Unraveling the synergy between gold nanoparticles and chromium-hydrotalcites in aerobic oxidation of alcohols

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A B S T R A C T

The combination of gold nanoparticles (AuNPs) with chromium-substituted hydrotalcite (Cr-HT) supports makes very efficient heterogeneous catalysts (Au/Cr-HT) for aerobic alcohol oxidation under soluble-base-free conditions. The Au-support synergy increases with increasing Cr content of the support and decreasing AuNP size. In situ UV-Raman, X-ray absorption and photoelectron spectroscopic studies firmly establish that the strong Au–Cr synergy is related to a $Cr^{3+} \leftrightarrow Cr^{6+}$ redox cycle at the Au/Cr-HT interface, where O_2 activation takes place accompanied by electron transfer from Cr-HT to Au. The interfacial Cr^{6+} species can be reduced by surface Au–H hydride and negative-charged Au species to close the catalytic cycle. A study of kinetic isotope effect indicates that alcohol O–H cleavage is facilitated by the presence of Cr, making α-C–H bond cleavage step more rate-controlling. Accordingly, a dual synergistic effect of Au/Cr-HT catalysts on the activation of O_2 and alcohol reactants is proposed.

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1. Introduction

Supported gold nanoparticles (AuNPs) are attractive catalysts for selective oxidation reactions with molecular oxygen [1–4]. The use of AuNP catalysts for aerobic oxidation of alcohols to carbonyl compounds is at the center of attention [5–8], primarily as a result of the great desire for green alternatives of conventional environmentally stressing stoichiometric oxidation processes. In general, the size of the AuNP and the interaction between gold and support are believed to be crucial in determining the catalytic activity of supported AuNP catalysts [9–32]. Despite the increasing number of potential applications in alcohol oxidation, the mechanistic details of gold catalysis are not well understood. In particular, the nature of gold-support interactions [12–14,17–20, 28,30–32], the origin of the activity of gold and the way molecular oxygen and the alcohol reactant are activated in the absence of base additives [10,12–14,18,19,27,31,32] remain unclear. Unraveling these aspects of the mechanism would provide important guidance for the design of novel supported AuNP catalysts with enhanced performance.

An important topic in the field of heterogeneous gold catalysis is the synergistic effect between gold and the support [1,4,5,33]. In this regard, the classification of supports into unreducible (e.g., SiO_2, Al_2O_3, and MgO) and reducible (e.g., TiO_2, CeO_2, and Fe_2O_3) oxides has turned out to be useful [34]. For the well-studied CO oxidation reaction, the use of reducible supports usually makes much more active gold catalysts than their unreducible counterparts. This is most likely related to facile O_2 activation on the reduced support or at the gold-support interface [1,35–38]. In contrast, the beneficial effect of using reducible supports is largely absent when gold catalysts are used for liquid-phase aerobic oxidation of alcohols, except for nanosized CeO_2 [12]. At the same time, some unreducible oxide-supported AuNP catalysts exhibit very high activity, even in the absence of base additives [19,23,27,28]. For instance, Au/TiO_2 can catalyze CO oxidation at temperature as low as $-77\,°C$ [1] but is a poor catalyst for alcohol oxidation when no bases are added [21,23,28,29]. Base additives are generally believed to facilitate the cleavage of the alcohol O–H bond [2,5,15]. Due to their Lewis acidic nature, AuNP and TiO_2 cannot catalyze the initial alcohol activation step [5]. The α-C–H bond cleavage of alcohols on gold surface is understood to be the key step in their aerobic oxidation, resulting in Au–H intermediates [13,39,40]. Nevertheless, the nature (oxidation state) of the active gold phase is still under debate [12,20,22,41]. Similar to alcohol

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oxidation by Pd catalysts [42], it has been argued that the role of molecular oxygen is to remove the surface hydrides on gold [13,39]. Another role advocated for O_2 is the regeneration of OH^- via formation and decomposition of peroxide (OOH) and hydrogen peroxide (HOOH) intermediates [25,40]. Despite these important insights, it has not yet been established how the alcohol and O_2 reactants are activated by the reducible oxide-supported AuNP catalysts in the absence of soluble base.

Since the presence of base additives is important for AuNP-catalyzed alcohol oxidation, from the viewpoint of green and sustainable chemistry, it is desirable to use solid base instead of soluble base. To this end, bifunctional catalysts combining AuNP with a solid base support should be developed [17,21,23,28,29]. Obviously, if the solid base supports also possess redox properties, there would be great opportunity to further enhance the activity of supported AuNPs by a dual synergistic effect on the activation of alcohol by the basic sites and oxygen by the redox functionality of the support. Examples of such a dual synergy are scarce. Moreover, the redox behavior of the reducible supports associated with O_2 activation largely remains unclear. Therefore, the development of supported AuNP catalysts with dual synergistic effect on alcohol and O_2 activations for aerobic alcohol oxidation has become a significant challenge.

Hydrotalcites (HT, typically $Mg_6Al_2(OH)_{16}CO_3 \cdot nH_2O$) are layered double hydroxides with unique and tunable surface basic properties [43–47]. The application of HT as support for AuNP has shown its promise in oxidation [23,28,29,48–50], deoxygenation [51,52], and dehydrogenation [53,54] reactions of organic chemicals. We have recently demonstrated the benefit of doping transition-metal cations into HT to render highly active AuNP catalysts for the aerobic oxidation of alcohols [28]. As the particularly strong synergy between Cr^{3+}-containing HT (Cr-HT) supports and AuNP cannot be explained by the higher basicity of Cr-HT, we unravel here in detail the Au/Cr-HT catalyst system with the aim to understand the origin of its unprecedented activity in aerobic alcohol oxidation and to provide guidance for the design of improved supported gold catalysts. We will provide compelling evidence for the importance of Cr-HT on the activation of alcohol and O_2 reactants by employing a combination of surface and bulk-sensitive spectroscopic techniques as well as kinetic studies. We will show that O_2 activation is facilitated by a $Cr^{3+} \rightarrow Cr^{6+}$ oxidation occurring at the Au/Cr-HT interface, which involves electron transfer from the Cr-HT support to AuNP. In line with this, Cr^{6+} species can only be reduced by the alcohol reactant in the presence of negatively charged AuNP to close the catalytic cycle. Kinetic investigations point to α-C–H bond breaking of the Au–alcoholate intermediate preceded by O–H bond cleavage as the most rate-controlling step in overall alcohol oxidation. Increasing the amount of Cr in the HT support enhances the synergy and overall catalytic performance, as also does the decrease in the AuNP size to subnanometer size.

2. Experimental

2.1. Materials

Various inorganic chemicals such as $HAuCl_4 \cdot 3H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ were obtained in high purity from Sigma–Aldrich. Various benzylic alcohols such as 4-methoxybenzyl alcohol (98%), 4-methylbenzyl alcohol (98%), benzyl alcohol ($\geqslant$99%), 4-chlorobenzyl alcohol (99%), 4-nitrobenzyl alcohol (99%), and benzyl alcohol-α,α-d_2 ($C_6H_5CD_2OH$, 98 atom% D) were purchased from Sigma–Aldrich. Benzyl alcohol-OD ($C_6H_5CH_2OD$) was prepared by the following procedure [55]: a Schlenk flask was charged with 0.75 g NaH under nitrogen atmosphere and then 3.0 g benzyl alcohol in 50 mL dry tetrahydrofuran solution was

added. The resulting suspension was stirred at room temperature for 1 h before adding 3 equiv. of D_2O (99.9 atom% D). The deuterated benzyl alcohol-OD was extracted with dry diethyl ether for three times, and the combined organic phase was dried over Na_2SO_4. The solvent was removed in vacuo to afford $C_6H_5CH_2OD$ (>97 atom% D by ^1H NMR).

2.2. Catalyst preparation

The various hydrotalcite supports, $Mg_{12}Al_{(4-x)}Cr_x$-HT (denoted as Crx-HT, $x = 0, 1, 2, 3$, and 4), were prepared by a modified coprecipitation method [28]. Typically, a mixed aqueous solution of Mg^{2+}, Al^{3+}, and Cr^{3+} nitrates (with molar ratio $Mg/(Al + Cr) = 3.0$) was added dropwise to an aqueous Na_2CO_3 solution (with molar ratio $Na_2CO_3/(Al + Cr) = 1.0$) at 70 °C under vigorous stirring. The pH of the slurry was adjusted to 10.5 ± 0.1 by adding aqueous NaOH (1.0 M) solution, and the resulting slurry was transferred to an autoclave and incubated at 160 °C for 48 h. The resultant solid was separated by filtration, followed by washing with deionized water (till the pH of filtrate close to 7.0) and drying at 110 °C overnight to yield Crx-HT.

The reduced Au/Crx-HT catalysts were prepared by a sequential deposition-reduction approach. Typically, the Crx-HT support (1.0 g) was added to 50 mL of an aqueous solution of $HAuCl_4$ (1.0 mM, theoretical Au loading is ~1.0 wt%). After stirring for 2 min, aqueous NaOH (0.5 M) was added to adjust the pH of slurry to 9.0. The resulting mixture was stirred at room temperature for 12 h. This slurry was filtered, washed with deionized water and dried at room temperature in vacuo. The solid was subsequently treated with aqueous $NaBH_4$ (threefold excess) solution at room temperature for 2 h, then filtered, washed and dried to yield the reduced Au/Crx-HT catalyst. The unreduced Au/Crx-HT catalysts were prepared by the similar procedure as the reduced ones, with the pH of slurry increased to 10.0 and without the $NaBH_4$ reduction step.

2.3. Catalyst characterization

X-ray diffraction (XRD) was performed on a Bruker Endeavour D4 with Cu K_α radiation (40 kV and 30 mA). Transmission electron microscopy (TEM) was conducted using a FEI Tecnai 20 electron microscope at an acceleration voltage of 200 kV with a LaB_6 filament. The average Au particle size was calculated by counting ~200 Au particles. The BET surface areas were recorded on a Tristar 3000 automated gas adsorption system. The samples were degassed at 180 °C for 6 h prior to analysis. The gold loading of the catalysts was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) after an aliquot of the sample was dissolved in a mixture of HCl and HNO_3. Basicity measurements were carried out by suspending 10 mg of catalyst in 3 mL freshly distilled water and stirring for 0.5 h. The pH of the upper clear liquid of the sedimented suspension was measured by an Inolab 730 pH meter.

X-ray photoelectron spectra (XPS) were measured on a Thermo Scientific K-Alpha spectrometer. Data analysis was performed using CasaXPS software. The binding energy was corrected for surface charging by taking the C 1s peak of contaminant carbon as a reference at 284.5 eV. Ultraviolet–visible (UV–vis) absorption spectra were recorded by a Shimadzu UV-2401 PC spectrophotometer. Diffusive reflectance ultraviolet–visible (DR UV–vis) spectra were collected in a diffusion reflectance mode with $BaSO_4$ as a reference.

Temperature programed surface reaction (TPSR) experiments were carried out as follows: after the catalyst (50 mg) was activated at 200 °C for 2 h under He stream (50 mL min^{-1}), it was cooled to room temperature and exposed to isopropanol vapor (by introducing 50 mL min^{-1} He stream through an isopropanol