Cobalt carbide catalyst for Fischer–Tropsch Synthesis: in situ monitoring during the transition to metal state and its application as Fischer–Tropsch catalyst in slurry phase

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Introduction
Fischer–Tropsch synthesis (FTS) converts synthesis gas (CO + H₂) into clean hydrocarbon fuels and valuable chemicals. Because of the high conversion per pass that can be achieved, and the low deactivation rate during FTS, cobalt catalysts are ideal for synthesizing long-chain hydrocarbons [1]. Cobalt-catalyzed FTS typically proceeds at 220–240 °C, 20 bar, and a H₂/CO ratio of 2 on metal cobalt sites dispersed on the surface of a refractory oxide support. The formation of Co₂C occurs easily under low H₂/CO ratio (< 1) and has been considered rather as a deactivation route of cobalt-based catalyst during FTS. However, according to the previous works, the inactive Co₂C upon FTS can be readily converted to metal cobalt at about 200 °C via its subsequent hydrogenation. In addition, the transformed cobalt metal phase from Co₂C mainly contains cobalt metal with hexagonal closed packed (Cohcp) phase, which shows more active catalysis for CO hydrogenation than the cobalt face centered cubic (Cofcc) phase obtained from the reduction of cobalt oxide phase [2].

Based on the previous studies, the present work focused on in situ characterizations of cobalt carbide in the temperature range at which chemical conversion to metal cobalt occurred, and the transition mechanism was also elucidated using time-resolved analysis of gas molecules emitted during the hydrogenation. We also considered the application in slurry phase FTS of the carburized cobalt rapidly transformed at lower temperatures to a more active metal cobalt.

Materials and Methods
A typical catalyst, CoPt/Al₂O₃ with 23 wt% cobalt, promoted with 0.05 wt% Pt, was successively prepared using a stepwise impregnation method in a slurry of γ-alumina support with ethanol as solvent. Prior to carburization, the CoPt/Al₂O₃ catalyst was sufficiently reduced to metal cobalt in H₂ at 400 °C. The carburization of the reduced catalyst was sequentially performed at 220 °C and 2.0 MPa with a flow of pure CO for 5 h. The transition of cobalt carbide to metal cobalt species in a H₂ environment was studied using in situ analyses, including temperature-programmed decarburization (TPDC), in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFT), X-ray absorption spectroscopy (XAS), and time-resolved gas chromatography profiles, during hydrogenation of cobalt carbide. The catalytic performances of the prepared Co₂C and CoPt/Al₂O₃ catalysts were compared in a slurry-phase FTS reactor under the same conditions: 220 °C, 2.0 MPa, GHSV = 4.0 Lsyn/(gcat/h), and H₂/Co = 2.

Results and Discussion
The prepared cobalt carbide passed through a rapid transition to the cobalt metal phase at relatively low temperature in a H₂ environment. This work focused on this low temperature rapid transition and attempted to verify the fundamental phenomena related to hydrogenation of Co₂C, using in situ analyses of hydrocarbons produced during hydrogenation, as a function of hydrogenation temperature. The analysis results revealed that the onset of hydrogenation of Co₂C in excess H₂ typically occurred at around 160 °C. The cobalt metal hcp phase obtained after completion of hydrogenation showed higher activity than the cobalt metal fcc phase derived from the CoPt/Al₂O₃ did in slurry-phase FTS. The relatively low-temperature transition of Co₂C to cobalt metal with high catalytic activity in FTS could have useful applications in slurry-phase FTS.

Table 1. Activation conditions and catalytic activities of Co₂C and CoPt/Al₂O₃ catalysts in slurry phase FTS reaction

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activation conditions</th>
<th>CO conversion (%)</th>
<th>CTY* [10⁻⁵ mol CO/(gcat·s)]</th>
<th>Hydrocarbon Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₂C</td>
<td>in situ at 220 °C in H₂ for 2 h</td>
<td>70.0</td>
<td>4.29</td>
<td>1.9</td>
</tr>
<tr>
<td>CoPt/Al₂O₃</td>
<td>ex situ at 400 °C in H₂ for 12 h</td>
<td>58.0</td>
<td>3.55</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Figure 1. XANES profiles for (a) Co₂C and (b) CoPt/Al₂O₃ reduced in H₂ at different temperatures, and reference standards, namely CoO (powder), Co₃O₄ (powder), and cobalt metal foil. The spectra were measured in situ at the corresponding temperatures.

Significance
We verified that the cobalt carbide can be considered to be a more effective FT-catalyst, due to its rapid transition at lower temperatures and higher catalytic performance.

References