Towards a greener approach for the preparation of highly active gold/carbon catalyst for the hydrochlorination of ethyne

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A B S T R A C T

Gold on activated carbon (Au/AC) materials are promising alternative catalysts for ethyne hydrochlorination. The preparation of active, stable Au/AC catalysts without *aqua regia* for ethyne hydrochlorination remains a significant challenge. A novel catalyst preparation protocol involving impregnation using a H_2O_2/HCl mixture is established for highly active Au/AC catalysts comprising primarily of single-site cationic Au species, as identified by systematic X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR) analyses and transmission electron microscopy (TEM) imaging. In addition, evaluation of the Au-C interface by temperature-programmed desorption (TPD) analyses showed that the oxidation of activated carbon by the H_2O_2/HCl mixture, which creates surface oxygen-containing functional groups (SOGs), is a crucial step for the formation of active Au/AC catalysts. The structure determination and comprehensive experimental evidence allow density functional theory (DFT) to predict that single-site cationic AuCl species stabilized by SOGs via -O- linkages are efficient active sites for Au-catalyzed ethyne hydrochlorination. In addition, these catalysts can be reused for several times with negligible changes in performance after treatment with the H_2O_2/HCl mixture. The H_2O_2/HCl mixture is thus envisioned as a viable, green alternative to toxic *aqua regia* for the preparation of Au/AC catalysts for ethyne hydrochlorination.

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1. Introduction

The potential applications of supported high evenly atomically dispersed gold in the field of catalysis have been widely discussed since Hutchings reported that gold was highly active for ethyne hydrochlorination [1] and Haruta's report of CO oxidation catalyzed by gold dispersed on metal oxides [2]. Generally, the activity of a Au catalysts is frequently discussed in terms of metal dispersion, the perimeter interface between gold and the support and the oxidation states of gold. When the dispersions are high, a greater number of active metal atoms may be expose to the surface, which is accessible to substrates and available for catalysis. In addition, the active species of the gold catalysts are not limited to the metallic state (such as Au⁰), and numerous catalytic reactions involved high-valent cationic Au species as the active sites in these Au-based catalysts. For example, for CO oxidation [3] and water-gas shift reactions [4], cationic Au species are more active than metallic Au⁰ species. Additionally, the reaction between ethyne and hydrogen chloride for the direct production of the industrially valuable vinyl chloride monomer (VCM) has been extensively studied, and recently, great progress was made in this field [5,6].

Most studies on supported Au catalysts involve the use of metal oxides as supports [7]. Compared with oxide materials, however, carbon materials have many advantages: they have higher chemical stability, and the supported metals can easily be retrieved by burning the carbon materials [8]. In addition, the properties of carbon materials (e.g., the texture properties and the surface chemistry) can easily be adjusted for particular applications [9,10]. Au cationic species can also be stabilized by surface groups of carbon materials, and such stabilized species may serve as the active sites for certain reactions [11]. However, due to the low melting point of Au, the high surface energy of small Au particles and the redox properties of carbon materials, such ultra-small or even atomically dispersed gold containing active cationic species are challenging to synthesize and stabilize on the carbon material support using traditional catalyst preparation methods (e.g., deposition-precipitation and impregnation) [12].

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Recently, Hutchings et al. proposed that deposition of $HAuCl_4$ as a precursor onto a carbon support in the presence of *aqua regia* as an impregnation solvent led to considerably active hydrochlorination catalysts because of the formation of single-site cationic Au entities ($AuCl_x$), which act as the active sites in the final material [13,14]. The study also demonstrated that the active species consist of a single-site Au^+ and Au^{3+} cationic species [14]. However, metallic Au^0 species are inactive and are not involving in the reaction [15]. Despite the demonstrated high activity of the Au/C catalyst prepared using *aqua regia*, there are several drawbacks to this technique that make it incompatible with common industrial manufacturing processes. First, *aqua regia* is the origin of toxic NOCl, Cl_2 and NO_x, which would cause serious environmental impacts and limit process safety. Second, the Au/C catalysts made with *aqua regia* are unstable during long reactions due to the dynamic nature of the surface Au species [16]. Finally, the use of the *aqua regia* for the preparation of Au/AC catalysts lead to considerable agglomeration of the gold on the carbon support, which makes it impossible to decreasing the metal loading [17–19]. To circumvent those issues, alternative catalyst preparation methods that are greener and more effective are necessary.

Thus, as a continuation of Hutchings' efforts, we describe an environmentally benign approach using a mixture of hydrogen peroxide and hydrochloric acid (H_2O_2/HCl), i.e., a "green *aqua regia*", which provides facile entry to the production of active Au/AC catalysts and is suitable for practical use. This H_2O_2/HCl mixture was also found to efficiently produce single-site active $AuCl_x$ entities on the carbon support through a combination of the oxidizing effect of the H_2O_2/HCl mixture on the metallic Au^0 species which was related with the reduction property of carbon towards Au^{3+} and the carbon support, which facilitates high-valent and atomically dispersed cationic Au sites. These observations were supported by substantial catalyst characterization studies. Then, the catalytic performances of the prepared Au-based catalysts were investigated in the hydrochlorination of ethyne. In contrast to the catalyst prepared using *aqua regia* (Au/ROX08(AQ)), we demonstrated that the new preparation method using the H_2O_2/HCl mixture leads to catalysts (Au/ROX08(AP)) with improved activity and stability. Mechanistic studies revealed that the surface oxygen-containing functional groups (SOGs) created by the H_2O_2/HCl mixture are better than *aqua regia* at stabilizing single-site cationic Au sites. More importantly, density functional theory (DFT) calculations showed that isolated cationic AuCl entities directly bonded to SOGs (e.g., carbonyl groups) on the carbon support could catalyze the reaction more effectively than AuCl on a graphite surface. In addition, the used catalyst could be efficiently reactivated using H_2O_2/HCl mixture treatment. This strategy allows the green preparation of highly dispersed and active gold/-carbon catalysts.

2. Experimental

2.1. Catalyst preparation

A commercially extruded activated carbon species, Norit ROX08 (surface area of 1100–1200 m^2/g, pore volume of 0.63 cm^3/g, density of 400 g/L, maximum diameter of 0.5 mm, and length of 1–5 mm; ROX08 is a steam-activated carbon that can be thermally reactivated) was used as the catalyst support. First, the ROX08 carbon was ground to obtain a powder (80–100 mesh) and then pretreated with HCl (>36 wt%) to remove residual metal ions (such as trace amounts of K^+ and Al^{3+}). The pretreated ROX08 carbon was filtered, washed with deionized water until the pH of the filtrate was 7, and then dried for use.

A series of carbon-supported Au catalysts were prepared via a wet impregnation method. In a typical synthesis of the 1.0 wt% Au/ROX08(AP) catalyst, 0.6 mL of $HAuCl_4$ (0.05 g_{Au}/mL) aqueous solution was added into 5.4 mL of H_2O_2/HCl mixture (1:3 H_2O_2(30 wt%): HCl (36 wt%)) in a 20 mL flask under magnetic stirring. The solution was stirred for 1 h after complete addition of the $HAuCl_4$ solution. Then, the solution of the gold precursor was added dropwise to 2.97 g of pretreated ROX08 carbon support. The mixture was stirred vigorously for 4 h and then dried at 110 °C under vacuum for 12 h. The synthetic procedures for preparing Au/ROX08(AP) with different Au loadings ranging from 0.1 wt% to 0.5 wt% were similar to that for 1.0 wt% Au/ROX08 (AP), except for the concentration and amount of $HAuCl_4$ solution. $HAuCl_4 \cdot 4H_2O$ solutions in 36 wt% hydrochloric acid or 30 wt% hydrogen peroxide solutions were also prepared to obtain Au catalysts with 1.0 wt% loading. The samples were designated Au/ROX08(A) and Au/ROX08(P), respectively. For comparison, the Au/ROX08(AQ) catalyst was also prepared using *aqua regia* (1:3 HNO_3 (>65 wt%): HCl (>36 wt%)) as solvent in an identical procedure. This catalyst was used as a reference.

The catalysts prepared using deionized water as the solvent on the untreated ROX08 carbon or ROX08 carbon pretreated by the H_2O_2/HCl mixture or *aqua regia* were labeled Au/ROX08-H_2O, Au/ROX08(AP)-H_2O and Au/ROX08(AQ)-H_2O, respectively.

2.2. The regeneration of used Au/ROX08(AP) catalyst

Regeneration treatments of the used catalysts were carried out in a sealed glass vial. In a typical treatment, 2 mL of the H_2O_2/HCl mixture (1:3 H_2O_2: HCl) was prepared in a sealed sample vial. After that, 1 g of the used Au/ROX08(AP) catalyst was added to the mixed solution. The samples were vigorously stirred at 70 °C under ambient pressure for 4 h. After treatment, the samples were dried at 110 °C for 12 h to give the regenerated catalyst, which was labeled Au/ROX08(AP)-R.

2.3. Catalyst characterization and computational procedures

X-ray diffraction (XRD) measurements were carried out on a PANalytical-X'Pert PRO generator with Cu Kα radiation (λ = 0.1541 nm) operating at 60 kV and 55 mA. Diffraction patterns were recorded at a scanning rate of 2° min^{-1} and at a step angle of 0.02°. Transmission electron microscopy (TEM) images were acquired on a Cs-corrected FEI Titan G2 60–300 Microscope operating at 300 kV using an HAADF detector. The solid samples were finely ground and dispersed ultrasonically in ethanol and then transferred to a carbon/Cu grid. Images that clearly reveal single Au atoms were typically recorded at 10 M x direct magnification. Because the nanoparticles and sub-nm species have almost equal chances to be imaged on the support surfaces, the various gold species (>200 total counts) near the edges of the samples in different regions were counted and analyzed. X-ray photoelectron spectroscopy (XPS) was performed with a Kratos AXIS Ultra DLD spectrometer to determine the elemental surface composition of the catalysts. The monochromatized aluminum X-ray source was 1486.6 eV, and the passed energy with an electron analyzer was 40 eV. The pressure in the analysis chamber was lower than 5×10^{-10} Torr during data acquisition. The samples were outgassed under vacuum for 4 h before loading. Binding energies were referred to the C1s line at 284.8 eV. Temperature-programmed reduction (TPR) was performed in a micro-flow reactor fed with hydrogen (10% in Ar) at a flow rate of 45 mL min^{-1}. The temperature was increased from 30 °C to 850 °C at a rate of 10 °C min^{-1}. A thermal conductivity detector (TCD) was used to measure the hydrogen consumption. The integrated TPR signal using CuO as a standard was used to calibrate the TCD. The $AuCl_x$ amount is