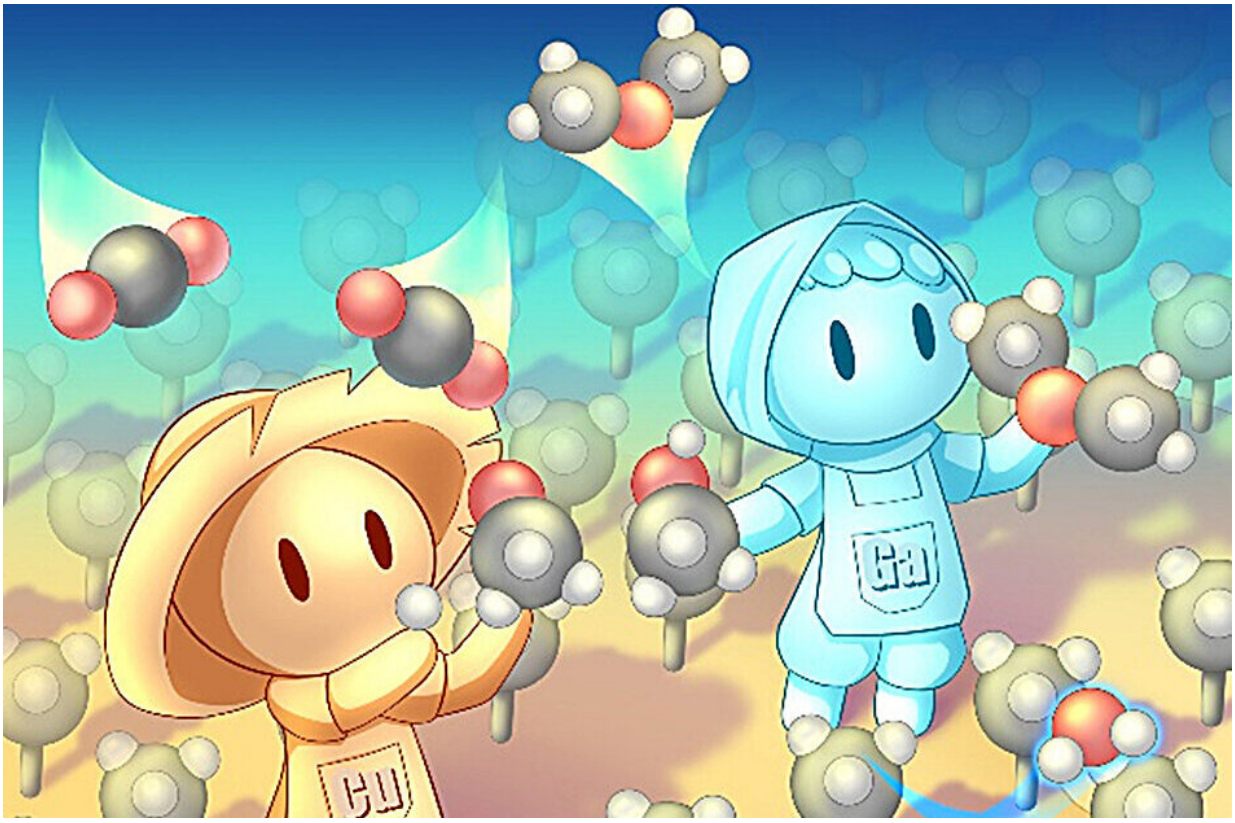
Selective conversion of CO_2 into dimethyl ether over hydrophobic and gallium-modified copper catalysts

January 1 2024



The proximity of Cu and Ga species over Cu/Ga-SiO_2-20Me catalyst could simultaneously realize tandem reactions of hydrogenation of CO_2 to methanol and dehydration of methanol to DME, where further transportation and re-adsorption of methanol intermedia to the hydrophobic catalyst was avoided. Moreover, the methyl groups efficiently removed the water generated in these two reactions, shifting the reaction equilibrium forward. In this case, CO_2

conversion and DME selectivity were both promoted over Cu/Ga-SiO_2-20Me catalyst. Credit: *Chinese Journal of Catalysis*

The selective conversion of CO_2 and H_2 into valuable chemicals and fuels is a promising route for carbon recycling. Multiple routes have been developed for the CO_2 hydrogenation to methanol, higher alcohols, dimethyl ether (DME), aromatics, hydrocarbon, and olefins. Among these products, DME is attractive because it is nontoxic and noncorrosive and has been used as a platform chemical in industry, a carrier for hydrogen, and an additive for fuels.

A series of catalysts has been synthesized for the direct hydrogenation of CO_2-to-DME via cascade catalysis involving methanol synthesis and methanol condensation to DME over a supported copper catalyst. However, high DME selectivity was only achieved at low conversion of CO_2, resulting in poor one-pass productivity.

When the CO_2 conversion increased, abundant by-products of CO, methanol, and hydrocarbons were produced. A recent trend is CO_2 to DME conversion over bifunctional catalysts, such as acid oxide-supported copper nanoparticles, but their performance is still unsatisfactory. In addition, the copper nanoparticles were sintered during catalysis, resulting in poor durability.

Recently, a research team led by Prof. Feng-Shou Xiao and Prof. Liang Wang from Zhejiang University, China, has overcome these limitations by developing a highly active, selective, and durable copper nanoparticle catalyst for converting CO_2 to DME. This was achieved by loading Cu nanoparticles onto hydrophobic and Ga-modified silica supports. The Ga-modified silica provided moderate acidity for methanol dehydration to DME, which hindered deep dehydration to hydrocarbons.

Importantly, the hydrophobic catalyst surface efficiently hinders the sintering of the Cu nanoparticles, which is usually triggered by water and methanol. Consequently, under the following reaction conditions (6000 mL $g_{cat}^{-1} \cdot h^{-1}$, 3 MPa, 240 °C), the CO_2 conversion of 9.7%, DME and methanol selectivities of 59.3% and 28.4%, and CO selectivity of only 11.3% were obtained. In a continuous evaluation for 100 h, the performance was well maintained without any deactivation trend, outperforming the general supported Cu catalysts.

The research is published in the *Chinese Journal of Catalysis*.

More information: Hangjie Li et al, Selective hydrogenation of CO2 into dimethyl ether over hydrophobic and gallium-modified copper catalysts, *Chinese Journal of Catalysis* (2023). DOI: 10.1016/S1872-2067(23)64535-8