FACTORS AFFECTING THE EXTENT OF BRANCHING IN FISCHER-TROPSCH SYNTHESIS PRODUCTS WITH IRON-BASED CATALYSTS

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Summary

Branched products are mainly formed during secondary isomerization reactions, and not in the main synthesis reaction itself. The extent of branching is a function of the catalyst formulation. High acidity and a low hydrogenation strength of the catalyst (normally found in catalysts with a high basicity) favour branching. The latter can be explained by the fact that the rate of skeletal isomerization of alkenes is much higher than the rate of hydrogenation. If the former rate is higher than the latter, hydrogenation will take place rapidly before any isomerization can occur. Little variation with time on stream is observed in the extent of branching with non-acidic catalysts. Acidic catalysts yield initially a much more branched product, the extent of which decreases with time on stream, to eventually reach levels only marginally higher than those observed with non-acidic catalysts.

The extent of branching is different for products with different carbon numbers. It does not follow a random probability pattern, as results from a hydrocarbon synthesis in which single carbon units are linked to the growing chains at random places, but rather a pattern which depends on the hydrogenation strength of the catalyst used. With low hydrogenation strength catalysts, branching occurs preferentially in the lighter products. Branching is favoured in the heavier products when higher hydrogenation strength catalysts are used. This is explained in terms of the higher surface mobility of lighter products.

Introduction

The extent of branching of hydrocarbons greatly affects the reactivity of olefins and the quality of gasoline and diesel oil produced. Since the Fischer-Tropsch synthesis products are predominantly linear hydrocarbons, very few studies on factors affecting the extent of branching in Fischer-Tropsch products have been reported to date. Frohning et al. [1] report that the concentration of branched hydrocarbons produced with iron catalysts...
increases with their carbon number. Anderson [2] supports this observation
and adds that the extent of branching was greater for hydrocarbons from
iron catalysts than those produced with cobalt catalysts. In a review [3]
the same author points out that the hypothesis has been proposed that the
main sequence of chain growth leads only to straight chains, and methyl-
substituted species are produced by the incorporation of propene into the
growing chain. A survey of available data led to the conclusion that propene
incorporation does indeed occur on Co, but not to any appreciable extent
on Fe. However, incorporation and kinetic studies suggest that propene is
not an important source of branched species. Moreover, attributing all the
branched molecules being produced to propene requires the consumption of
a ridiculously large amount of propene.

Pichler and Schulz [4] have suggested a reaction scheme where
branched hydrocarbons are produced via methylation by surface methyl
groups. Since there are presumed to be few CH₃ units present on the surface,
the scheme has the merit that it predicts a low degree of branching, as is
indeed observed in practice. However, Dry [5] points out that the reaction
scheme fails to account for the very considerable production of oxygenated
molecules over Fe catalysts and also over Co catalysts at lower temperatures.

Leconte et al. [6] observed that catalysts giving the highest degree of
branching give the lowest degree of secondary hydrogenation of primary
between the silica content of silica-supported iron catalysts and the branched
hydrocarbon product selectivities.

To date, no adequate explanation of the factors affecting the extent of
branching is available. It is the purpose of this communication to investigate
such factors by addressing in particular the following questions:

(i) Does the extent of branching of any given hydrocarbon in the
product obtained with various catalysts vary with time on stream?
(ii) Does the extent of branching of any given hydrocarbon in the
product obtained with various catalysts vary with the catalyst formulation?
(iii) Is the extent of branching of saturated and unsaturated products
equal for any given carbon number?
(iv) Does the extent of branching of alkanes follow a random
probability pattern and, if not, is there a correlation with the catalyst
formulation?

Methods and definitions

The number of isomers which may exist for any given hydrocarbon
increases rapidly with their carbon number. If it is assumed that the
formation of the isomers is random, i.e. no catalytic or other influence
causes the preferential formation of one or more isomers, then the theoretical
random extent of branching can be expressed as the ratio of the probabili-
ties for the formation of a branched isomer, P(B), and that for the
formation of a linear isomer, \( P(L) \). Random probability calculations result in:

\[
P(B)/P(L) = 0.5 \frac{n_C(n_B/n_L + 1) - 1}{n_C/n_L - 1}
\]

where \( n_C \) is the number of carbon atoms in the feed molecule from which the product molecule is to be formed by addition of a single carbon atom; \( n_L \) and \( n_B \) are the number of linear and branched isomers, respectively, in the feed mixture. Use of the relation can be demonstrated with the following example.

Up to \( C_3 \), no branching is possible. Formation of \( C_4 \) alkanes by random addition of a single \( C \) unit to any of the three \( C \) atoms of a \( C_3 \) molecule results in twice as many linear as branched \( C_4 \) alkanes. In \( C_4 \) formation, \( n_C = 3, n_L = 1 \) and \( n_B = 0 \). Consequently \( P(B)/P(L) = 0.5 \). Formation of \( C_5 \) from this mixture of \( C_4 \) alkanes entails \( n_C = 4, n_L = 2 \) and \( n_B = 1 \), resulting in \( P(B)/P(L) = 2 \). Values for some lower alkanes are given in Table 1.

In order to obtain a measure of the extent of branching in the hydrocarbon products obtained from the various catalysts studied in this work, a branching index for hydrocarbons, \( B_{I_n}^u \) (unsaturated) or \( B_{I_n}^s \) (saturated), is introduced. The index is defined as the ratio of the sum of the concentrations of branched saturated (s) or unsaturated (u) hydrocarbons having \( n \) carbon atoms, and the sum of the concentrations of the corresponding linear isomers.

The relative extent of branching of the hydrocarbons as a function of the carbon number involved may then be arrived at by normalizing the indices in such a way that the index for butanes is unity. Values derived in this fashion can be compared directly with the \( P(B)/P(L) \) values listed in Table 1, so that any deviation from the random formation statistics can be revealed.

Some difficulty is experienced in determining the index values because of the number of isomers involved. This problem is particularly severe in the case of alkenes. Positive identification, in particular of \( C_5 \) alkenes, is not always practicable. The number of possible isomers of the corresponding alkanes is much lower, and positive identification of these compounds up to the hexanes is in most cases possible. Therefore, only the indices for \( C_4-C_6 \) alkanes and \( C_4 \) alkenes were determined.

**TABLE 1**

**Possible number of isomers and extent of branching of alkanes**

<table>
<thead>
<tr>
<th>Carbon number</th>
<th>Number of branched isomers</th>
<th>( P(B)/P(L) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Experimental

The catalysts used in this study were prepared by partial degradation of iron complexes [8]. The oxidic catalyst precursors have the general formula Fe_<x>O_<y>C_<z>, where the values for x and y are close to 2 and 3 respectively. The value for z has been shown with scanning Auger electron microscopy to be between 0.5 and 1 in the outermost surface layer of the precursor, and decreases to approach zero at the fourth atomic subsurface layer. K-promotion was effected by means of incipient wetness impregnation.

The behaviour of the catalysts studied has been reported elsewhere, separately, for three groups of catalyst: unsupported [9], semi-supported [10] and supported [11] complex-derived catalysts. The unsupported catalysts are compared with an alkalized fused iron ammonia synthesis catalyst BASF 6 - 10, designated catalyst BASF. Unpromoted complex-derived iron is denoted as catalyst C-Fe, iron–cobalt (atomic ratio Fe/Co = 1) as catalyst C-FeCo, and the latter catalyst promoted with 0.4 atm.% K as catalyst C-FeCo–K. Semi-supported catalysts are mixed-metal oxides prepared by the complex method, containing iron and another metal in equiatomic amounts. Four different materials were used: C-Fe–Ca, C-FeMg, C-FeMn and C–FeAl. Only one supported catalyst was used in this study, complex-derived iron on a low-acidity amorphous silica–alumina [12, 13] containing 1 mass % Fe, designated catalyst Fe–SA.

The catalyst precursors were crushed, screened to particle sizes in the range of 0.2 to 0.6 mm and partially reduced in a hydrogen flow (VHSV = 2000) at a pressure of 300 kPa. The reduction temperature was kept at 433 K for 3 - 5 h and subsequently at 573 K for 16 - 20 h.

The catalytic behaviour of the materials was evaluated in a fixed bed microreactor system [14] based on the concentric tube design [15]. The product was analyzed by means of a sophisticated on-line gas chromatographic data system [16 - 18]. Reaction was carried out at a pressure of 2.0 MPa, a temperature of 543 K and a flow (VHSV = 1000) of synthesis gas with a mol ratio H₂/CO = 0.5.

Unsupported catalysts

Except for a slight decrease during the first 100 ks on stream, no significant change is observed in the index values of hydrocarbons obtained from the unsupported iron-based catalysts. Variations during the initial synthesis periods are not unexpected, since during this time variations in the catalyst structure and associated catalytic behaviour are known to occur. It is, however, of interest to note that the initial product obtained from the catalysts is somewhat more branched. Typical values obtained with the four catalysts are reported in Table 2.

All index values obtained with catalyst C-FeCo are lower than those obtained with the other catalysts, indicating that the hydrocarbons in the
TABLE 2
Branching indices for the product obtained with unsupported iron-based catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Olefin selectivity (% m/m)</th>
<th>BI$_4^u$</th>
<th>BI$_4^s$</th>
<th>BI$_5^s$</th>
<th>BI$_6^s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASF</td>
<td>80</td>
<td>0.095</td>
<td>0.098</td>
<td>0.178</td>
<td>0.192</td>
</tr>
<tr>
<td>C-Fe</td>
<td>80</td>
<td>0.088</td>
<td>0.085</td>
<td>0.180</td>
<td>0.195</td>
</tr>
<tr>
<td>C-FeCo–K</td>
<td>68</td>
<td>0.074</td>
<td>0.049</td>
<td>0.120</td>
<td>0.140</td>
</tr>
<tr>
<td>C-FeCo</td>
<td>56</td>
<td>0.066</td>
<td>0.028</td>
<td>0.104</td>
<td>0.138</td>
</tr>
</tbody>
</table>

The product obtained from this catalyst are less branched. Therefore, it can be concluded that the extent of branching of the catalyst is influenced by the catalyst formulation.

In the case of catalysts BASF and C-Fe, a good agreement exists between the values for alkenes and alkanes, suggesting that the latter have been formed from the former by hydrogenation only.

In contrast, with catalyst C-FeCo the product is characterized by alkanes which are branched to a lower extent than is the case for the alkenes. Since branched alkenes are known to be hydrogenated more slowly than their linear isomers, a possible explanation for the observation is that when primary products undergo secondary hydrogenation, the linear alkenes are preferentially hydrogenated. An additional explanation is that as a consequence of the higher hydrogenation activity of the cobalt-containing catalyst, hydrogenation occurs so rapidly that the probability of a perhaps possible but less rapid isomerization, decreases.

Promotion of catalyst C-FeCo with K results in a more branched product, albeit not as branched as that obtained with catalyst Fe. The difference in extent of branching between alkenes and alkanes has decreased, but is still significant.

The relative extent of branching of alkanes (Table 3) does not follow the random probability pattern shown in Table 1, but rather one which depends on the type of catalyst used. Two entirely different patterns may be discerned. At one extreme, with catalyst BASF, the values suggest that branching occurs preferentially in the lighter products. At the other extreme, with catalyst C-FeCo, branching is favoured in the heavier products. The other two unsupported catalysts show intermediate behaviour. The pattern obtained definitely seems to be related to the catalyst formulation.

In line with reports by Leconte et al. [6], it is suggested that all results presented above can be explained in terms of the hydrogenation activity of the four catalysts. For this reason, the catalysts are listed in Tables 2 and 3 in the order of increasing hydrogenation activity, as judged on the basis of olefin selectivity (Table 2). In passing, it may be noted that the catalysts are then automatically listed in the order of decreasing basicity [8].
TABLE 3
Relative extent of branching of light alkanes in the product obtained with unsupported iron-based catalysts, as compared with literature data [20]

<table>
<thead>
<tr>
<th>Catalysta</th>
<th>Butanes</th>
<th>Pentanes</th>
<th>Hexanes</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASF</td>
<td>1.0</td>
<td>1.5</td>
<td>1.8</td>
</tr>
<tr>
<td>C-Fe</td>
<td>1.0</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>C-FeCo–K</td>
<td>1.0</td>
<td>2.4</td>
<td>2.9</td>
</tr>
<tr>
<td>C-FeCo</td>
<td>1.0</td>
<td>3.7</td>
<td>4.9</td>
</tr>
<tr>
<td>I</td>
<td>1.0</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>II</td>
<td>1.0</td>
<td>2.3</td>
<td>3.2</td>
</tr>
<tr>
<td>III</td>
<td>1.0</td>
<td>2.6</td>
<td>4.5</td>
</tr>
<tr>
<td>IV</td>
<td>1.0</td>
<td>2.9</td>
<td>5.0</td>
</tr>
</tbody>
</table>

aI and II are Sasol fused iron Arge catalysts used at 2.1 MPa and at 493 and 514 K respectively. Catalyst III is a Sasol Synthol catalyst used at 2.2 MPa and 593 K. Catalyst IV consists of 100 Co/100 kieselguhr/18 ThO2 and is used at atmospheric pressure and 462 K.

In view of reports by Dartigues et al. [19], which show increasing skeletal isomerization activity with decreasing hydrogenation activity with Pt catalysts, an effect which is considered to be of more general applicability, it is not unreasonable to expect the isomerization activity to decrease in the same order as the catalysts are listed.

Since the catalyst with the highest hydrogenation activity is expected to have the lowest skeletal isomerization activity, its products may be expected to be closest to those originally produced in the hydrocarbon synthesis, i.e. the product distribution is not greatly influenced by concurrent isomerization processes. Therefore, the data presented in Table 3 suggest that branching is preferentially produced in the heavier products and that no random process is followed.

This conclusion is supported by results reported by Pichler et al. [20] (Table 4). These data and that in Table 3 contradict Anderson's observation that chain branching is greater with Fe than with Co catalysts [3]. It is possible that the observation is biased as a result of differences in the reactor temperatures employed. In Table 4, it is seen clearly that an increase of only 21 K results in a large difference in the indices obtained with fixed bed Fe catalysts. A similar difference is observed for the Co catalysts at 463 K (Table 4) and 543 K (Table 3).

The influence of temperature and catalyst formulation on the extent of branching can be used to advantage, as shown in Table 4. Sasol's Arge process is geared towards the production of diesel oil and waxes, and hence the production of branched hydrocarbons is undesirable. By choosing proper conditions of temperature and catalyst formulation (catalyst II, Table 4), this criterion is met. In fact, the index values increase only slightly with increasing carbon number, to level out at a maximal value of about 0.06 at C6. However, in Sasol's Synthol process, the emphasis lies on the production
TABLE 4
Branching indices calculated from literature data [20]; catalysts I to IV refer to literature data described in Table 3.

<table>
<thead>
<tr>
<th>Branching index</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi_{14} u+s</td>
<td>0.037</td>
<td>0.042</td>
<td>0.092</td>
<td>0.048</td>
</tr>
<tr>
<td>Bi_{15} u+s</td>
<td>0.054</td>
<td>0.096</td>
<td>0.242</td>
<td>0.139</td>
</tr>
<tr>
<td>Bi_{16} u+s</td>
<td>0.064</td>
<td>0.133</td>
<td>0.414</td>
<td>0.241</td>
</tr>
<tr>
<td>Bi_{17} u+s</td>
<td>0.063</td>
<td>0.159</td>
<td>0.721</td>
<td>0.359</td>
</tr>
<tr>
<td>Bi_{18} u+s</td>
<td>0.066</td>
<td>0.181</td>
<td>0.866</td>
<td>0.473</td>
</tr>
<tr>
<td>Bi_{19} u+s</td>
<td>0.062</td>
<td>0.185</td>
<td>0.988</td>
<td>0.580</td>
</tr>
<tr>
<td>Bi_{20} u+s</td>
<td>0.066</td>
<td>0.193</td>
<td>1.000</td>
<td>0.656</td>
</tr>
<tr>
<td>Bi_{12} u+s</td>
<td>0.058</td>
<td>0.185</td>
<td>0.955</td>
<td>0.789</td>
</tr>
<tr>
<td>Bi_{13} u+s</td>
<td>0.056</td>
<td></td>
<td>1.469</td>
<td>0.812</td>
</tr>
<tr>
<td>Bi_{14} u+s</td>
<td>0.058</td>
<td></td>
<td>1.358</td>
<td>1.062</td>
</tr>
<tr>
<td>Bi_{15} u+s</td>
<td>0.052</td>
<td></td>
<td>1.695</td>
<td>1.146</td>
</tr>
<tr>
<td>Bi_{16} u+s</td>
<td>0.059</td>
<td></td>
<td>1.725</td>
<td>1.152</td>
</tr>
<tr>
<td>Bi_{17} u+s</td>
<td>0.056</td>
<td></td>
<td>2.268</td>
<td>1.289</td>
</tr>
<tr>
<td>Bi_{18} u+s</td>
<td>0.059</td>
<td></td>
<td>2.367</td>
<td>1.268</td>
</tr>
</tbody>
</table>

of gasoline, and thus on branched hydrocarbons. The results attained with catalyst III indicate that a highly branched product can be obtained with Fe catalysts. In this case the index values rise steeply with increasing carbon number, and no maximal value is observed in the reported range up to \( n_C = 17 \).

Semi-supported catalysts

As is the case with the unsupported catalysts, no significant changes are observed in the branching indices of hydrocarbons obtained from the semi-supported catalysts, except for a slight decrease during the first 100 ks on stream. Typical values obtained with the four catalysts are reported in Table 5, where it is shown that the indices do vary with catalyst formulation.

TABLE 5
Branching indices for the product obtained with semi-supported iron-based catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Olefin selectivity (% m/m)</th>
<th>Bi_{14} u</th>
<th>Bi_{14} s</th>
<th>Bi_{15} s</th>
<th>Bi_{16} s</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-FeCa</td>
<td>70</td>
<td>0.071</td>
<td>0.044</td>
<td>0.128</td>
<td>0.151</td>
</tr>
<tr>
<td>C-FeMg</td>
<td>81</td>
<td>0.076</td>
<td>0.065</td>
<td>0.144</td>
<td>0.164</td>
</tr>
<tr>
<td>C-FeMn</td>
<td>85</td>
<td>0.089</td>
<td>0.103</td>
<td>0.217</td>
<td>0.399</td>
</tr>
<tr>
<td>C-FeAl</td>
<td>77</td>
<td>0.070</td>
<td>0.070</td>
<td>0.162</td>
<td>0.192</td>
</tr>
</tbody>
</table>
In Table 5 the catalysts are listed again in order of decreasing basicity [8]. For these catalysts no direct relationship between basicity and hydrogenation activity exists, as evidenced by the observed catalytic behaviour depicted in Fig. 1. Here the relative values of the activity (\(r_{HC} = \text{rate of CO conversion to hydrocarbons}\)) and selectivities to olefins and methane are plotted against the possible shift in the catalyst basicity relative to that of iron. Earlier [10] we described this relation as a Schwab basicity effect [8] for C-FeCa, C-FeMg and C-FeMn and in the case of C-FeAl as a Lewis acid amplified Schwab basicity effect. The observed catalytic behaviour is reflected in the relationship depicted in Fig. 2, where again the branching indices are directly related to the olefin selectivity.

Concerning the extent of branching, except for catalyst C-FeCa, a reasonable agreement exists between the observed values for alkenes and alkanes, suggesting that the latter have been formed from the former by hydrogenation only. The products obtained with catalyst C-FeCa show a much higher degree of branching in the alkenes than is the case for the alkanes. This observation is similar to that made for catalyst C-FeCo, and again either a preferential hydrogenation of linear alkenes may be responsible, or the rate of hydrogenation is much faster than that of isomerization.

The relative extent of branching of alkanes (Table 6) does not follow the random probability pattern shown in Table 1, but one which is based on the relations shown in Fig. 2. From the data presented in Fig. 1 and Table 6, it is clear that catalyst C-FeMn not only produces the highest degree of branching in each of the three alkanes investigated, but also produces branching preferentially in the heavier products. The last statement is not only valid

![Figure 1](image-url)

**Fig. 1.** Influence of the difference in electron work function of iron and the parent metal of the support on the relative catalytic behaviour of the four semi-supported iron catalysts. *\(r_{HC}\), △methane, ○olefins.
Electron work function shift, eV

![Graph showing Electron work function shift](image)

Fig. 2. Comparison of branching index and olefin selectivity obtained with the four semi-supported iron catalysts as a function of the difference in electron work function between iron and the parent metal of the support.

**TABLE 6**

Relative extent of branching of light alkanes in the product obtained with semi-supported iron-based catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Butanes</th>
<th>Pentanes</th>
<th>Hexanes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-FeCa</td>
<td>1.0</td>
<td>2.9</td>
<td>3.4</td>
</tr>
<tr>
<td>C-FeMg</td>
<td>1.0</td>
<td>2.2</td>
<td>2.5</td>
</tr>
<tr>
<td>C-FeMn</td>
<td>1.0</td>
<td>2.1</td>
<td>3.9</td>
</tr>
<tr>
<td>C-FeAl</td>
<td>1.0</td>
<td>2.3</td>
<td>2.7</td>
</tr>
</tbody>
</table>

for this particular catalyst; all four catalysts are associated with products in which the heavier alkanes are more branched than the lighter ones.

Clearly the extent of branching of alkanes does not follow a random probability pattern. Moreover, the observed pattern appears to be correlated with the catalyst formulation. It is significant that all four questions posed in the introduction can be answered in the same way for both the unsupported and semi-supported catalysts.
Supported catalyst

In line with the acidic nature of the carrier, the silica-alumina-supported catalyst exhibited pronounced isomerization activity, as may be judged from the initial branching index values (Fig. 3). This observation is consistent with earlier reports [7]. However, the extent of isomerization decreases with time on stream, in line with an expected decrease in acidity. Therefore, no variations in the extent of branching occur with time on stream when the catalyst becomes stable.

The index values, even after one week on stream, differ significantly from those observed with other catalysts (Tables 2 and 5). However, final steady values of the branching indices obtained are only marginally higher than those observed with the other catalysts discussed in the two preceding sections. The extent of branching of saturated and unsaturated products at a given carbon number was not found to differ significantly. Finally, as observed with the other catalysts, the extent of branching of the alkanes does not follow a random probability pattern.

Fig. 3. Branching index values obtained with catalyst Fe-SA with time on stream. $x \ n = 6$, $\triangle \ n = 5$, $\circ \ n = 4$.

The nature of the formation of branched products

In the introduction four questions were asked. The first question, concerning variations of the branching indices with increasing time on stream, can be answered in the affirmative only for the first week on stream, and for the supported catalyst only. In this case, acidity of the support was responsible for the observed high extent of branching. Gradual loss of acidity during reaction caused a decrease in the indices. For all other catalysts investigated, the index values remained essentially constant with
increasing time on stream. The second question, concerning variations of the index values with catalyst formulation, is answered in the affirmative for all catalysts investigated. An inverse relationship between the indices and the hydrogenation strength of the catalyst was observed in all cases.

The third question concerned differences between the extent of branching in saturated and unsaturated hydrocarbons. In most cases, a reasonable agreement was found between the extent of branching in alkenes and alkanes. Deviations were observed for those catalysts which exhibit the highest hydrogenation activity (C-FeCo and C-FeCa). In these cases, a much higher degree of branching was observed in the alkenes than in the alkanes. This is attributed to a combination of the preferential hydrogenation of linear alkenes and the hydrogenation rate much faster than that of isomerization. In both cases, the branched products are formed in secondary reactions involving skeletal isomerization of linear alkenes. This finding supports the generally held view that the main formation of branched products is not via the synthesis reaction itself, but via secondary reactions.

The fourth question concerned the relative branching of products. This was found to be a function of the catalyst used, and in none of the cases did it follow the random probability pattern. It was observed that branching was more favoured in the light products when catalysts with low hydrogenation strength were used. In contrast, high hydrogenation strength catalysts were characterized by branching predominantly in the heavy product slate. This is in line with normally observed alkene hydrogenation kinetics, where the rate of hydrogenation falls when the molecular size of the alkene is increased. As discussed before, a decrease in the rate of hydrogenation favours isomerization.

That the indices for heavier products are much less influenced by the hydrogenation strength of the catalyst than for light products is reflected in the difference between values of the indices obtained with the low hydrogenation strength catalyst BASF and the higher hydrogenation strength catalyst C-FeCo (Table 2). For the light C₄ product, the index value obtained with the latter catalyst was 29% of that obtained with the former. For the heavier C₆ product, this figure is 72%.

It has been demonstrated that catalyst basicity and hydrogenation strength have a great influence on the extent of branching of the product. However, this influence appears to be chain-length dependent, and could indicate that mechanistic influences, such as suggested by Pichler and Schulz [4] play an additional role.

Conclusions

It can finally be concluded that:

(1) The extent of branching is a function of the catalyst formulation. High acidity and a low hydrogenation strength of the catalyst (normally found in catalysts with a high basicity) favour branching.
(2) The extent of branching does not change with time on stream when non-acidic catalysts are used. Acidic catalysts are characterized by a much more branched product, the extent of which decreases with time on stream to eventually reach values only marginally higher than those observed with non-acidic catalysts.

(3) The extent of branching is different for products with different carbon numbers. It does not follow a random probability pattern, but rather one which depends on the hydrogenation strength of the catalyst used. With low hydrogenation strength catalysts, branching occurs preferentially in the lighter products. Branching is favoured in the heavier products when higher hydrogenation strength catalysts are used.

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