spectra to the measured spectra. The Mössbauer spectra which were used as a base are the single phase carbide spectra used in our previous study [4], completed with the spectra of α-Fe and the subspectra of doublets belonging to the unreduced iron phases in the catalyst after reduction. Results of this analysis are shown in Figure 7.

According to the Mössbauer spectra and the X-ray diffraction pattern (Figure 6), the α-Fe is converted into the carbides ε'-Fe$_{2.2}$C and x-Fe$_{5}$C$_{2}$. In this conversion Fe$_{x}$C, which is known from our Mössbauer and X-ray investigation to represent poorly defined structures between α-Fe and a crystallographically well defined carbide, appears as an intermediate.

The X-ray diffraction lines of MnO are still the same as those in Figure 2B; because the contribution of the unreduced iron phases Fe$^{2+}$ and Fe$^{3+}$ is also constant during the time interval studied, these results indicate that during the Fischer Tropsch synthesis not much reduction or oxidation of the catalyst occurs.

When the synthesis gas mixture is led over pure MnO, no reaction products are formed at 513 K.
Fischer Tropsch synthesis on sulphur containing iron manganese oxide catalysts

The reaction rate and the selectivities of the sulphate impregnated iron manganese oxide at 513 K are shown in Figure 8. The maximum reaction rate is lower than the maximum rate of the original iron manganese oxide catalyst but, as the final activities are about equal, evidently the sulphated catalyst also deactivates less. The smaller deactivation is accompanied by a higher ethane to ethene ratio during the complete time interval studied, as is shown in Figure 5.

The Mössbauer spectrum of the reduced sulphated catalyst contains contributions of the same subspectra as the unsulphated catalyst, only the contribution of α-Fe for the former is less, so the degree of reduction is somewhat lower for the sulphated catalyst.

However, after a reaction period of 30 ks iron is still present in the sulphated catalyst (see Figure 9); probably the sulphur compounds prevent this iron from being carbided by the synthesis gas. The composition of the spectra with respect to the carbides is not essentially different. Here also the phase $\text{Fe}_x\text{C}$ remains visible in the spectra as long as α-Fe is present.

In the introduction we mentioned that manganese oxide has been advocated as an effective promotor of Fischer Tropsch catalysts to produce light olefins. Because the unsulphated as well as the sulphated iron manganese oxide catalysts behave at
FIGURE 8  A) Reaction rate during Fischer Tropsch synthesis on a sulphated Fe/MnO catalyst at 513 K. B) The corresponding methane, ethane and ethene selectivities.

FIGURE 9  Relative contributions from reduced α-Fe to the Mössbauer spectra during Fischer Tropsch synthesis over A) an unsulphated Fe/MnO catalyst (o) and B) a sulphated Fe/MnO catalyst (∆) at 513 K.

513 K in about the same way as a pure iron catalyst, i.e., no beneficial influence on the olefinicity is found at this temperature; the catalysts were further studied
at a reaction temperature of 623 K.

At 623 K the reaction rate of the pure iron catalyst increases very quickly, but the catalyst is deactivated within 3.6 ks by the formation of inactive graphite carbon species (after a short initial period of a few minutes the carbon deposition increases at a constant rate of 3 wt % carbon h\(^{-1}\)). The methane selectivity varies between 80 and 90 %.

The activation and deactivation of the manganese oxide promoted iron catalyst proceeds at 623 K just as found for the pure iron catalyst, although a little more activity remains (see Figure 10) and the main product is also methane.

However, the sulphate impregnated iron manganese oxide catalyst behaves totally differently at 623 K, as is also shown in Figure 10. The catalyst is again quickly

\[ \text{(\mu mol CO)} / (\text{kg Fe}_2 \text{O}_3) \]

\[ \% \]

FIGURE 10 Reaction rates during Fischer Tropsch synthesis at 623 K over A) an unsulphated Fe/MnO catalyst (solid line) and over a sulphated Fe/MnO catalyst (broken line); B) the methane, ethane and ethene selectivities on a sulphated Fe/MnO catalyst.
activated, but the reaction rate remains rather high. Even more remarkable is the observation that the main product is no longer methane, but ethene. The ethane/ethene ratio levels out to a value of about 0.03 after 50 ks Fischer Tropsch reaction at 623 K.

Unfortunately, the mechanical strength of this particular sulphated catalyst was much lower than that of the unsulphated iron manganese oxide catalyst. On the sulphated as well as the unsulphated catalyst very much carbon is deposited at 623 K, but the sulphated catalyst particles disintegrate to a fine powder after a few hours; this effect causes a slow increase in the reaction rate after 25 ks.

The addition of higher quantities of ammonium sulphate to the iron manganese oxide catalyst results in an improved resistance against the deposition of carbon, thus preventing catalyst disintegration, while the olefin selectivity remains very high. However, the amounts of sulphate added have to be restricted to below 1 wt % sulphur, otherwise the catalyst is completely deactivated. In our laboratory, Kieffer [12] has produced quantitative data about the optimum addition of sulphate to Fe/ZnO catalysts and found these catalysts to be very stable and very selective.

DISCUSSION

The degree of reduction of the sulphated and unsulphated catalysts varies between 70 and 80 %. The rather small quantities of unreduced Fe$^{2+}$ and Fe$^{3+}$ compounds are observed as superparamagnetic phases in Mössbauer spectroscopy; these compounds also cause the shift of the X-ray diffraction lines of MnO. During the Fischer Tropsch reaction the amount of the unreduced iron does not change. These unreduced iron compounds are probably associated with the MnO phase of the catalyst. Reduction at higher temperatures leads to a lower activity, presumably due to sintering.

The increase of the reaction rates on unsulphated and sulphated catalysts during the first 3 ks at 513 K was accompanied by an increase of the ethane to ethene ratio. This was also observed on pure iron catalysts by Ott et al. [13] and also in our laboratory. As we have some indications from experiments in our laboratory [12,14] that the hydrogenation reactions involved in the formation of methane and in the formation of higher paraffins are different in nature, we will, for a discussion of the hydrogenation activity, restrict ourselves to a comparison of the formation of ethane and ethene, as we may assume that these products are formed from the same precursor. In a recent kinetic study, Rautavauma and Van der Baan [15] conclude that the precursors C$_n$H$_{2n}$** are bound to the catalyst surface with one carbon atom to two metal sites. We will thus assume that ethane and ethene are formed according to the following reactions:

$$C_2H_4^{**} \xrightarrow{k_1} C_2H_4 + 2* \quad \text{fast equilibrium}$$

(2)
\[ C_2\text{H}_4^{**} + 2\text{H}^* \xrightarrow{k_2} C_2\text{H}_6 + 4^* \]  

(3)

The formation rates of these products can be expressed as:

\[ \frac{r_{C_2\text{H}_4}}{r_{C_2\text{H}_6}} = \frac{k_{e}C_2\text{H}_4}{k_{e}C_2\text{H}_4 + \theta^2} \]  

(4)

\[ \frac{d(C_2\text{H}_6)}{dt} = k_{e}C_2\text{H}_4 \cdot \theta^2 \]  

(5)

where \( F \) is the gas rate in \( m^3 \text{ s}^{-1} \), \( W \) the catalyst weight in kg, \( (C_2\text{H}_4) \) the concentration of ethene in kmol m\(^{-3} \) and \( K \) the ratio between \( k_1 \) and \( k_{e} \).

As (2) and (3) are parallel reactions starting from the same substrate we can write:

\[ \frac{r_{C_2\text{H}_6}}{r_{C_2\text{H}_4}} = k' \cdot \theta^2 \cdot \theta_H \cdot \frac{W}{F} \]  

(6)

The surface coverage of empty sites \( \theta_e \) will presumably decrease in the course of a reaction and therefore can initially not be very low. The low ethane to ethene ratio is then caused by either a low surface coverage of hydrogen \( \theta_H \) or by a low number of ensembles of sites that can perform the hydrogenation reaction. Since we expect that the equilibrium of the dissociative hydrogen adsorption is quickly reached, we suggest that \( k' \) must increase in the course of the reaction, i.e., that the iron surface requires first some kind of activation by which action the hydrogenation ensembles are formed.

If we would assume with Sachtler et al. [17] that the surface compounds are of the composition \( C_n\text{H}_{2n+1} \) and single bonded, we can derive relations that lead to the same conclusions as have been derived on the basis of equation (6).

The deactivation of the catalysts is accompanied by a decrease of the ethane to ethene ratios. This decrease can be caused by carbon deposition that results in a decrease of either the hydrogenation ensembles mentioned above or of the empty sites \( \theta_e \) or even of both. The former factor influences \( k' \) of equation (6), whereas the latter has its influence on both \( \theta_e \) and \( \theta_H \).

As during the overall deactivation process the rate of ethene formation actually increases, we are inclined to ascribe this deactivation to a decrease in empty
sites, for that would, according to equation (4), explain the observed rate increase for ethene.

As opposed to an iron catalyst a cobalt catalyst has a high initial activity; on these cobalt catalysts some deactivation is observed, which is also coupled with a decreasing ethane to ethene ratio [16].

During the activation/deactivation process the sulphated catalyst is always somewhat less active than the unsulphated catalyst, although in the final (pseudo) steady state the difference in activity is small. It is noteworthy that during the whole activation/deactivation process at 513 K the ethane to ethene ratio is higher for the sulphated catalyst than for the unsulphated catalyst.

Since no relation has been found at 513 K between the olefin selectivity of the catalyst and the amount of manganese oxide added, the manganese oxide itself is not considered to be an effective promotor for the production of light olefins. This is not in agreement with the results of Köbel [1], Büssemeier [2] and Yang [3]. We also did not observe any influence of manganese oxide additions on the molecular mass distribution of the product mixture. A fully carburized iron manganese oxide catalyst revealed a Schulz-Flory distribution which was quite similar to that of a carburized iron catalyst without manganese oxide.

However, a great difference between sulphated and unsulphated catalysts is observed at higher temperatures. The sulphated catalysts are stable at 623 K and give a product with a high olefin content and a relatively low \( \text{CH}_4 \) production, whereas the unsulphated catalyst deactivates quickly and produces only methane. Kieffer [12] has argued that the effect of sulphur is basically an increased stability of the catalyst at higher temperatures and that the higher olefinicity is mainly caused by the higher reaction temperature.

Results comparable to those we obtained with sulphated catalysts at 623 K were obtained by Büssemeier [21] with manganese promoted iron catalysts. In connection with our negative results with manganese oxide alone, we are inclined to think that the olefin selectivity of the catalysts of Büssemeier is caused by one of the other further promotors that are added to his catalysts, or to the use of less pure starting materials.

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