Supporting Information

From CO or CO$_2$?: Space-resolved insights into high-pressure CO$_2$ hydrogenation to methanol over Cu/ZnO/Al$_2$O$_3$

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Experimental

Chemicals

A commercial methanol synthesis catalysts (Cu/ZnO/Al₂O₃, Product No.: 45776) was purchased from Alfa Aesar. A CO₂/H₂/Ar (23/69/8%) gas mixture cylinder was purchased from Abelló Linde (Spain). A sapphire capillary reactor with outer diameter = 1.5 mm, inner diameter = 1 mm, and length = 100 mm was purchased from Saint-Gobain Crystals, USA.

High-pressure reactor setup

The details of a high-pressure reactor setup are explained elsewhere. High-pressure CO₂ was dispensed from a syringe pump and H₂ was pressurized and controlled by a gas booster and a mass flow controller, respectively. The total pressure of the reactor was controlled by a back-pressure regulator. The commercial Cu/ZnO/Al₂O₃ catalyst was packed in a specific type of reactor explained later. Two pressure indicators were used to measure the pressure drop over the catalyst bed, which was negligible in all experiments (<2 bar). Prior to running reaction, the catalyst was reduced with 90% H₂/He at 330 °C for 30 min then cooled down to room temperature. The reactor was pressurized by the feed gas to the desired pressure before started heating to the reaction temperature.

Experimental setup for space-resolved gas analysis using SS reactor

The space-resolved gas analysis was performed in a high-pressure setup explained elsewhere. The commercial Cu/ZnO/Al₂O₃ catalyst with a particle size of 100-300 μm was packed in a 1/8” SS tube reactor. As shown in Figure 1B, the catalyst was separated into three catalyst beds, B1, B2, and B3, with 60 mg each. Each catalyst bed was supported on a 10 μm frit to avoid moving due to high-pressure flow. The space before/between each catalyst bed (P1, P2, P3, and P4) was created for gas sampling purpose and a sampling rate of 2 mL min⁻¹ was controlled by a needle valve. The impact of gas sampling on catalytic performance was minimized by meticulous valve opening to maintain overall pressure and flow pattern. The gas composition from four different positions was analyzed by online GC and MS.

Experimental setup for operando Raman spectroscopy

The sapphire capillary reactor setup for operando Raman spectroscopy is shown in Figure S1. The most crucial part for operating at a pressure up to 200 bar is a leak-tight sealing between the sapphire capillary and SS VICI fitting. For this purpose, the polyimide film was coated at the end of the capillary to provide adhesion between graphite-reinforced polyimide ferrule and the sapphire surface. The commercial Cu/ZnO/Al₂O₃ catalyst with a particle size of 63-80 μm was packed in the same manner
as the previous setup. As shown in Figure S2, three catalyst beds (5 mg and 5 mm each) were supported on quartz wool and SS rods (OD 0.6 mm), and separated with 10-12 mm void sections for gas analysis purpose. The gas products and intermediates in the void sections were analyzed by a Raman microscope (Renishaw, InVia, λ=532 nm) in backscattering mode, as reported elsewhere. A fiber-coupled Raman probe was mounted and motorized remotely along the axial direction of the reactor by a linear actuator. The probe was focused on the P1-P4 positions shown in Figure S2 to analyze the unreacted feed and the product after each catalyst bed. The phase condensation in void sections was inspected simultaneously by a white-light camera. Eventually, the outlet composition was analyzed by an online GC.

The H₂:CO₂ feed ratio was decreased from the usual stoichiometric ratio of 3:1 to 2.5:1 in order to improve the signal-to-baseline ratio and the quality of the Raman spectra as a result of increasing density. An increase in density lessened the light transmittance through the transparent reactor and improved the light-collection efficiency. However, the decrease in signal intensity due to complicated light-matter interactions (e.g., refraction and reflection) still existed.

**Figure S1.** High-pressure reactor setup for operando Raman spectroscopy.
Figure S2. (a) The picture of the sapphire capillary reactor packed with the catalyst, (b) Schematic of the catalyst bed configuration with multiple catalyst beds and void sections. P1-P4 denote the positions analyzed by Raman microscopy.
Characterization of the spent catalysts by XRD

XRD patterns were recorded on Bruker AXS D8 advance diffractometer equipped with a Cu tube, a Ge (111) incident beam monochromator (1.54184 Å), and Vantec-1 PSD operated in transmission mode. Signal was recorded in 20-80° 2θ with a step size of 0.02° and counting time of 4 seconds per step. Crystal phases were confirmed using Bruker X'Pert Pro software and JCPDS database. The spent catalyst beds extracted from P1-4 were analyzed by XRD, as shown in Fig. S3. The bulk copper oxidation state was found to remain in metallic copper (Cu$^{0}$). However, the crystallite size of Cu (111) has increased since the presence of water in the fluid phase can promote Cu crystallite growth. The ZnO phase has also been transformed to ZnCO$_3$ at the bed positions towards outlet due to the production water that likely induces the formation of carbonic acid (H$_2$CO$_3$) by contacting with high-pressure CO$_2$. However, the presence of ZnCO$_3$ in the catalyst does not seem to pose any negative influence on the activity of the Cu-based catalyst, and in turn either ZnO or ZnCO$_3$ has probably the coordinating assistance to the catalytic activity of Cu-based catalyst.

Table S1. Crystallite size of Cu (111) calculated from the Scherer equation of the spent catalyst under CO$_2$ hydrogenation at various temperatures and 360 bars.

<table>
<thead>
<tr>
<th>Catalyst bed</th>
<th>180 °C</th>
<th>260 °C</th>
<th>340 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>14</td>
<td>12</td>
<td>18</td>
</tr>
<tr>
<td>B2</td>
<td>18</td>
<td>15</td>
<td>21</td>
</tr>
<tr>
<td>B3</td>
<td>25</td>
<td>19</td>
<td>27</td>
</tr>
</tbody>
</table>

Figure S3. PXRD analysis of the catalyst beds B1, B2, B3 placed between P1-P2, P2-P3, and P3-P4 respectively. The reaction was performed at 180, 260 and 340 °C at 360 bars.
Thermodynamic calculations

In order to facilitate the interpretation and discussion of the results, the thermodynamic equilibrium of CO$_2$ hydrogenation was calculated by Aspen HYSYS V8.6 simulation software using the Soave Redlich Kwong (SRK) equation of state (EOS). The binary interaction parameters for CO, CO$_2$, H$_2$, methanol and water were modified according to van Bennekom et al.$^6,7$ The equilibrium CO$_2$ conversion and product selectivity from CO$_2$ hydrogenation and RWGS at the temperature range of 150-400 °C, and pressure of 184 and 331 bar were shown in Figure S3 and S4, respectively.

Figure S4. Thermodynamic equilibrium of CO$_2$ conversion and methanol selectivity (the rest is CO) at CO$_2$:H$_2$ = 1:3 at 184 and 331 bar. The steep increase in CO$_2$ conversion shows the phase transition due to liquid phase condensation at lower temperatures.

Figure S5. Thermodynamic equilibrium of CO$_2$ conversion from RWGS reaction : at H$_2$/CO$_2$ = 3, 150-400 °C, and 184 and 331 bar.
Raman spectroscopy for quantitative analysis

A typical Raman spectrum of the reaction stream obtained at 260 °C at the reactor outlet (P4) is shown in Figure S5. The rotational transitions of H\textsubscript{2} (355, 587, 812, 1033, 1246, 1447 cm\textsuperscript{-1}) and the Fermi dyad of CO\textsubscript{2} and satellite bands (1265, 1286, 1387, 1408 cm\textsuperscript{-1}) are clearly identified.\textsuperscript{8} Due to a small Raman scattering cross-section, the characteristic feature of CO at 2140 cm\textsuperscript{-1} and the features of methanol at 2840 and 2945 cm\textsuperscript{-1} are too weak for quantitative analysis. Therefore, the most intense bands of H\textsubscript{2} at 587 cm\textsuperscript{-1}, and CO\textsubscript{2}, at 1387 cm\textsuperscript{-1} are considered for quantitative composition analysis. All band areas were normalized with respect to the most intense band of all (H\textsubscript{2} at 587 cm\textsuperscript{-1}) to correct for the difference in focal depth. The initial area ratio at P1 is scaled to 2.5 to match the molar ratio of unreacted feed confirmed by online GC analysis at room temperature.

![Representative Raman spectrum at 260 °C, 184 bar at P4.](image)

Figure S6. Representative Raman spectrum at 260 °C, 184 bar at P4.
Figure S7. CO₂ conversion ($X_{\text{CO}_2}$), selectivity of methanol and CO ($S_{\text{MeOH}}, S_{\text{CO}}$ respectively) observed in CO₂ hydrogenation over the commercial Cu/ZnO/Al₂O₃ catalyst using sapphire reactor tube at 180, 230, 260 and 290 °C at 184 bar, at CO₂:H₂ = 1:3 at P1-P4 at 80,000 hr⁻¹.

Figure S8. Phase condensation at P4 position during CO₂ hydrogenation to methanol over Cu/ZnO/Al₂O₃ catalysts, at 260 °C, 184 bar, and 80,000 hr⁻¹.

Reactor setup for thermal imaging using IR camera

The CO₂ hydrogenation at stoichiometric ratio (H₂:CO₂ = 3:1) was carried in a sapphire capillary reactor as previously mentioned in the operando Raman spectroscopy. In this setup, however, a heat gun (Bosch, GHG 660) was used to control the reaction temperature to minimize the infrared interference. The reactor was covered with firebricks to minimize heat loss and light disturbance. The thermal images during the reaction were taken from the top of the reactor by an IR camera (Sensors Unlimited, Micro-SWIR 320CSX). The IR camera took 1000 images at 60 frames per second before averaging into a single image shown in Figure S8. After the reaction, the thermal image under H₂ flow at 1 atm was used for temperature calibration. Finally, the thermal image taken during the reaction was
subtracted with calibration to investigate the temperature change contributed by exothermic and endothermic reactions.

Figure S9. Thermal images during CO$_2$ hydrogenation to methanol reaction at 340 °C, 184 bar, and 80000 hrs$^{-1}$ over the commercial Cu/ZnO/Al$_2$O$_3$ catalyst.

Figure S10. (A) IR thermogram along the catalyst bed and (B) temperature deviation ($\Delta T$) profile and during CO$_2$ hydrogenation to methanol over the commercial Cu/ZnO/Al$_2$O$_3$ catalyst. $\text{H}_2$/CO$_2$ = 3, $T = 260$ and 340 °C, $P = 184$ bar, and GHSV = 80,000 hr$^{-1}$. 
References


