Reviews

Recent development of supported monometallic gold as heterogeneous catalyst for selective liquid phase hydrogenation reactions

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ABSTRACT

The great potential of gold catalysts for chemical conversions in both industrial and environmental concerns has attracted increasing interest in many fields of research. Gold nanoparticles supported by metal oxides with high surface area have been recognized as highly efficient and effective green heterogeneous catalyst even at room temperature under normal reaction conditions, in gas and liquid phase reactions. In the present review, we discuss the recent development of heterogeneous, supported monometallic gold catalysts for organic transformations emphasizing mainly liquid phase hydrogenation reactions. Discussions on the catalytic synthesis procedures and the promoting effect of other noble metals are omitted since they are already worked out. Applications of heterogeneous, supported monometallic catalysts for chemoselective hydrogenations in liquid phase are studied including potential articles during the period 2000–2013.

1. Introduction

In the perspective of environmental pollution, heterogeneous catalysis has acquired a vital role since it is a very efficient green approach. The main concepts of green catalysis are as follows: (1) usage of eco-friendly solvents; (2) avoidance of hazardous wastes; (3) usage of recyclable catalysts; (4) mild reaction conditions; and (5) high efficiency and selectivity [1]. Over the past few years, heterogeneous catalysis by nano-gold catalysts has attracted the attention of researchers because it is a highly proficient substitute for non-separable and pollutant homogeneous catalysis. Recent studies on the applications of nano-gold catalyst have opened many enchanting doors in the world of nanotechnology, since it meets all the criteria to be an excellent green recyclable heterogeneous catalyst. Metallic gold is catalytically inactive due to less stability of gold oxide according to the Tanaka–Tamaru rule [2]. Although it is a prized metal, it is more available and economical compared to other noble metals such as Pt and Pd and the peculiarities of nano-gold catalysts attract the attention to be a heterogeneous recyclable catalyst [3]. The applications of nano-gold catalysts are not confined in a particular field. Although about 83% of mined gold is demanded for jewelry applications, the rest is used for the environmental matters, chemical processing, fuel cells and medicinal purpose especially in tumor diagnosis [4].

The first observed gold catalysis was in 1906 accidently during oxidation of hydrogen on gold gauze. Studies were then carried on to apply gold as a catalyst [5]. In 1971 Yolles *et al.* [6] reported the use of gold catalyst for hydrogenation reaction. Bond *et al.* [7] in 1973 proved

the surprising performance of oxide supported nano-gold in the alkyne hydrogenation reactions and it was shown that gold supported by alumina or silica can actively catalyze hydrogenation of alkenes at 100 °C even at low percentage gold loading [8]. In 1980s Haruta *et al.* [9] reported the amazing catalytic activity of nano-gold on metal oxide support towards CO oxidation at lower temperatures. In 1996 Hutchings *et al.* [10] recognized that ethyne could be hydrochlorinated by $AuCl_3$, with catalytic activity owing to the high standard electrode potential of gold. The initial work for liquid phase reactions was done by Prati and Rossi in 1998 [11]. It is proposed that the astonishing catalytic activity of nano-gold catalysts may be due to quantum size effects, development of charge on nano-gold particle due to the interactions with imperfections in the oxide support, presence of easily available low coordinated nano-gold particles, large surface area of nano-gold particles [12], and largely available oxygen free surface [13]. The Lewis acidity of nano-gold catalyst facilitates the formation of carbon–carbon and carbon hetero atom bond in unsaturated compounds such as alkenes, alkynes, and allenes *via* activation of sp, sp^2, and sp^3 carbon hydrogen bonds by pre-coordination [14,15]. The major advantages of nano-gold catalysts are their long time stability [16–18] and poison resistivity [19].

The role of support is very important for the supported nano-gold catalysts. Support will influence the electronic structure of gold by charge transfer between negatively charged defects on the support and gold particles [20]. The support functions as a nucleating agent, stabilizing small sized Au particles by strong support-gold interactions and mobilizing them to prevent sintering during calcination [21]. The more active state of gold is still uncertain and metallic gold clusters [22], cationic gold [23], and anionic gold species [24] have been reported as active sites. The mechanism with nano-gold as catalyst is still unknown because of the intricacy of the reaction and it is thought to be followed

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by weakening of bonds in reactants due to adsorption of the nano-gold catalyst [25].

Supported nano-gold is found to be resourceful catalysts for liquid phase organic reactions in addition to reactions in the gas phase. There are hundreds of reports on the applications of nano-gold catalysts for liquid phase reactions. Nano-gold can be used as a redox catalyst and studies shows that the catalysts are highly active and extraordinarily selective. Nano-gold catalyzed reactions in liquid phase present advantages such as heterogeneity, reusability and feasibility under mild reaction conditions. The surprising activity and selectivity of nano-gold catalysts are governed by the nature of support and the method of preparation [26]. The pH value, temperature, percentage of gold loading, aging period, calcination temperature, *etc.* largely affect catalyst particle size, catalyst morphology and oxidation state of Au [27]. It has been proved that oxide supported nano-gold catalysts are capable of accelerating redox reactions.

Gold has less ability to chemisorb hydrogen compared to other metals such as Pt and Pd [28–31] and catalytically less active for hydrogen reactions including hydrogen dissociation [32]. By studying dissociative hydrogen chemisorption on unsintered thin gold film, Stobinski *et al.* proposed that hydrogen reacts with low coordinated gold atom on edge sites and corner sites [33]. A study by Lin and Vannice [34] on titania supported nano-gold suggested reversible and weak adsorption of hydrogen and it was then substantiated by Bus *et al.* using Au/Al$_2$O$_3$ [35]. Observations by Boronat *et al.* [36] concluded that small gold particles with a higher fraction of low coordinated gold atoms occupied edges and corners will have a higher number of active gold sites for hydrogen dissociation. Fujitani *et al.* [37] carried out a study over Au/TiO$_2$ and suggested that H$_2$ dissociation was not so much related to a change in the fraction of edge and corner sites or a change in the electronic nature caused by the quantum size effect.

There are many reviews in the field of gold catalysis. A recent publication by Zhang *et al.* reviewed the use of nano-gold catalysts in fine chemical synthesis [38]. Hashmi and Hutchings in 2006 published the most comprehensive review in gold catalysis [39]. Rudolpha and Hashmi updated the recent developments in gold catalysis in total synthesis [40]. McEwan *et al.* reviewed the use of gold catalysts in selective hydrogenation reactions particularly for chemoselective hydrogenation of α, β-unsaturated aldehydes and selective partial hydrogenation of lower hydrocarbons (C$_2$–C$_6$) [41]. One of the latest reviews is on the development of gold catalysts for use in hydrogenation reactions [42], focusing on recent model hydrogenation experiments and theoretical calculations on a well-structured gold surface to get more information on reaction mechanism [43].

The present paper reviews recent development of supported monometallic gold as heterogeneous catalyst for selective liquid phase hydrogenation reactions. The main concern of this review is the establishment of the role of supported nano-gold as reusable green heterogeneous catalyst in liquid phase hydrogenation reactions. We concentrate only on the applications of supported monometallic nano-gold as heterogeneous catalyst and a comparative study between catalytic activity of nano-gold as homogeneous and heterogeneous catalyst is beyond this study. Through this review, we aim to highlight the potential role of supported monometallic gold catalyst for a wide range of hydrogenation reactions and discuss catalytic results and the mechanism of hydrogenation in brief.

2. Selective Hydrogenation Reactions

Catalytic hydrogenation is one of the most important reactions extensively employed in industry. The main problem with catalytic hydrogenation reactions is their chemical and stereo-selectivity [44]. Nanoparticles of Pd, Ni, Ru, or Pt are generally used for hydrogenations [45], because dissociatively adsorbed hydrogen is easily available on these metals. It has been found that supported nano-gold is an efficient catalyst for selective hydrogenation reaction since the reports by Haruta

et al. [9] and other researchers at the end of 1980s [46]. Supported nano-gold is highly selective for hydrogenation of various functional groups including C=O, CH=O, NO$_2$, and C=C. The mechanism of hydrogen adsorption on the nano-gold catalysts and the hydrogen active sites are still not confirmed [47]. The nano-gold catalysts are found to be good for a variety of hydrogenation reactions.

2.1. Hydrogenation of α, β-unsaturated aldehydes

The selective hydrogenation of C=O bond in α, β unsaturated aldehydes is thermodynamically less preferred over C=C bond since C=C bond is an active center for hydrogenation due to electron transfer from support to metal [44,48]. Supported gold catalysts are found to be good for the selective hydrogenation of α, β unsaturated aldehydes to corresponding α, β unsaturated alcohols. Hydrogenation with conventional hydrogenation catalysts results in the formation of saturated alcohols and aldehydes. C=O or C=C bond in α, β-unsaturated aldehydes can be selectively oxidized with nano-gold on suitable supports.

2.1.1. Hydrogenation of crotonaldehyde

Schematic representation of hydrogenation of crotonaldehyde to crotyl alcohol is shown in Fig. 1. Zanella *et al.* [49,50] prepared Au/TiO$_2$ by deposition precipitation method with NaOH and urea and activated the catalyst under hydrogen or air. The activity of the catalyst was tested for crotonaldehyde hydrogenation. It was noted that the catalytic activity and turn over frequency (TOF) increased with particle size, independent of preparation method. The average particle size of the catalyst did not increase drastically with the increase of reduction temperature, confirmed by transmission electron microscopy (TEM) images. X-ray absorption near-edge structure (XANES) spectra for catalyst systems pretreated at different temperatures were the same and similar to that of Au^0 reference of gold foil. The catalytic activity reached maximum when particle size was 2 nm and decreased to 1/10 as particle size increased to 4 nm. Up to 50% crotonaldehyde conversion and 60%–70% selectivity to crotyl alcohol were maintained. It is suggested that the dissociation of hydrogen on the low coordinated sites of gold particles is the rate-determining step and crotonaldehyde is adsorbed on gold particles through a η^3 or η^4 mode of adsorption. The η^3 and η^4 adsorption modes of crotonaldehyde are represented in Fig. 2.
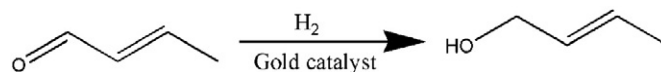

Fig. 1. Selective hydrogenation of crotonaldehyde to crotyl alcohol.

Campo *et al.* [51] studied crotonaldehyde hydrogenation over Au/Nb$_2$O$_5$ and Au/CeO$_2$ with isopropanol as solvent. It was found that Au/CeO$_2$ was less selective to crotyl alcohol in liquid phase hydrogenation and Au/Nb$_2$O$_5$ was unselective in both cases (conversion only 20%). In the X-ray diffraction (XRD) patterns of both catalysts, the peak corresponding to noble metal was absent, which indicates that the gold metal particles are smaller in size. Unlike the temperature-programmed reduction (TPR) profile of Au/Nb$_2$O$_5$, strong modification was observed for Au/CeO$_2$, which reveals that gold increases reduction. The less selectivity of Au/CeO$_2$ was assumed to be due to secondary reactions. In the case of Au/Nb$_2$O$_5$ it was proposed that Nb$_2$O$_5$ favors the presence of gold crystallites with low concentration of edges as reported by Claus and coworkers [46], which results in unselective of Au/Nb$_2$O$_5$. Campo *et al.* further investigated the influence of surface area of the Au/CeO$_2$ system in crotyl alcohol selectivity [52]. Considerable selectivity to crotyl alcohol (29%) was obtained only for Au/CeO$_2$ system with the highest surface area (240 m^2·g^{-1}) because of high gold dispersion, the selectivity of