ones under realistic PEMFC conditions. The catalyst is deposited directly on the TEM grid, so atomic-resolution IL-(S) TEM can be used to observe the same nanoparticle before and after being given electrochemical treatment (like PCA or ADT). By marking the difference between picture before and picture after, atomic columns that disappear or appear upon the exposure of a given nanoparticle to a particular electrochemical treatment are identified. IL-(S)TEM further allows the strain analysis, so all these data can be combined to investigate and understand how the local structures affect (local) stability of a given nanoparticle.

The described approach provides the most in-depth information about relations between local structures and nanoparticle stability to date.

This approach seems like the best alternative to the *in situ* liquid microscopy, the most straightforward approach to study nanoparticle degradation under operating conditions, limited by the unresolved problem of beam-induced re-

actions.[5] Nevertheless, the described concept has some room for improvement. Namely, the data showing the changes of nanoparticles are 2D projections of actually existing 3D nanoparticles. The use of 3D atomically resolved STEM tomography would be the next natural step. With 3D structures, generalized coordination numbers[6] could be calculated as activity descriptors. However, the atomic-level structural data are still linked to the electrochemical measurements using the MFE approach, i.e., averaged data over the nanoparticles ensemble. For this reason, the measurements of catalytic activity of single nanoparticles would be a step further. Until this is possible, the solution could be using computational techniques to evaluate strain-dependence of local chemisorption properties and catalytic activity, knowing that the effects of the chemical environment are rather localized for the case of metal nanoparticles and thin metal films.[7]

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The role of Pt in α-MoC on the water-gas shift reaction at low temperatures

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Improving the CO conversion efficiency and hydrogen production in water-gas shift reaction at low-temperatures is strictly tied to developing a catalyst material with simultaneous high activity a long-term stability which has proven to be a challenge. Recently, Ma et al. demonstrated in a *Nature* article that Pt loaded in α-MoC has a high activity and a long-lasting stability in water-gas shift reaction at low temperatures.

The water-gas shift (WGS) is an exothermic chemical reaction with a reported enthalpy of −0.43 eV[1] and is essential for hydrogen production and carbon monoxide removal. This reaction has a broad application range in various energy-related chemical processes, such as increasing the efficiency of fuel cells, the synthesis of hydrocarbons through the Fischer-Tropsch process and the synthesis of ammonia and methanol.[2,3] CO conversion is a crucial step in technologies that depend on the purity of H₂. The WGS reaction can be used as an H₂ purifier in processes such as steam reforming, autothermal reforming, or catalytic partial oxidation.

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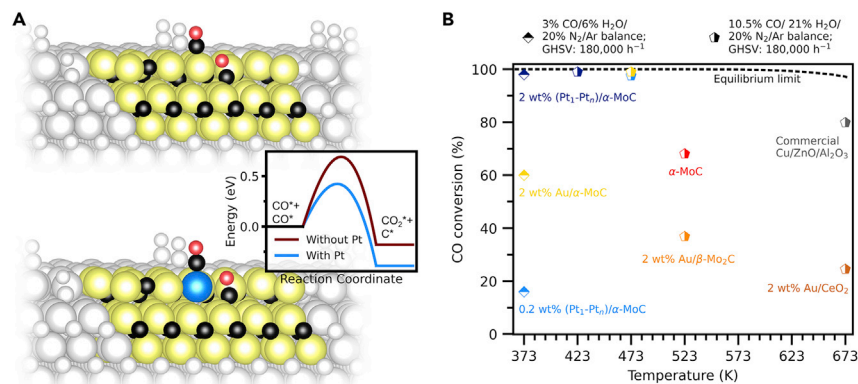*Correspondence:
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Figure 1. Increase of α-MoC efficiency by depositing scattered platinum atoms on the surface
(A) Illustration of α-MoC(111) without and with platinum. Energy barriers are calculated with DFT for α-MoC (red) and Pt/α-Moc (blue). Reference energies are CO adsorbed on their respective surfaces. Color coding is as follows: Mo, yellow; Pt, blue; C, black; O, red; and periodicity, gray.
(B) Maximum conversion of carbon monoxide (%) using different catalysts at a gas hourly space velocity of 180,000 h^{-1}. The gas composition at 373 K is 3% CO/ 6% H_2O/ 20% N_2/Ar balance, whereas between 423 K and 673 K is 10.5% CO/ 21% H_2O/ 20% N_2/Ar balance. Data taken from Yao et al.[4] and Zhang et al.[8]

Fuel-cell operating conditions and the formation of hydrocarbons are two examples in which the efficiency of the WGS depends on the low temperatures. Finding suitable catalysts with high performance below 523 K has proven to be a challenge.[2] Reported copper, zinc oxide, and aluminum oxide (Cu, ZnO, and Al_2O_3) commercial catalysts have low activity at the low-temperature regime. In the meantime, several low-temperature WGS catalysts have been reported in the literature, such as Ir_1/FeO_x, Au_1/CeO_2, and Au_1-Na/mesoporous silica. Recently, Yao et al. reported an efficient catalyst made of one-layer Au cluster/α-MoC for low-temperature WGS. Hydrogen formation is detected from 303 K and has notable CO conversion (%) between 393 and 523 K at a gas hourly space velocity of 180,000 h^{-1}.[4] We note that the current challenge is to maintain the catalyst stability against agglomeration under reaction-required temperatures. Support deactivation due to oxidation under reaction conditions is another unsolved challenge.

Nørskov and co-workers investigated the WGS reaction on copper through a kinetic model based on a statistical mechanical treatment of the redox mechanism, to develop an in-depth understanding of the key steps of the reaction, and showed that the rate-limiting step depends strongly on the CO:H_2O ratios, being either CO oxidation or water dissociation under higher or lower ratios, respectively.[5] Mavrikakis et al. used density functional theory (DFT) calculations and microkinetic modeling, showing that the initial hydrogen abstraction from water is the rate-limiting step under CO:H_2O ratios of 0.33 and 1,[6] which is in line with the work of Campbell et al., published early in the 1980s.[7] Although the focus in this work is not on the Cu-based catalysts, reported theoretical studies on such systems are fundamental in an endeavor to understand the kinetic behavior of other materials.

Writing in *Nature*, Ma et al. developed a new catalytic system by loading Pt clusters in α-MoC, which catalyzes the WGS reaction in the 303–373 K range.[8] This system has a high loading of surface atomic Pt species, which helps to boost the turnover of adsorbed oxygen species on the α-MoC substrate, thereby preventing the substrate deactivation during WGS reaction.[8,9] The key to in-

crease the catalytic activity is to control the density of the metal-support interface so that sufficient Pt atoms are on the interface to promote Pt interactions with the reactants but not on an excessive amount, in which particles will coalesce, reducing the catalyst's activity. It has been proposed before that Pt-OH_x species are active for low-temperature WGS.[10] This indicates that, for this process, Pt is a good additive to boost the catalytic activity.

Using DFT calculations, the authors predicted that Pt_1 species adsorbed on the α-MoC surface reduce energy barriers for the conversion of carbon monoxide (Figure 1A) and water dissociation. They also explained that the Pt/α-MoC catalyst has a high conventional WGS reactivity. But an unconventional WGS route co-exists, which contributes to 35% of the H_2 production. The co-existence of conventional and unconventional WGS routes results in the high catalytic potential of their catalyst.

The catalytic conversion of CO using different catalysts, with a CO:H_2O gas ratio of 0.5 is depicted in Figure 1B. The CO conversion peaked at ~80% for commercial catalysts (at 673 K), whereas metal/α-MoC catalysts reach nearly 100% CO conversion in the range of 373–473 K. Pt/α-MoC outperforms Au/α-MoC below 473K, and pure α-MoC catalysts have maximum CO conversion below 70% at 523 K. This indicates crowding the surface of α-MoC with Pt species to be essential for efficient CO conversion.

In this study, different Pt loaded (0.02–8 wt%) α-MoC samples were prepared using the incipient wetness impregnation method. The size of the clusters formed depended on Pt loadings, forming dispersed Pt_1 species to nano-sized particles across the surface. Pt_n clusters are formed at 2 and 8 wt%, which exhibit lower mole-specific activity (mol H_2 per mol Pt per second)

compared to 0.02 and 0.2 wt%, where the surface is covered mostly with dispersed Pt_1 species. This activity drop is presumed to be due to Pt coalescence, where Pt atoms from the interior of the clusters formed are now inaccessible to aid the catalytic reaction. Ma and co-workers show that Pt/α-MoC outperforms reducible oxide supports, alkali-promoted inert supports, Au/α-MoC, or pure α-MoC, regardless of the distinct activity under different Pt loadings.[8]

Near-ambient-pressure (NAP) X-ray photoelectron spectroscopy (XPS) experiments were used to unravel the reasons behind the high catalytic efficiency of Pt/α-MoC samples. After dosing with water, XPS peaks confirm OH-bound species to α-MoC due to water adsorption and dissociation, whereas parallel water treatment experiments via transient kinetic analysis (TKA) confirm H_2 production at room temperature. The surface with pre-adsorbed OH species was exposed to 5 mbar of CO at 303 K, where subsequent CO_2 formation was detected through TKA experiments. This indicates that CO binds to Pt and will readily react with adjacent OH species bound to the α-MoC, recovering the surface sites for further water dissociation.

The stability of 0.02 wt% Pt_1/α-MoC and 2 wt% (Pt_1-Pt_n)/α-MoC was measured in steady-state, at 523 K. These samples were also measured through *in situ* XPS to investigate Pt_1/α-MoC and (Pt_1-Pt_n)/α-MoC's surface composition. An oxidized α-MoC surface was detected after long exposures to H_2O+CO, leading to reduced activity, whereas Pt/α-MoC (2 wt%) remains highly active for over 250 h. This indicates that high loadings of surface Pt atoms help to remove the additional adsorbed oxygen species on α-MoC substrate resulting in higher stability in 2 wt% Pt/α-MoC. In contrast with the α-MoC surface with low density of Pt_1 species (0.02 wt%), which was mostly oxidized after 8 h, the bulk α-MoC region remained unoxidized regardless of the Pt density on the surface.

In summary, the gradual α-MoC's deactivation is correlated with the amount of OH species that adsorb onto the surface, which is counteracted by CO-adsorbed Pt particles. CO reacts with oxygen deposited on α-MoC, resulting in increased CO conversion. Although higher loadings of Pt lead to particle coalescence and reduce the catalyst's mole-specific activity, 2 wt% (Pt_1-Pt_n)/α-MoC shows long-term stability for over 250 h. On the other hand, 0.02 wt% Pt_1/α-MoC starts twice as active but rapidly decays to non-existent activity after 5–8 h because of surface oxidation. We also note that despite 2 wt% (Pt_1-Pt_n)/α-MoC not being as highly active as α-MoC with lower Pt concentration, it still excels by far, in terms of mass-specific activity, compared to other reported catalysts at 523 K and below. Increased activity by scattered Pt_1 species on the α-MoC surface, compared to pure α-MoC, is also supported by DFT calculations, which predict a reduction in the transition states by up to 0.29 eV. The takeaway message by Ma et al. emphasizes the relevance of crowding the surface with Pt particles to increase the catalyst's long-term stability.

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