CO₂ HYDROGENATION

Bimetallics encaged

ChemCatChem <http://doi.org/c9qmq> (2019).

The stability of a heterogeneous catalyst is a key parameter for its practical utilization, and is one of the most sought-after properties when developing new conversion schemes for carbon dioxide conversion. Take, as an example, the valorization of CO₂ via hydrogenation to formate. Palladium nanoparticles on different supports have shown good activity for this reaction, however, the stability of such catalysts is often compromised by severe deactivation caused by particle sintering and aggregation. Now, Qiming Sun, Ning Yan and colleagues report a method to prepare Pd–Co bimetallic nanoparticles encapsulated within mesoporous silica nanospheres (MSNs) that feature remarkable activity and stability for the reduction of CO₂ to formate.

MSNs have recently found application as supports for heterogeneous catalysts, due to their high porosity. However, the functionalization of MSNs by conventional means — that is, incipient wetness impregnation — often leads to large particles and aggregates. Here, the authors developed instead a one-pot synthesis method (pictured), which relies on the use of cetyltrimethylammonium bromide (CTAB). In the presence of the metal precursor — a H_2PdCl_4 solution — this surfactant forms micelles that are further incorporated into a solid silicate upon addition of tetraethoxysilane (TEOS). As bimetallic systems usually show improved

catalytic properties, they employed CoCl₂ as a second metal precursor. Calcination and further reduction were thus performed to activate the system.

A number of characterization techniques, including transmission electron microscopy and X-ray absorption spectroscopy confirmed the formation of finely dispersed Pd–Co bimetallic nanoparticle — with an average diameter of 1.8 nm — encapsulated in the mesoporous channels of the silica nanospheres. Particles with a specific Pd/Co ratio ($\text{Pd}_{0.8}\text{Co}_{0.2}\text{@MSN}$), achieved an excellent performance in the hydrogenation of NaHCO₃ to sodium formate (used as the model reaction). At 373 K and 20 bar H_2 , the catalyst features an activity of 408 mol mol_{Pd}⁻¹ h⁻¹, two times higher than the corresponding monometallic Pd@MSN, and an order of magnitude higher than control catalysts prepared by simple impregnation, for example, Pd/SiO₂. The activity of the catalyst proved stable over five recycling experiments, while post-catalysis characterization revealed an essentially unchanged structure. This study is an interesting example of the potential of encapsulation strategies in heterogeneous catalysis.

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