



Vital roles of hydroxyl groups and gold oxidation states in Au/ZrO₂ catalysts for 1,3-butadiene hydrogenation

Xin Zhang^{a,b}, Hui Shi^{a,1}, Bo-Qing Xu^{a,*}

^a Innovative Catalysis Program, Key Lab for Organic Optoelectronics & Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China

^b State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Changping, Beijing 102249, China

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ABSTRACT

Hydrogenation of 1,3-butadiene over Au/ZrO₂ catalysts with different gold loadings and calcination temperatures was reported. The catalysts were characterized in depth to understand their structure–property relationship. Gold oxidation states and surface hydroxyl groups, which were found to be sensitive to the gold loading, calcination temperature, and treatment with water, were shown to play vital roles in the hydrogenation activity of Au/ZrO₂. Continued activity decrease was seen when the density of surface hydroxyl groups was lowered by elevating the pre-calcination temperature of ZrO₂. Fully dehydroxylated Au/ZrO₂ was essentially inactive, but became very active after partial regeneration of the hydroxyl groups by water treatment. Moreover, the activity of Au/ZrO₂ increased with increasing Au³⁺/Au⁰ ratio. Isolated Au³⁺ ions at the support surface showed up to two orders of magnitude higher activity than Au⁰ atoms on Au particles. Several models are proposed to address the structural features of active sites for H₂ activation in Au/ZrO₂ catalysts.

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1. Introduction

Supported gold catalysts have unexpectedly been found to be active for a wide variety of reactions [1]; however, most of the studies have been devoted to the unprecedented activity of nano-sized gold catalysts for CO oxidation. The nature of active sites and reaction mechanisms for CO oxidation on gold catalysts has been extensively studied [1–6]. In contrast, little work has been done to gain insight into the activity and nature of gold catalysts for hydrogenation reactions [7,8], especially for the hydrogenation of unsaturated hydrocarbons [9–13], in spite of some elegant documentation on gold-catalyzed hydrogenation of α,β -unsaturated aldehydes/ketones [14–18]. This is surprising, since catalytic hydrogenation represents a well-studied and industrially important category of chemical reactions on conventional transition metal catalysts [19].

Supported gold catalysts prepared by the conventional impregnation method were found to show very low catalytic rates for the hydrogenation of unsaturated hydrocarbons in the 1970s [9,10]. The first report was made by Bond et al. [9], who investigated impregnated Au/SiO₂ and Au/ γ -Al₂O₃ catalysts for the hydrogenation of 1-pentene, 1,3-butadiene, and 2-butyne. These authors

speculated, without direct evidence, that the hydrogenation activity of their gold catalysts arose from small gold particles having a large number of defects, or resided in even smaller particles not witnessed by electron microscopy. Buchanan and Webb [10] studied the reaction of 1,3-butadiene with H₂/D₂ over Au/Al₂O₃ catalysts with widely varied Au sizes. They claimed that the special sites capable of activating molecular hydrogen would reside in extremely small gold particles not sensed by their electron microscopy. Due to the limitations of the impregnation method for preparing gold catalysts (e.g., wide Au size distribution and possible contamination by poisonous chloride residues [1,4,12]), these earlier attempts to understand the catalytic sites might be severely distorted. Using improved preparation methods (e.g., deposition–precipitation), Au nanoparticles on oxide supports were prepared and tested as catalysts for the hydrogenation of unsaturated hydrocarbons [12,13]. For the hydrogenation of acetylene over Au/Al₂O₃, a maximum reaction rate was observed over the sample having an average Au particle size of 3 nm [13]. For hydrogenation of 1,3-butadiene, however, the reaction rates over oxide-supported Au catalysts appeared almost insensitive to the Au particle size as well as to the nature of the oxide supports [12].

In contrast to the well-established knowledge of H₂ chemisorption/activation over Group VIII metals (e.g., Pd, Pt), H₂ chemisorption/activation on supported gold catalysts is far from clear. Chemisorption of H₂ molecules does not occur on clean “bulky” gold surfaces but is occasionally reported on supported small gold nanoparticles [7,11,20,21]. Theoretical calculations of H₂ activation

* Corresponding author. Fax: +86 10 6279 2122.

E-mail address: bqxu@mail.tsinghua.edu.cn (B.-Q. Xu).

¹ Present address: Department Chemie, Technische Universität München, Lichtenbergstr. 4, D-85748 Garching, Germany.

by dissociation on single-crystal Au surfaces or gold clusters with varying numbers of Au atoms provide some information [22–24], but these theoretical models can be far from real catalysts and sometimes produce controversial results. It should be pointed out that these earlier experimental and/or theoretical assessments of H₂ chemisorption and hydrogenation reactions were in most cases done on supported metallic gold catalysts, which could have neglected possible involvements of cationic gold species and the underlying support surfaces in H₂ activation.

For CO oxidation [25–28] and water–gas shift reactions [29], cationic gold species (Au³⁺ and/or Au⁺) sometimes are found to be superior to metallic gold (Au⁰), at least on several oxide supports. The first demonstration of high activity of immobilized Au³⁺ ions for olefin hydrogenation was documented using MgO-supported mononuclear Au (III) complex catalyst for ethene hydrogenation [30]. It was clearly shown with in situ X-ray absorption near-edge structure (XANES) that mononuclear Au³⁺ complexes, but not metallic gold clusters, were responsible for the hydrogenation activity [30]. We previously communicated that isolated Au³⁺ ions on a ZrO₂ surface were highly active for the selective hydrogenation of 1,3-butadiene [27,31]. These cationic gold species were also found to be active for olefin (propene) hydrogenation [32]. These results are encouraging, which identified that immobilized surface cationic gold species have potential as new catalyst for the hydrogenation of unsaturated hydrocarbons, even though H₂ could potentially be a reducing agent to the cationic gold species.

It was reported that moisture (water vapor) in the reaction feed or in some cases hydroxyl groups on the catalyst surface [33,34] could influence the catalytic activity of oxide-supported gold for CO oxidation. Nevertheless, effects of moisture and surface hydroxyl groups on the gold-catalyzed hydrogenation of unsaturated hydrocarbons have not yet been explored. Here, a series of Au/ZrO₂ catalysts, with different gold loadings and calcination temperatures, are prepared by deposition–precipitation and investigated for the selective hydrogenation of 1,3-butadiene. A detailed analysis of the catalyst structure is provided, based on characterizations using a variety of techniques. We attempt to gain insight into the structure–performance relationship for 1,3-butadiene hydrogenation over these Au/ZrO₂ catalysts. Particular attention is paid to the effects of moisture in the reaction feed, density of hydroxyl groups on the support surface, and percentage of Au³⁺ species in gold. Several model structures are envisaged to discuss the structural features of active sites in Au/ZrO₂ catalysts.

2. Experimental

2.1. Catalyst preparation

Two kinds of zirconia were prepared, using ZrO(OH)₂ hydrogel obtained by hydrolysis of zirconyl chloride in aqueous ammonia, as described previously [5,35]. Following our earlier sample coding, ZrO₂-CP-*t* denotes the sample prepared by calcination for 5 h in flowing air of the ZrO(OH)₂ hydrogel at temperature *t* = 673, 873, 973 and 1073 K, respectively. A ZrO(OH)₂ alcogel was prepared by extensive washing with anhydrous ethanol of the ZrO(OH)₂ hydrogel [35]. A follow-up calcination for 5 h of the ZrO(OH)₂ alcogel in flowing N₂ at temperature *t* produced the ZrO₂-AN-*t* samples.

Zirconia-supported gold catalysts were prepared using a deposition–precipitation method. Briefly, zirconia powders (2 g) were added into an appropriate amount of aqueous HAuCl₄ solution. The solution pH was adjusted to ca. 9 by controlled addition of 0.2 M NH₃·H₂O solution. The aqueous dispersions were stirred for 6 h, aged for 2 h, and suction filtered. Extensive washing with deionized water was then continued until it was free of Cl⁻ ions.

Conductivity of the final filtrate was less than 10⁻⁵ S m⁻¹. The samples were dried at 393 K overnight and then calcined in flowing air (60 ml min⁻¹) at temperature *T* for 5 h (ramp rate: 10 K min⁻¹). The samples were denoted as Au/ZrO₂-CP(AN)-*t*-*T*. *t* refers again to the pre-calcination temperature of ZrO₂ support (before gold was loaded) and *T* is the catalyst calcination temperature (after gold was loaded). Unless specified, the actual gold loadings were between 0.63 and 0.76 wt.% by ICP-AES analysis, but the nominal gold loading in the preparation was 1.0 wt.% for these Au/ZrO₂-CP-*t*-*T* and -AN-*t*-*T* samples. Variation in gold loading in the range of 0.01–1.0 wt.% was intentionally made within the Au/ZrO₂-CP-673-473 samples, by adjusting the amounts of aqueous HAuCl₄ during the deposition–precipitation stage; these samples are labeled as *m*%Au/ZrO₂-CP-673-473 and *m*% denotes the actual gold loading by weight percentage. In addition, a 0.08%Au/ZrO₂-CP-673-473 was prepared by treatment of the Au/ZrO₂-CP-673-473 (1.0% nominal Au loading) with a 2% KCN solution as described previously [31].

2.2. Catalyst characterizations

The catalysts were characterized by a number of techniques including XRD, TEM, XPS, TPR, ESR, IR, TG-DTA, N₂ adsorption, and element analysis (ICP-AES), the details of which are given in the Supplementary material. H₂-TPD measurements were performed on a TPR apparatus [31] equipped with both TCD and MS (Balzers MSC 200) detectors. Typically, the catalyst sample (200 mg for 0.05%Au/ZrO₂-CP-673-473, 100 mg for the others) was put into a U-shaped quartz reactor (i.d. 4 mm) and pretreated in flowing Ar at the catalyst calcination temperature *T* for 1 h. After the sample was cooled to 393 K (the reaction temperature of 1,3-butadiene hydrogenation), the reactor was switched to H₂ flow (45 ml min⁻¹) for 1 h. The reactor was then switched back to Ar and purged for 0.5 h, followed by cooling to room temperature. TCD and MS (*m/z* = 2) signals were recorded when the reactor was heated from room temperature up to 1073 K at a rate of 10 K min⁻¹ in flowing Ar (45 ml min⁻¹).

2.3. Catalytic hydrogenation of 1,3-butadiene

Hydrogenation of 1,3-butadiene was carried out at 393 K in a fixed-bed flow stainless reactor (i.d. 6 mm) under atmospheric pressure. Unless otherwise specified, the reaction feed was a gas mixture of 2.15 vol.% 1,3-butadiene in H₂, which was introduced into the reactor at a space velocity (GHSV) of 8100 ml h⁻¹ (g cat.)⁻¹. The catalyst (ca. 100 mg Au/ZrO₂ in 80–120 mesh) was diluted with 500 mg of quartz sand before being loaded into the reactor. Before it was switched to the reaction feed gas, the catalyst was pretreated in flowing Ar (30 ml min⁻¹) at 473 K for 2 h. The reaction conditions were similar to those applied by Okumura et al. [12]. In some experiments, a 0.05%Au/ZrO₂-CP-673-473 catalyst was pretreated with flowing H₂ (30 ml min⁻¹) at 473 or 523 K for 2 h to investigate the effect of hydrogen reduction on catalyst activity; the reduced catalyst was then cooled to 393 K in flowing Ar (30 ml min⁻¹) to evaluate its catalytic activity for the hydrogenation reaction. Any significant mass-transfer limitation was precluded in a series of pre-experiments at a fixed space velocity (e.g., GHSV = 8100 ml h⁻¹ (g cat.)⁻¹) so that the conversion of 1,3-butadiene over a highly active Au/ZrO₂ catalyst was not significantly affected by changing the flow rate of the reaction feed and the catalyst pellet size in 40–120 mesh. The reactor effluent was analyzed on line using a GC-8A gas chromatograph equipped with a GDX-501 column and a FID detector.

To study the effect of moisture on the hydrogenation reaction, the reaction feed gas was set to pass through a glass vessel (250 ml) containing ca. 50 g H₂O. The temperature was varied

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