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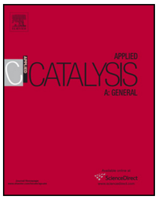

NiO-doped Au/Ti-powder: A catalyst with dramatic improvement in activity for gas-phase oxidation of alcohols

Guofeng Zhao[a], Huanyun Hu[a], Zheng Jiang[b], Shuo Zhang[b], Yong Lu[a,*]

[a] *Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China*
[b] *Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China*

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ABSTRACT

An active and stable NiO@Au/Ti-powder catalyst, which can be obtained by doping Au/Ti-powder (Au: 35–40 nm) with NiO, has been developed for the gas-phase oxidation of alcohols. Gold particles are found to be partially covered with tiny NiO segments to form specific NiO@Au ensembles thereby leading to a dramatic conversion improvement from only ~5% (without NiO doping) to ~94% for the benzyl alcohol oxidation at 280 °C. Additionally, the selective oxidation of cyclopropyl carbinol can proceed over this catalyst at 280 °C with a selectivity of 94% and a conversion of 72–80% throughout the entire 300 h test. The hybrid active-sites, Ni_2O_3-Au^+, on the NiO@Au ensemble are identified using X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS).

1. Introduction

Selective oxidations of alcohols to carbonyl compounds are some of the most important processes in organic chemistry, both in laboratory and in industrial manufacturing [1–9]. However, the use of various toxic and expensive stoichiometric inorganic oxidants (notably Cr reagents) and volatile organic solvents in the existing oxidation processes causes serious problems in product separation and environmental issues, obviously conflicting the atom-economical concept of green chemistry [1–9]. Therefore, there should be a paradigm shift away from traditional approaches, aimed at using atmospheric air and recyclable heterogeneous catalysts under solvent-free conditions [1–9].

Supported gold catalysts have been extensively studied for the aerobic oxidation of alcohols [1–9]. Generally, their activity is related to the size of gold nanoparticles (Au NPs) [2,4,10–13], the chemical state of the gold [14–16], the support properties [17–21], and the gold-support interactions [22]. The small Au NPs (<5 nm) has been widely accepted to be essential for good catalytic activity [12], and the other factors are all discussed based on the use of the small Au NPs. Recently, however, some reports disclosed the occurrence of the opposite behavior, which warrants the reconsideration of this fundamental belief. For example, catalysts comprising a transition metal oxide deposited on a single crystal of gold, such as CeO_2/Au(1 1 1) [23,24] and TiO_2/Au(1 1 1) [25], are not even nano-scale but still show higher catalytic activity than Au NPs supported on oxides. Therefore, particle size is not the only parameter that strongly affects the activity of these catalysts. There should be another model to explain the excellent activity displayed by the large gold particles in some reactions.

More recently, NiO@Au ensembles (*i.e.*, partial coverage of 20–30 nm Au particles with NiO segments) have been reported by our group, which are highly active and selective for the gas-phase oxidation of alcohols [26–28]. Guided by our previous results, we attempted to place NiO@Au ensembles on a suitable support for obtaining a practical and versatile catalyst with high activity/selectivity, good stability and high heat conductivity. Because gas-phase alcohol oxidation reactions are highly exothermic, it is desirable to endow the catalyst with high heat conductivity for rapidly dissipating reaction heat from the catalytic reactor bed. The oxide-supported catalysts demonstrated good low-temperature activity, but their poor heat conductivity causes hotspots to form in the reaction bed [3]. Therefore, metal support is a reasonable alternative. Compared to the metallic Ni [26–28] and Cu [29,30] microfibrous supports, Ti powder was a good support candidate because of its low price, low coking activity, high oxidation-/acid-corrosion resistance, inert behavior toward the alcohol oxidation, and relatively high heat conductivity. In order to further elucidate the activity origin of the NiO@Au/Ti-powder catalyst, X-ray

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* Corresponding author. Tel.: +86 21 62233424; fax: +86 21 62233424.
E-mail address: ylu@chem.ecnu.edu.cn (Y. Lu).

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photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) were employed to reveal the active-sites on the NiO@Au ensembles.

2. Experimental

2.1. Catalyst preparation

The Au/Ti-powder catalyst (5 wt% Au, denoted as Au-5/Ti) was prepared by impregnating Ti-powder (200–300 mesh, Alfa Aesar) with $HAuCl_4$ solution, followed by calcination at 300 °C in air for 4 h. Au-5/Ti catalyst was then impregnated with aqueous $NiCl_2$ solution (to 1 wt% NiO) and calcined at 400 °C in air for 4 h, which transformed the $NiCl_2$ into NiO. By doing so, a NiO-doped Au-5/Ti catalyst was obtained and denoted as NiO-1@Au-5/Ti-Cl. NiO-1@Au-5/Ti-N and NiO-1@Au-5/Ti-C catalysts were also prepared by using this method except that $Ni(NO_3)_2$ and $Ni(Ac)_2$ were used as precursors, respectively. Catalysts with different Au and NiO loadings were prepared by following the same procedure and simply tuning the amount of $HAuCl_4$ and nickel salts in the corresponding solutions.

Additionally, the NiO-1/Ti-Cl catalyst was prepared by impregnating Ti-powder with a $NiCl_2$ solution to NiO loading of 1 wt%, followed by calcination at 400 °C in air for 4 h. The Au-5@NiO-1/Ti-Cl catalyst was prepared by impregnating the NiO-1/Ti-Cl catalyst with a solution of $HAuCl_4$ to Au loading of 5 wt%, followed by calcination at 300 °C in air for 4 h.

2.2. Catalyst characterization

The catalysts were characterized with X-ray diffraction (XRD, Rigaku Uitima IV diffractometer (Cu Kα)), scanning electron microscopy (SEM, Hitachi S-4800) equipped with an energy dispersive X-ray analysis (EDX) unit (Oxford, UK), and transmission electron microscopy (TEM, JEOL-JEM-2010 instrument at 200 kV). XPS were recorded on a VG EscaLab 220i spectrometer, which used a standard Al Kα X-ray source (300 W) and an analyzer pass energy of 20 eV. All binding energies are referenced to the C1s line at 284.9 eV. XAS data of the Au L^{III}-edge (11,919 eV) and Ni K-edge (8350 eV) were collected in transmission mode on the BL14W1 beam line of the Shanghai Synchrotron Radiation Facility (SSRF). The typical electron beam energy was 3.5 GeV, and the current was 300 mA. A cryogenically cooled double-crystal Si (1 1 1) monochromator was used to minimize the harmonics. The extended X-ray absorption fine structure (EXAFS) spectra were analyzed with the ATHENA software. The loading of gold for all of the samples was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Thermo Scientific iCAP 6300 ICP spectrometer.

2.3. Reactivity tests

The gas-phase oxidation of alcohols was performed on a fixed-bed quartz tube reactor (700 mm length by 16 mm inner diameter) under atmospheric pressure as described previously [31,32]. Catalyst used in each test was 0.3 g (200–300 mesh). Alcohols were fed continuously *via* a high-performance liquid pump in parallel with O_2 (oxidant) and N_2 (diluted gas of 100 ml/min) feeding, which used calibrated mass flow controllers, into the reactor under steady-state temperature conditions. The weight hourly space velocity (WHSV) was calculated by dividing the mass flow rate of the alcohol feedstock by the catalyst mass. The effluent was cooled using an ice-salt bath (−15 °C) to condense the vapors for analysis using a Shimadzu-2014 gas chromatography-flame ionization detector (GC-FID) with a 60 m HP-5ms capillary column. The gas-phase products, such as H_2, CO_x, and C1–C3 hydrocarbons, were analyzed using an HP-5890 GC with a thermal conductivity detector (TCD) and a 30 m AT-plot 300 capillary column. The reproducibility of the conversion and selectivity of the product was high and the error range was ±0.2%. A carbon mass balance close to 100% was achieved.

3. Results and discussion

3.1. Highly active NiO@Au ensembles

$HAuCl_4$ and $NiCl_2$ were chosen as the preferred precursors in the fabrication of the NiO@Au ensembles because of the previously reported galvanic exchange reaction that yielded metallic gold particles and $NiCl_2$ from $HAuCl_4$ and Ni fiber [26,27]. First, we prepared an Au/Ti-powder catalyst (5 wt% Au; denoted as Au-5/Ti) by impregnation of Ti-powder with a $HAuCl_4$ solution and subsequent calcination at 300 °C in air for 4 h. Specific surface area of the Au-5/Ti catalyst is only 0.2 m^2/g, close to that (0.1 m^2/g) for the Ti-powder support itself (Table S1). SEM (Fig. 1A), XRD (Fig. 1B) and TEM (Fig. 1C) measurement results clearly showed that the $HAuCl_4$ decomposed to form metallic gold particles on Ti-powder surface. As shown in Table 1 and Fig. S1, gold particles of the Au-5/Ti catalyst, with size around 35–40 nm, are much larger than the small Au particles (<5 nm) desired for achieving good catalytic activity [12]. When subjected to oxidation of benzyl alcohol, not surprisingly, the Au-5/Ti catalyst delivered very low benzyl alcohol of <6%, comparable to the Ti-powder support itself (entries 1,2 in Table 1). Subsequently, the Au-5/Ti catalyst was impregnated with $NiCl_2$ solution to a NiO loading of 1 wt%, followed by calcination at 400 °C. The XRD patterns demonstrated that $NiCl_2$ was transformed into NiO, which co-existed with Au particles to produce a NiO-doped Au/Ti catalyst (denoted as NiO-1@Au-5/Ti-Cl; Fig. 2, Scheme S1). The EDX results indicated that the Ni was on the surface of the Au particles (Fig. S2). Most interestingly, NiO-doping resulted in a dramatic improvement in activity for the gas-phase oxidation of benzyl alcohol. Benzyl alcohol conversion of only 5.2% was observed over the Au-5/Ti (entry 2 in Table 1), but a high conversion of 93.7% was obtained over the NiO-1@Au-5/Ti-Cl (entry 3 in Table 1). Note that the specific surface area of the catalysts almost remained unchanged (*i.e.*, 0.2 m^2/g; Table S1) with or without NiO-doping. Thus, the dramatic conversion promotion assignment to the surface area change can be reasonably ruled out. For reference, NiO-1/Ti-Cl was prepared and, when subjected to the benzyl alcohol oxidation, yielded a conversion of only 2.3% (entry 4 in Table 1). Clearly, the singular use of Au or NiO particles was ineffective for the gas-phase oxidation of alcohols.

Figs. 1D and S3 show the TEM images of the NiO-1@Au-5/Ti-Cl catalyst. Clearly, large Au particles (∼40 nm) were partially covered with small NiO segments to form NiO@Au ensembles. Additionally, when we placed 5 wt% Au onto the NiO-1/Ti-Cl catalyst, the resultant Au-5@NiO-1/Ti-Cl catalyst did not show dramatic activity improvement yet (entry 5 in Table 1). This catalyst delivered a benzyl alcohol conversion of only 21.1%, much lower than that (93.7%) for the NiO-1@Au-5/Ti-Cl. Note that the Au-5@NiO-1/Ti-Cl catalyst was obtained by placing NiO (1 wt%) firstly onto the Ti-powder support to form NiO-1/Ti-Cl and subsequently depositing gold (5 wt%) on the NiO-1/Ti-Cl. By using this method, it is difficult to form the NiO@Au ensembles when compared to the method for the NiO-1@Au-5/Ti-Cl catalyst preparation. The above results indicated that the formation of the NiO@Au ensembles is essential for the high activity of the Au-5@NiO-1/Ti-Cl catalyst. This observation is in agreement with our previous report for the Au/Ni-fiber catalyst system [26,27].