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Synthesis of Liquid Fuels

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A Step Closer to the Electrochemical Production of Liquid Fuels

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The efficient and large-scale synthesis of liquid fuels from renewable sources is one of grand challenges of modern chemistry.[1] One important low-toxicity liquid fuel that can be produced sustainably is ethanol, in particular cellulosic ethanol made from second-generation biomass sources that do not compete with food production.[2,3] Large-scale plants for producing cellulosic ethanol already exist, demonstrating the viability of this technology. The main advantage of the production of cellulosic ethanol is that we can make extensive use of (photo-)catalytic technology that nature has already developed: the photosynthesis of sugar monomers and cellulose polymers by plants through carbon dioxide fixation, and the subsequent enzymatic "cracking" of cellulose to ethanol.

However, from a purely chemical point of view, the production of cellulosic ethanol is inelegant and wasteful. The detour from carbon dioxide via cellulose to ethanol is highly unfavorable energetically; even by the most optimistic estimates, the efficiency of the conversion of photon energy to chemical energy is not more than 1%.[1] Besides the chemical inefficacy, tremendous agricultural investments will be needed if we wish to produce such biofuels on a large scale.[1]

A promising long-term alternative for the large-scale production of liquid fuel is to replace nature's catalytic technology by tailored man-made catalytic technology, that is, to convert CO_2 to ethanol (or another liquid fuel) through a limited number of sensible intermediates using efficient, durable, and cost-effective synthetic catalysts, which preferably operate at ambient temperature. In contrast to the production of cellulosic ethanol, this new technology does not yet exist, but researchers worldwide are making progress in understanding the intricacies of two key reactions in the process—CO_2 reduction and water oxidation.

In a recent letter to *Nature*, the research group lead by Matthew Kanan at Stanford University reports on an exciting new development in a possible final step of such a future technology: the selective conversion of carbon monoxide to ethanol and other oxygenates on a copper electrode.[4] Copper has been known to be a good catalyst for the electrochemical conversion of CO_2 and CO to methane and ethylene since the seminal work of Hori in the 1980s.[5] Kanan et al. have now shown that nanocrystalline oxide-derived copper (OD-Cu) electrodes, prepared from the reduction of thick Cu_2O layers, produce mainly ethanol, as well as acetate and *n*-propanol, at low overpotentials (-0.25 to -0.5 V versus RHE (reversible hydrogen electrode)) with an unprecedented Faraday efficiency of up to 57%. No C_1 products were observed, indicating rapid C–C coupling at low overpotential. By comparing their OD-Cu to electrodes composed of commercial Cu nanoparticles, Kanan et al. conclude that the exceptional CO reduction activity of OD-Cu is related to the constrained environment of the grain boundaries formed during its synthesis. In addition, OD-Cu has a substantially lower hydrogen evolution activity than Cu nanoparticles, which also contributes to the high selectivity of the OD-Cu catalyst towards hydrocarbons.

Another copper surface that mediates the highly selective formation of C_2 products through CO reduction is the Cu(100) single-crystal electrode, on which the selective formation of ethylene can be observed at -0.3 V versus RHE.[6] In good agreement with the results of Kanan et al., this selective C_2 formation at low overpotential is also observed only in alkaline media, whereas at higher overpotentials, C_2 selectivity decreases and methane is formed on Cu(100) as well. The low-potential C–C coupling in alkaline media has been explained by the formation of surface-bound CO dimers through a rate-limiting proton-decoupled electron transfer, a reaction step which, according to recent density functional theory (DFT) calculations, strongly prefers (100) surface sites.[7] The subsequent hydrogenation of this dimer leads to the formation of a CH_2CHO(ads) intermediate, a kind of oxymetallacycle that binds to the copper surface through both C and O (see Figure 1). The DFT calculations suggest that this intermediate can be either reduced to ethylene, as observed on Cu(100) single-crystal electrodes, or to ethanol, as observed by Kanan et al. The factors determining whether ethylene or ethanol is formed are not yet understood, but presumably the pH and the local surface

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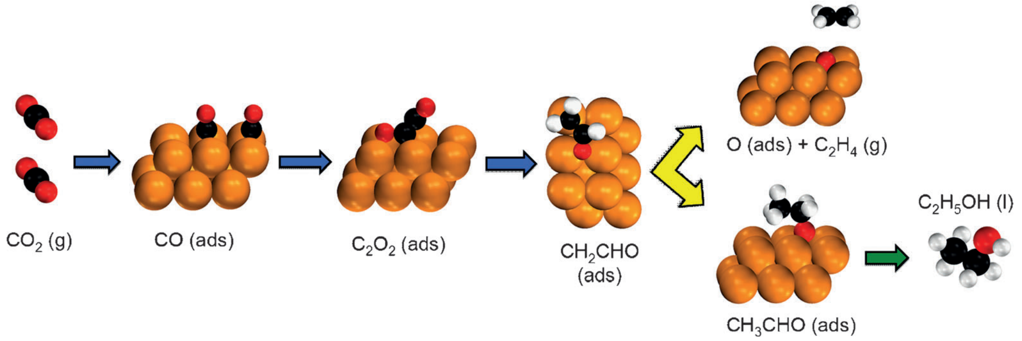

Figure 1. Suggested mechanism of the reduction of CO_2 to C_2 products. Initially, CO_2 is converted to CO on the same or on another catalyst. CO binds to the catalyst and may dimerize in alkaline media to form C_2O_2(ads). Hydrogenation of this species produces CH_2CHO(ads). The pathways towards ethylene and ethanol bifurcate from this intermediate: hydrogenation of C in the carbonyl group leads to ethylene and O(ads) (which quickly forms H_2O), whereas hydrogenation of the CH_2 group leads to acetaldehyde, which is ultimately reduced to ethanol.

structure play a decisive role. On Cu(100), the free energy of O(ads) + C_2H_4(g) is approximately 0.2 eV lower than that of CH_3CHO(ads).[7] The activation barriers, and hence the reaction rates, likely depend on the fine interplay between the local structure of the catalyst and the degree of solvation of the key adsorbed intermediates. It is expected that these free energy differences can be altered by atomic-scale effects, taking advantage of the fact that the strong chemisorption of O(ads) is significantly weakened by, for example, lattice strain effects,[8,9] which Kanan et al. have shown to exist in their oxide-derived Cu electrodes. The weak adsorption of acetaldehyde will, on the other hand, be less affected by changes in the Cu–Cu distance at the catalyst surface.

Kanan et al. suggest that eventually their catalyst may be incorporated into a two-step conversion process, in which the first step converts CO_2 to CO and the second step converts CO to liquid fuel. Both steps may be powered by renewable electricity, since electrolytic synthesis is a "more direct, versatile, and energetically efficient route to distributed liquid fuel production".

The eventual feasibility of such a process will depend on 1) the price of the electrochemical production of ethanol versus the production of cellulosic ethanol and 2) the potential reduction in CO_2 emissions offered by electrochemical CO_2 reduction, the latter often used as an argument in favor of (photo-)electrochemical CO_2 reduction.

Currently, the price of ethanol is around $600 per ton for fuel-grade ethanol. Further decreases may be expected because of the decreasing price of corn. If the price is calculated from the kilowatt hours (kWh) needed to reduce CO_2 to ethanol, assuming a cell voltage of 2 V (CO_2 reduction + water oxidation) and a price of $0.06 per kWh, the price per ton would be at least $830. This price only accounts for the cost of electrolysis, not for the energy needed for the other steps in the process, for example, distillation, as well as labor costs and capital investments.

It is instructive to perform the same calculation for the production of formic acid and methanol, two other liquid fuels that can be obtained from the reduction of CO_2. The current market prices for methanol and formic acid are $500 and $500–900 per ton, respectively. The electricity costs per ton for the electrochemical production from CO_2 are roughly $600 for methanol and $140 for formic acid, with the same assumptions as those made for ethanol. Basically, since we assume that the same overpotential is needed, the price depends only on the molecular weight (number of molecules per ton of product) and the number of electrons needed per molecule. The actual kWh needed for the production of formic acid might be a bit lower, as it should in principle require a lower overpotential. Although these numbers are only rough estimates, they show that the electrochemical reduction of CO_2 to more-reduced products, requiring more electrons per molecule, is at present not the best option from a purely economic point of view, considering also that for these costs we did not take into account the significant capital investments. Nevertheless, the estimated costs do not differ by orders of magnitude from current market prices. Therefore, the electrolytic production of liquid fuels seems a realistic future option, in addition to the electrolytic production of hydrogen, currently the most competitive electrolytic fuel.

To what extent the production of cellulosic ethanol and electrolytic ethanol can actually contribute to reducing CO_2 emissions is a matter of strong debate. Recent work has suggested that fuels produced from biomass may be associated with even higher CO_2 emissions than fossil fuels.[10] The photo-electrochemical reduction of CO_2 into fuels is also unlikely to make a substantial contribution to reducing CO_2 emissions. Parkinson and Turner have recently argued that to deploy electricity from renewable sources to totally reverse the CO_2 output of a typical fossil-fuel-fired plant, the capacity of renewable energy would be at least three times that needed to simply replace the electrical output of the same power plant with photovoltaic panels and windmills.[11] In other words: the most efficient way to reduce CO_2 emissions is to abandon CO_2-emitting technologies.

Although it is more efficient to use the electrical energy derived from renewable power sources directly, their variability poses a problem, since most applications require a stable energy supply. We believe that renewable energy storage could be one of the most promising future applications for the electrochemical conversion of CO_2 into liquid fuels, since the products of CO_2 reduction have a higher energy density than that of other energy storage technologies such as Li ion batteries, and are safer and easier to store than gaseous fuels such as hydrogen. From this point of view, ethanol has a higher energy density than formic acid and methanol, and is therefore a more desirable product. However, the most promising process for energy storage should also be as reversible as possible, that is, with a high "round-trip" efficiency, implying that low overpotentials are needed both for the reduction of CO_2 to store electricity and for the oxidation of the fuel back into work or electricity. Building an efficient and simple mimic of photosynthesis that can produce a variety of fuels will remain an important goal of future energy research. The work by Kanan et al. represents an important contribution to this grand challenge.

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