



Design of single-atom metal catalysts on various supports for the low-temperature water-gas shift reaction

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ABSTRACT

Herein we give an account of our work on catalyst design for the low-temperature water-gas shift (WGS) reaction. The reaction is catalyzed by single-site, oxygen coordinated metal cations on various supports. Using two different metals, namely Au and Pt, we have found that the two metals form similarly-structured active sites, comprising isolated metal cations, coordinated with several –O bonds to a metal oxide that serves as the support of the active gold or platinum species. The support can be a reducible oxide, e.g. CeO₂, FeO_x, TiO₂, a non-reducible oxide, e.g. silica, zeolites, alumina, or even a non-oxide support, like carbon nanotubes. In the latter cases, alkali (Na, K)-O_x- linkages are used as a first shell around the metal ion center, stabilizing it, and supplying the –OH species necessary for the reaction. The turnover rates per catalytic site are similar on any support, specific only to the nature of the metal cation of the active site: Au(I) or Pt(II). Accordingly, the apparent activation energy, E_{app} , is different for each metal; 45 ± 5 kJ/mol for gold, and 70 ± 10 kJ/mol for the platinum catalysts. The evolution of preparation methods from those involving mixed metal structures (nanoparticles, clusters, and atoms) to novel ones that give exclusively single-atom metal catalytic centers on a support is discussed. The latter materials may be used as a platform to check whether a reaction occurs via single-atom catalytic centers. The findings are general and can be easily extended to other oxygen-coordinated metal ions on supports for the WGS reaction. They may also find broader applications to different reactions in fuel conversion and green chemicals production.

1. Introduction

The water-gas shift (WGS) reaction is ubiquitous in the processing of fuels and in the conversion of carbonaceous feedstocks to hydrogen or chemicals. From the early studies of the reaction on Pt used for the automotive exhaust catalysts, it was understood that only a small fraction of the Pt coordinated with the part of the support that contained ceria was active and sinter-resistant, and this small fraction of Pt was present as distinct Pt-O_x- sites stabilized by CeO₂, a reducible oxide [1,2]. In 2003, we reported similar findings in WGS reaction for Pt/CeO₂, the ceria doped with lanthana [3], which preserves a nanosized ceria even after high temperature annealing [4]. Pt nanoparticles were carefully removed from the surface to show that the catalyst activity did not depend on their presence. The nanoscale ceria contains a large number of defects [5], thus it can anchor a correspondingly large number of Pt-O_x- species. Many studies have demonstrated the ability of nanoscale ceria to stably disperse Pt (and other metal) atoms on its surface. Examples from the more recent automotive exhaust treatment literature are papers by the Toyota Motor Co. in

the 2000s [6]. Ceria can be used to prepare atomic dispersions of other platinum group metals, and of base metals like copper and nickel [7], and this is a well-studied subject [8,9]. In our work, we were first to show that gold can also be stabilized as single-site Au-O_x- species on ceria, and these are the exclusive active sites for the water-gas shift (WGS) reaction [3,10–13]. Gold is more active than platinum for the WGS reaction, so interest in the preparation of active and stable gold catalysts remains high.

While ceria provides a nice platform to prepare a number of atomically dispersed metals, and is certain to be used in industrial applications, it is also fundamentally interesting and practically important to examine other supports, especially the supports that have much higher elemental abundance in the earth. Indeed, there are examples of very good platinum or gold WGS catalysts supported on iron oxide [14–16], titania [17–20], zirconia [21–23], or even on irreducible oxides such as silica and alumina [24,25], zeolites [26,27], and non oxide carbon supports [28,29], if alkali metal ions are added along with the active metal species.

Preparations of atomically dispersed metals on various supports

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may require different approaches depending on the type and structural properties of the support. They are important to classify in order to prepare high loadings of the active species on a given support, but also to compare in terms of the eventual stability of the metal atom species under realistic reaction conditions. Atomic metal-centered catalyst designs offer 100% atom efficiency, and more importantly, they may have distinct product selectivity, different from that of extended metal surfaces comprising mixed structures. Various experimental methods to prepare atomically dispersed catalysts at practical loadings are discussed in this article, mainly drawn from our recent work. The aim is to prepare stable atomically dispersed metals on supports for the efficient use of precious metals for the WGS reaction, but also for broader applications to different reactions in fuel conversion and green chemicals production.

2. Preparation of single-atom supported metal catalysts

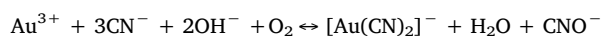
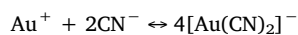
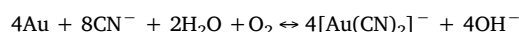
We have adopted different preparation methods, depending on the nature of the supports, to increase the population of the atomically dispersed platinum and gold species. For reducible support oxides, such as ceria and iron oxide [3,10,13–15,30] utilizing the surface lattice defect sites to build the [Metal Atom]-O_x⁻ structure is the essence of successful preparations. For the photoresponsive titania, UV irradiation was identified as an efficient technique to activate the surface vacancies of titania and bind the Au-O(OH)_x⁻ species on the titania surfaces [20]. For the earth-abundant irreducible supports, such as the alumina, silica, zeolites, and for non-oxide supports such as carbon nanotubes, the support surfaces do not provide enough –O_x species to coordinate with and stabilize a metal atom. Under these circumstances, alkali ion additives were used to stabilize the metal cation through –O_x binding and to supply the –OH necessary for the reaction. While the addition of alkali on supports, such as alumina, increases the amount of surface oxygen species, these are reducible only at high temperatures (> 350 °C) [24,31]. The presence of a metal is necessary to interact with these oxygens and shift their reduction temperature to below 100 °C [24–27]. The detailed preparation steps for building atomically dispersed gold and platinum species on various types of supports will be discussed in the following sections.

2.1. Atomically dispersed gold on various supports

For the Au/Ce(La)O_x catalysts, two preparation methods were used in our early work; namely coprecipitation and deposition precipitation [3,10,32]. Coprecipitation (CP) involves mixing aqueous solutions of HAuCl₄, cerium(III) nitrate and lanthanum nitrate with (NH₄)₂CO₃ at 60–70 °C, keeping a constant pH value around 8 and aging the resulting precipitate at 60–70 °C for 1 h. After aging, the precipitate is filtered and washed with distilled water until no residual Cl⁻ ions remain, as tested by AgNO₃ solution. Typically, the precipitate was dried at 100–120 °C, then heated to 400 °C in air at a heating rate of 2 °C/min; calcination at 400 °C continued for 10 h. Alternatively, deposition–precipitation (DP) was used to prepare the Au/Ce(La)O_x catalysts. The catalyst support was already prepared and calcined prior to its use in the DP method. The 10 at.% La-doped or Gd-doped ceria was prepared by the urea gelation/coprecipitation (UGC) method. Urea was added into the aqueous nitrate solutions and heated to 90 °C under vigorous stirring and addition of deionized water. The resulting gel was kept at ~ 90 °C for 8 h. The subsequent filtering and heating steps were the same as described above. The DP preparation took place by adding the desired amount of HAuCl₄ dropwise into an aqueous slurry of the thus prepared ceria. The pH of the aqueous slurry had already been adjusted to the value of 8 using (NH₄)₂CO₃. The resulting precipitate was aged at room temperature (RT) for 1 h, then filtered, washed and heat treated as above described.

These preparation routes do not necessarily yield the atomically dispersed gold species exclusively. Typically, gold nanoparticles and

clusters bound weakly onto the support surfaces especially at high gold loadings, are present as well. To fully remove the weakly bound gold nanoparticles (NP) and clusters, which quickly sinter into large particles during reaction at elevated temperatures and/or in a reducing atmosphere, we searched for strong ligands that can bind strongly to the transition metals like gold and take the weakly bound surface species into the aqueous solution. The search brought up several possibilities. Water-soluble ligands such as –CN (lgK[Au^I-CN] = 18.99), –NH₃ (lgK[Au^I-NH₃] = 5.58), –I (lgK[Au^I-I] = 11.09), and –SCN (lgK[Au^I-SCN] = 8.21) are promising candidates, and the cyanide ligand is the strongest leaching species among the candidates. As a result of equilibrium during the cyanide leaching, any type of weakly bound gold (both cationic and metallic) will be removed from the catalyst surface into the aqueous solution by the cyanide ligands. The typical reactions are listed below:



In our preparation of the Au/CeO_x catalysts, leaching of gold took place in an aqueous solution of 2 wt.% NaCN at RT. Sodium hydroxide was added to keep the pH around 12. The leached samples were washed, dried (at 120 °C for 10 h), and heated in air (at 400 °C for 2 h). More than 90% of the Au loading was removed from the ceria by this leaching procedure. Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) showed no Au particles remaining. X-ray photoelectron spectroscopy (XPS) identified cationic gold as the dominant Au species present in the leached materials [3,10] (see Fig. 1).

We also investigated the Au/FeO_x materials as low-temperature WGS catalysts [14]. The as-received 2.2 at.% Au-FeO_x catalyst was supplied by the World Gold Council, which was prepared through the CP method and had been calcined in air at 400 °C. Another series of 1.7 at.% Au/FeO_x catalysts was prepared in our lab by a two-step method. The iron oxide was prepared through precipitation, by adding an iron nitrate aqueous solution drop wise into water containing sodium carbonate at pH = 8. The precipitate was washed with water at 60 °C for three times, dried in a vacuum oven at 60 °C overnight, and calcined in air at 400 °C for 4 h. Leaching of gold from the Au/FeO_x samples took place in an aqueous solution of 2 wt.% NaCN under O₂ gas sparging at RT and pH ~ 12. After washing with DI water, the leached catalysts were dried for 12 h at 100 °C and calcined at 400 °C for 2 h. The leached catalysts contained only 0.1–0.7 at.% Au and comprised isolated sub-surface gold cations, stable in air calcination at 400 °C. Even after many hours of reaction in a reducing fuel gas mixture up to 350 °C, the used catalyst still contained a large fraction of isolated gold atoms along with sub-nm clusters, as shown by ac-HAADF/STEM [15] (see Fig. 2). Thus, similar to ceria, the iron oxide has good capacity to stabilize active mononuclear gold species on its surface under reaction conditions up to 350 °C.

For the preparation of Au/TiO₂ catalysts, a schematic is shown in Fig. 3 to illustrate the key steps of the conventional DP method and the UV-assisted deposition method developed in our lab [20]. Two types of titania (purity > 99%), namely P25 (30% rutile and 70% anatase, BET surface area: 45 m²/g) from Degussa, and G5 (100% anatase, 270 m²/g) from Millennium, were investigated in this work, and are designated as P25 and G5, respectively. While the gold deposition in weak base solution is followed by air calcination after filtering and drying in the conventional DP method, the UV-assisted method further treated the uncalcined Au/TiO₂ catalysts with UV irradiation in ethanol solution to produce reduced Ti(III) sites and enhance the Au-TiO₂ interface interaction [33]. A UV chamber (365 nm, 10 mW/cm², Spectronics Corp.) was used for the irradiation of the samples. A slurry of 300 mg

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