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Methanol from Synthesis Gas over Iron-rich Iron–Iridium on Silica Catalysts

Diederik C. Koningsberger, Christian P. J. H. Borgmans, Antoon M. J. van Elderen, Bert J. Kip, and Johannes W. Niemantsverdriet*

Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

Bimetallic FeIr/SiO₂ catalysts with Fe/Ir atomic ratios between 0.1 and 5 produce, under steady state conditions, MeOH from CO + 3 H₂ at 542 K and 4.0 MPa with selectivities of 75% and higher.

Supported bimetallic catalysts consisting of iron and one of the more noble group 8 metals Rh, Pd, and Ir show favourable activities for the production of oxygenates from syngas (CO–H₂) at elevated pressures.¹–³ Fukushima et al.³ report MeOH selectivities of over 80% for Fe-promoted Ir/SiO₂ catalysts with Fe/Ir atomic ratios between 0.02 and 0.2. For catalysts of higher Fe content the selectivity falls off rapidly, to only 22% for the 1:1 FeIr/SiO₂ system. Methane and small hydrocarbons are the dominant products here. It should be noted, however, that all data reported by Fukushima et al.³ were obtained after a relatively short time on stream (4 h).

The purpose of this communication is to show that high
was carried out in a copper-coated stainless steel reactor in \( \text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} \) (Merck p.a.) to the \( \text{SiO}_2 \) support (Grace K) overnight at 295 K, heated at 15 K/h to 400 K, and held at 400 K for \( 1 \text{ h} \). Dried catalysts were reduced in flowing \( \text{H}_2 \) (50 \text{ ml/min}) by linear programming the temperature at 5 K/min to 725 K followed by \( 1 \text{ h} \) at this temperature. CO hydrogenation was carried out in a copper-coated stainless steel reactor in 3 \( \text{H}_2 \) + CO (flow 1.1 ml/s) at 4.0 MPa (gauge) and 542 K.

CO hydrogenation results obtained with a few representative \( \text{FeIr/SiO}_2 \) catalysts are shown in Figure 1. The Ir-rich 1:5 \( \text{FeIr/SiO}_2 \) catalyst changes only slightly during reaction. This catalyst produces MeOH from the beginning at a favourable selectivity of 80—90%, in agreement with ref. 3. In contrast to this, the iron-rich 1:1 and 5:1 \( \text{FeIr/SiO}_2 \) start as typical Fischer–Tropsch catalysts with high selectivities for lower hydrocarbons, but change gradually to MeOH-producing catalysts (Figure 1). At steady state, reached after 30—40 h on stream, the 1:1 and 5:1 \( \text{FeIr/SiO}_2 \) catalysts produce MeOH with a selectivity of about 75% and at a total activity which is significantly higher than that of the catalysts with a low iron content.

Figure 1 illustrates that it is imperative to study the behaviour of \( \text{FeIr/SiO}_2 \) catalysts as a function of time on stream and to report catalytic data obtained under steady state conditions. If we had compared the behaviour of our catalysts after 4 h on stream, as done by Fukushima et al., the favourable performance of the iron-rich \( \text{FeIr/SiO}_2 \) catalysts would have gone unnoticed.

Table 1 lists the steady state CO conversion, as well as selectivities and yields of the products MeOH, EtOH, and \( \text{CH}_4 \), for all the \( \text{FeIr/SiO}_2 \) catalysts. The data show that MeOH selectivities of at least 75% can be obtained for \( \text{FeIr/SiO}_2 \) catalysts with Fe/Ir ratios between 1 and 5. In terms of yield, the iron-rich \( \text{FeIr} \) catalysts are by no means inferior to the catalysts of low iron content. For completeness we note that high pressure is a prerequisite for appreciable MeOH formation. At atmospheric pressure or even at 3 atm the \( \text{FeIr/SiO}_2 \) catalysts produced predominantly \( \text{CH}_4 \), \( \text{C}_2\text{H}_4 \), and \( \text{C}_3\text{H}_8 \) and the MeOH selectivity did not exceed 10%.

CO hydrogenation can also be obtained with iron-rich \( \text{FeIr/SiO}_2 \) (Fe/Ir > 1) catalysts. These catalysts, however, need 20—40 h to reach steady state conditions. The results underline the need for time-dependent studies to ascertain steady state conditions and raise the question whether iron is a promoter or a catalyst itself.

Catalysts were prepared by adding dropwise an aqueous solution of \( \text{IrCl}_3\cdot\text{H}_2\text{O} \) (53.1 wt% Ir, Drijfhout) and \( \text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} \) (Merck p.a.) to the SiO\(_2\) support (Grace Type 332, 320 m\(^2\)/g) until the incipient wetness point was reached. The catalysts with atomic ratios Fe/Ir = 1 and lower contained 4 wt% Ir, and those with atomic ratios higher than 1 contained 3 wt% Fe. Impregnated catalysts were dried in air overnight at 295 K, heated at 15 K/h to 400 K, and held at 400 K for 24 h. Dried catalysts were reduced in flowing \( \text{H}_2 \) (50 ml/min) by linear programming the temperature at 5 K/min to 725 K followed by 1 h at this temperature. CO hydrogenation was carried out in a copper-coated stainless steel reactor in 3 \( \text{H}_2 \) + CO (flow 1.1 ml/s) at 4.0 MPa (gauge) and 542 K.

![Figure 1. Yields (mmol converted CO (mol Ir s\(^{-1}\)) of methanol, ethanol, and methane in CO hydrogenation over 1:5, 1:1, and 5:1 FeIr/SiO\(_2\) catalysts at 542 K and 4.0 MPa of 3 \( \text{H}_2 \) + CO.](image-url)

<table>
<thead>
<tr>
<th>Fe/Ir ratio</th>
<th>Ir wt%</th>
<th>% Conversion</th>
<th>% Selectivity</th>
<th>Yield*</th>
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<tr>
<td></td>
<td></td>
<td>MeOH EtOH CH(_4)</td>
<td>MeOH EtOH CH(_4)</td>
<td></td>
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<td>0</td>
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<td>1.1</td>
<td>2.79 4.7 27.8</td>
<td>6.99 0.57 3.37</td>
<td></td>
</tr>
</tbody>
</table>

Fe 3 wt% 1.0 1.2 1.5 3.3 5.7 11.2 2.0 2.7 5.8 10.0

*In mmol converted CO (mol Ir s\(^{-1}\)).

In contrast to this, the iron-rich 1:1 and 5:1 \( \text{FeIr/SiO}_2 \) start as typical Fischer–Tropsch catalysts with high selectivities for lower hydrocarbons, but change gradually to MeOH-producing catalysts (Figure 1). At steady state, reached after 30—40 h on stream, the 1:1 and 5:1 \( \text{FeIr/SiO}_2 \) catalysts produce MeOH with a selectivity of about 75% and at a total activity which is significantly higher than that of the catalysts with a low iron content.

The fact that iron-rich \( \text{FeIr/SiO}_2 \) produces MeOH almost as efficiently as catalysts with a low Fe/Ir ratio raises the question whether iron should be considered as a promoter for Ir, as suggested by Fukushima et al., or as a catalyst itself. In situ Mössbauer and X-ray photoelectron spectroscopy have shown that a reduced 1:1 \( \text{FeIr/SiO}_2 \) catalyst contains zero-valent Ir and zero-valent Fe in a face-centred cubic FeIr alloy and highly dispersed iron(III). Mössbauer spectroscopy revealed furthermore that the iron(III) is accessible for and affected by CO. Hence, in principle both unreduced and reduced iron may be involved in catalytic sites for MeOH production.

The time scale on which the 1:1 and 5:1 \( \text{FeIr/SiO}_2 \) develop their MeOH activity suggests that a chemical or morphological
transformation of the catalyst particles occurs during high pressure CO hydrogenation. It has been suggested that transition metal ions play a key role in the formation of MeOH from syngas. In this respect, it is worthwhile to investigate whether the transformation of the iron-rich FeIr/SiO₂ samples from typical Fischer–Tropsch to MeOH-producing catalysts is accompanied by oxidation of either iron or iridium, caused by H₂O formed during the reaction. In situ characterization with EXAFS, Mössbauer, and e.s.r. spectroscopy is in progress to investigate this point.

In conclusion, bimetallic FeIr/SiO₂ with Fe/Ir atomic ratios between 0.1 and 5 produce MeOH from CO + 3 H₂ at 542 K and 4.0 MPa with selectivities of 75% and higher. The iron-rich FeIr/SiO₂ catalysts behave initially as normal Fischer–Tropsch catalysts, but develop their interesting MeOH selectivity during the first 30—40 h of the reaction. The results underline the importance of reporting catalytic data obtained under steady state conditions.

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References