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Silica-supported Au–Cu alloy nanoparticles as an efficient catalyst for selective oxidation of alcohols

Wanjun Li[a,b], Aiqin Wang[a], Xiaoyan Liu[a], Tao Zhang[a,*]

[a] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023, PR China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

Silica-supported Au–Cu and Au–Ag alloy nanoparticles were synthesized, characterized, and tested for the aerobic oxidation of alcohols. The results showed that Au–Cu alloy catalyst exhibited good activity and selectivity to aldehydes for a variety of structurally diverse alcohols and a strong synergistic effect was found between Au and Cu. In contrast, Au–Ag alloy catalysts were less active and selective for the oxidation of alcohols although they have very similar particle sizes to the Au–Cu alloy catalysts. Besides the chemical compositions, the pretreatment conditions were found to affect significantly the catalytic performances, and the reduction treatment is necessary for obtaining a high activity and selectivity, suggesting Au–Cu alloy is the active phase. Moreover, the catalyst could be reused if only the catalyst after the reaction was subjected to reduction treatment.

1. Introduction

Selective oxidation of alcohols to corresponding aldehydes or ketones is one of the most important tasks in the fine chemicals industry [1]. Traditional synthesis is performed by using stoichiometric amounts of oxidants (such as chromate) which always lead to environmental problems or even more economic problems [2]. Therefore, a green process involving the use of molecular oxygen as a primary oxidant in the presence of a catalyst, producing water as the only by-product, has attracted much attention [3–6]. Transition metal nanoparticle catalysts, such as Pd [7,8], Pt [9,10], and Ru [11–14] have been widely investigated, and many of them show good activity and selectivity. In comparison with these platinum group metal catalysts, supported gold nanocatalyst is emerging as a new and highly selective catalyst for the aerobic oxidation of alcohols [15–17]. For example, Abad et al. showed that nanosized ceria supported gold nanoparticles were highly active and selective for the oxidation of alcohols to corresponding aldehyde [18], and Su et al. employed Ga–Al mixed oxide as a support of gold nanoparticles and found that the resultant catalyst could efficiently catalyze the aerobic oxidation of various alcohols [19]. Gold nanoparticles supported on a Cu–Mg–Al-mixed oxide was also reported to be highly active for the alcohol oxidation reaction [20,21]. In these examples, the basic supports played important roles in promoting dehydrogenation of alcohols which is generally considered as a rate-determining step. In contrast, when gold is supported on an inert support such as silica or alumina, the activity or selectivity is relatively poor due to the absence of a base promoter [22,23].

In order to get a highly active and selective nanogold catalyst, alloying gold with another metal has proved as an effective method in addition to choosing a proper support [15,16,24]. For example, Enache et al. showed that Au–Pd/TiO_2 catalyst gave very high turnover frequencies for the oxidation of alcohols including less reactive primary alkyl alcohols [15]. Prati and coworkers showed that Au–Pd/AC and Au–Pt/AC were more active and selective for the oxidation of alcohols and glucose [16,25,26]. Miyamura et al. found that the addition of Pt to Au could efficiently enhance the catalytic activity for oxidation of a variety of alcohols at room temperature [27]. These examples demonstrate that alloying gold with platinum group metals can dramatically enhance the activity or selectivity in the oxidation of alcohols. Nevertheless, the platinum group metals are expensive and scarce in their resources.

An alternative strategy is to alloy Au with a less expensive metal, in particular with the same group metals such as Cu or Ag. In our earlier work [28–34], we have successfully prepared thermally stable and very uniform Au–Ag and Au–Cu alloy nanoparticles on silica support, and found that they were much more active than pure gold catalyst for CO oxidation. Considering that both Ag [35–37] and Cu [38–40] are active for dehydrogenation of alcohols, we explored the potentials of Au–Cu and Au–Ag alloy

* Corresponding author. Tel.: +86 411 84379015; fax: +86 411 84691570.
E-mail address: taozhang@dicp.ac.cn (T. Zhang).

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