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Propene epoxidation with O₂ and H₂: 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). ¹²⁹Xe 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 O₂ and H₂, 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 byproduction of toxic chlorinated organic compounds as well as salts such as CaCl₂. 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 O₂ and H₂ could be catalyzed by gold nanoparticles (Au NPs, 2.0–5.0 nm) deposited on anatase TiO₂ 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 H₂ 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 TiO₂ [4,12], mesoporous Ti-silicate (Ti-SiO₂) [5-7,9,10] and microporous titanosilicalite-1 (TS-1) [8,11,15-19]. Although Au/TiO₂ could present high PO selectivity (>90%), C₃H₆ 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-SiO₂ and Au/TS-1 could be used at higher reaction temperature, and both high C₃H₆ conversion and high PO selectivity could be achieved. Promoted by Ba(NO₃)₂, 0.30 wt% Au/mesoporous Ti-SiO₂ displayed a high C₃H₆ 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/TiO₂ 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 CO₂ and Au clusters smaller than 2.0 nm lead to propene hydrogenation [4]. Although Au/mesoporous Ti-SiO₂ and Au/TS-1 are more active for PO synthesis than Au/TiO₂, 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-SiO₂ 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 (~0.55 nm) of TS-1, such as Au₃ 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} k g_{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 darkfield 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 alkalinetreated 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. ¹²⁹Xe 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, ¹²⁹Xe 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 ¹²⁹Xe 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, ¹²⁹Xe 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 ¹²⁹Xe 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 H₂O 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 HAuCl₄ 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 HAuCl₄ 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 [(CH₃)₂Au(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.% H₂ 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 ¹²⁹Xe 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 HAuCl₄ 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 ¹²⁹Xe NMR analysis, Au catalysts were used to catalyze propene epoxidation with O₂ and H₂ mixture at 473 K for 2.0 h according to the procedures described in the following Part 2.5. Catalytic tests. During ¹²⁹Xe NMR measurements, supports or Au catalysts were first placed in an NMR tube equipped with I. Young valves, where the samples were dehydrated by slowly raising temperature to 473 K in a vacuum $(1.33 \times 10^{-4} \text{ kPa})$ 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, ¹²⁹Xe 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.

The chemical shift was referenced to xenon gas extrapolated to zero pressure. The ¹²⁹Xe NMR experiments can be repeated very well. The peaks were sufficiently narrow, and the error associated with chemical shift value is roughly 0.10 ppm.

2.5. Catalytic tests

Gold catalysts prepared by SG were first reduced at 423 K by H_2 (10 vol.% H_2 in Ar) and then cooled down to room temperature in the same stream. Gold catalysts prepared by DP were first dried under vacuum at room temperature overnight and then used directly without treatment. In both cases, 0.15 g of gold catalyst was weighed and then loaded into a vertical fixed-bed U-shaped quartz reactor with an inner diameter of 10 mm. The reactant feed gas of C_3H_6 , O_2 , H_2 and Ar with volume ratio of 10/10/10/70 was passed through at a flow rate of 20 mL min⁻¹, which corresponded to a space velocity of 8000 mL g_{cat}^{-1} h⁻¹. Reaction temperature was raised slowly from room temperature to 473 K with a heating rate of 1.0 K min⁻¹ and then kept at 473 K. Reactants and products were analyzed by on-line GCs equipped with TCD (Porapak Q column) and FID (HR-20M column) detectors.

3. Results

3.1. Catalytic activity

In our previous work, we found that Au loading could be easily adjusted by SG [8]. Thus, herein we first prepared Au/TS-1 by the DP method, and then after analyzing the real Au loading, we prepared Au/TS-1 with the same Au loading by the SG method. As shown in Table 1, Au/TS-1(DP) with a Au loading of 0.11 wt% was prepared by DP and gave only a low C_3H_6 conversion of 1.4% with a PO selectivity of 82% and with a H_2 efficiency of 31%, presenting a low PO formation rate of 22 g_{PO} kg_{cat}⁻¹ h⁻¹. Then, similar Au content was loaded by SG on TS-1, which has been treated in a similar manner to the DP method by replacing HAuCl₄ with HCl to remove K element and did not contain mesopores based on N₂ adsorption measurements, but the catalytic performance was inferior. In contrast, over 0.10 wt% Au/TS-1-Na1(SG), a greatly enhanced C₃H₆ conversion of 7.4% was achieved with a PO selectivity of 85% and with a H₂ efficiency of 30%, corresponding to a high PO formation rate of 119 g_{PO} kg_{cat}⁻¹ h⁻¹. In order to eliminate the effect of different supports (TS-1 vs. TS-1-Na1) on the very different catalytic activity over 0.11 wt% Au/TS-1(DP) and 0.10 wt% Au/TS-1-Na1(SG), the same support (TS-1-Na1) was selected to deposit Au at about 0.20 wt% by the SG and the DP method (Table 1). The PO formation rate over 0.20 wt% Au/TS-1-Na1(SG) prepared by SG is 127 $g_{PO} kg_{cat}^{-1} h^{-1}$, much higher than that of 74 $g_{PO} kg_{cat}^{-1} h^{-1}$ over 0.23 wt% Au/TS-1-Na1(DP) prepared by DP.

The catalytic stability of 0.10 wt% Au/TS-1-Na1(SG), 0.20 wt% Au/TS-1-Na1(SG) and 0.23 wt% Au/TS-1-Na1(DP) was also investi-

gated (Fig. 1). All the catalysts displayed good catalytic stability at reaction temperature of 473 K, especially C_3H_6 conversion and PO selectivity. These results are consistent with previous reports [8,16]. Interestingly, the steady state over 0.10 wt% Au/TS-1-Na1(SG) and 0.20 wt% Au/TS-1-Na1(SG) could be rapidly reached when the temperature was elevated to 473 K. However, that over 0.23 wt% Au/TS-1-Na1(DP) could be reached only after time on stream of 2.0 h at 473 K due to the necessity of in situ activation of Au species [17].

It is interesting that the increase of Au loading from 0.10 wt% to 0.20 wt% in Au/TS-1-Na1(SG) can only lead to a relatively small effect on the PO formation rate per gram of catalyst. This result might be explained as follows. A key step in propylene epoxidation with O₂ and H₂ is assumed to be the formation of Ti–OOH species [7,10]. Therefore, the formation of H_2O_2 on the Au surfaces and its effective transfer to isolated Ti sites are very important. Higher density of Au clusters will produce larger amount of H₂O₂ but covers larger amount of isolated Ti sites. Thus, the amount of effective (free, uncovered by Au clusters) isolated Ti sites in capturing H_2O_2 will be reduced. In addition, higher density of Au clusters will enhance the direct decomposition of H₂O₂ over the Au surfaces to H₂O. Finally, the increase of Au loading can only lead to a relatively small increase in the amount of Ti-OOH species and thus a relatively small increase in PO formation rate per gram of catalyst. This interpretation might be supported by reduced H₂ efficiency with Au loadings in our previous research [8].

3.2. ¹²⁹Xe NMR characterization

Fig. 2 and Fig. 3 show the effect of the amount of adsorbed xenon (Xe atoms per g of catalyst) on the ¹²⁹Xe NMR chemical shift. It should be noted that in our experiments, all the ¹²⁹Xe NMR spectra showed only a single and symmetrical peak. Therefore, in Figs. 2 and 3, only one curve could be plotted for each sample. Fig. 2 shows that the ¹²⁹Xe NMR chemical shift over TS-1 increases almost linearly with Xe concentration, which is the common behavior of xenon adsorbed in micropores. On the contrary, over 0.11 wt% Au/TS-1(DP), the ¹²⁹Xe NMR chemical shift first decreases gradually and then increases linearly with Xe concentration. Actually, at high xenon loading, both curves are parallel. At the lowest Xe loadings with Xe pressure of about 30 Torr, the chemical shift over 0.11 wt% Au/TS-1(DP) is 110.5 ppm, 12.4 ppm higher than that of 98.1 ppm over TS-1.

Compared with TS-1 (Fig. 2), TS-1-Na1 displayed a very different ¹²⁹Xe NMR chemical shift curve, which first decreases and then increases almost linearly with Xe concentration (Fig. 3). At the lowest Xe concentration with Xe pressure of about 30 Torr, a chemical shift of 74.1 ppm was obtained over TS-1-Na1, much lower than that of 98.1 ppm over TS-1. Over 0.23 wt% Au/TS-1-Na1(DP) and 0.20 wt% Au/TS-1-Na1(SG), similar chemical shift curves to that over TS-1-Na1 were obtained (Fig. 3). At the lowest Xe loadings

Table 1

Propene epoxidation with O2 and H2 mixture over Au catalysts prepared by DP and SG.

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	Au catalysts ^a	Mean Au diameter (nm)	Na (wt.%)	K (wt.%)	C ₃ H ₆ conv. (%)	H_2 effici. (%)	PO sel. (%)	PO formation rate $(g_{PO} kg_{cat}^{-1} h^{-1})$
	0.11 wt% Au/TS-1(DP)	4.3	0.95	<0.01	1.4	31	82	22
	0.10 wt% Au/TS-1(SG) ^b	4.0	0.95	< 0.01	0.9	32	90	16
	0.10 wt% Au/TS-1-Na1(SG)	1.6	0.93	< 0.01	7.4	30	85	119
	0.20 wt% Au/TS-1-Na1(SG)	1.8	0.93	< 0.01	8.3	24	84	127
	0.23 wt% Au/TS-1-Na1(DP)	1.7	0.96	<0.01	4.8	27	81	74

Reaction conditions: feed gas, $C_3H_6/O_2/H_2/Ar = 10/10/10/70$ in vol.%; space velocity, 8000 mL g_{cat}^{-1} h⁻¹; temperature, 473 K. All the data were taken under a steady state after 2.0 h duration.

PO: propene epoxide; conv.: conversion; sel.: selectivity; effici.: efficiency.

^a wt.% shows the real gold loadings obtained by ICP-AES analyses. Ti content is 1.8 wt% in all the catalysts.

^b Before solid grinding, TS-1 was treated in a similar manner to the DP method by replacing HAuCl₄ with HCl.



Fig. 1. Catalytic performance of 0.10 wt% Au/TS-1-Na1(SG) (\diamond), 0.20 wt% Au/TS-1-Na1(SG) (\blacktriangle) and 0.23 wt% Au/TS-1-Na1(DP) (\triangledown) in C₃H₆ epoxidation with an O₂ and H₂ mixture. Reaction conditions: catalyst, 0.15 g; temperature, 473 K; feed gas, C₃H₆/O₂/H₂/Ar = 10/10/10/70 in vol.%; space velocity, 8000 mL g_{cat}^{-1} h⁻¹. When the reaction temperature just reached 473 K, time on stream began.

with Xe pressure of about 30 Torr, the chemical shift over 0.23 wt% Au/TS-1-Na1(DP) is 86.6 ppm, 12.5 ppm higher than that of 74.1 ppm over TS-1-Na1; however, the chemical shift over 0.20 wt% Au/TS-1-Na1(SG) is 77.6 ppm, only \sim 3.5 ppm higher than that over TS-1-Na1.

3.3. HAADF-STEM observations

Fig. 4a shows one of the typical HAADF-STEM pictures of 0.11 wt% Au/TS-1(DP) taken in many different regions. In this picture, only three Au particles can be observed with diameters of 1.8, 3.7 and 7.5 nm. Counting all the Au particles revealed a very low population density of 6.4 Au particles per $100 \text{ nm} \times 100 \text{ nm}$. In addition, the diameter distribution of Au particles was also very broad (1.0-10.5 nm), and only 18% of Au particles existed as clusters (<2.0 nm), finally leading to a relative large mean diameter of 4.3 nm (Fig. 4b and Table 1). In addition, Au species were deposited by SG on TS-1 which was treated in a similar manner to the DP method by replacing HAuCl₄ with HCl (see Part 2.2. Deposition of Au by DP). Only Au NPs (>2.0 nm) but not Au clusters (<2.0 nm) could be formed. In contrast, a large number of Au particles could be clearly observed over 0.10 wt% Au/TS-1-Na1(SG) (Fig. 4c), and a high population density of 49.7 Au particles per 100 nm \times 100 nm was achieved. Furthermore, the diameter distribution of Au particles was very narrow (1.0-5.0 nm), giving a mean diameter of 1.6 nm (Fig. 4d and Table 1), and about 90% of Au particles were clusters (<2.0 nm).

In addition, Au with a higher loading of about 0.20 wt% was also deposited on TS-1-Na1 by both SG and DP method (Table 1). HAADF-STEM observations showed that in 0.20 wt% Au/TS-1-Na1(SG), the population density of Au particles per 100 nm \times 100 nm was 51.4 (Fig. 5a), higher than that of 17.4 Au particles per 100 nm \times 100 nm in 0.23 wt% Au/TS-1-Na1(DP) (Fig. 5c). In addition, in 0.20 wt% Au/TS-1-Na1(SG), the diameter distribution is very narrow and 87% of Au particles existed as clusters smaller than 2.0 nm (Fig. 5b), while in 0.23 wt% Au/TS-1-Na1(DP), only 66% of Au particles existed as clusters (Fig. 5d).

It should be noted that after the deposition of Au on TS-1-Na1 by SG, the color of Au/TS-1-Na1(SG) was white, the color of TS-1-Na1 itself. However, during the deposition of Au on TS-1 without alkaline pretreatment by SG, the color of Au/TS-1(SG) changed from white (the color of TS-1) to slight pink (the color of Au particles). This color change over Au/TS-1(SG) during SG clearly indicates that $(CH_3)_2Au(acac)$ can easily decompose in air by virtue of surface Ti-OH species and/or Si-OH species to form $-O-Au(CH_3)_2$ [30]. The formed $-O-Au(CH_3)_2$ species adsorbed on Au/TS-1(SG) will be reduced and coagulate to form Au particles during solid grinding in air.

4. Discussion

In order to obtain the high catalytic performance for PO synthesis not TS-1 but TS-1 treated with alkaline solution is indispensable as a support for Au clusters (Table 1). Second, the SG method is superior to the DP method. The results of the characterizations indicated that support materials (TS-1 and TS-1-Na1) in all the five Au catalysts (shown in Table 1) possess very similar crystalline MFI structure (based on XRD and ²⁹Si MAS NMR analysis), similar coordination circumstance of Ti sites (based on UV–vis and XANES) and similar particle morphology (based on TEM). In addition, these Au catalysts also possess similar Na content and the same Ti content (Table 1). Therefore, the very different catalytic activity among them should be caused by the different size and different size distribution of Au particles.

In the preparation of Au/TS-1 and Au/TS-1-Na1 by DP or SG, there are mainly two possible locations for Au deposition. One location is in the microporous channels of the supports, where Au should exist as tiny clusters such as Au₃ with diameters smaller than the size of channels, \sim 0.55 nm. The other is on the exterior surfaces of TS-1 and TS-1-Na1, where Au particles could exist as clusters (<2.0 nm) and NPs (>2.0 nm).¹²⁹Xe NMR characterizations and HAADF-STEM have been utilized to detect Au particles inside microporous channels and over the exterior surfaces, respectively.

Before analyzing the ¹²⁹Xe NMR results of supported Au catalysts, we first focus on the ¹²⁹Xe NMR results of supports (TS-1 and TS-1-Na1). As described in Part 3.2., ¹²⁹Xe NMR characterization, TS-1 (Fig. 2) and TS-1-Na1 (Fig. 3) displayed very different chemical shift value (98.1 vs. 74.1 ppm) at low xenon loadings and very different shapes of the curves (linear vs. nonlinear). Since both supports possess similar elemental contents, similar crystalline structures and similar morphologies, the differences above can be ascribed to their different pore structures. Although TS-1



Fig. 2. Effect of adsorbed Xe atoms per gram of samples on $^{129}\!\text{Xe}$ NMR chemical shifts (*T* = 291 K) on TS-1 (○) and 0.11 wt% Au/TS-1(DP) (●).

(treated with aqueous NaOH solution at pH of 9.0) possesses only micropores, TS-1-Na1 possesses both mesopores (created during alkaline treatment at pH of 12) and micropores based on N₂ adsorption measurements and ¹²⁹Xe NMR characterization at 210 K (described in the following). For TS-1 and TS-1-Na1, the ¹²⁹Xe NMR chemical shift could be

expressed as follows: $\delta = \delta_0 + \delta_{Xe-W} + \delta_{Xe-Xe}$, where δ_0 is the chem-



Fig. 3. Effect of adsorbed Xe atoms per gram of samples on ¹²⁹Xe NMR chemical shifts (*T* = 291 K) on TS-1-Na1 (■), 0.20 wt% Au/TS-1-Na1(SG) (▲) and 0.23 wt% Au/ TS-1-Na1(DP) (♥).

ical shift of reference and has been fixed to zero, $\delta_{\text{Xe-W}}$ is the parameter due to collisions between xenon atoms and zeolite walls, δ_{Xe-Xe} is caused by xenon-xenon collisions. At high loadings of xenon, δ_{Xe-Xe} determines the value of δ , while at low loadings of xenon, δ_{Xe-W} plays a crucial role. Related investigation showed that the interaction of adsorbed Xe atoms with microporous wall was



Fig. 4. HAADF-STEM images (a and c) and diameter distribution of Au particles (b and d) for 0.11 wt% Au/TS-1(DP) (a and b) and 0.10 wt% Au/TS-1-Na1(SG) (c and d). HAADF-STEM observation of Au catalysts was carried out after catalytic tests at 473 K for 2.0 h. D_{Au} denotes diameters of Au particles.



Fig. 5. HAADF-STEM images (a and c) and diameter distribution of Au particles (b and d) for 0.20 wt% Au/TS-1-Na1(SG) (a and b) and 0.23 wt% Au/TS-1-Na1(DP) (c and d). HAADF-STEM observation of Au catalysts was carried out after catalytic tests at 473 K for 2.0 h. D_{Au} denotes diameters of Au particles.

much stronger than that with mesoporous wall and thus gives a higher chemical shift [31,32]. Since ¹²⁹Xe NMR spectroscopy at low temperature is very sensitive to the pore structure of supports, the ¹²⁹Xe NMR characterizations of TS-1-Na1 at low temperature were carried out. As shown in Fig. 6, when the operation temperature decreased to 210 K, two peaks could be clearly observed. The peak at high δ is due to xenon adsorbed in micropores, and the peak with low δ is due to xenon adsorbed on mesopores. The successful detection of mesopores in TS-1-Na1 by ¹²⁹Xe NMR spectroscopy confirms the analyses based on N₂ adsorption measurements.

Now, it appears reasonable that at a low Xe loading, the chemical shift over TS-1 at 291 K (Fig. 2) is higher than that over TS-1-Na1 at 291 K (Fig. 3), because the former corresponds to only strong δ_{Xe-W} (microporous wall), while the latter corresponds to an average δ_{Xe-W} of both strong δ_{Xe-W} (microporous wall) and weak δ_{Xe-W} (mesoporous wall) due to the fast exchange of Xe atoms in micropores and in mesopores. With an increase in Xe loading, over TS-1-Na1 the contribution from δ_{Xe-W} (mesoporous wall) will increase, and thus the chemical shift decreases correspondingly (Fig. 3). After the chemical shift reaches the minimum, it will increase with Xe loadings due to the contribution of δ_{Xe-Xe} contribution. At high xenon loadings, the slopes of chemical shift versus xenon amount over both TS-1 (Fig. 2) and TS-1-Na1 (Fig. 3) are similar, which suggests that at high xenon loadings, xenon-xenon collisions contribute more significantly to give smaller difference in chemical shift. However, the chemical shift values are not exactly the same probably due to the differences in the porous network of these samples.

For metal/zeolites, the ¹²⁹Xe NMR chemical shift could be expressed as follows: $\delta = \delta_0 + \delta_{Xe-M} + \delta_{Xe-W} + \delta_{Xe-Xe}$, where δ_{Xe-M} is

the parameter due to collisions between xenon atoms and metal clusters incorporated into the channels of zeolite. Previous investigation showed that the incorporation of metal clusters into microporous channels of zeolites led to a great increase in ¹²⁹Xe chemical shifts at low Xe loading range, indicating that the interaction of adsorbed Xe atoms with incorporated metal clusters is much stronger than that with microporous wall of zeolites [24-28]. Therefore, at low Xe loadings, the observed chemical shifts δ $(\delta = \delta_0 + \delta_{Xe-M} + \delta_{Xe-W} + \delta_{Xe-Xe})$ can be ascribed mainly to δ_{Xe-M} . Accordingly, we will focus on the ¹²⁹Xe NMR chemical shift curve at low Xe loading. As shown in Fig. 2, 0.11 wt% Au/TS-1(DP) displays at a low xenon loading a chemical shift of 110.5 ppm, 12.4 ppm higher than that (98.1 ppm) of TS-1, indicating that tiny Au clusters have been incorporated into microporous channels of TS-1 by DP. In addition, it is also found that after the deposition of Au on TS-1 by DP, the slope of the curve δ versus xenon amount increases, meaning the decrease in the volume accessible to xenon due to the presence of Au species. This further confirms the incorporation of tiny Au clusters into microporous channels of TS-1 by DP. The successful detection of Au clusters incorporated in the microporous channels of TS-1 by Xe NMR technique indicates that Xe atoms can freely diffuse into the microporous channels. Although the pore structure of TS-1 is 3D interconnected and Xe atoms can diffuse into the microporous channels from anyone of the surface pore openings, the exterior pore openings are also the preferential adsorption sites for Au species during DP process. Therefore, tiny Au clusters incorporated might be located at defect sites inside microporous channels because the size of channels of TS-1 was only \sim 0.55 nm and the diameter of Au atoms is about 0.29 nm. This finding is consistent with the prediction by Joshi et al. [21] based on theoretical calculations that in Au/TS-1

294 K

273 K



68.0 ppm

Fig. 6. Temperature dependence of the ¹²⁹Xe NMR spectrum in TS-1-Na1 sample equilibrated at 300 Torr of xenon.

prepared by DP, tiny Au clusters are preferentially adsorbed on defect sites of microporous channels.

As shown in Fig. 3 the chemical shift over 0.23 wt% Au/TS-1-Na1(DP) is 12.5 ppm higher than that over TS-1-Na1 (86.6 vs. 74.1 ppm) at a low Xe loading, similar to the phenomenon observed over 0.11 wt% Au/TS-1(DP) and TS-1, indicating the incorporation of tiny Au clusters into the microporous channels of TS-1-Na1 by DP. On the contrary, 0.20 wt% Au/TS-1-Na1(SG) displays only a slightly higher chemical shift than that of TS-1-Na1 (77.6 vs. 74.1 ppm). The low values of observed chemical shifts in 0.20 wt% Au/TS-1-Na1(SG) suggest that Au species were not incorporated into microporous channels by the SG method but were located over the exterior surfaces as Au clusters and/or nanoparticles. Actually, the slopes of asymptote of curve Au/TS-1-Na1(SG) are very close to those of TS-1-Na1, supporting the hypothesis that Au species were preferentially located on the external surfaces. However, the possibility that small amount of Au species were incorporated into microporous channels and/or mesoporous channels could not be ruled out due to the slightly higher chemical shift over 0.20 wt% Au/TS-1-Na1(SG) than that over TS-1-Na1 at a low Xe loading. Therefore, further ¹²⁹Xe NMR characterizations of TS-1-Na1 and 0.20 wt% Au/TS-1-Na1(SG) at 210 K were carried out.

As shown in Fig. 7, chemical shift due to xenon adsorbed in micropores is very close for TS-1-Na1 and 0.20 wt% Au/TS-1-Na1(SG) samples. However, the chemical shifts due to xenon adsorbed in mesopores for 0.20 wt% Au/TS-1-Na1(SG) are slightly higher than that for TS-1-Na1, especially at low Xe loadings. This clearly indicates that during the preparation of Au/TS-1-Na1 by SG, Au species could not be deposited into microporous channels, but a small amount of Au species could be deposited into mesoporous channels probably owing to the relatively easier diffusion of bulky (CH₃)₂Au(acac) into mesoporous channels than into microporous channels.

It should be noted that ¹²⁹Xe NMR chemical shift curve over TS-1 increases almost linearly with Xe concentration (Fig. 2), while those over TS-1-Na1, Au/TS-1(DP), Au/TS-1-Na1(DP) and Au/TS-1-Na1(SG) first decrease and then increase almost linearly with Xe concentration, giving a minimum of chemical shift at low Xe loadings (Figs. 2 and 3). The presence of these minimum usually means the presence of strong adsorption sites (SAS) [33]. For



Fig. 7. Effect of adsorbed Xe atoms per gram of samples on ¹²⁹Xe NMR chemical shifts (*T* = 210 K) of xenon adsorbed in micropores of both TS-1-Na1 (\blacksquare) and 0.20 wt% Au/TS-1-Na1(SG) (\blacktriangle) and in mesopores of both TS-1-Na1 (\Box) and 0.20 wt% Au/TS-1-Na1(SG) (\triangle).

Au/TS-1(DP) and Au/TS-1-Na1(DP), tiny Au clusters incorporated into microporous channels should be the strong adsorption sites. However, it is not the case for TS-1-Na1 and Au/TS-1-Na1(SG). As shown in Fig. 7, TS-1-Na1 displays one minimum in chemical shift curve (at low Xe loadings and at 210 K) attributed to Xe atoms adsorbed into microporous channels, while Au/TS-1-Na1(SG) displays two minimum (at low Xe loadings and at 210 K) in chemical shift curves of Xe atoms adsorbed both into microporous channels and into mesoporous channels, respectively. For TS-1-Na1, the only strong adsorption sites might correspond to the defects created during the alkaline treatment of TS-1. However, for Au/TS-1-Na1(SG), the two strong adsorption sites might correspond to both the defects and Au species incorporated into mesoporous channels, respectively.

HAADF-STEM observation shows that over the exterior surfaces, the population density of Au particles over 0.23 wt% Au/TS-1-Na1(DP) is 17.4 Au particles per 100 nm \times 100 nm (Fig. 5c), lower than that of 51.4 Au particles per 100 nm \times 100 nm over 0.20 wt% Au/TS-1-Na1(SG) (Fig. 5a), although 0.23 wt% Au/TS-1-Na1(DP) possesses a slightly higher Au loading and a similar mean diameter of Au particles in comparison with 0.20 wt% Au/TS-1-Na1(SG) (Au loading, 0.23 vs. 0.20 wt%; mean diameter, 1.7 vs. 1.8 nm; respectively). Interestingly, even Au/TS-1-Na1(SG) with a lower Au loading of 0.10 wt% and with a mean diameter of 1.6 nm also displays much higher population density of 49.7 Au particles per 100 nm \times 100 nm than 0.23 wt% Au/TS-1-Na1(DP). Therefore, it is likely that some part of Au atoms in 0.23 wt% Au/TS-1-Na1(DP) were invisible by HAADF-STEM with a detection limit of \sim 0.6 nm, and they should exist as tiny clusters with atoms less than 11 (Au₁₁: ~0.8 nm in diameter). Recent experiments by Liu et al. [34] have showed that even under vacuum conditions, Au₁₁ clusters incorporated into mesoporous channels of mesoporous silica (SBA-15) and protected by the rough surfaces of mesoporous wall are not stable at 473 K. Therefore, it is probable that in 0.23 wt% Au/TS-1-Na1(DP), tiny Au clusters such as Au₃ deposited on the exterior surfaces and in mesoporous channels would sinter to form Au clusters larger than Au₁₁ and/or NPs under our reaction conditions (temperature, 473 K; feed gas flow, 20 mL min⁻¹), whereas tiny clusters could be stabilized inside the microporous channels, which is consistent with ¹²⁹Xe NMR characterizations.

Based on the combined analyses by 129 Xe NMR and HAADF-STEM, a conclusion can be drawn that tiny Au clusters such as

Au₃ are incorporated into microporous channels of both TS-1 and alkaline-treated TS-1 by DP but not by SG, while Au clusters (1.0–2.0 nm) and NPs (>2.0 nm) are deposited on the exterior surfaces of TS-1 and alkaline-treated TS-1 by both DP and SG methods. In addition, for Au/TS-1-Na1 prepared by both DP and SG, some Au species might be incorporated into mesoporous channels as Au clusters (larger than Au₁₁) and/or as NPs. However, the loading of Au incorporated into mesoporous channels should be much smaller than that over the exterior surfaces because the amount of mesopores in TS-1-Na1 is very small [8] and the diffusion and adsorption of Au species on the exterior surfaces is much easier than that into mesoporous channels during the preparation of Au/TS-1-Na1 by both DP and SG, especially by SG.

Joshi et al. [20,21] have predicted based on theoretical calculations that in Au/TS-1, tiny Au clusters incorporated into the microporous channels of TS-1 could be active for PO synthesis by the reaction of propene with O₂ and H₂ mixture. However, our experiments strongly indicated that Au clusters (1.0-2.0 nm) deposited on the exterior surfaces of alkaline-treated TS-1 were mainly responsible for PO synthesis [8]. The PO formation rate over 0.23 wt% Au/TS-1-Na1(DP) is 74 g_{PO} k g_{cat}^{-1} h⁻¹, much lower than that of 127 g_{PO} kg_{cat}⁻¹ h⁻¹ over 0.20 wt% Au/TS-1-Na1(SG) and even lower than that of 119 g_{PO} k g_{cat}^{-1} h⁻¹ over 0.10 wt% Au/TS-1-Na1(SG) (see Table 1). In Au/TS-1-Na1(DP), the DP method produces both tiny Au clusters (<0.55 nm) inside microporous channels and Au clusters (1.0-2.0 nm) on the exterior surfaces, while in Au/TS-1-Na1(SG), the SG method produces Au clusters (1.0-2.0 nm) selectively on the exterior surfaces. The lower catalytic activity over Au/TS-1-Na1(DP) than that over Au/TS-1-Na1(SG) suggests that Au clusters (1.0-2.0 nm) deposited on the exterior surfaces might be more active than tiny Au clusters (<0.55 nm) incorporated into microporous channels.

5. Conclusions

HAADF-STEM combined with ¹²⁹Xe NMR and elemental analyses indicate that by the SG method, Au is selectively deposited on the exterior surfaces of alkaline-treated TS-1 as clusters (1.0–2.0 nm) and partly as NPs (>2.0 nm), while by the DP method, Au is deposited not only over the exterior surfaces of TS-1 and alkaline-treated TS-1 as clusters (1.0–2.0 nm) and partly as NPs (>2.0 nm) but also inside the microporous channels (~0.55 nm) as tiny clusters. These tiny Au clusters might reside on the defect sites inside microporous channels, agreeing with the analyses by Joshi et al. based on theoretical calculations. In propene epoxidation with an O₂ and H₂ mixture, PO formation rate over 0.23 wt% Au/TS-1-Na1(DP) with a mean diameter of 1.7 nm is 74 g_{PO} kg⁻¹_{cat} h⁻¹, much lower than that of 127 g_{PO} kg⁻¹_{cat} h⁻¹ over 0.20 wt% Au/TS-1-Na1(SG) with a mean diameter of 1.8 nm. The only difference between the two catalysts is the location of Au

clusters, and accordingly, Au clusters (1.0–2.0 nm) over the exterior surfaces are more active for PO synthesis than tiny Au clusters inside the microporous channels.

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