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A highly active Au/Al_2O_3 catalyst for cyclohexane oxidation using molecular oxygen

Li-Xin Xu, Chao-Hong He, Ming-Qiao Zhu,* and Sheng Fang

Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, China

Received 22 November 2006; accepted 12 January 2007

The selective oxidation of cyclohexane to cyclohexanone and cyclohexanol has been investigated over Au/Al_2O_3 catalysts using molecular oxygen in a solvent-free system. The catalysts were prepared by a modified direct anionic exchange method and characterized by AAS, N_2 adsorption and TEM. The results showed that the catalytic performance of Au/Al_2O_3 is very high in terms of turnover frequency. Moreover, the nano-size effect of gold is also reported in the reaction.

KEY WORDS: gold catalyst; selective oxidation; cyclohexane; alumina.

1. Introduction

The development of catalytic methods for the selectively oxidative functionalization of alkane carbon-hydrogen bonds remains a challenge in modern chemisty [1]. Of particular importance is the selective cyclohexane oxidation to cyclohexanone and cyclohexanol, which are key intermediates for the production of adipic acid and caprolactam [2]. The present commercial process for cyclohexane oxidation using molecular oxygen or air is carried out at 150–160 °C and 1–2 MPa, affording 4% conversion and 70–85% selectivity to cyclohexanone and cyclohexanol [3]. The greater demand for these oxidation products and the increased environmental concerns warrant the introduction of catalytic systems over heterogeneous catalysts using environmentally benign oxidants such as molecular oxygen or hydrogen peroxide [4]. In the last decade, great efforts have been made to this reaction over heterogeneous catalysts such as (Cr) MCM-41, TS-1, VPO, VMCM-41 and metal-containing AlPO redox molecular sieves [5–9]. However, cyclohexane oxidation with hydrogen peroxide shows low efficiency and is, therefore, not interesting for industrial applications [10]. Therefore, solvent-free catalytic processes using molecular oxygen should be preferred.

An increasing interest has been directed to the catalytic potential of gold catalysts in the last few years, as various selective oxidation reactions are now known to be catalyzed by gold [11–15]. Moreover, gold-based catalysts including Au/ZSM-5, Au/MCM-41 and hybrid Au/SBA-15 have been shown to be highly active to perform the selective cyclohexane oxidation using molecular oxygen [16–19]. To prepare active gold catalysts on inert supports such as SiO_2 or Al_2O_3, gold must exist in highly dispersed state [20]. However, both Au/ZSM-5 and Au/MCM-41 catalyst were prepared directly during the synthesis of molecular sieve supports by an *in–situ* addition of gold precursor. Large Au particles resulted from this method due to the high calcination temperatures needed to remove the templating agents [21]. Hybrid Au/SBA-15 catalysts were synthesized after the surface modification of mesoporous silica with organic bifunctional materials. Unfortunately, the catalyst preparation was troublesome and the bifunctional materials could also interfere with catalytic reactions by capping active sites [22].

On the other hand, metal oxide-supported gold catalysts take advantage of facile preparation and low cost. To date, few of them have been investigated in cyclohexane oxidation. Al_2O_3 is a most common industrial material as a catalyst support material because of its relative stability, high surface area and workability. In particular, the amphoteric character of Al_2O_3 (iso-electric point = 8–9) facilitates it to support gold in a wide pH range using cheap chloroauric acid in aqueous medium, thus affording flexibility for catalyst synthesis by varying preparation parameters and activation conditions [23–25]. More recently, a direct anionic exchange (DAE) method has been developed for preparing metal oxide-supported catalyst, and this method permits to have a high and homogeneous dispersion of gold on Al_2O_3 [26, 27].

In this work, we report an Au/Al_2O_3 catalyst prepared by a modified DAE method. The Al_2O_3 catalyst shows a very high activity for the selective cyclohexane oxidation using molecular oxygen in a solvent-free

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*To whom correspondence should be addressed.
E-mail: zhumingqiao@zju.edu.cn

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system. Moreover, the nano-size effect of gold is also reported for the reaction.

2. Experimental

Au/Al_2O_3 catalysts with varied gold loadings were prepared by a modified direct anionic exchange method. Typically, a suitable amount of chloroauric acid tetrahydrate (47.8% Au, SCRC) was dissolved in 200 mL deionized water. The commercial γ-Al_2O_3 powder (266 $m^2\ g^{-1}$) was sieved to obtain the fraction of 74–125 μm. 2 g of the γ-Al_2O_3 was stirred in the chloroauric acid solution for 1 h at 70 °C, and the pH of the slurry was kept at 4 by 1 M NaOH solution. Following filtration and washing with 4 M NH_3 solution until the washings contained no chloride, the resulting product was dried in an oven at 80 °C overnight and calcined in a flowing gas containing 10% H_2 and 90%N_2 for 2 h at 250 °C.

The gold loadings of the calcined Au/Al_2O_3 samples were determined by an atomic absorption spectrometer (AAS, Hitachi 180-50). The sample was completely dissolved by aqua regia. The specific surface areas and pore volumes of the samples were obtained from the N_2 adsorption isotherms at −196 °C by the Brunauer-Emmett-Teller (BET) method using an Autosorb-1-C instrument. Transmission electron microscopy (TEM) images were collected on a JEM-200CX at 160 kV.

In a typical oxidation reaction, 20 mL cyclohexane and 50 mg catalyst were magnetically stirred in a 100 mL autoclave lined with polytetrafluoroethylene (PTFE) under the conditions of 150 °C, 3 h and a pressure of 1.5 MPa controlled by O_2. After reaction a suitable quantity of acetone was added into the cold reactor to dissolve all the reactants and products. The liquid samples were analyzed by gas chromatography (GC) with a SE-54 capillary column (30 m × 0.25 mm) and a FID. The identity of the components was verified by GC-MS analysis. It is essential that the samples are doublly analyzed by GC, before and after reducing cyclohexyl hydroperoxide (CHHP, the first and indispensible oxygenated product of cyclohexane oxidation and acting as the precursor of cyclohexanone and cyclohexanol) to cyclohexanol with triphyl phosphine [28]. As CHHP partially decomposes upon injection to form some cyclohexanone and cyclohexanol, an appreciable positive deviation for quantifying cyclohexanone could be caused while the samples were directly analyzed by GC. Blank reactions with and without pure Al_2O_3 were also conducted under the same reaction conditions.

3. Results and discussion

3.1. Catalyst charaterization

Table 1 shows the chemical composition, specific surface areas and pore volumes of Al_2O_3 and Au/Al_2O_3 samples. With the increase of gold loadings the specific surface areas and pore volumes of Au/Al_2O_3 catalysts differ only slightly, which means loading gold has little effect on the support. TEM technique was subsequently used to confirm the formation of gold nanoparticles. Figure 1 (a)–(c) compare the gold sizes of calcined Au/Al_2O_3 with a gold content of 0.2, 0.6 and 1.0%, respectively. As Al_2O_3 displays a strong background of the images, it is relatively difficult to distinguish the supported gold particles with the sizes smaller than 3 nm in the micrographs [29]. Fortunately, a few black dots representing gold particles monodispersed on the support can be discerned from the background in Figure 1 (a) and (b), and the particle sizes are around 3–6 nm, agreeing well with the results in an earlier report [27]. However, a number of gold particles are bigger than 10 nm in Figure 1 (c), which means the gold loading greatly affect the particle size.

Table 1

Physical properties of Al_2O_3 and Au/Al_2O_3 samples

Samples	Au content (%)	S_{BET} ($m^2\ g^{-1}$)	Pore volume (mL g^{-1})
Al_2O_3	–	266	0.53
Au/Al_2O_3	0.2	258	0.52
Au/Al_2O_3	0.6	257	0.47
Au/Al_2O_3	1.0	251	0.46

3.2. Catalytic oxidation of cyclohexane

In preliminary experiments, an uncatalyzed oxidation reaction was carried out under the typical reaction conditions in order that the promotion effect of the reactor wall on the reaction was evaluated. As shown in Table 2(entry 1), the PTFE-lined autoclave wall is inert for the oxidation reaction. Moreover, the pure Al_2O_3 support was also found to be inactive for cyclohexane oxidation under the same conditions.

The catalytic performances of Au/Al_2O_3 catalysts were investigated for cyclohexane oxidation using molecular oxygen as an oxidant in a solvent-free system, and the results are given in Table 2. The best catalytic performance previously reported is Au/ZSM-5 (0.55% Au), which presents a conversion of 7% with a turnover frequency (TOF) of 3092 h^{-1} [16]. In this work, a conversion of 11.5% as well as a TOF of 4508 h^{-1} was obtained over Au/Al_2O_3 (0.6% Au) under almost the same reaction conditions. Furthermore, a surprisingly high TOF up to 16136 h^{-1} was attained over Au/Al_2O_3 (0.2% Au), which endows this system with the best activity ever reported in terms of TOF. In the synthesis of Au/Al_2O_3 catalyst, loading gold on the support proceeds by a direct anionic exchange of $[Au(OH)_nCl_{4-n}]^-$ (n = 0–4) ions with other anions chemsorbed on the surface of Al_2O_3, making gold dispersed on a molecular scale. Moreover, the subsequent activation of the catalyst precursor by H_2 reduction at low temperature might

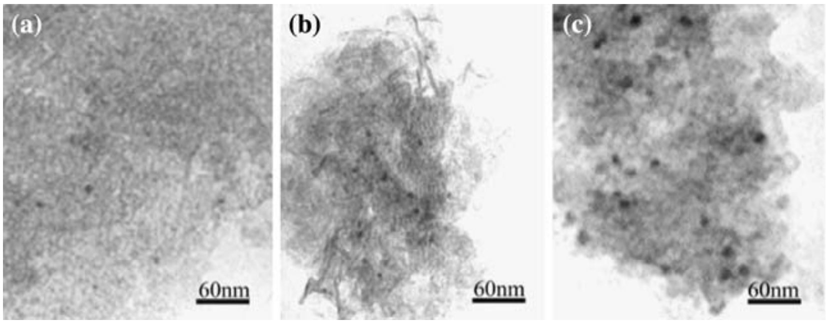

Figure 1. TEM images of Au/Al_2O_3 catalysts of (a) 0.2%, (b) 0.6% and (c) 1.0% Au.

suppress the conglomeration of the gold nanoparticles. These lead to a high dispersion as well as fine size control of gold on the support, thus resulting in a high activity for cyclohexane oxidation in spite of a relatively low gold loading of the catalyst. The recently reported Au/ZSM-5 and Au/MCM-41 catalysts generally show better conversion with an increase of gold loading. However, as the gold loadings of our samples increased from 0.2 to 1.0%, both the conversion of cyclohexane and the total selectivity to the three oxygenated products decreases, and a sharp decrease of the TOF value is evident at the same time. These effects are more likely caused by a decrease of highly active gold particles since the particles grow bigger according to the TEM analysis. To our knowledge, this is the first observation of a nanosize effect of gold in cyclohexane oxidation. On the other hand, the selectivity to cyclohexanone as well as the total selectivities to cyclohexanone, cyclohexanol and CHHP is not very high according to Table 2. One possible explanation is that the strong hydrophilicity of Al_2O_3 facilitates the catalytic esterization of byproduced ring-opened acids with cyclohexanol via the surface acid/base sites of Al_2O_3.

As Au/Al_2O_3 (0.6% Au) shows the best results with respect to the conversion and the selectivity to cyclohexanone among the three catalysts, it is employed to investigate the progress of the reaction with time under the typical conditions. As shown in Figure 2, the oxidation of cyclohexane proceeds appreciably at 1.0 h, affording a conversion of 4.3% and 98.6% selectivity to the three desired oxygenates. However, under almost the same conditions no oxidation reaction occurs over Au/ZSM-5 (1.30% Au) [16]. It is also evident that the oxidation reaction gradually slowdowns with time, suggesting a gradual loss of catalytic activity of the catalyst. We believe this could be ascribed to a strong affinity of Al_2O_3 with water formed increasingly in the reaction, through which the adsorption of apolar cyclohexane on the catalyst can be suppressed and the catalytic esterization side-reaction of cyclohexanol with byproduced ring-opened acids may be enhanced on the support as well. In addition, the products shift gradually from CHHP to cyclohexanol and cyclohexanone with time, which means that CHHP could be the first oxygenated product in the oxidation. It is also noted that the higher the CHHP selectivity, the higher the total selectivity to the three oxygenated products, which is consistant with the results reported earlier [30].

Recycling tests were performed using Au/Al_2O_3 (1.0% Au) under the typical reaction conditions, and the results are given in Figure 3. Both the conversion and the overall selectivity to the three oxygenates are well retained with a slightly enhanced selectivity to cyclohexanone, suggesting a high stability of the catalyst.

In summary, we have shown that Au/Al_2O_3 catalysts with the gold particles of 3–6 nm are highly active for

Table 2
Results of cyclohexane oxidation over Au/Al_2O_3 catalysts[a]

Catalyst	Conversion (%)	Selectivity(%)			TOF[b] (h^{-1})
		Cyclohexanol	Cyclohexanone	CHHP	
No catalyst	–	–	–	–	–
Al_2O_3	–	–	–	–	–
0.2% Au/Al_2O_3	12.6	52.6	32.1	3.8	16136
0.6% Au/Al_2O_3	11.5	49.2	37.5	1.6	4508
1.0% Au/Al_2O_3	10.9	54.0	30.3	2.8	2592
0.55% Au/ZSM-5[c]	7	36	55		3092

[a] Reaction conditions in this work: cyclohexane 20 ml, catalyst 50 mg; 150 °C, 1.5 MPa, 3 h; 100 ml PTEE-lined autoclave.
[b] Calculated by moles of cyclohexane converted per mole of Au per hour.
[c] Reaction conditions of reference 16: cyclohexane 2 ml, catalyst 5 mg; 150 °C, 1.0 MPa O_2, 3 h.

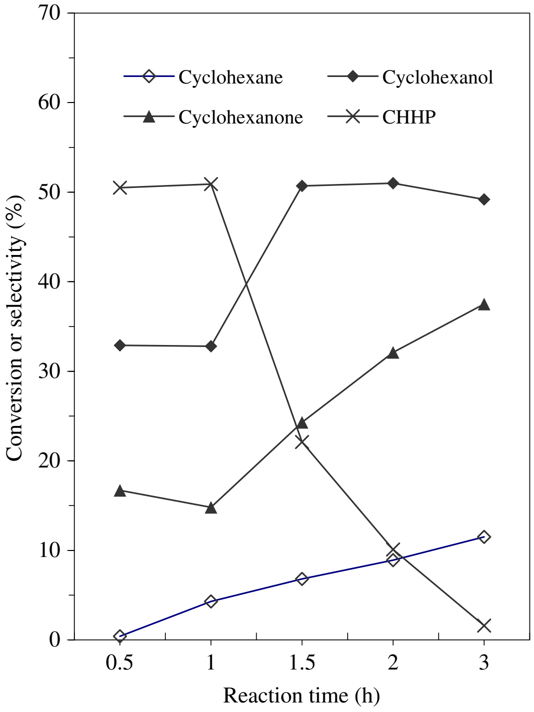

Figure 2. Cyclohexane oxidation over Au/Al_2O_3 (0.6% Au) with different reaction time.

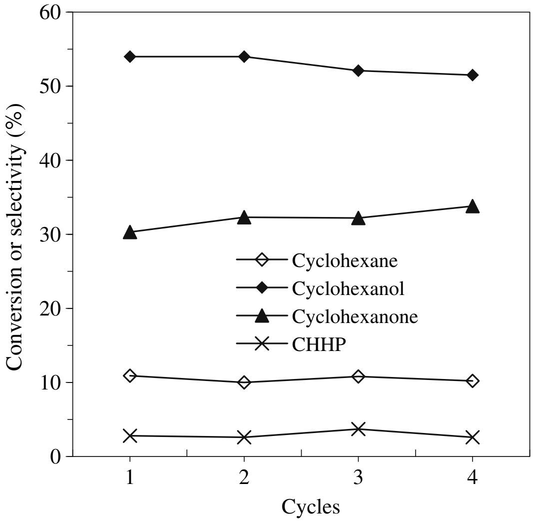

Figure 3. Results of recycling test over Au/Al_2O_3 (1.0% Au).

the selective cyclohexane oxidation to cyclohexanone and cyclohexanol under relatively mild conditions. The nano-size effect of gold is found in the reaction for the first time. On the other hand, the selectivity to cyclohexanone and cyclohexanol combined is not very high. Therefore, improvement of the selectivity to cyclohexanone and cyclohexanol as well as the stability of Au/Al_2O_3 catalysts should be directed to modify the surface chemistry of the support.

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