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Control of Solid Catalysts Down to the Atomic Scale: Where is the Limit?

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Dedicated to the MPI für Kohlenforschung on the occasion of its centenary

electron microscopy · heterogeneous catalysis · nanostructures · scanning probe techniques · surface chemistry

Solid catalysts are the workhorses of the chemical industry. It is estimated that 90% of all chemical processes are catalyzed, and the majority of these by solids.[1] The catalytic effect of solids has been known since the 19th century, even before Berzelius coined the term "catalysis".[2] Catalysts which were structured on the nanometer scale were already known early in the 20th century, around the founding date of the MPI für Kohlenforschung, when supported noble metal catalysts were introduced, although at that time it was unclear just how well the nanostructuring was performed. The reason for this was the lack of imaging methods, which meant that only bulk properties, such as the adsorption behavior—associated with the name of Irving Langmuir[3]—could be measured, from which one could infer to some extent the nanostructure, that is, the dispersion of the noble metal particles.

Now, about 100 years later, we have learnt to manipulate the arrangement of atoms and particles in solids down to the atomic scale, at least for some examples, and we also have the means to analyze such solids at the atomic level. In particular, the advances in imaging techniques over the last few decades have helped tremendously in the analysis of nanostructured catalysts. This began with the development of atomic probe microscopies, such as STM (scanning tunneling microscopy)[4] and AFM (atomic force microscopy), by which single atoms on surfaces could be probed and even manipulated, and by which bond breaking and making on the single molecule level could be studied.[5] However, these scanning probe techniques also highlighted a problem in controlling catalysts at the atomic level: it was observed that atoms moved about on the surfaces, unless the studies were carried out at low temperatures, often at 4 K; in exceptional cases, structures that were even stable for a certain time at room temperature were created.[4] Thus, unless methods can be developed to stabilize surface-atom positions, it seems improbable that catalytic surfaces that could work for extended periods of time at higher than ambient temperatures can be constructed at will down to the single-atom level.

For supported catalysts, advanced electron microscopy methods give atomic level insight into the localization of the different components.[6] Aberration correction in electron microscopy has allowed unprecedented imaging capabilities, so that individual atoms can be imaged almost on a routine basis. Figure 1a shows a high-angle annular dark-field scan-

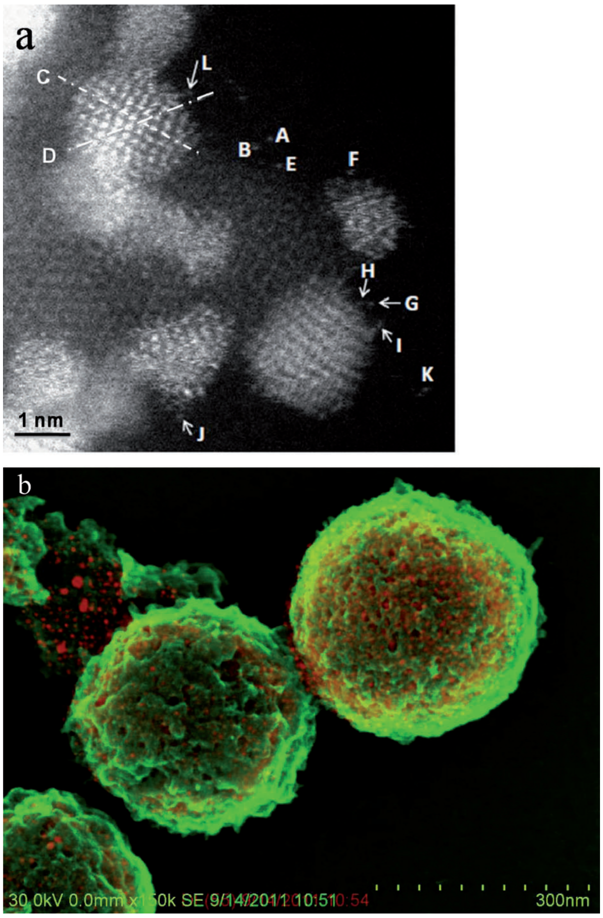

Figure 1. a) HAADF-STEM image of gold particles on iron oxide. The letters indicate individual gold atoms which were used for intensity calibration of the line scan along C and D to determine the number of atoms in the imaged column. Reproduced from Ref. [7] with kind permission. b) Superposition of the SEM (green) and STEM (red) images of hollow graphitic spheres loaded with 3–4 nm platinum particles. Reproduced from Ref. [10] with kind permission.

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ning transmission microscopy (HAADF-STEM) image of gold nanoparticles supported on iron oxide, in which the atomic columns of gold particles are seen, in addition to individual gold atoms which had been removed from the catalyst under the influence of the electron beam. By modeling the image, it was possible to even determine the number of gold atoms in the atom columns of the particles.[7] With scanning electron microscopy (SEM), one can nowadays reach nanometer resolution,[8,9] and this method is especially valuable in the analysis of the distribution of nanoparticles over complex supports (Figure 1b). Here, the distribution of platinum nanoparticles with sizes of 3–4 nm over graphitic hollow carbon shells is analyzed, and the overlay of the SEM and STEM images allows discrimination of particles on the surface and in the pores system of the carbon spheres.[10] Similar information can also be obtained using SEM alone, by imaging with different acceleration voltages. If the methods mentioned above are combined with electron tomography,[11] unprecedented insight is obtained into the distribution of the active phase of the catalyst on the support, as was recently demonstrated by Prieto et al. for metal particles on ordered mesoporous silica.[12]

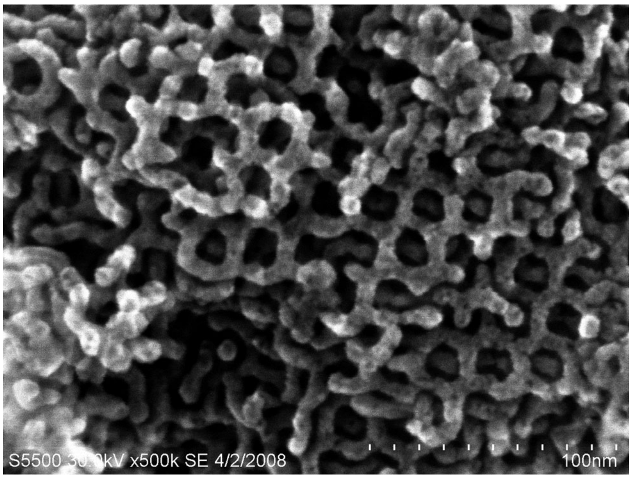

Figure 2. HR-SEM image of ordered mesostructured Co_3O_4 synthesized by nanocasting from ordered mesoporous silica. Reproduced with permission from H. Tüysüz and Hans Bongard, MPI für Kohlenforschung.

The advances in the analysis of nanostructures were paralleled by synthetic methods that allowed the synthesis of known structures with improved control on the nanometer level and access to novel materials which are intrinsically nanostructured. The first example is the novel porous materials which have emerged over the last 20 years. Until the early 1990s, zeolites were the prototypical materials with an ordered porosity, with the faujasite family having a maximum pore size of less than 0.8 nm. The aluminum phosphate VPI-5[13] with a pore size of almost 1.3 nm—although rather unstable—heralded the advent of various new families of porous materials, which exceeded the pore sizes hitherto possible. Zeolite structures were discovered with pore sizes about three times greater than those of the faujasite family;[14] the use of germanium to substitute some of the silicon atoms in the conventional zeolites was instrumental in achieving these structures. Tetrahedral germanium favors the formation of small atom rings, such as four rings or double four rings, which in turn also favors the simultaneous presence of very large rings. In 1992, scientists at Mobil Oil Corporation discovered surfactant templating, in which supramolecular arrays of surfactant molecules serve as templates, instead of the molecular templates used in zeolite synthesis.[15] This opened up new methods for the creation of regular pores larger than 10 nm, initially for silica, but later on many other compositions were synthesized, some of them through templating from the surfactant-templated silica by so-called nanocasting processes[16] (see Figure 2 for the example of Co_3O_4). Finally, a third prominent new group of highly porous materials was opened up with the family of "porous coordination compounds" or "metal–organic frameworks", as they are alternatively called, in which metal–oxo vertices are three-dimensionally connected through organic linkers with more than one functionality, so that 3D polymerization becomes possible.[17] These materials allow record porosities and often show highly interesting adsorption properties, such as, for example, the occurrence of gate pressures, since the materials are able to adapt their structures to the adsorbed molecules.[18]

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Such—and other—porous materials provide the matrix into which catalytically relevant functionalities can be deposited. Great progress has also been made here over the last few years. The methods of choice for the deposition of metal particles include impregnation or ion-exchange techniques, which are still predominant in industrial catalyst synthesis. However, one problem of this synthetic method is the intimate coupling between the support and the forming supported particles, so that the particle properties cannot be controlled independently of the support. This can be circumvented by the colloidal deposition method,[19] in which colloidal metal particles—typically stabilized by ligands—are first synthesized in solution. These are then, in a separate step, deposited on the support material, so that the particle formation and supporting steps are effectively separated. However, although these steps are decoupled, the particles can change substantially upon deposition. For example, it has been shown that colloidally synthesized gold particles that are more or less spherical in solution are strongly facetted after deposition on the support, as shown in Figure 3.[20] This effect is certainly dependent on the interaction with the support

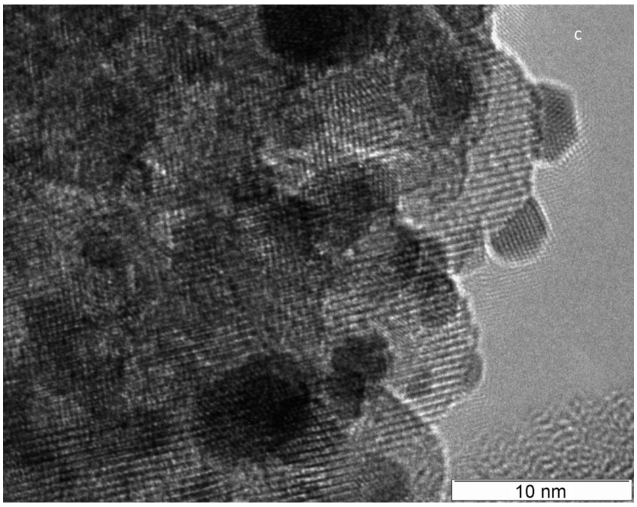

Figure 3. TEM image of colloidally deposited gold particles on zirconia. The particles in the upper right corner are clearly facetted, although they were more or less round in solution. Reproduced from Ref. [20] with kind permission.

material, since the energetic contribution arising from the interaction between the metal and support leads to a new equilibrium shape of the deposited particles, and seemingly small effects, such as the presence of heteroatoms, can lead to pronounced changes.[21] This problem would probably also hold for any other method[22] based on the deposition of preformed clusters on supports. Extremely well controlled metal clusters can be produced in the gas phase in a cluster source, and then size selected to contain precisely controlled numbers of atoms. If they are then "soft landed" on a substrate, one can synthesize model catalysts to study fundamental effects.[23] However, it is questionable whether such clusters indeed remain unaffected by the deposition process, or whether they are changed in a similar manner as the colloidally synthesized particles. In any case, even if the particles change shape, the size of the presynthesized particles at least is not altered during or after the deposition process.

The methods of preformation also allow the controlled synthesis of alloy nanoparticles from mixed precursors.[24] These are also accessible by other techniques, such as thermal treatment of supports impregnated with two different metal species or synthesis of monometallic particles, which are then exposed to a second component.[25] However, since the mobility of metal atoms in small particles is rather high at somewhat elevated temperatures, it is difficult to stabilize compositions or elemental distributions which are far away from the thermodynamic equilibrium.[26] Core–shell bimetallic particles are highly desirable, since precious-metal catalysts could be saved if they could be supported on a base-metal core. They have thus gained high importance in fuel cell catalysis, where the presence of an alloy element in addition to platinum may also increase the activity. However, depending on the gas-phase compositions, such core–shell structures tend to mix or reverse the order of the components if the interaction of the core with the gas phase is more favorable, thus minimizing the total energy of the system.[27] It will be very difficult, at least for reactions at temperatures substantially above room temperature, to stabilize alloy nanoparticles or structured nanoparticles, that is, core–shell systems, which are not at least in a deep local energetic minimum for extended periods of time. On the other hand, alloys might be thermodynamically stable in the nanoparticle range that are not accessible for bulk materials.[25]

The discussion on core–shell materials has already addressed a topic which has also gained substantial momentum over the last few years, that is, the deposition of functionality in catalysts at desired locations, such as only on the surface of nanoparticles or in pores, where optimal stabilization of a particle is possible. Approaches to achieve this rely on a number of different concepts, such as reversible protection of part of a solid,[28] nanocasting using sacrificial templates,[29] or spatially controlled modification of surfaces.[30] By using such methods, we have placed particles in thermally stable, hollow shells to avoid sintering (Figure 4),[31] or functionalized the mesopores and micropores of ordered mesoporous SBA-15 differently to elucidate the importance of acidic sites in different environments.[32] CMK-5, an ordered mesoporous carbon consisting of hexagonally packed carbon tubes, seems to be an ideal substrate for such approaches, since the pores within the carbon tubes and the pores between the tubes are formed in separate steps, so that it should be possible to functionalize them independently of each other. A first step has been taken by the selective deposition of iron oxide particles exclusively in the pores inside the tubes,[33] and we are currently exploring pathways to place one functionality within the tubes and the other on the other surface of the tubes, that is, in the pores between the tubes.

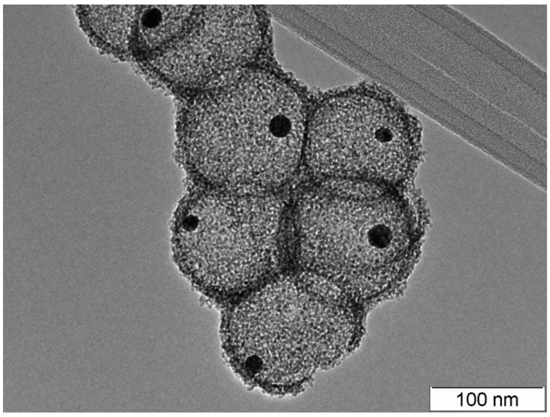

Figure 4. Gold nanoparticles embedded in porous zirconia shells, forming a sinter-resistant catalyst. Reproduced with permission from P. Arnal and B. Spliethoff, MPI für Kohlenforschung.

Finally, the structuring of solids down to the scale corresponding to molecular catalysts has also been achieved. A long-known pathway is the anchoring/grafting of molecular catalysts to solid surfaces, for which many different anchoring groups are available. By combining the special properties of ordered porous materials with anchored molecular catalysts, enantioselective systems could even be produced, where the metal center provides the catalytic activity and the confining pore directs the approach of the reagents.[34] One problem with grafted molecular catalysts is the possible lability of the tether. Often the anchoring proceeds through a group which might be prone to hydrolysis or other cleavage reactions, so that eventually the anchored catalyst is leached. A solid with ligand sites as an integral part of the solid framework could help in this respect. This principle has been used for the synthesis of a solid analogue of the molecular Periana catalyst for the oxidation of methane to methyl bisulfate in concentrated sulfuric acid.[35] A carbon–nitrogen framework with structural elements resembling the bipyrimidyl ligand of the molecular catalyst allows a tight anchoring of the atomic platinum species. During use as a catalyst, the platinum is not only retained by the framework, but clustered species which exist after synthesis of the catalyst even distribute over the solid so that eventually a fully atomically dispersed platinum distribution is obtained. The ligand environment realized here clearly immobilizes the platinum so efficiently that it even withstands the harsh reaction environment, that is, oleum at temperatures exceeding 200 °C. This is an interesting example of a solid analogue of a molecular catalyst. However, it currently seems that any such system is unique, and needs to be designed with great care.

Have we reached the limits, yet? First of all, one should note that most of the synthetic procedures for tailored catalysts, as discussed above, are only suitable for the small-scale production of materials. However, this does not necessarily mean that these methods are not useful practically. On the one hand, in the future we might also develop scalable methods for the production of similar materials on a larger scale. Moreover, in many cases it is not necessary to retain all the features of these model catalysts for industrial application. For example, in the case of sinter-resistant nanoparticles encapsulated in hollow shells, there is no need for all the shells to be exactly the same size, and even if some of the shells were partly broken, the diffusion pathways for nanoparticles would still be longer than in conventional supported catalysts, and thus part of the stabilizing function would be maintained.

For fundamental studies, it would be extremely tempting to place individual atoms on surfaces in arrangements which are optimized for a given catalytic reaction. For example, three different atoms placed on a surface would create a chiral arrangement (Figure 5), which would be a more general way of constructing chiral sites on a surface than the chiral kink sites, the study of which was pioneered by Gellman and coworkers.[36,37] Furthermore, simultaneous functionalization of a substrate molecule at two different positions might be possible by placing two or more catalytically active sites on a surface at just the correct distance, or correctly placed adsorption sites might be combined with catalytic sites to first preorient a molecule through the adsorption site and then effect the catalytic reaction. Going even further, one might think about "catalytic assembly lines" on surfaces, in which different catalytic functions placed in a spatially controlled manner, combined with "transfer ligands" to move the substrate between them, could perform sequential multistep reactions.

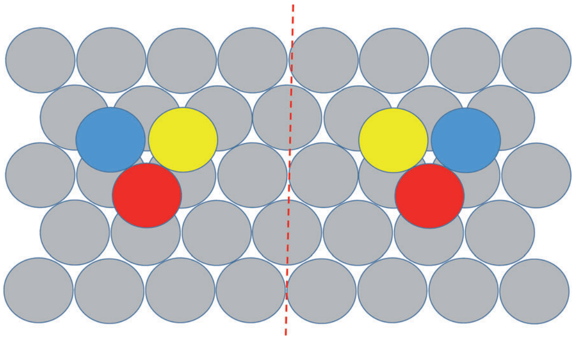

Figure 5. Hypothetical surface chiral site. Three different atoms are sufficient on a surface to create chirality, since the underlying surface prevents access from the back. If three different atoms could be placed stably on a surface, an enantioselective catalyst might be obtained.

However, there are some fundamental limits for the nanostructuring of catalysts. Not everything that seems conceptually possible also appears to be feasible in practice. Thermal mobility certainly sets a limit to constructed structures; too high a reactivity of very low coordinated atoms may also be a limit. The patterning of the structure of surfaces by placing individual atoms at desired locations can be taken as an example, as was first demonstrated by Eigler and Schweizer.[38] In the seminal publication, helium atoms were manipulated to spell "IBM". Helium atoms are certainly catalytically not very relevant, but in subsequent work, iron atoms were placed in a ring on a copper surface (a so-called "quantum corral"), two elements which are certainly catalytically important.[39] However, such experiments are typically carried out at 4 K to minimize thermal diffusion. Individual atoms bound to a flat surface have contact with three to four—depending on the nature of the surface—other atoms, which results in rather weak bonding. Self-diffusion of gold on a gold surface was found to have an activation energy of around 30 $\mathrm{kJ\,mol^{-1}}$.[40] Even metal clusters diffuse on surfaces at a substantial rate below room temperature. For example, activation energies on the order of only some tens of $\mathrm{kJ\,mol^{-1}}$ have been observed in the case of small gold clusters with sizes of 2–4 nm on Ru(0001);[41] these energies are too low to keep such clusters immobile at typical temperatures of catalytic reactions. The onset of surface mobility is already observed in such cases below room temperature. Thus, any defined arrangement created on a metal surface would probably be destroyed after short reaction times under catalytically relevant conditions. Better possibilities for persistent, atomically defined structures appear to be possible, if individual atoms are "plucked out" of a complete and perfect surface layer, since the remaining atoms have more bonds to neighboring atoms compared to isolated atoms placed on a flat surface. This has, for example, been shown for individual atoms removed from MoS_2 layers, where the defects created were even stable for a certain time at room temperature (Figure 6).[42] A similar stabilization could be obtained if individual sites were created at kinks on a substrate surface. Atoms specifically placed there would be more tightly bound, so that chances are higher for such arrangements to be persistent.

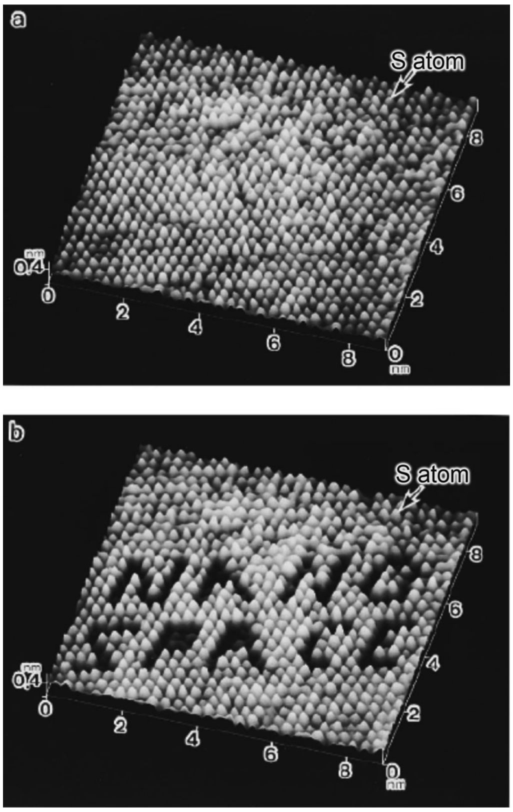

Figure 6. STM image of a room-temperature stable structure created in a MoS_2 surface by removal of individual sulfur atoms. Top: initial state, bottom: after removal of atoms.

Similar considerations would also hold for core–shell structures. Thin layers of a second component on the core formed from another metal are probably not sufficiently stable, unless the system is in a deep local energy minimum or even in the global minimum. In general, global minima will be difficult to achieve, since a system in which the surface energy is sufficient to stably coat one material with another, would typically also form even more stable alloys. The diffusion of metal atoms has relatively high diffusion coefficients, so that at least a local energy minimum structure will eventually be reached. Such (meta)stable structures, however, can have the desired properties, and there are many studies which suggest that judicious choice of the constituents and compositions can lead to a wide variety of different nanoparticle structures.[43]

In contrast to metallic nanostructures, where mobility of atoms is relatively high, since low activation energy pathways exist for diffusion because of the low directional character of the bonds in metals, the situation is somewhat better for covalent systems. Organic molecules are stable under the typical conditions of molecularly catalyzed reactions, since the typical directional bonds, such as C−C or C−H bonds, in such molecules have bond energies of several hundred $kJ\,mol^{-1}$. Metal–carbon bonds are weaker, on the order of 200–300 $kJ\,mol^{-1}$.[44] This would still be sufficient for them to be stable under the conditions of many catalytic reactions. However, in the presence of reactants and/or solvents, these bonds do not have to be broken to destabilize an arrangement which had been created at will, since ligand-exchange reactions with much lower activation energies are possible to break these bonds—which incidentally is one of the reasons why metal complexes can catalyze organic reactions. Therefore, one would most probably need arrangements in which catalytic centers are stabilized by more than one bond, for example in chelating arrangements, as are observed in the stable solid Periana analogue, where the platinum atoms are strongly bonded to two nitrogen atoms. Thus, similar to the metallic systems, detailed insight into the energetics of the relevant species is required for the atomic-scale design of catalysts which would not lose their structure after very short reaction times.

We have seen tremendous progress in the manipulation of the constituents of solid catalysts on the atomic scale. The ingenuity of future scientists will certainly move the frontiers further and further ahead. However, there seem to be fundamental limitations which will be difficult to circumvent. This may not be in research: catalytic effects of single atoms on a surface might be observed even at very low rates with sophisticated equipment at the low temperatures at which such structures could be stabilized, or stable arrangements could be produced at step sites. One could even think about a row of different sites along a monoatomic step. However, in practice the rough conditions of industrial chemistry seem to set a limit to atomically constructed catalysts which are not in a local energetic minimum state at least. Where exactly this limit will be, however, remains an open question. With extremely active catalysts, industrially relevant reactions might be possible at high rates at room temperature where sophisticated structures could also survive sufficiently long. Nature proves that this is indeed possible, and it is the ingenuity of chemists which will be required to create similarly efficient artificial systems.

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