Bifunctional Titanosilicate with Hollow Structure

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Introduction

Titanosilicate has been widely investigated for the selective oxidation of organic reactants with aqueous hydrogen peroxide (H_2O_2, HP) as oxidant, which is one of the earliest classes of molecular sieves containing transition metal cations (Ti^{4+}) in framework positions.[1] Especially for TS-1, one type of titanosilicate with MFI topology, has been used as a highly-efficient heterogeneous catalyst for selective oxidation of industrially important organic compounds.[2] Containing a high fraction of active oxygen and generating water as its only byproduct, HP is regarded as a green oxidant. However, the existing manufacturing processes for HP are not very green because of the generation of wastes, low efficiency and high energy consumption. Direct synthesis of HP from H_2 and O_2 is an attractive technology as it is the most atom-efficient method by which HP can be synthesized.[3] Moreover, it is desirable to use *in situ* synthesized HP (coupling the direct synthesis of HP from H_2 and O_2, with the oxidation of reactants in one reaction zone) to replace preproduced HP, and hence, this one pot route has been investigated extensively over the past decade.[4] The catalysts used are bifunctional and usually with noble metal loaded on "support" (mainly Ti-containing molecular sieves).[5]

The presence of micropores in molecular sieves may limit the diffusion of reactant molecules into internal catalytic sites, while molecular transport in the channels or pores can be remarkably improved by creating intracrystalline mesoporosity or macroporosity (intraparticle voids).[6] In our earlier studies,[7] we have presented one type of titanosilicate with hollow structure (RTS, having intraparticle voids), and quite recently, one new bifunctional titanosilicate crystals with hollow structure (NHTS) was prepared by a semi *in situ* procedure (including partial dissolution and recrystallization process),[8,9] their bifunctional catalytic performance was investigated and very excellent,[10] while the synthetic procedure is relative complex (protector and reducer needed) and not easy to repeat completely. Here, we load noble metal on RTS via a simple but very effective route, thereby make the product become bifunctional titanosilicate with hollow structure (denoted as Pd-HTS$_x$, where subscript x stands for the noble metal content added in gel by weight percent). Pd-HTS$_x$ samples were characterized by various analytic techniques, such as X-ray fluorescence (XRF), X-ray powder diffraction (XRPD), transmission electron microscopy (TEM), N_2 adsorption-desorption isotherms (BET), Fourier transform infrared spectrometry (FTIR), and UV-Visible diffuse reflectance spectroscopy (UV–Vis). Their catalytic performances for the direct propylene epoxidation in one pot process (probe reaction) were also investigated.

Experimental

Synthesis

Titanosilicate with hollow structure (RIPP Titanosilicate, RTS for short) was prepared using the procedure similar to that described in the literature,[7] and the typical synthesis process was as follows: Tetraethyl orthosilicate (TEOS) was first hydrolyzed for 30 min in an aqueous solution of tetrapropylammonium hydroxide (TPAOH) and followed by the addition of tetrabutyl orthotitanate preliminary dissolved in dry isopropanol, then heated at 85°C for 3 h under stirring. The resulting mixture with the mole composition of SiO_2-0.4TPAOH-0.02TiO_2-45H_2O was transferred to a Teflon-lined stainless steel autoclave and shelved at 170°C for 72 h. After crystallization, the solid was recovered by centrifugation, washed with distilled water, dried at 120°C for 6 h, and calcined at 550°C in air for 6 h. The aforementioned solid was mixed with TPAOH and water in a weight ratio of the solid:TPAOH:water = 10:1:25, and the obtained mixture was transferred to Teflon-lined autoclave again at 170°C for 48 h. Then cooled and depressed. The mixture was centrifuged, washed, dried (120°C for 3 h), and calcined (550°C for 5 h).

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Table 1. XRF Results, Porous Parameters, and Catalytic Performance

				BET surface area (m^2/g)		Pore volume (cm^3/g)				
Samples	Pd (wt %)	TiO_2 (wt %)	SiO_2 (wt %)	S_{Micro}*	Total	V_{Micro}*	Total	C_{PO} (wt %)	S_{PO} (mol %)	V_{prop} (mol %)
RTS	–	2.14	97.86	388	442	0.19	0.38	–	–	–
Pd-HTS$_{0.5}$	0.47	2.11	97.42	379	417	0.18	0.34	1.4	94.1	18.9
Pd-HTS$_{1.0}$	0.94	2.08	96.98	373	409	0.18	0.32	2.3	92.7	25.6
Pd-HTS$_{1.5}$	1.36	2.01	96.63	368	395	0.17	0.28	2.2	89.5	25.2

*Microporous part.

Three bifunctional titanosilicate samples with different Pd contents (Pd-HTS$_{0.5}$, Pd-HTS$_{1.0}$, and Pd-HTS$_{1.5}$) have been prepared by a simple but very effective way, and the detailed loading procedures were as following: in a quartz beaker, 10.0 g RTS, 0.5 – 5.0 g TPAOH, and 25.0 – 50.0 g deionized water were added and then heated to 40 – 80°C with continuous stirring. Then amount of $PdCl_2$ (ammonia solution) were added into aforementioned solution, the mixture obtained was kept stirring at 45°C for 4 – 24 h. The solid was recovered by routine filtering and washing, drying at 110°C for 12 h, calcining in air at 350°C for 3 h, and reducing by H_2 at 120°C for 6 h.

Characterization techniques

XRF analyses were measured using a Rigaku 3271E XRF spectrometer. XRD data were recorded on a Siemens D5005 diffractometer. TEM images were gained on a Tecnai G^{2}F20S-TWIN electron microscope. FTIR spectra as well as the spectra of pyridine adsorption were recorded on a Nicolet 8210 infrared spectrometer. UV-Vis spectra were obtained on a Perkin-Elmer Lambda 20 UV-Vis spectrometer. The nitrogen isotherms were measured on a micromeritics ASAP 2010M system.

Catalytic test

The experiments for direct propylene epoxidation (one pot process) were carried out in a stainless steel high pressure reactor equipped with a Teflon beaker. 1.0 g catalyst, 40 g methanol, and 5 g water were charged to the reactor. First, 0.6 MPa of propylene was introduced into the reactor; second, H_2 and O_2 (mol ratio is 1:1) was continuously fed into the vessel until the pressure reaches 2.5 MPa. The slurry was kept at 60°C for 2 h under pressure and vigorous stirring, finally, cooled down to the temperature below 10°C and depressed. The catalyst was filtered off and the liquid phase analysis was performed on gas chromatograph (GC, Agilent 6890N, equipped with a flame ionization detector and FFAP capillary column). Here, the mole conversion of the propylene (V_{prop}), the weight concentration of target product (propylene oxide, PO) (C_{PO}), and the mole selectivity to PO (S_{PO}) in the reacted solution were used to describe their catalytic performance. Quantitative analysis data are obtained using authentic samples (external standard method).

Results and Discussion

Characterization

With the increase of Pd contents in Pd-HTS$_x$ samples, their SiO_2 and TiO_2 contents decrease slightly (Table 1), in view of the presence of certain content of Pd in Pd-HTS$_x$, the data match well with what expected. All samples exhibit the same main diffraction peaks (not shown), in agreement with that of the typical titanosilicate with MFI topological structure (TS-1), which indicates that the load of Pd on RTS have no evident effect on their crystal structures.[11] Furthermore, XRPD patterns of Pd-HTS$_x$ do not show any obvious characteristic signals of Pd species, demonstrating the high dispersion of Pd species in titanosilicate matrix (RTS).[12]

The particles of Pd-HTS$_x$ samples have intraparticle voids (Figure 1), which means that the load of Pd on RTS does

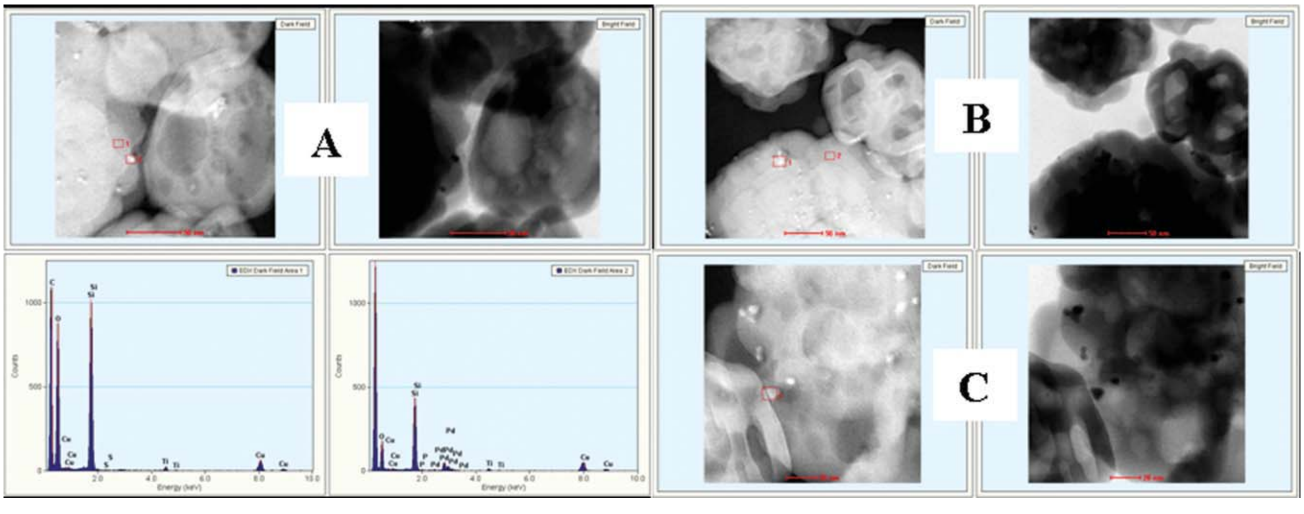

Figure 1. TEM images of samples: (A) Pd-HTS$_{0.5}$, (B) Pd-HTS$_{1.0}$, (C) Pd-HTS$_{1.5}$.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

not change their morphologies especially for the hollow structure. There are some characteristic particles of Pd species found in the TEM images of Pd-HTS$_x$ via a contrast between dark field images and bright field images (Figure 1), and the particle sizes of Pd species are almost less than 5 nm. Furthermore, with the increase of Pd content in Pd-HTS$_x$, the Pd particle sizes increase slightly.

Pd-HTS$_x$ samples give one strong UV absorption bands at 212 nm, indicating the existence of framework Ti^{4+}. One broad absorption band with the center around 500 nm also appeared in UV–Vis spectra of Pd-HTS$_x$, which is assigned to the absorption of noble metal species.[13] Moreover, with the increase of Pd content in Pd-HTS$_x$, UV–Vis absorption intensity of band at 500 nm increases slightly. The main FTIR absorption bands are consistent with the typical FTIR spectra of TS-1.[14] For Pd-HTS$_x$, the characteristic fingerprint band at 960 cm^{-1} is clearly detected, and there are no great changes in the fingerprint bands of RTS after the load of Pd (between RTS and Pd-HTS$_x$), suggesting that the effect of noble metal on RTS is almost negligible. The spectra of pyridine adsorption IR show that the adsorption band is only at 1450 cm^{-1}, implying Pd-HTS$_x$ and RTS only have L-acidic site. Moreover, L-acid quantities decrease with the increase of Pd content, indicating much less L-acidic sites in Pd-HTS$_x$ and some interactions between noble metal and RTS.

Evidently, the N_2 adsorption-desorption isotherm curves of Pd-HTS$_x$ and RTS (not shown) exhibit the pronounced hysteresis loop, clearly indicating the presence of significant mesoporosity, and the abrupt closure on the desorption branch is one characteristic of intracrystalline voids (hollow structure).[7] The aforementioned phenomena also illuminate that the synthesis procedure not only can make Pd load on Pd-HTS$_x$ but also maintain the intraparticle voids fully consistent with TEM analysis. The different amounts of noble metal load on RTS make the porous parameters of Pd-HTS$_x$ a little difference (Table 1), the slight decreases of surface area and pore volume are found, and the decreases are almost their corresponding mesoporous parts (subtracting microporous corresponding parts from total surface area or pore volume), which would be related to their catalytic performance.

Catalytic performance (Propylene direct epoxidation)

Under such evaluating conditions, RTS has no catalytic activity, whereas Pd-HTS$_x$ samples exhibit certain activity (Table 1). The mole conversion of the propylene (catalytic activity, V_{prop}) are given at 18.9, 25.6, and 25.1% for Pd-HTS$_{0.5}$, Pd-HTS$_{1.0}$, and Pd-HTS$_{1.5}$, the weight concentrations of PO (C_{PO}) are at 1.4, 2.3, and 2.2%, with the mole selectivity to PO (S_{PO}) at 94.1, 92.7, and 89.5%, respectively. The aforementioned catalytic results demonstrate that Pd-HTS$_{1.0}$ has better catalytic performance than that of other samples (Pd-HTS$_{0.5}$ and Pd-HTS$_{1.5}$), which can directly synthesize more quantities of HP from H_2 and O_2, and epoxidize more propylene, thus forming more target product PO. In one separate experiment without addition of propylene, the formation of HP from H_2 and O_2 at reaction conditions is proven directly.[14] In another separate experiment with addition of HP instead of H_2 and O_2, the formation of PO at reaction conditions is also proven directly. On the basis of aforementioned catalytic results, it can also be deduced and further testified that the formation of HP could occur over Pd species, and the direct propylene epoxidation process involving onsite HP formation followed by HP oxidizing propylene to PO, and Pd-HTS$_x$ are exactly bi-functional catalyst.[9] Such phenomena may be due to the special preparation treatment of Pd-HTS$_x$, which cannot only make the introduction of Pd, but also can maintain the hollow structure in Pd-HTS$_x$, thereby affording facilities for the molecular diffusions in Pd-HTS$_x$.

In summary, Pd-HTS$_x$ is one type of bi-functional catalyst used in one pot process. With high dispersed noble metal loading and hollow structure, Pd-HTS$_x$ may be applicable in direct catalytic oxidations.

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