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CO$_2$ Utilization

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# Mixing Copper Nanoparticles and ZnO Nanocrystals: A Route towards Understanding the Hydrogenation of CO$_2$ to Methanol?

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Recent work by Tsang and co-workers addresses important topics in environmental science and heterogeneous catalysis, that is, CO$_2$ utilization and the economic viability of doing so, methanol synthesis, and metal–support interactions.[1] The experimental study carried out by Tsang and co-workers was based on an innovative approach using catalytic materials made up of a physical mixture of two model components each having a controlled morphology. The components were copper and ZnO nanoparticles. While the use of nanoparticles with well-defined size and morphology has been documented over the past years,[2] the utilization of a multi-component model nanocatalyst powder in a conventional flow reactor is far less common, if not unique. (Note: of course, studies in surface science have offered a vast number of structurally well-defined multi-component nanostructures, yet those rarely allowed catalytic activity to be measured under realistic conditions.) The investigation by Tsang and co-workers[1] focused on the preparation of Cu/ZnO-based catalysts for the synthesis of methanol using a CO$_2$/H$_2$ feed [Eq. (1)].

$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O \qquad (1)$$

Cu/ZnO-based catalysts are among the most active formulations for CO$_2$ hydrogenation.[3] Fujita et al.[4] proposed that the reaction pathway (investigated at atmospheric pressure) involved the formation of formates on both the copper and ZnO phases, which are further hydrogenated to form methoxides located on the ZnO, with the methoxide eventually being hydrolyzed to methanol. The reaction rate-determining step would be the formate hydrogenation on the copper phase.[4] These reports suggest that both the copper and ZnO phases are crucial catalyst components. Importantly, methanol was shown to be a primary reaction product formed from CO$_2$ (and not via another intermediate, such as CO). Carbon monoxide and water were both found to inhibit the reaction.[3] Therefore, it would be beneficial for many aspects to prevent CO formation, in particular by preventing the reverse water–gas shift reaction [Eq. (2)].

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (2)$$

Tsang and co-workers addressed the question of the selectivity to methanol formation [Eq. (1)] or carbon monoxide [Eq. (2)] formation.[1] Markedly higher selectivity to methanol (ca. 70 %) at isoconversion could be achieved when physically mixing Cu particles (diameter 35 nm) with platelet-like ZnO crystals, in which the polar (002) face was exposed, as compared mixing the Cu particles with rod-like ZnO crystals (selectivity to methanol ca. 40 %), which mostly presented the apolar faces (100) and (101).[1]

The presence of strong electronic interactions between the Cu nanoparticles and the (002) faces of the ZnO platelets was demonstrated by several techniques.[1] Temperature-programmed reduction showed that the reducibility of some of the oxygen from the ZnO (002) faces was dramatically increased in the presence of Cu. The onset of reduction was observed at approximately 200 °C, while the same oxygen in a Cu-free system would be reduced at around 750 °C. The binding energies (measured by X-ray photoelectron spectroscopy (XPS)) of electrons in the atoms present revealed a greater interaction between the Cu and platelet ZnO, than between the Cu and ZnO rods. The XPS data suggested the transfer of electrons from the conduction band of ZnO (a n-type semiconducting oxide) to the Cu, resulting in a Schottky–Mott junction at the interface between the two phases. This interpretation was further supported by electron paramagnetic resonance data.

Tsang and co-workers have therefore convincingly shown that 1) the interaction between Cu nanoparticles and the (002) polar planes of ZnO platelets is stronger than that observed between Cu nanoparticles and rod-like ZnO crystal exhibiting mostly apolar faces, 2) a Schottky–Mott junction was formed in the case of the Cu/ZnO platelets which modifies the electronic properties of both Cu and ZnO at the interface, and 3) the Cu/ZnO platelet was intrinsically more selective to methanol formation, leading to less CO formed through the reverse water–gas shift. These results by themselves are important and, in particular, highlight the complex interactions existing at the interface between the supported

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metal and the support and the means by which those interactions can be characterized.

As Tsang and co-workers indicated,[1] the exact details of the mechanism of methanol synthesis from syngas ($CO/CO_2/H_2$ mixtures)[5] and from $CO_2$ hydrogenation[3,4] on formulations based on Cu–ZnO are still matters of controversy. Most researchers seem to agree that the main reaction pathway is similar for both reactions and methanol formation occurs 1) through the hydrogenation of $CO_2$ and 2) that metallic surface copper atoms are the sites associated with the rate-determining step of the reaction.[3] The main role of the ZnO support is therefore to disperse the metallic copper. (note: an additional role of ZnO is to trap poisons thus protecting the metal.) A recent report suggests that the active Cu surface area of Cu/ZnO catalysts is correlated with the degree of Zn incorporation into the zinc malachite precursor, from which the most active catalysts are obtained by subsequent meso- and nanostructuring.[6]

In addition to dispersing and stabilizing the active Cu phase, ZnO is also thought to somehow promote the intrinsic activity of the Cu sites. The origin of this improvement is still unclear. The formation of a specific Cu–Zn site (surface alloy) that enhanced the activity of Cu was reported by various groups.[7] Earlier, Frost had proposed the formation of Schottky–Mott junction at the metal–support interface and the increased formation of oxygen defects, which were thought to be the main active sites.[8] However, Waugh dismissed the catalytic importance of such sites in the case of Cu–ZnO-based materials,[5a] while stressing that those could yet be important in the case of copper-free ZnO. Tsang et al.[1] suggest a model remotely derived from the junction effect as described by Frost[8] to explain the improved activity of their Cu–ZnO platelets, in which some electrons and oxygen atoms migrate from the ZnO to Cu to form CuO and oxygen vacancies in the ZnO phase near to the interface.

The comments above underline that further studies will be needed to ascertain the origin of the selectivity differences observed by Tsang and co-workers.[1] In particular, operando techniques need to be used, since Grunwaldt et al.[9] showed that Cu wetted differently ZnO depending on the experimental conditions. It would be interesting to assess 1) possible changes in shape and size of the copper particles under reaction conditions, 2) the possibility of Zn–Cu surface alloys formation, and 3) the Cu surface area in situ after reaction (by $N_2O$ reactive frontal chromatography[5a]) in the case of Cu–ZnO platelets and Cu–ZnO rods.

The marked difference of selectivity observed is related to the difference in the structure of the catalytic materials derived from the original mechanical mixtures.[1] The water–gas shift is a structure-sensitive reaction on $Cu/ZnO/Al_2O_3$ and according to the principle of microscopic reversibility, it is likely that the reverse reaction is too.[10a] Methanol synthesis from $CO/CO_2/H_2$ is mostly structure insensitive, as the methanol formation rate is essentially only proportional to the copper metal area, although deviations have been related to minor structure sensitivity effects.[10b] Surely, the model catalysts prepared by Tsang and co-workers and the exciting preliminary results that these authors have reported should help resolve the controversial matters discussed in the previous paragraphs and allow the design of highly active and selective catalysts for the synthesis of methanol from $CO_2$ and $H_2$.

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