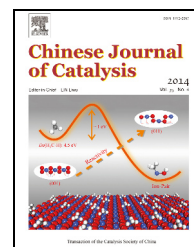




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Research Perspective

What and where are the active sites of oxide-supported nanostructured metal catalysts?

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The oxide-supported metal catalysts constitute the most investigated catalyst in both academia and industry. This perspective highlights recent research progresses on the topic, which may shed light on the nature and location of the active sites.

Keywords: Supported catalyst; Nanoparticle; Metal support interaction; Perimeter atom; Interface

Received 30 December 2013. Published 20 April 2014.

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Oxide-supported metal catalysts are important catalysts that are much investigated in academia and industry [1–4]. When these catalysts are prepared by traditional techniques, they comprise a heterogeneous population of particles, nanoclusters, subnanometer species, and isolated atoms/ions on the support surface, which make the identification of the active sites difficult. The catalyst support generally has three functions: (i) it provides a thermally stable and mechanically robust platform for metal particle dispersion [5]; (ii) it provides a suitable environment for mass transfer (large pores, hydrophilic/hydrophobic surface) [6]; and (iii) it accelerates catalytic reactions via the so-called strong metal support interaction (SMSI) [7]. Recent studies have advanced knowledge on the role of the support in catalysis [8], and these have been well reviewed [9]. The support can modify the electronic state of the metal by electron transfer between the metal and support, to influence catalytic performance [10]. The knowledge gained has shed light on the two basic questions for oxide-supported metal catalysts: what is the active site and where is it located?

Oxygen vacancy sites on reducible metal oxides, such as MgO and MoO_x, can stabilize negatively charged metal species. Häkkinen et al. [11] reported that gold octamers (Au₈) bound to

F-center defects on MgO(001) are the sites that catalyzed the low temperature oxidation of CO to CO₂, whereas the clusters deposited on non-defective magnesia surfaces are chemically inert. Charge transfer from oxygen vacancy sites to the deposited metal clusters underlies the catalytic activity of the gold octamers (Au₈). This charge activates the CO molecule by the back donation of electrons to the CO antibonding orbital. Wang et al. [12] recently found that surface-confined electrons in the oxygen vacancy sites can be transferred to the supported Au nanoparticles on partially reduced MoO_x (Fig. 1). As a result, the gold species is negatively charged. This species is responsible for the formation of the active oxygen species, for example, superoxo- or peroxy-species, in the oxidative dehydrogenation of alcohols to aldehydes and ketones.

Ceria (CeO₂) has wide applications in catalysis due to the easy formation of oxygen vacancy sites on it at low temperature [13,14]. Interactions between CeO₂ and the supported

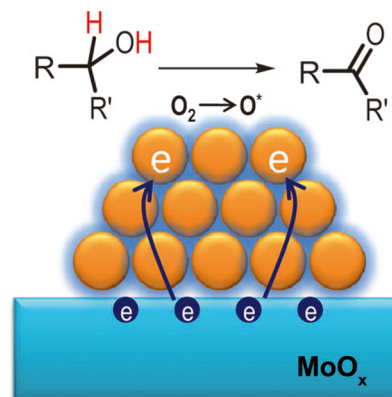


Fig. 1. Electron transfer from partially reduced MoO_x to gold nanoparticles. Reproduced from Ref. [6] with permission from Wiley.

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This work was supported by the National Natural Science Foundation of China (21303189, 21273231, and 21233008), and the Hundred Person Project of the Chinese Academy of Sciences.

DOI: 10.1016/S1872-2067(14)60073-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 4, April 2014

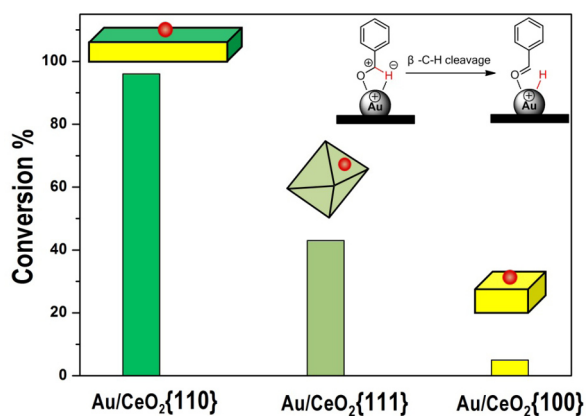


Fig. 2. Gold deposited on the {110} plane of ceria showed the highest activity for alcohol oxidation. Reproduced from Ref. [9] by permission of The Royal Society of Chemistry.

metal greatly enhanced the rates for a number of reactions, such as CO oxidation, alcohol oxidation, and the water gas shift (WGS) reaction [15–17]. It is commonly recognized that the metallic particles are the active sites. Fu et al. [18] showed that the active species in the WGS reaction is the charged metal species on the CeO₂ supported catalyst and that the metal nanoparticles did not participate in the reaction. Recently, we found that the active metal species are mainly located on the {110} surface plane of CeO₂ (Fig. 2) [19]. However, the exact nature of the active atoms and their location are still unclear.

A recent work by Murray and coworkers [20] suggested that the atoms at the interfacial rim of the nanoparticle and support (CeO₂) are the active sites. A similar site has been proposed for other catalysts [21]. The reaction rate can be enhanced by increasing the length of the ceria-metal interface. Murray and coworkers [20] prepared three different sizes of nanocrystals (Ni, Pd, and Pt) and deposited these on an inert support, Al₂O₃, and an active support, CeO₂. The preparation of the catalyst was carefully controlled to give a narrow site distribution and similar shape. This was critical for making a computer model of the interface between the nanocrystal and support for comparing the performance in CO oxidation. For the Al₂O₃ support, no difference was observed in the catalytic activity between the differently sized particles when this was normalized per number of metal atoms. However, they found that the activity of the CeO₂ supported catalysts displayed a strong size dependence on the three metals. The smaller particles were more active than the larger ones. This showed that a structural difference in the particles led to different active sites for the reaction.

From the model of the interface between the metal particle and support, they calculated the number of perimeter atoms and correlated these interfacial atoms with the catalytic activity. They found that the activity increased with an increase in the fraction of interfacial atoms (Fig. 3). This indicates that the perimeter atoms are the active sites for the CO oxidation in CeO₂ supported metals.

Concerning the exact nature of the active atoms and their location, the above studies have together partially answered the questions although the debate will remain open. It is the catalytic environment created by the supported metal and

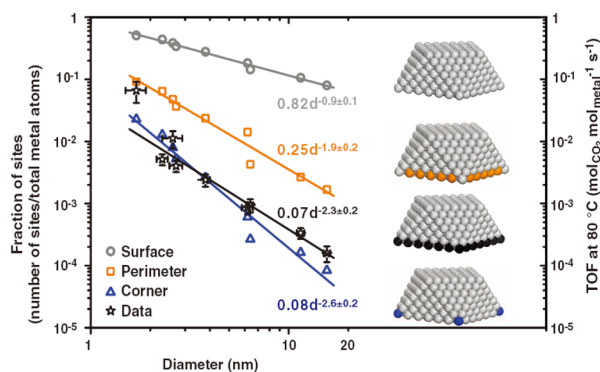


Fig. 3. Calculated number of sites for a particular geometry (surface and perimeter or corner atoms in contact with the support) as a function of Pd diameter and TOF at 80 °C for the nine ceria supported samples. Reproduced from Ref. [10] with permission from AAAS.

support that plays a pivotal role in the catalysis. Charge transfer from or to the supported metal on the environment it is in contact with has the decisive effect, and this depends on the charge state of the support or additive. For a catalytic site located at the perimeter site of the metal and oxide, charge transfer easily takes place, and the transferred charge gets stabilized.

Over the past decade, significant advances have been made in oxide-supported metal catalysis, especially for the transformation of small molecules such as CO. These studies have emerged as powerful tools for understanding the catalytic nature of metal catalysts, in particular, the “what” and the “where” in the title. The rational preparation of metal particles using size, shape, and morphology controlled ways and their interaction with the oxide support are critical to the development of highly active and selective catalysts. Although much progress has been made in the past, more research is needed to be conducted. The challenges lie in the design and preparation of multifunctional and robust metal particles and their controlled immobilization on the support, which provides the control of the perimeter sites at the metal-support interface. This nano- or sub-nano-structure emphasizes the importance of the location of the active sites. In situ and operando combined characterizations are required to give timely feedback and information on the nano- or sub-nanoscale. Besides the use of model catalysts, the use of the complex information from real catalysts remains challenging, and these should be carefully analyzed, so that underlying useful information can be extracted. The work should not be limited to small molecules, and the broad application of metal oxide supported catalysts to large, complex, and multifunctionalized molecules targeting high atomic efficiency, yield, chemo-selectivity, and enantioselectivity in a one-pot system can revolutionize synthesis chemistry and open new avenues for green and sustainable chemical processes.

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