Ti–Si Mixed Oxides by Non-hydrolytic Sol–Gel Synthesis as Potential Gold Catalyst Supports for Gas-phase Epoxidation of Propylene in H_2 and O_2

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The amorphous Ti–Si mixed oxides prepared from chloride precursors using a one-step nonhydrolytic sol–gel route could serve as efficient gold catalyst supports for gas-phase epoxidation of propylene in O_2 and H_2. A propylene conversion of 6.8% at the initial 60 min and 4.0% after 4 h of time-on-steam, keeping a selectivity to propylene oxide as high as 95%, was obtained over the gold supported on a Ti–Si mixed oxide containing 10 mol % of Ti.

Nonhydrolytic sol–gel process which is based on the formation of M–O–M or M–O–M′ bridges by thermal condensation between metal chlorides and metal alkoxides at moderate temperature, dividing as halide–ether route and halide–alkoxide route, may offer an alternative way to prepare mixed oxides with good homogeneity and high surface area.[1] The Ti–Si xerogels by the nonhydrolytic sol–gel have been reported as promising catalysts for epoxidation of alkenes and might be potential for the preparation of supported catalysts.[2] On the other hand, much attention has been paid on the epoxidation of propylene using O_2 with gold nanoparticles deposited on Ti-containing supports since the pioneer work of Haruta and co-workers.[3] The propylene oxide (PO) selectivity is larger than 90% over the catalysts, but it is necessary to remove several hurdles such as the lower conversion of propylene, rapid catalyst deactivation, and regeneration problems before making the process commercially viable. Three factors are believed as the key issues for overcoming these barriers: a molecular scale dispersion of the Ti atoms which are in synergism of the reduced dimensions of the metal particles (2–4 nm), supports with mesopores for effective dispersion of Au nanoparticles inside the pores, and support hydrophobicity for better PO desorption. Indeed, selected supports such as TS-1, Ti-MCM-41, Ti-MCM-48, Ti-containing hydrophobic silsesquioxanes, and 3D mesoporous titanosilicates have been claimed as being adequate for preparing active supported Au catalysts.[4] Herein, we present the first supported Au catalysts with the Ti–Si mixed oxides prepared by a one-step nonhydrolytic sol–gel synthesis for the gas-phase epoxidation of propylene in O_2 and H_2.

We chose the halide–ether route to prepare Ti–Si mixed oxides according to the procedure in the literature.[1c] The gels were formed in a well-sealed autoclave at 393 K for 96 h without contacting air. Calcination of the xerogels was performed in a furnace under flowing dry air for 5 h at 773 K with a heating rate of 1 K/min. The samples were labeled as Ti–Si–N_x (where x stands for the Ti mol % in the initial gel). The preparation hydrolysis sol–gel was based on the reported procedure using $TiCl_4$ and $SiCl_4$ as precursors[5] and labeled as Ti–Si–H_x. The deposition of gold on all the supports was carried out by a deposition–precipitation (DP) method at 333 K,[4] using an aqueous solution of $HAuCl_4$ (4 wt % Au loading based on the support) and a pH of 7.5 ± 0.1 adjusted by 0.05 mol·L^{-1} aqueous solution of NaOH. The solids were collected by filtration followed by washing for three times. The final samples were calcined in air at 673 K for 4 h. Catalytic reactions were carried out at 393 K in a fixed-bed flow reactor operated at atmospheric pressure with a feed containing 10 vol % each of C_3H_6, H_2 and O_2 in nitrogen (space velocity 4000 cm^3·h^{-1}·g$^{-1}_{\mathrm{cat.}}$).[4] The products were analyzed by two on-line gas chromatographs equipped with TCD detectors (5A, 3 m and Porapak Q, 3m) and FID detector (Porapak T, 2 m).

The XRD measurements clarified that the amorphous Ti–Si–N_x oxides were formed when $x \leq 12$. They possessed mesopores and higher surface areas by the results of N_2-adsorption/desorption (Table 1). No Au crystalline diffraction lines were observed with the samples of Au/Ti–Si–N_x (Figure 1a). High-resolution TEM images (not shown) revealed that the size of Au nanoparticles was about 2–4 nm. The UV–vis spectra (Figure 1b) showed that the samples with Ti contents up to 12.0 mol % exhibited absorbance peaks at 220–245 nm, which might result from tetrahedrally and octahedrally coordinated Ti centers. The broad band and that at longer wavelength region than 250 nm suggested that the presence of polymeric octahedral coordination was possible and also might be due to the Ti in a distorted tetrahedral environment, although no peak at ca. 330 nm was observed for the segregated TiO_2 phase when $x < 14$.[4] In addition, the typical plasmon band at 500–600 nm for small Au particles at the catalyst surfaces is evident as shown in Figure 1b.[3b,6]

Table 1 shows the catalytic performance of Au deposited on different supports for the gas-phase epoxidation of propylene. As for Au/Ti–Si–N_x, the propylene conversion and PO selectivity

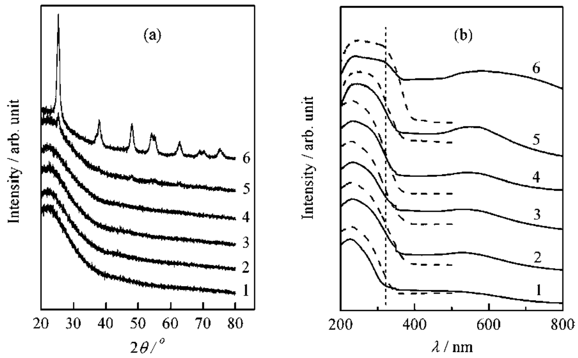

Figure 1. (a) XRD patterns and (b) diffuse-reflectance UV–vis spectra of Au/Ti–Si–N_x catalysts (the short dashs in UV–vis stands for the supports of Ti–Si–N_x). Ti contents: 1) 6.0 mol %; 2) 8.0 mol %; 3) 10.0 mol %; 4) 12.0 mol %; 5) 14.0 mol %; 6) 20.0 mol %.

Table 1. Catalytic performance of Au deposited on different supports for gas-phase epoxidation of propylene[a]

Support	Ti loading /mol %	S_{BET} /m^2 g^{-1}	Average pore diameter/nm	Conversion /%	Selectivity/%				
					PO	CH_3CHO	C_2H_3CHO	$(CH_3)_2CO$	CO_x
Ti–Si–N_6	6.0	452	3.0	1.2	81.5	4.5	1.6	0.3	6.7
Ti–Si–N_8	8.0	481	3.4	2.9	90.1	3.0	1.1	0.1	5.7
Ti–Si–N_{10}	10.0	664	3.6	6.8	95.0	2.3	1.0	0.1	1.6
Ti–Si–N_{12}	12.0	463	3.9	2.8	89.8	2.7	1.4	0.1	6.6
Ti–Si–H_8	8.0	354	4.8	2.1	95.5	0.4	1.5	1.8	0.1
Ti–Si–H_{10}	10.0	360	3.7	2.7	95.0	0.5	1.4	1.3	0.1
Ti–Si–H_{12}	12.0	267	3.6	2.5	92.1	1.4	0.5	1.2	4.7
P-25[b]	100	45	14.4	0.7	99.9	0.0	0.0	0.0	0.0
TS-1	2.5	526	4.1	0.3	8.0	35.0	43.2	16.4	0.0

[a] Reaction conditions: Feed gas $C_3H_6/O_2/H_2/N_2 = 1/1/1/7$ (vol %); GHSV = 4000 cm^3·h^{-1}·g$^{-1}{}_{cat}$; catalyst weight = 0.15 g; reaction temperature = 393 K; Data were taken at 60 min of time-on-stream. [b] Reaction temperature = 343 K.

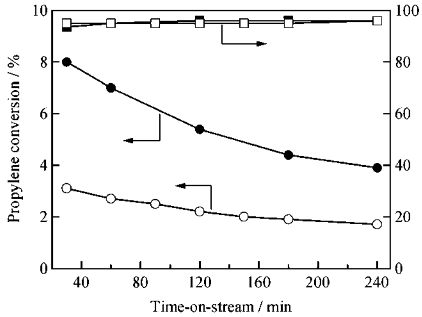

Figure 2. Epoxidation of propylene over Au/Ti–Si–N_{10} (solid symbols) and Au/Ti–Si–H_{10} (blank symbols) catalysts as a function of time-on-stream. The reaction conditions are the same as in Table 1.

increased with increasing Ti contents and reached maximum values at 10.0 mol % Ti content. Above this Ti content the propylene conversion tended to decline quickly. It is worth noting that the sample of Au/Ti–Si–N_{10} afforded a propylene conversion of 6.8% at the initial 60 min and 4.0% after 4 h of time-on-steam, keeping a selectivity to PO as high as 95% throughout 4 h of run (Figure 2). In contrast, when the Au deposited on the similar Ti-containing Ti–Si–H_x mixed oxides, the propylene conversion was lower in the case of Ti contents ranging at 8–12 mol %, although the PO selectivity was as high as 92–95.5% (Table 1). The lower selectivity to PO over Au/TS-1 sample might be due to the limited isolated Ti sites available.[4a]

Using the reaction conditions in Table 1, we have investigated the catalytic behaviors of Au/Ti–Si–N_{10} sample prepared by a variety of parameters, such as the aging time of nonhydrolytic sol–gel, calcination temperature for the xerogels and pH for the Au DP. With the Ti–Si–N_{10} obtained by aging time longer or shorter than 96 h, the catalyst generated afforded a propylene conversion and PO selectivity lower than 4.0 and 92%, respectively. The calcination temperature for the xerogels influenced the homogeneity and surface area as evidenced by the XRD and BET measurements, leading to different catalytic performances. Our results showed that the calcination at 673 K for 5 h was adequate. Moreover, when using a pH of 6.5 for the Au DP, the catalyst showed a propylene conversion of 5.6% and PO selectivity of 92.5%. Also, the propylene conversion and PO selectivity dropped to 2.2 and 90.1%, respectively, when pH for the Au DP was set at 8.5.

In summary, we have found that the Au nanoparticles dispersed on the amorphous Ti–Si–N_{10} mixed oxide by a non-hydrolytic sol–gel synthesis showed promising catalytic performance for the epxoidation of propylene to PO in the presence of O_2 and H_2. The catalyst preparation is relatively simple.

This work was supported by the NSFC (Nos. 20473065 and 20433030), the Key Project of Fujian Province (No. 2005HZ01-3), the RFDP and the Key Project of Chinese Ministry of Education (Nos. 20050384011 and 106099).

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