Supplementary information

Role of carbon atoms of supported iron carbides in Fischer-Tropsch synthesis
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Preparation of catalysts

Commercial amorphous silica (CARIACT Q-10, Fuji Silysia) and carbon nanotubes (Chengdu Company CNT, purity ≥ 95%, outer diameter 20 - 30 nm) were used as catalytic supports. The Fe/SiO\(_2\) and Fe/CNT catalysts were prepared by incipient wetness impregnation of the relevant supports with aqueous solutions of hydrous iron nitrate (Fe(NO\(_3\))\(_3\)·9H\(_2\)O). The concentrations of the impregnating solutions were calculated to obtain 10 wt. % iron in the final catalysts. After the impregnation, the catalysts were dried overnight in an oven at 100°C. Then they were calcined in air (Fe/SiO\(_2\)) or N\(_2\) flow (Fe/CNT) at 400°C for 6 h with 1°C/min temperature ramping. The catalysts were activated in a flow of carbon monoxide at 350°C. A very small amount of O\(_2\) was introduced in the flowing N\(_2\) (1% O\(_2\) in N\(_2\)) for passivation of the catalysts activated in carbon monoxide before their removal from the reactor at room temperature for ex-situ characterization.

Characterization

The BET surface area, pore volume and average pore diameter were determined by N\(_2\) physisorption using a Micromeritics ASAP 2000 automated system. The samples were degassed under vacuum at <10 μm Hg in the Micromeritics ASAP 2000 at 300°C for 4 h prior to N\(_2\) physisorption.

*Ex situ* X-ray powder diffraction (XRD) experiments were conducted using a Bruker AXS D8 diffractometer using Cu(Kα) radiation (λ=0.1538 nm). The XRD patterns were collected in 20-70° (2θ) range. The identification was carried out by comparison with JCPDF standard spectra software. The average crystallite size of Fe\(_3\)O\(_4\), Fe\(_2\)O\(_3\) or iron carbides was calculated using the diffraction peaks according to the Scherrer equation.
The in-situ X-Ray diffraction patterns were measured using a D8 Advance diffractometer (Brüker AXS) using Cu (Kα) radiation. For the in-situ measurements the catalyst was placed in a high temperature chamber on D8 Advance (Brüker AXS) to record the evolution of XRD patterns as a function of the increasing temperature (6 °C/min, with 20~15 s) under 3 vol% H₂ in nitrogen.

The TEM analyses were carried out on a Jeol 2100F (field emission gun) microscope operating at 200 kV equipped with probe corrector for the spherical aberrations. Prior to the analysis, the sample was dispersed by ultrasound in ethanol solution for 5 min, and a drop of solution was deposited onto a carbon membrane onto a 300 mesh-copper grid.

TPR (temperature programmed reduction) measurements were performed on a Micromeritics AutoChem II 2920 instrument. 0.1 g sample was firstly pretreated with pure CO flow at 350 °C for 3h in a quartz reactor. Then, the sample was flushed with He and cooled to 100 °C. 5%H₂/Ar (20 mL/min) was introduced into the reactor at 100 °C, and the temperature was raised to 800 °C at a rate of 6 °C/min. The generation of CH₄ was monitored by MS at m/e = 15.

**Catalytic tests**

Carbon monoxide hydrogenation was carried out on the REALCAT platform in a Flowrence® high-throughput unit (Avantium) equipped with 16 parallel milli-fixed-bed reactors (d=2 mm) operating at a total pressure of 20 bar, H₂/CO= 2 molar ratio and GHSV from 16 L h⁻¹ g⁻¹. The catalyst loading was 50 mg per reactor. Prior to the catalytic test all the samples were activated in a flow of CO at atmospheric pressure during 10 h at 350°C. During the activation step, the temperature ramp was 3°C/min. After the reduction, the catalysts were cooled down to 180°C and a flow of premixed syngas was gradually introduced to the catalysts. When pressure attained 20 bar, the temperature was slowly increased to 300°C. Gaseous reaction products were analyzed by on-line gas chromatography. Analysis of permanent gases was performed using a Molecular Sieve column and a thermal conductivity detector. Carbon dioxide and C₁-C₄
hydrocarbons were separated in a PPQ column and analyzed by a thermoconductivity detector. C₅-C₁₂ hydrocarbons were analyzed using CP-Sil5 column and a flame-ionization detector. High-molecular-weight products were collected at atmospheric pressure in vials heated at 80°C. The carbon monoxide contained 5% of helium, which was used as an internal standard for calculating carbon monoxide conversion. The reaction rates were defined as iron time yields and expressed as moles of CO converted per mole of total iron per hour. The product selectivity (S) was reported as the percentage of CO converted into a given product and expressed on carbon basis.

The static hydrogenation tests of the catalysts have been conducted in the same unit at 300 ºC, 20 bars and H₂ flow with GHSV=0.75 L/g·h after different pretreatments.

GC-MS tests were conducted by sampling during the test in the single fixed bed reactor at the same reaction conditions as in the high-throughput unit. The catalyst Fe/CNT has been pretreated by CO¹³ at 350°C for 10 h. The unit has been connected at the exit to 16 way valves with periodic sampling. The samples have been analyzed afterwards over GC-MS. The products have been identified by GC-MS Varian 3800 over the column HP-PLOT Q PT, 0.32 mm x 30 m. The composition of the mixture of different isotopic variants of the reaction product is calculated from the fragmentation spectrum. The fragmentation pattern is a linear combination of the individual patterns of all isotopic components of the reaction product. By minimizing the difference between the observed and the calculated values for every m/e position in the fragmentation pattern, the contribution of each isotopic variant has been determined.
TEM analysis

Figure S1. TEM images of Fe/SiO$_2$ and Fe/CNT after calcination in N$_2$ (a), pretreatment in CO (b) and after reaction (c)
Figure S2. Catalytic activity of iron catalysts (P=2 MPa, H₂/CO=2.1, GHSV=16 L h⁻¹ g⁻¹, T=300°C)
Mössbauer analysis

![Mössbauer Spectrum](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Iron sites</th>
<th>HF (T)</th>
<th>IS (mm s(^{-1}))</th>
<th>QS (mm s(^{-1}))</th>
<th>Relative area%</th>
<th>Phase quantification (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/SiO(_2)</td>
<td>Fe(_3)C (I)</td>
<td>20.82</td>
<td>0.245</td>
<td>0.020</td>
<td>10.6</td>
<td>Fe(_3)C : 11.7±2%</td>
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<tr>
<td></td>
<td>Fe(_3)C (II)</td>
<td>-</td>
<td>0.359</td>
<td>0</td>
<td>1.1</td>
<td>χ-Fe(_5)C(_2) : 58.4±2%</td>
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<tr>
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<td>χ-Fe(_5)C(_2) (I)</td>
<td>18.66</td>
<td>0.207</td>
<td>-0.006</td>
<td>25.7</td>
<td>ε-Fe(_2)(_2)C : 12.7±2%</td>
</tr>
<tr>
<td></td>
<td>χ-Fe(_5)C(_2) (II)</td>
<td>22.09</td>
<td>0.266</td>
<td>0.014</td>
<td>32.7</td>
<td>Oxides : 17.2±2%</td>
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<td>ε-Fe(_2)(_2)C</td>
<td>17.28</td>
<td>0.150</td>
<td>0.020</td>
<td>12.7</td>
<td>(11.3%Fe(_3)O(_y)</td>
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<tr>
<td></td>
<td>Fe(_x)O(_y)</td>
<td>13.55</td>
<td>0.367</td>
<td>-0.071</td>
<td>11.3</td>
<td>+ 5.9%Fe(_3)O(_4))</td>
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<tr>
<td></td>
<td>Fe(_3)O(_4)</td>
<td>48.23</td>
<td>0.275</td>
<td>-0.449</td>
<td>5.9</td>
<td></td>
</tr>
</tbody>
</table>

Figure S3. Mössbauer spectrum and parameters of supported Fe/SiO\(_2\) activated in CO
Static hydrogenation of carbides

Figure S4. Hydrogenation of Fe/CNT and Fe/SiO$_2$ catalysts after different pretreatments
Figure S5. TPR and in-situ XRD analysis during catalysts hydrogenation
Catalysts hydrogenation before and after GC-MS test

Figure S6. Hydrogenation of labeled carbide Fe/CNT before and after the test