Isolated Zr Surface Sites on Silica Promote Hydrogenation of CO_2 to CH_3OH in Supported Cu Catalysts

Erwin Lam, Kim Larmier, Patrick Wolf, Olga Safanova and Christophe Copéret*

Department of Chemistry and Applied Biosciences, ETH Zürich,
Vladimir Prelog Weg 1-5, CH-8037
elam@student.ethz.ch

The increasing amount of carbon dioxide (CO_2) in the atmosphere has a direct impact on global warming and is a direct consequence of the use of fossil fuels as our main energy sources. One way to mitigate its increase is to incorporate CO_2 in a carbon-energy-cycle and to transform it into more valuable compounds such as methanol following the concept of the "methanol economy".[1] The hydrogenation of CO_2 to methanol is possible with Cu-based catalysts, of which promising catalytic efficacy (methanol activity and selectivity) can be reached by choosing specific metal oxide supports, such as zirconia, while a silica support favors the reverse water gas shift reaction.[2] We have recently shown that the improved activity and selectivity in zirconia-supported Cu nanoparticles is due to the favored formation of CH_3OH at the interface between copper and zirconia.[3]

In order to further understand the role of the support and in particular of the Zr surface species for selectively forming CH_3OH, a surface organometallic chemistry approach has been used to tailor a silica support containing isolated Zr(IV) surface sites, on which copper nanoparticles are generated. This catalyst exhibits increased CH_3OH activity and selectivity compared to those supported on SiO_2, reaching catalytic performances comparable to the corresponding Cu/ZrO_2. *In situ* spectroscopy reveal that the Zr sites on silica remain isolated and in their +4 oxidation state and shows that similar mechanisms are involved with the single-site support and ZrO_2. These observations imply that Zr(IV) surface sites at the periphery of Cu particles are responsible for promoting CH_3OH formation on Cu-Zr based catalysts.

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