CO2 electroreduction to formic acid on copper based catalysts: on the role of the carbon support

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PURPOSE OF THE ABSTRACT
Electroreduction is an attractive way for converting CO2 to energetically relevant molecules due to the mild conditions of temperature and pressure used in these processes. CO2 reduction to formic acid is also of great interest since the latter is a very promising hydrogen carrier. Therefore, there is a need in the development of cheap and efficient electrocatalysts able to perform the CO2 reduction reaction at low overpotential for the further development of energetically efficient CO2 conversion systems. One the most attractive metal catalyst for this reaction is copper due to its unique ability to reduce CO2 into a wide class of compounds. The way the catalyst is synthesized can dramatically tune the selectivities. Thus, a careful control of the catalyst surface properties as well as the supporting material are critical to reach high current densities and high faradaic yields. In this study, we discuss on the role of the carbon support morphology on the global performances of this electrochemical reaction. Copper nanoparticles are supported on several carbon morphologies, from amorphous (Vulcan X72R) to highly organized mesoporous structures (CMK3, FDU15). The nucleation and growth of the nanoparticles are also investigated by using the microwave assisted polyol synthesis and a one pot soft templating method. Electron tomography allowed evidencing that copper nanoparticles can be embedded inside the mesoporous structure while keeping the pore structure unaffected (Fig. 1a), thus ensuring efficient diffusion path for CO2 access to the catalytic sites. Cu nanoparticles supported onto mesoporous carbon are found to be ideal candidates to increase the active electrode surface area and to reach current densities in the range of 10 mA cm-2 (Fig. 1b). The activity of the different electrocatalysts is following the trend of the exposed metallic surface area, as determined by a novel methodology based on the surface statistics on a truncated octahedron cluster structure. Nevertheless, the competitive water reduction reaction leading to hydrogen levels off the faradaic yield for formic acid to ca. 24%. This intrinsic limitation is related to the onset potentials of the two competitive reactions, as evidenced by a coupled electrochemical and mass spectroscopic study.
FIGURE 1

Figure 1
Electron tomography of Cu nanoparticles embedded in a mesoporous carbon structure (a). Normalized limiting current densities obtained for CO2 electrolyses at E = -0.72 V vs. RHE along with faradaic yield for formic acid as a function of the carbon substrate.

FIGURE 2

KEYWORDS
CO2 electroreduction | mesoporous electrocatalysts | formic acid | copper

BIBLIOGRAPHY