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Propene epoxidation with O_2 and H_2: Identification of the most active gold clusters

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ABSTRACT

Gold was deposited on alkaline-treated TS-1 (TS-1-Na1) to prepare Au/TS-1-Na1(DP) by deposition–precipitation (DP) and Au/TS-1-Na1(SG) by solid grinding (SG). ^{129}Xe NMR technique has detected that tiny Au clusters have been incorporated into the microporous channels of Au/TS-1-Na1(DP), while they were absent inside the microporous channels of Au/TS-1-Na1(SG). On the other hand, HAADF-STEM observation showed that the amount of Au clusters (1.0–2.0 nm) over the exterior surfaces was much larger in Au/TS-1-Na1(SG) than in Au/TS-1-Na1(DP). In propene epoxidation with O_2 and H_2, Au/TS-1-Na1(SG) exhibited much higher PO formation rate (127 $g_{PO}\ kg_{cat}^{-1}\ h^{-1}$) than Au/TS-1-Na1(DP) (74 $g_{PO}\ kg_{cat}^{-1}\ h^{-1}$), indicating that Au clusters with diameters of 1.0–2.0 nm are more active for PO synthesis than tiny Au clusters incorporated inside the microporous channels.

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1. Introduction

Propene epoxide (PO) is a very important feed stock in chemical industry and widely used to produce a variety of derivatives such as polyether polyols and propylene glycol. In Industry, the chlorohydrin process and several organic peroxide processes are used to produce PO [1]. However, these processes suffer from the environmental unfriendliness and market mismatch of co-products, respectively. The chlorohydrin process is accompanied by the by-production of toxic chlorinated organic compounds as well as salts such as $CaCl_2$. The organic peroxide processes usually require multiple reaction steps in liquid phase and often suffer from the mismatch in market demand of co-products such as tert-butanol. The latest PO production plants are based on H_2O_2 as an oxidant [2] or on cumene recycling by the reduction of co-product, cumyl alcohol with H_2 [3].

Direct epoxidation of propene (C_3H_6) with oxygen (O_2) and hydrogen (H_2) is a promising process for PO synthesis, because it is simple (one-step reaction in gas phase) and green (with H_2O as the only by-product). Since Hayashi et al. [4] first reported in 1998 that propene epoxidation with O_2 and H_2 could be catalyzed by gold nanoparticles (Au NPs, 2.0–5.0 nm) deposited on anatase TiO_2 with PO selectivity above 90%, many efforts have been devoted to this reaction [5–19]. So far, great progresses have been made, and C_3H_6 conversion (5.0–9.8% [5]), PO selectivity (90–96% [5]) and H_2 efficiency (30–47% [8]) have approached the estimated industrial targets (10%, 90% and 50%, respectively).

For Au catalysts, there are two key factors that define their catalytic performance: the type of supports and the size of gold particles. For supports, usually materials containing Ti cations are required, and until now, three materials have been widely used as supports, anatase TiO_2 [4,12], mesoporous Ti–silicate (Ti–SiO_2) [5–7,9,10] and microporous titanosilicalite-1 (TS-1) [8,11,15–19]. Although Au/TiO_2 could present high PO selectivity (>90%), C_3H_6 conversion is usually very low, less than 1.0%, due to the low reaction temperature (usually lower than 373 K). In contrast, Au/mesoporous Ti–SiO_2 and Au/TS-1 could be used at higher reaction temperature, and both high C_3H_6 conversion and high PO selectivity could be achieved. Promoted by $Ba(NO_3)_2$, 0.30 wt% Au/mesoporous Ti–SiO_2 displayed a high C_3H_6 conversion of 9.8% with a high PO selectivity of about 90% at 433 K [5], while 0.05 wt% Au/TS-1(Si/Ti = 36) without promoters could also present a high C_3H_6 conversion of 8.8% with a PO selectivity of 81% at 473 K, which corresponded to a PO formation rate of 116 $g_{PO}\ kg_{cat}^{-1}\ h^{-1}$

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[16]. As for the catalytic stability, among these three types of Au catalysts, Au/TS-1 is superior.

Beside supports, the size of gold particles is also critically important. For example, for Au/TiO_2 only hemispherical Au NPs with size of 2.0–5.0 nm are active for PO synthesis, whereas spherical Au NPs larger than 5.0 nm favor the complete combustion of propene to CO_2 and Au clusters smaller than 2.0 nm lead to propene hydrogenation [4]. Although Au/mesoporous Ti-SiO_2 and Au/TS-1 are more active for PO synthesis than Au/TiO_2, the exact size or size range of Au particles most active for PO synthesis is not clear yet. Lu et al. [9] have observed that in Au/mesoporous Ti-SiO_2 catalysts, small Au clusters (0.9 nm from EXAFS) showed much higher catalytic performance than both large Au clusters (2.0 nm from TEM or 1.4 nm from EXAFS) and Au NPs (2.5 nm from TEM). Yap et al. [15] speculated that in Au/TS-1, Au clusters (<2.0 nm) which were hardly visible by TEM would be responsible for PO synthesis. Joshi et al. [20,21] proposed based on theoretical calculations that in Au/TS-1 tiny Au clusters incorporated in microporous channels ($\sim$0.55 nm) of TS-1, such as Au_3 clusters, should be active for PO synthesis.

Our recent results showed that Au/alkaline-treated TS-1 prepared by solid grinding (SG) could display a high PO formation rate of 137 $g_{PO}\ kg_{cat}^{-1}\ h^{-1}$ [8], comparable to the best results reported by Cumaranatunge and Delgass [17] over Au/TS-1 prepared by deposition–precipitation (DP). HAADF-STEM (high-angle annular dark-field scanning transmission electron microscopy) observations, which could provide stronger contrast for Au against the support, showed that Au clusters with diameters of 1.0–2.0 nm were situated on the exterior surfaces of alkaline-treated TS-1. It is likely that those Au clusters are responsible for the excellent catalytic performance. On the other hand, it could not be denied that tiny Au clusters incorporated inside microporous channels of alkaline-treated TS-1 exhibited high catalytic activity for PO synthesis. Accordingly, a key question is which is more active for PO synthesis, Au clusters (1.0–2.0 nm) on the exterior surfaces or tiny Au clusters incorporated inside microporous channels.

In this context, xenon is a monoatomic probe to sense free spaces such as pores. ^{129}Xe is chemically inert, small with a diameter of 0.44 nm and very sensitive to the chemical surroundings of microporous channels of zeolites [22]. Therefore, ^{129}Xe NMR spectroscopy is a powerful technique to detect metal clusters incorporated into the channels of zeolites [23]. Previous research showed that once metal clusters such as Ir, Pt, Rh, Os and Au were incorporated into microporous channels of zeolites, much greater ^{129}Xe chemical shifts at low Xe loading could be detected than those on pure zeolites due to the strong interaction of Xe atoms with metal clusters [24–28]. Herein, ^{129}Xe NMR spectroscopy was utilized to characterize Au/alkaline-treated TS-1 prepared by SG and DP to examine whether tiny clusters could be incorporated into the microporous channels or not. For comparison, Au/TS-1 prepared by DP and supports (TS-1 and alkaline-treated TS-1) were also characterized by ^{129}Xe NMR spectroscopy.

2. Experimental

2.1. Alkaline treatment of TS-1 with NaOH aqueous solution

Microporous TS-1 with molar ratio of silicon (Si) to titanium (Ti) of 48 was synthesized according to the previous report [8]. The alkaline treatment of TS-1 was as follows. First, 1.0 g of calcined TS-1 was added to the water (100 mL). Second, to the suspension, 1.0 M NaOH aqueous solution was added dropwise under vigorous stirring at 303 K until the pH reached 12. The pH was maintained at this value for 1.0 h by continuing to add a small amount of NaOH aqueous solution. Finally, the solid was collected by filtration, washed five times with 2000 mL (total amount) of H_2O to remove residual NaOH and then dried at 373 K in air. The obtained alkaline-treated TS-1 was named as TS-1-Na1, where 1 stands for 1.0 h of alkaline treatment period.

2.2. Deposition of Au by DP

The procedure of Au deposition on TS-1 and TS-1-Na1 by the DP method in aqueous solution at room temperature is as follows. First, 1.0 g of support was added to 50 mL of 9.1 mM $HAuCl_4$ aqueous solution (Au/Support = 9.0 wt.%), and then the aqueous solution of NaOH was added dropwise until the pH reached 9.0. The suspension was stirred vigorously at room temperature for 3.0 h, and meanwhile the pH of 9.0 was kept constant by adding a small amount of NaOH aqueous solution. Finally, the solid was centrifuged out, washed in 50 mL of water, centrifuged again and then dried under vacuum at room temperature overnight. The Au catalysts thus prepared were denoted as Au/TS-1(DP) and Au/TS-1-Na1(DP).

2.3. Deposition of Au by SG

The preparation of Au/TS-1 and Au/TS-1-Na1 by the SG method was done according to the procedure previously reported [8,29]. Since TS-1 contains 0.75 wt% K [8], before SG, TS-1 was treated in a similar manner to the DP method by replacing $HAuCl_4$ with HCl to eliminate the potential effect caused by K element and then dried at 373 K in air overnight. First, the powder of TS-1 or TS-1-Na1 and the required amount of dimethyl Au(III) acetylacetonate [$(CH_3)_2$Au(acac)] having a vapor pressure of 1.1 Pa at 298 K were ground in an agate mortar in air for 15 min at room temperature and then reduced by 10 vol.% H_2 in Ar (20 mL min^{-1}) at 423 K for 1.0 h. The temperature was raised from room temperature to 423 K at a heating rate of 1.0 K min^{-1}. The Au catalysts thus prepared were denoted as Au/TS-1(SG) and Au/TS-1-Na1(SG).

2.4. Characterization of catalysts

HAADF-STEM was utilized to observe gold particles on a JEOL JEM-3000F transmission electron microscope equipped with a digitally processed STEM imaging system. The operating voltage was 300 kV, and the resolution was about 0.20 nm. Here, not fresh but used gold catalysts in propene epoxidation with O_2 and H_2 mixture were selected and directly dispersed on a micro-grid supported on a copper mesh without solvent. Elemental compositions were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Xenon gas (Praxair, 99.999%) was used for the ^{129}Xe NMR measurements. Two sets of samples were selected. One set of samples consist of TS-1 and 0.11 wt% Au/TS-1(DP) and the former was also treated in a similar manner to the DP method by replacing $HAuCl_4$ with HCl to eliminate the potential effect caused by different Na content. The other set of samples consist of TS-1-Na1, 0.20 wt% Au/TS-1-Na1(SG) and 0.23 wt% Au/TS-1-Na1(DP). Before ^{129}Xe NMR analysis, Au catalysts were used to catalyze propene epoxidation with O_2 and H_2 mixture at 473 K for 2.0 h according to the procedures described in the following Part 2.5. Catalytic tests. During ^{129}Xe NMR measurements, supports or Au catalysts were first placed in an NMR tube equipped with J. Young valves, where the samples were dehydrated by slowly raising temperature to 473 K in a vacuum (1.33×10^{-4} kPa) and keeping the temperature at 473 K for 2.0 h. Then, dehydrated samples were contacted with different pressures of xenon at 291 K. Finally, ^{129}Xe NMR spectra were recorded between 210 and 291 K in a Bruker DMX-500 spectrometer operating at 138.34 MHz. Single excitation pulses were used, and at least 1000 scans were collected with a delay time of 2 s.

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