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Heterogeneous Catalysis

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An Exceptionally Active Catalyst for Generating Hydrogen from Water**

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clean technology · fuel cells ·
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In the context of the hydrogen economy and all its promise, it would be difficult to overemphasize the importance of the water–gas shift (WGS) reaction [Eq. (1)].

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H^{\circ}_{298} = -41\ \text{kJ mol}^{-1} \qquad (1)$$

Although of ancient lineage and one of the most fundamental chemical reactions—it has been known since the late eighteenth century—it came into full prominence over ninety years ago when Carl Bosch at BASF introduced it (during steam-reforming) as a source of hydrogen for the synthesis of ammonia. Currently the WGS reaction is of profound academic and commercial interest as a convenient means of producing H_2 for fuel cells and other applications in the drive towards clean technology.

A remarkably interesting and important paper has recently been published,[1] which reports how a simple, cheap catalyst may well take center stage and be of great practical value, provided the exciting results reported therein (in a laboratory study) can be scaled up to meet the ever-growing demand for high-purity H_2. What this study offers is a viable alternative catalyst to replace the one extensively used in the current (low-temperature, LT) WGS reaction which is based on finely divided copper metal supported on zinc oxide and alumina.

It is universal industrial practice to effect the WGS reaction in two steps, for reasons that are fully explained elsewhere.[2] One of these steps is done at high temperature (300 to 500 °C) for which a good, Fe_3O_4-based, catalyst exists. The second step, the LT WGS, uses the widely popular $Cu/ZnO/Al_2O_3$ catalyst in the region 200 to 300 °C. It is in the LT process that high-purity H_2 is generated from H_2O and CO, such that the concentration of the latter is so low that it does not poison the catalysts for ammonia synthesis (or the electrocatalysts utilized in fuel-cell applications).

To appreciate the full significance of the results reported in reference [1], it is relevant to recall prior efforts aimed at capitalizing on the demonstrated exceptional catalytic activity of nanoparticle gold in a variety of commercially important reactions, including WGS and its reverse. Haruta et al.[3] and later Andreeva et al.[4] compared the activities of Au nanoparticles (on supports such as α-Fe_2O_3 and Al_2O_3) with that of the traditional $Cu/ZnO/Al_2O_3$ catalysts, for the LT WGS reaction. It transpired that the Au/α-Fe_2O_3 catalyst showed better performance than the commercial, Cu-based one. This work spawned much interest in the design of newer variants of nanometal-supported catalysts for the LT WGS reaction. Many support materials, especially the reducible ones CeO_2 and TiO_2, were used, and nanoparticles/nanoclusters (the terms are not synonymous[5]) of both Au and Pt were investigated.

In one significant study, Flytzani-Stephanopoulos and coworkers[6] came to the conclusion, greeted with some surprise at the time as it ran counter to popular belief, that, for the class of nanostructured Au/CeO_2 or Pt/CeO_2 catalysts, metal nanoparticles do not participate in the WGS reaction. These entities are simply spectators. The authors maintained that nonmetallic Au or Pt, strongly associated with the oxygen atoms of the CeO_2 support (through ionic–covalent Au–O–Ce bonds), is responsible for the activity. In another study Park et al.[7] observed extremely high activity for the production of H_2 through the WGS reaction (using CeO_{2-x} and TiO_2 supports for Au). They concluded that the "*exploration of mixed-metal oxides at the nanometer level may open new avenues for optimizing catalysts through stabilization of unconventional surface structures with special chemical activity*".

In effect, what the joint efforts of Flytzani-Stephanopoulos and Mavrikakis and their colleagues[1] amount to is a precise fulfilment, in a dramatically unexpected manner, of the quintessence of the above quotation. Through a series of elegant and meticulous experimental and theoretical analyses these workers have shown that alkali-metal ions (Na^+ or K^+) added in small amounts, activate atomically dispersed Pt on alumina or silica for the LT WGS reaction for producing high-purity H_2. There is no doubt whatsoever that metallic Pt is not involved in the catalysis because the white-line intensity (in the in situ X-ray near-edge absorption spectra) of the Pt-L_{III} edge clearly signifies an electron-deficient metal in the Pt-3Na-SiO_2 and Pt-3K-SiO_2 catalysts (see Figure S4 of refer-

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ence [1]). All this points to the fact that the alkali-metal ions associated with surface OH groups are activated by CO at a temperature as low as 100 °C in the presence of atomically dispersed Pt. The nature of the active center (which is single-site but multinuclear as with other highly active catalysts[5]) is as represented in Figure 1.

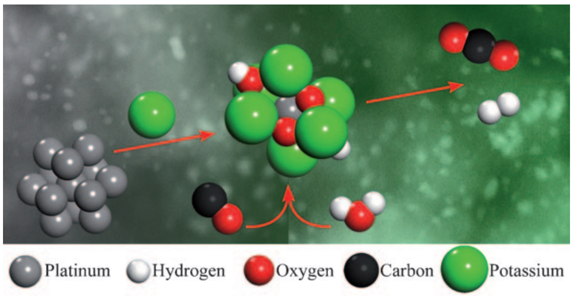

Figure 1. Schematic depiction of how the alkali metal ion stabilized Pt–OH$_x$ species (center) catalyzes the water–gas shift reaction at low temperature.

If this new catalyst possesses adequate longevity, it will be considerably more advantageous to use than the current one (Cu/ZnO/Al_2O_3) for the LT WGS reaction. One disadvantage with the current catalyst is that it is pyrophoric when exposed to air, a serious problem if used in fuel cells.[8] An advantage of the new catalyst is that the support materials (SiO_2 and Al_2O_3) are much cheaper and more plentiful than the CeO_2 support thought to be essential to[6] the WGS reaction until very recently.[9] Moreover, because the Pt is atomically dispersed, this catalyst will be far less expensive than rival ones that require nanoparticle Pt (or Au). Compare similar arguments made by Liu et al.[10] concerning their description of optimized Au-based catalysts for the selective hydrogenation of 1,3-butadiene over Au/ZrO_2.

Of late there has been lively debate[5,11–16] on whether nanoparticles, nanoclusters, or individual atoms of Au and Pt are the crucial determinants in a wide range of industrially important reactions. Small double-layer atomic entities of Au as well as small neutral nanoclusters and ionic species have all been implicated. On the basis of the evidence presented in reference [1] there seems little doubt that none of these entities dominates in the WGS reaction. Rather it is the stabilized atomically dispersed electron-deficient Pt that constitutes the locus of catalytic turnover in the WGS reaction.

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