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Propylene epoxidation with O_2 and H_2: a high-performance Au/TS-1 catalyst prepared *via* a deposition–precipitation method using urea†

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Gold nanoparticles could only be highly dispersed onto the as-synthesized TS-1 zeolite (TS-1-*syn*: with template) rather than the calcined one (TS-1-*calc*: template removed), *via* a deposition–precipitation method using urea. The Au-1/TS-1-*syn* (Au loading: 1 wt%) is promising for propylene epoxidation with O_2 and H_2, delivering a conversion of 8.1% with ~82% selectivity to propylene epoxide (PO). The pores of TS-1 may not be essential for PO synthesis as they are blocked by the organic template.

Propylene epoxide (PO) is an important organic chemical intermediate which is mainly used for the production of polyether polyols and propylene glycol. In principle, PO can be produced through stoichiometric chlorohydrin and organic peroxide (later H_2O_2) processes. However, the environmental issues (*e.g.*, waste and toxic chemical production) and unsatisfactory cost-efficiency (*e.g.*, multi steps and market mismatch of co-products) accompanying these processes are exigently calling for much greener and more atom-efficient methods that adopt solid catalysts and O_2 as an oxidant.

One-step catalytic epoxidation of propylene with O_2 in the presence of H_2 using solid catalysts has been attracting particular attention as a promising route for PO production. In 1998, Haruta *et al.* reported for the first time a nano-gold catalyst supported on TiO_2 that can selectively catalyse the epoxidation of propylene with H_2 and O_2 to produce PO.[1] From then on, supported Au NP catalysts for propylene epoxidation have been extensively studied in order to reach the estimated industrial targets (10% conversion and 90% selectivity), with most of the attention focused on the screening of Ti-containing supports (including TS-1,[2,3] Ti-MCM-41,[4,5] Ti-MCM-48,[4,6] and Ti-TUD[7]), the tuning of chemical properties by additives (such as $Ba(NO_3)_2$),[8] and the preparation of Au-particles with controlled size and location.

Among these catalysts, the Au supported on TS-1 showed promising catalytic activity with high selectivity and relatively good stability in the epoxidation of propylene with O_2 in the presence of H_2.[9] Delgass *et al.* have studied the influence of the precipitant, the pretreatment conditions and the support in the Au/TS-1 catalyst system,[10] the kinetics and the formation of hydrogen peroxide over Au cluster by density functional theory (DFT) calculation.[11–13] They showed that the supported Au catalyst can reach a higher activity when TS-1 with poor crystallinity was used as the support,[14] which indicated that the morphology and some structural defects of TS-1 have an important impact on the performance of the catalyst. Recently, the interest for Au catalysis has moved toward Au cluster catalysts that are obtainable with very low Au loadings and offer much higher intrinsic activities compared to the traditional supported Au catalysts.[15,16] Haruta *et al.* compared the Au/TS-1 catalysts prepared by the deposition–precipitation (DP) and solid grinding (SG) methods, and they indicated that the Au clusters deposited on the exterior surface were mainly responsible for PO synthesis,[17] as they might be more active than the tiny Au clusters incorporated into the microporous channels.[9]

DP urea and NaOH methods[18–20] are well established techniques for the deposition of either Au nanoparticles (Au NPs) or Au clusters onto various oxide supports with point of zero charge (PZC) in the range 6–8 rather than on ones with PZC of ~2. The DP urea (DPU) method has been receiving growing interest for the preparation of supported Au catalysts.[20–22] Since the hydrolysis of urea can gradually release hydroxyl ions, the pH value of the suspension can rise by degrees. As a result, the Au can be deposited onto the support adequately with rare losses.[20] In addition, DPU can avoid metal contaminants such as Na^+ residues. However, no success has been reported in highly and uniformly dispersing Au NPs on TS-1 zeolites with the DPU method.[20,21]

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Table 1 Epoxidation of propylene with O_2 and H_2 over Au-1/TS-1[a]

Catalyst	C_3H_6 conv. (%)	PO select.[d] (%)	PO yield (%)
Au-1/TS-1-*syn*[b]	8.1	81.5[e]	6.5
Au-1/TS-1-*calc*[c]	0.6	65.7	0.4

[a] Catalyst preparation conditions: light-free DPU, DPU time 4.5 h, DPU temperature 90 °C, urea–Au molar ratio of 100 and calcination in air at 300 °C for 4 h. Catalyst testing conditions: catalyst 0.3 g, 150 °C, $C_3H_6 : O_2 : H_2 : N_2 = 1 : 3 : 9 : 12$ (vol/vol), total gas hourly space velocity (GHSV) 12 000 ml h^{-1} g^{-1}. Au loading was 1 wt% for both catalysts and they were pre-reduced in H_2 at 250 °C for 1 h before testing. [b] Using as-synthesized TS-1 zeolite (TS-1-*syn*, with template) as the support. [c] Using calcined TS-1 zeolite (TS-1-*calc*, template removed) as the support. [d] Byproducts were propanol, acetone and CO_2. [e] H_2 utilization efficiency, defined as PO produced per molar amount of hydrogen converted, was estimated to be 6%.

Herein, we demonstrate, for the first time to our knowledge, the successful high and uniform dispersion of Au NPs (4–6 nm) onto an as-synthesized TS-1 zeolite by employing a modified DPU method. Such catalysts provide a nice activity and selectivity for the direct epoxidation of propylene with O_2 and H_2. In addition, whether or not the pores of TS-1 zeolite are essential is also tentatively discussed.

As shown in Table 1, the conversion and selectivity of the Au/TS-1 catalysts were strongly dependent on whether we kept the organic template in the TS-1 zeolite or removed it by calcination before using TS-1 as the support. Note that both catalysts were activated and tested under optimal conditions, as shown in Fig. S1–S3 and Table S1 (ESI†). The representative Au-1/TS-1-*syn* catalyst (1 wt% Au loading), obtained by using as-synthesized TS-1 zeolite, could deliver a propylene conversion of 8.1% with a PO selectivity of ~82%, but it was associated with a low H_2 utilization efficiency of 6% (compared to a reported number of ~20%[16]). In contrast, the Au-1/TS-1-*calc* obtained by using calcined TS-1 was neither active nor highly selective.

The influence of the DPU parameters on the catalytic performance of the TS-1-*syn* supported Au (1 wt%) catalysts was carefully investigated as well as the catalyst calcination temperature, with the results shown in Fig. S4 (ESI†). It is clear that the catalyst activity was very sensitive to both the DPU temperature and DPU time (Fig. S4A and B, ESI†) but not to the urea–Au molar ratio (Fig. S4C, ESI†). The DPU temperature of 90 °C, higher than previously reported ones (≤80 °C),[20] was mostly preferred for activity promotion; but a high DPU temperature of 100 °C caused a decline of the activity (Fig. S4A, ESI†). The optimal DPU time length was around 5 h rather than previously reported times of ≤4 h.[20] Increasing the DPU time from 1 to 6 h would almost double the propylene conversion (Fig. S4B, ESI†). Thus, the optimized DPU conditions were absence of light, DPU temperature 90 °C, DPU time 4.5 h and a urea–Au molar ratio of 100. In addition, the catalyst calcination temperature was found to be most crucial for both the activity and selectivity. The optimal calcination temperature was identified to be 300 °C (Fig. S4D, ESI†).

Fig. S5 in ESI† shows the conversion and selectivity for the epoxidation of propylene against the Au loading. When 1 wt % Au (relative to the mass of the TS-1-*syn* support) was loaded, the catalyst showed a good balance between conversion and selectivity. Lower Au loadings of <1 wt% favoured selectivity but conversion was too low while higher Au loadings of >1 wt% promoted the conversion but the selectivity was seriously degraded due to over-oxidation.

To gain insight into the nature of the high activity and selectivity of the TS-1-*syn* supported catalyst, the real Au loadings were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). It is clear from Table S1 (ESI†) that, under optimal DPU conditions (urea–Au molar ratio of 100, at 90 °C for 4.5 h), over 95% of Au could be deposited onto the TS-1-*syn* zeolite support even for a high Au loading of 3 wt%. In contrast, a relatively low value of 86% was obtained when depositing 1 wt% Au onto TS-1-*calc* zeolite support. We wonder whether Au loss was the main cause for such a big difference in activity and selectivity between Au-1/TS-1-*syn* and Au-1/TS-1-*calc*. To address this question, a 90% deposition of a 1 wt% Au loading (relative to the support mass) onto TS-1-*syn* was obtained by tuning the DPU parameters (*i.e.*, using a low DPU temperature of 50 °C or a short DPU time of 1 h; Table S1, ESI†), which is very close to the 86% obtained for Au-1/TS-1-*calc*. However, these two samples still delivered much better reactivity than the Au-1/TS-1-*calc.* (0.6% conversion, 65.7% selectivity): 5.8% conversion and 84.3% selectivity for 50 °C DPU temperature and 4.3% conversion and 81.1% selectivity for 1 h DPU time (Fig. S4 (ESI†) and Table 1). Moreover, over the Au-0.5/TS-1-*syn* (Au loading of 0.5 wt%, with 100% Au deposition as shown in Table S1, ESI†), a conversion higher than 5% could also be obtained with over 80% selectivity (Fig. S5, ESI†). It is thus rational to infer, from the above results, that Au loss during the DPU preparation was not the main cause for the reactivity difference between Au-1/TS-1-*syn* and Au-1/TS-1-*calc*.

It is widely accepted that particle size of the Au catalyst is critical for endowing them with an outstanding catalytic activity. After ruling out the possibility of Au loss as the main cause for the reactivity difference, we employed transmission electron microscopy (TEM) to check the Au particle size over as-synthesized Au/TS-1 catalysts, with the results shown in Fig. 1. Interestingly, a high dispersion of Au could be observed on the Au-1/TS-1-*syn* catalyst with a narrow Au particle distribution centred at ~5 nm (Fig. 1A and a). In contrast, larger Au particles were observed on the Au-1/TS-1-*calc* catalyst with a dual size particle distribution (~10 and ~30 nm; Fig. 1B and b). Clearly, a good correlation between the Au particle size and the catalyst activity–selectivity for propylene epoxidation using O_2 and H_2 can be obtained; a high activity can only be achieved when the Au particle size was reduced to ~5 nm. Recently, several research groups have indicated that the activity can be visibly promoted again by further reducing the Au particle size to ~1 nm (Au cluster).[15–17] Our observation together with the above mentioned literature results solidly indicates that the Au/TS-1 catalysts feature a

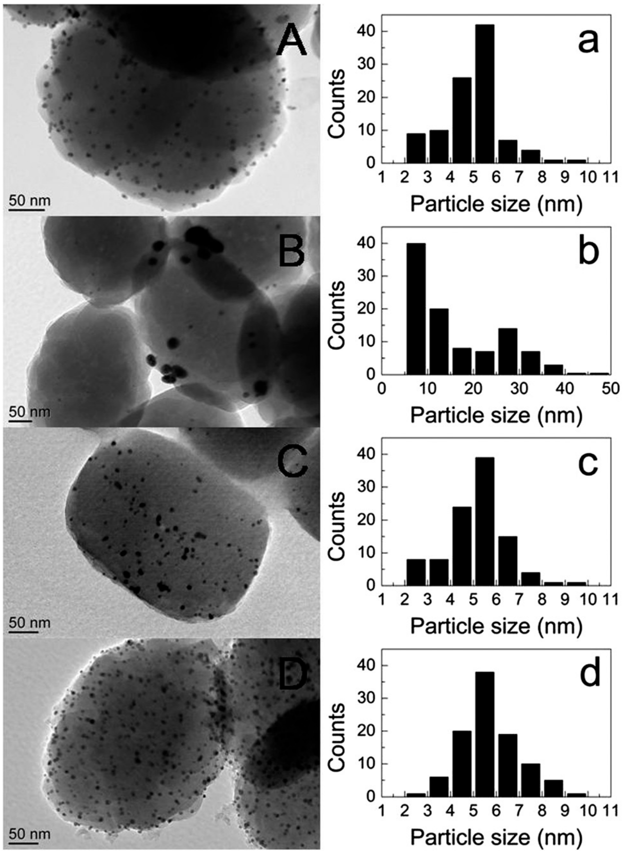

Fig. 1 TEM images and Au particle size distributions. (A) Au-1/TS-1-*syn*, (B) Au-1/TS-1-*calc*, (C) reduced Au-1/TS-1-*syn* in H_2 at 250 °C for 1 h, (D) Au-3/TS-1-*syn* (Au: 3 wt%). Note: the statistics were based on hundreds of Au particles in the samples except for Au-1/TS-1-*calc*.

Au-size-dependent activity in the direct propylene epoxidation process.

Based on the TEM results (Fig. 1A and B), we can draw the conclusion that the organic template filling the pores of TS-1 zeolites plays a determinant role in inducing a high and uniform dispersion of Au onto the external surface of the TS-1 crystals. A comprehensive understanding of the positive effect of the presence of the organic template in the zeolite pores is particularly desirable. As noted previously, the TS-1-*calc* has an isoelectric point of 2–3,[8] not matching the value (5–6) required by DP methods for Au NP deposition on oxides from the precursor $HAuCl_4$.[20] Interestingly, the presence of the organic template in TS-1-*syn* shifted the isoelectric point close to 5 (Fig. S6, ESI†) thereby permitting the DPU method to work efficiently. Additionally, the organic template occupied the TS-1 zeolite pores and therefore blocked the deposition of Au into them. Based on the above results, it is rational for us to infer that the pores of TS-1 may not be essential for this reaction. This agrees with the results from Haruta in that Au clusters on the exterior surface are mainly responsible for PO synthesis.[17] Notably, Delgass *et al.* recently showed that gold clusters inside the TS-1 channels are active for the PO reaction.[15]

After undergoing a pre-reduction with H_2 at 250 °C for 1 h, no significant growth of Au NPs on the Au-1/TS-1-*syn* catalyst was observed (Fig. 1C and c). Notably, the Au-3/TS-1-*syn* catalyst also showed a unique and high dispersion of Au NPs, with a narrow particle size distribution and an average particle size comparable to that of the Au-1/TS-1-*syn* catalyst (~5 nm), even though the Au loading was tripled (Fig. 1D and d). However, the Au-3/TS-1-*syn* catalyst provided very poor selectivity for the epoxidation of propylene. For instance, at 150 °C, a selectivity of only ~11% was obtained with a high conversion of ~15% (Fig. S5, ESI†). This is likely due to the high density of Au NPs which might significantly promote the deep oxidation of H_2 and propylene as well as the PO product with O_2 to form H_2O and CO_x while releasing a lot of heat. Indeed, under identical reaction conditions, a remarkable increase of the catalyst bed temperature was observed when using the Au-3/TS-1-*syn* catalyst, compared to the catalyst bed packed with Au-1/TS-1-*syn*.

In summary, a promising Au/TS-1 catalyst for the epoxidation of propylene with O_2 and H_2 has been successfully developed by using the DPU method with only as-synthesized TS-1 zeolite as support. The presence of the organic template results in a raised isoelectric point, which is crucial for high and uniform dispersion of Au on the TS-1 support. Most notably, the pores of TS-1 may not be essential for PO synthesis as the pores of the Au/TS-1-*syn* catalyst are blocked by the organic template. We anticipate that our findings will initiate attempts to develop high-performance gold catalysts for direct propylene epoxidation and to understand gold catalysis in more detail.

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Experimental section

Catalyst preparation

The hydrothermal synthesis of TS-1 zeolite with a Si–Ti molar ratio of 40 was performed under static conditions at 170 °C for 48 h, basically according to the literature,[23] from a gel having the following molar composition: 1TEOS : 0.025TBOT : 0.18TPAOH : $18H_2O$. Calcined TS-1 (TS-1-*calc*: template removed) was obtained by heating the as-synthesized TS-1 (TS-1-*syn*) sample in air at 550 °C for 6 h with a heating rate of 2 °C min^{-1}. Fig. S7 (ESI†) shows the XRD patterns for both as-synthesized and calcined TS-1 samples, indicating the presence of a highly crystalline phase evidenced by typical separated peaks.

Gold deposition onto the TS-1 zeolite was carried out by the DPU method as previously described elsewhere.[22] The following is the detailed procedure: TS-1-*syn* or TS-1-*calc* zeolite support (1.5 g) was added to a solution (80 ml) with the desired amount of $HAuCl_4$ and urea. The suspension was then heated at 50–100 °C under stirring for an appointed period of time. The DPU process proceeded under protection from light. After that, the solid was collected by filtration and washed 5 times to thoroughly remove residual Cl^- ($AgNO_3$ test). The obtained catalyst samples were dried at 100 °C overnight and calcined in air at 100–700 °C for 4 h.

Catalyst characterization

The catalysts were characterized by X-ray diffraction (XRD; Rigaku Ultima IV diffractometer [Cu-Kα]) and transmission electron microscopy (TEM; JEOL-JEM-2010 instrument at 200 kV). The Au loading of the catalyst samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Thermo IRIS Intrepid II XSP spectrometer. Electrophoresis measurements were undertaken using a Powereach JS94H instrument (China). Each value was calculated as an average of five parallel measurements.

Reactivity test

The gas-phase epoxidation of propylene was carried out in a fixed-bed quartz reactor with an inner diameter of 16 mm. The test was carried out under atmospheric pressure and 0.3 g of the catalyst was charged. The catalysts were pre-reduced with a H_2 flow at 200–350 °C for 0.5–5 h, prior to the reaction test. The gas effluent was quantitatively analysed by using two on-line HP 5890 GCs equipped with TCD (Plot Q and MS 5A parallel capillary column (DIKMA); for analysing O_2, N_2, CO, CO_2 and H_2O) and FID (60 m FFAP capillary column; for analysing organic and O-containing organic chemicals) detectors.

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