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Strong Metal-Support Interactions: An Extra Layer of Complexity

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relationships can also speed up evolution through selective pressures on capture-evasion mechanisms[5].

Using a system with only a few molecular components, the team has shown how even rudimentary protocells can interact with each other and potentially influence evolutionary trajectories. Furthermore, the acquisition of foreign DNA by the predator, as observed in this case, is not unlike natural mechanisms of transformation, transduction and conjugation, which often confers new phenotypes on recipient cells that are critical for survival (Fig. 1). However, it must be remembered that what has been shown in this synthetic ecosystem occurred because the protocells were specifically designed to interact and to transfer cargo. To answer whether similar predatory mechanisms could easily emerge from primitive cells or to investigate the effect of predator–prey interactions on the evolution of protocells and on the co-dependent dynamics of the synthetic ecosystem, some type of hereditary system needs to be incorporated. The most obvious way would seem to be to encode the components of the protocell within DNA, so that the transcription–translation of the genome of surviving protocells would lead to an enrichment of daughter protocells with selected phenotypes. The problem is that a fully encoded protocell has never been made before. Or maybe we are again too influenced by life as we know it. In other words, perhaps all that is needed is more ingenious chemistry. ❑

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STRONG METAL–SUPPORT INTERACTIONS

An extra layer of complexity

Strong interactions between oxide supports and catalytic metal particles can lead to inhibitive oxide layers forming over the active metal catalyst. Now, adsorbate-induced metal–support interactions have been shown to lead to a porous overlayer in the Rh/TiO_2 system that tunes catalyst activity, improving its selectivity for the partial reduction of CO_2.

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Heterogeneous catalysts are used extensively in petroleum refining and the production of bulk and fine chemicals, making them one of the most important technologies in industrial chemistry. These materials will continue to impact some of our most urgent societal and environmental needs for decades to come due to their applications in emissions abatement, photochemical energy conversion and fuel-cell catalysts, to name but a few. One of the most common classes of heterogeneous catalysts are supported metal catalysts, which typically consist of a high-surface-area oxide that has metal nanoparticles (typically 1–10 nm or roughly 100–100,000 atoms) dispersed across the surface.

Although the interface between the metal and the oxide support often plays an important role in catalytic activity, in many systems the metal–support interface is complex and not well understood. This is particularly true for noble metals deposited on reducible oxide supports, which can undergo peculiar structural rearrangements when subjected to high-temperature hydrogen treatments. These treatments were found to generate oxygen vacancies that interact strongly with the metal surface, causing the support to rearrange — essentially crawling up the metal nanoparticle — to maximize the interactions between the metal and the support. This process, which was described in terms of strong metal–support interactions (SMSIs), was extensively discussed by Tauster and colleagues, as well as other researchers, in the late 1970s and early 1980s[1,2]. Although fundamentally interesting and still under investigation, the traditional SMSI is generally considered to be undesirable — the effect can be so strong that a thin, impenetrable layer of the metal oxide encapsulates the metal nanoparticles, completely blocking gas-phase molecules from accessing the catalytic active sites.
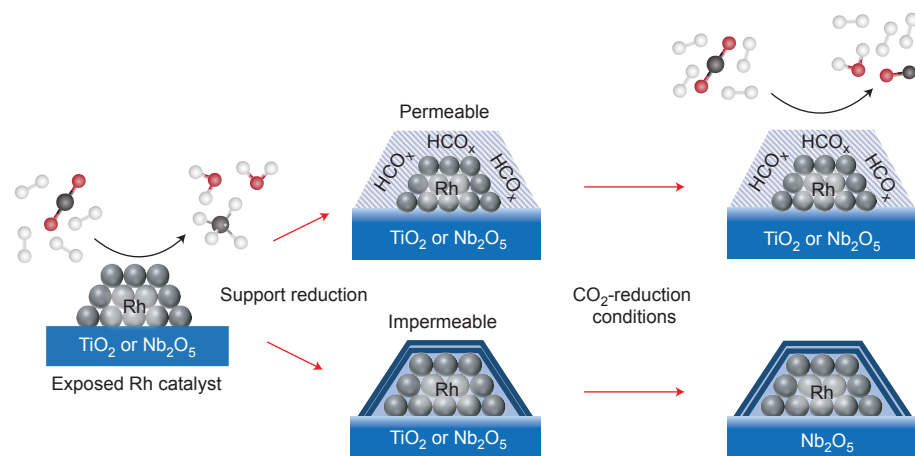

Figure 1 | Schematic comparing the activity of bare Rh to those with A-SMSI or SMSI layers. The bare Rh particles over-hydrogenate CO_2 and are highly selective for CH_4 production. The particles covered with a traditional SMSI overlayer (bottom) are unreactive, whereas particles covered with an A-SMSI overlayer partially reduce CO_2 to CO (top).

These deleterious effects have meant that the SMSI has been largely avoided for the past 30 or so years. However, writing in *Nature Chemistry,* Christopher and co-workers describe an intriguing new kind of SMSI, the adsorbate-induced SMSI or A-SMSI[3]. The discovery unfolded while the researchers were studying CO_2 reduction over heterogeneous catalysts comprised of rhodium (Rh) nanoparticles supported on titania (Rh/TiO_2). The goal is to partially reduce CO_2 to CO, and then mix the CO with additional hydrogen to make 'synthesis gas' ($CO + H_2$). Appropriate synthesis gas mixtures can be reacted over Fischer–Tropsch catalysts to prepare a wide variety of hydrocarbon fuels and commodity chemicals. This whole process requires energy, but if the energy sources are renewable, it provides a potential method for recycling CO_2 and reducing net CO_2 emissions from hydrocarbon combustion[4].

Supported Rh catalysts activate CO_2 at moderate temperatures (~200 °C); however, they over-hydrogenate the carbon, resulting in the selectivity for methane being greater than 90%. This also requires far more energy than simply reducing CO_2 to CO. However, when Christopher and co-workers pre-treated the Rh/TiO_2 catalyst at high temperatures under an atmosphere of CO_2 and H_2 the selectivity switched completely, favouring CO. After optimizing the pre-treatment (10:1 CO_2:H_2 at 250 °C), CO selectivity approached 90%. Further studies showed that the pre-treated catalyst essentially shut down the undesirable CO hydrogenation reaction, with C–H bond formation reactions proceeding roughly 40 times slower than on a typically reduced catalyst (Fig. 1). This dramatic selectivity switch was only observed for reducible supports such as TiO_2 and Nb_2O_5; when Rh/Al_2O_3 was used, the CO_2/H_2 pre-treatment had only minor effects on reactivity and selectivity.

Christopher and colleagues characterized the Rh/TiO_2 catalysts and saw something surprising: the low temperature CO_2/H_2 treatment caused the Rh nanoparticles to become encapsulated in a thin overlayer. Traditional SMSI overlayers are composed of a partially reduced version of the metal–oxide support, and completely block the metal surface. CO adsorption experiments on the A-SMSI catalysts (and the CO_2 reduction catalysis) on the other hand, showed that the A-SMSI overlayer is porous enough to allow small molecules to access the metal surface. Although it is only a few atomic layers thick, it was dense enough to be directly imaged with high-resolution transmission electron microscopy. The amorphous A-SMSI overlayer is composed primarily of the metal oxide combined with formate and carbonate-like species. Unlike the traditional SMSI, which re-oxidizes under O_2, the A-SMSI is relatively robust and stable against re-oxidation at moderate temperatures. Details of the overlayer formation mechanism remain uncertain, but there are several parallels with formic-acid-induced oxygen vacancy formation on titania[5,6].

Perhaps the most exciting aspect of this discovery is the degree to which the overlayer modifies the surface electronics of the Rh nanoparticle. The stretching frequency of CO adsorbed on the surface Rh atoms shifts nearly 50 cm^{-1} when the A-SMSI overlayer is present. This appears to be directly related to the interactions between the HCO_x species in the overlayer and the Rh surface. Further, it indicates that the HCO_x overlayer, which may contain some reduced Ti(III), acts as a strong electron donor. This is an exciting new development as it suggests potential new routes for modifying the surface chemistry of supported metal nanoparticles. It also highlights the strong influence that

adsorbates and the metal–support interface can have on the catalytic chemistry of metal nanoparticles[7,8].

Several intriguing uncertainties remain, such as the precise composition of the overlayer and the details of the species present. The origin of the electronic influence, particularly the nature of the interaction between the A-SMSI overlayer and the Rh surface, is also unclear at this early stage: how much of the modification is due to interactions with HCO_x species versus interactions associated with Ti(III) sites? Furthermore, what are the mechanistic implications of these interactions, *vis-a-vis* the catalysis? Christopher and colleagues suggest a few possibilities, but it is difficult to reconcile the electron-rich Rh surface with the poor CO hydrogenation activity and reasonable CO_2 activation activity. Perhaps the overlayer plays a more significant mechanistic role in this reaction beyond modifying the Rh nanoparticle surface. Future studies will probably sort this out, extend this new discovery to additional metal–support systems and exploit it to develop new catalytic chemistries. Time will tell, but this discovery may be an important new tool for developing highly active and selective metal catalysts. ❑

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