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Highlights

Heterogeneous Catalysis

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Heterogeneous Catalysis of CO_2 Conversion to Methanol on Copper Surfaces**

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Among the various valorization reactions of CO_2, the Cu-catalyzed hydrogenation to methanol belongs to the most promising conversions. Unlike many other approaches, a well-established large-scale process that converts synthesis gas (CO, CO_2, H_2) into methanol is already in operation (approx. 75 Mt/year, currently from fossil sources). In addition to its current role as mainly a base chemical, methanol is also a potential fuel,[1] and a promising storage molecule for the energy sector.[2] Provided a sustainable source of hydrogen becomes available at reasonable costs, this type of chemistry seems feasible to give CO_2 molecules from flue gases "a second life" as a synthetic fuel and, thus, to substantially mitigate greenhouse gas emissions already in a short- to medium-term scenario.

Given that there are still many open questions even with regard to the conventional syngas process, which has been studied for decades, it is no wonder that this field is currently experiencing a renaissance with many new insights into the structural and functional properties of Cu-based CO_2 hydrogenation catalysts and into their mode of operation. In their recent report,[3] Graciani et al. now present copper/ceria as a new promising catalyst system for the methanol synthesis reaction and propose a reaction mechanism based on surface scientific model studies and DFT calculations that deviates from the one that was thought to operate on conventional (Al_2O_3-promoted) copper/zinc oxide catalysts. Copper/ceria is known to be a powerful catalyst for CO oxidation, water–gas shift and methanol steam reforming, but until now only little attention has been paid to ceria as a promoter in methanol synthesis catalysts.

This is astonishing, because there are interesting parallels between the modern view on copper/zinc oxide catalysts and the model that the authors elaborate for copper/ceria. In both systems, there is ample evidence that copper alone, that is, without contact to the support, shows a lower performance than the oxide-containing systems (although there certainly is a distinct activity also of clean copper[4]). In their work, Graciani et al.[3] elegantly show this by comparing the activity of a clean Cu(111) single crystal surface with one on which small ceria islands have been deposited (Figure 1 a). The CeO_x/Cu(111) was found to be substantially more active—a result that also has been obtained by Fujitani et al. in the copper/zinc oxide system for a ZnO_x/Cu(111) model catalyst in a similar experiment.[5]

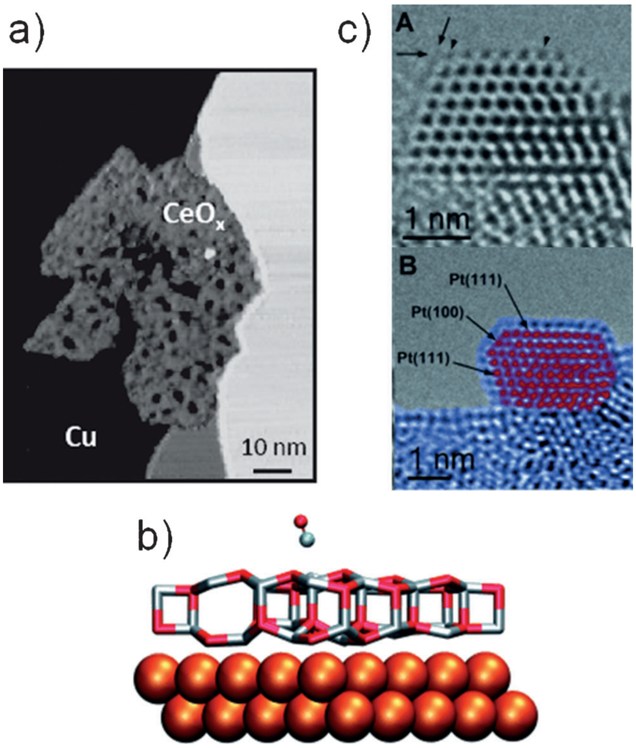

Figure 1. Images of advanced surface science models of metal/oxide arrangements that can occur in heterogeneous catalysts. a) STM micrograph of the CeO_x/Cu(111) inverse model catalysts studied by Graciani et al.[3] Reprinted with permission from Ref. [3]; b) DFT-optimized model of a ZnO bilayer surface phase supported on Cu(111) studied by Schott et al.;[8] c) HRTEM micrograph of an ultrathin FeO surface film on Pt nanoparticles supported on Fe_3O_4 by Willinger et al.[9]

In both cases, the "reducible" nature of the oxide is thought to be important for the synergistic effect in CO_2 hydrogenation. This synergistic effect of the oxide is in both

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catalysts related to the dynamic nature of the surface sites that originates from the metal oxide interfaces and the strongly reducing conditions during CO_2 hydrogenation.[6] In their treatment of the copper/ceria catalyst, Graciani et al.[3] observed the reduction of the initially present Ce^{IV} to Ce^{III} and used a Cu–"Ce_2O_3" perimeter site in their DFT model to explain the catalytic activity. In case of the copper/zinc oxide system, the oxidation state of those zinc atoms involved in the relevant surface sites is less clear, but zinc oxide was similarly found to be (partially) reduced under working condition. A recent paper by Kuld et al. provides evidence for a surface alloy, that is, complete reduction of zinc into the metallic state,[7] other authors have described the copper surface as being decorated with a film or islands of partially reduced ZnO_x. From a functional perspective, all three models have in common that the site likely to be responsible for the activation of CO_2—a Ce^{3+} perimeter atom, an oxophilic Zn metal atom of a surface alloy, or the oxygen vacancy of ZnO_x—is formed by a dynamic process and brought into close contact with the copper surface sites, which likely are responsible for the hydrogenation chemistry of the chemisorbed CO_2.

It is one of the persisting challenges in heterogeneous catalysis to understand (and finally control in an application) the involvement of support oxides in metal-catalyzed reactions. Besides CO_2 hydrogenation, there are also other reaction systems, in which these oxides are not only inert and static spacers, but a minor dynamic fraction of them additionally acts as a so-called electronic promoter for the reaction. By using DFT calculations and an "inverse" model catalyst, that is, small oxide islands deposited on an extended metal surface instead of vice versa, Graciani et al.[3] have successfully developed a comprehensive model for the methanol synthesis at the copper–ceria interface that accounts for this synergistic effect and its dynamics.

Catalysts form bonds to reactants and intermediates and thus are reactive and dynamic by definition. In real metal/oxide catalysts the dynamic behavior is usually not limited to the bond formation and breaking of single atomic sites, but many processes on different time and length scales can happen when the material is subjected to the chemical potentials of the actual reaction. It is important to recognize that the synthesized state might substantially differ from the working state of the catalyst. This is not undesired, but an optimal catalyst can be rather seen as a "smart material" that self-assembles its active sites under the reaction conditions. The in situ analysis of the valence change of CeO_x/Cu(111) by Graciani et al.[3] is a great example of how surface science models can contribute to combat this complexity.

Another recent example can be found in copper/zinc oxide catalysts. Using a similar inverse approach like Graciani et al.,[3] Schott et al. have presented a special surface phase of zinc oxide supported on Cu(111).[8] Compared to its bulk counterpart, it was only a few layers thick and crystallized in a boron nitride-like structure instead of the Wurzite type (Figure 1 b). Likely due to this 2D structure, it showed a strong wetting of the metal surface that comes along with a modification of the adsorption chemistry. Such dynamical wetting effects might play an important role for a self-assembled distribution of the $Zn(O_x)$ promoter on the copper surface in real catalysts. More recently, another illustrative example of oxide-decorated metal surfaces was presented by Willinger et al.:[9] The authors combined modern microscopy techniques and advanced synthesis methods for model catalysts to atomically resolve an ultrathin FeO film that was formed on Pt nanoparticles deposited on a Fe_3O_4 substrate (Figure 1 c) and discussed their results in the context of strong metal–support interactions—a phenomenon well-known also in CO_2 hydrogenation chemistry.[10]

Such sophisticated surface science models can be seen as well-defined "snapshots" of possible surface sites that might dynamically occur in real catalysts, in which they are extremely hard to detect. The next level of understanding can be reached if these snapshots are related with reactivity and stability data that allow deciding if they indeed represent the active sites at steady state as Graciani et al. have done with their copper/ceria catalyst.[3]

Thus, the increased complexity of modern model catalysts makes the models more realistic and more valuable to understand real systems, compared to for example, clean single crystal surfaces, but it has to be noted that these materials are also more heterogeneous despite being structurally well defined. This makes the results more prone to interpretation. For instance, the activity of metal catalysts is traditionally expressed as turnover frequency (TOF), which is often understood as the reaction rate normalized per metal surface site. This definition assumes that all metal surface sites are equally active, a concept that certainly does not apply for most real catalysts, in particular those that show synergistic effects with participation of oxide components. Graciani et al. account for this issue by normalizing their catalytic data per interfacial Cu atom, that is, they count only the fraction of Cu atoms covered by the CeO_x islands and neglect the larger Cu(111) terraces.[3] This strategy approaches the more fundamental definition of the TOF as rate per active site, whereas the amount of the latter is to be determined in each system. This is usually difficult, but it is in most cases a much more realistic concept as it assumes that there are certain (synergistic) sites that are sufficiently active to dominate the catalytic performance although they might be the clear minority.

However, this concept also holds the danger of losing comparability if not rigorously applied to all systems to be compared. Thus, the TOF-based comparison of copper/ceria and copper/zinc oxide presented in the work of Graciani et al.[3] might suffer from the fact that only the former catalyst has been evaluated according to a TOF definition per active site, whereas the rate measurement on the model catalyst for the latter was normalized by the total amount of copper atoms present. A similar discussion can be started with regard to spectroscopic results: If a distribution of surface sites is assumed with a low number of highly active sites (at the copper–ceria perimeter) and a large number of less active sites (on the clean Cu(111) terraces), the former will dominate the catalysis, but the latter will likely dominate the vibrational spectrum of adsorbed surface species. Thus, a detected surface species during the CO_2 hydrogenation like formate might well be a stable "spectator" on inactive sites, but a reactive intermediate on the small amount of active sites at the same time. The latter will be obscured in the spectra by the much larger amount of stable formate species.

There is a current debate about the mechanism of CO_2 hydrogenation.[4,11] Graciani et al. propose a mechanism of consecutive reverse water–gas shift (RWGS: $CO_2 + H_2 \rightarrow CO + H_2O$) and CO hydrogenation ($CO + 2H_2 \rightarrow CH_3OH$) on copper/ceria,[3] whereas on the copper/zinc oxide catalyst the majority of researchers appear to favor the direct hydrogenation of CO_2 likely via a formate intermediate, for which there is a larger body of evidence from real reactor studies. This difference is of fundamental importance for the development of future CO_2 hydrogenation catalysts: The formation of CO by RWGS is an undesired side reaction in the one case and a desired step in the reaction sequence toward methanol in the other. More work is needed here and it will be interesting to see if despite the chemical similarities of both systems (see above) a change in the reaction mechanism is induced by the change of the promoting oxide and/or by variations in the reaction conditions between model and high performance catalysis.

An important contribution to solve these issues is the relation to real performance catalysts to bridge the gap between model and applied catalysts. For instance, there are many tools of kinetic analysis that can be applied in real reactor studies to give hints on the reaction mechanisms.[4] Such studies should also involve the materials chemistry of high performance catalysts and are needed to validate the ideas developed on model catalysts as being really relevant for the catalytic synthesis of a product or as maybe only odd side aspects. These might be of academic interest, but can be even dead end roads on the way to understanding catalytic processes.

If we continue to do research in heterogeneous catalysis with a holistic approach involving model materials for structural definition, theoretical modeling for microkinetic function, and real catalysis data for the integration of high performance data, there is a good chance that this and other problems will be solved in the near future. The impressive results of Graciani et al.[3] are an encouraging example. Looking at this and the various other recent developments in methanol synthesis catalysis,[12] of which only a fraction can be mentioned here, this important reaction has the chance of becoming a reference case for the understanding of metal-catalyzed hydrogenations assisted by reducible oxides.

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