



Effects of pore structure of post-treated TS-1 on phenol hydroxylation

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ABSTRACT

The present study reports the effects of crystal size of TS-1 (micrometer sized umTS1 and nanometer sized nmTS1) and the post-treatment (TPAOH and NaOH treatment) on the porous structure and the catalytic performances of TS-1 in phenol hydroxylation. TPAOH post-treatment generates hollow crystal and increases the surface area of umTS1 without changing its pore structure. In contrast, NaOH treatment selectively dissolves framework silica to form mesopore and modify microporous structure through which hierarchical material is constructed with agglomerated crystals. The umTS1 sample gives a much lower conversion and lower selectivity of dihydroxybenzenes (DHB) than the nmTS1 sample. Its activity can be greatly improved by TPAOH post-treatment exhibiting a comparable catalytic activity and DHB selectivity with the nmTS1 sample. Furthermore, successive post-treatment by TPAOH following with NaOH can generate micropores larger than the pore size of TS-1. The higher titanium content and faster diffusivity associated with the successive post-treatment significantly improve the catalytic performance of TS-1.

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1. Introduction

EniChem Corporation successfully developed a new phenol hydroxylation process in 1986 by using TS-1 catalyst and hydrogen peroxide oxidant in replacement of the traditional Brichima process (homogeneous system using $\text{Fe}^{2+}/\text{Co}^{2+}$ catalyst) for the production of hydroquinone (HQ) and catechol (CT). Since then, the catalysis of titanium containing molecular sieves has been extended to many other oxidation reactions [1]. The TS-1 catalysis involves a five membered ring intermediate generated by reacting titanium peroxy species (Ti-OOH) with the hydroxyl group of solvent molecules [2]. Formation of the bulky five membered ring intermediate reduces the pore volume of TS-1 and, thus, imposes remarkable diffusion resistance of substrates upon TS-1 [3]. As a result, the catalytic performance of TS-1 is strongly affected by the molecular size of substrate and oxidant, nature of solvent, crystal size, pore structure and hydrophobicity [4,5]. Effect of crystal size on phenol hydroxylation is still not clear. Wilkenhöner et al. reported that smaller crystallite TS-1 has higher catalytic activity [4]. Kerton et al. reported that oxidation of crotyl alcohol does not require TS-1 structure, but phenol hydroxylation is catalyzed only by crystalline TS-1. Phenol hydroxylation occurs only on the exterior surface of large TS-1 crystallites, with smaller crystallites

of TS-1, the reaction could occur on the exterior of the crystallites or at sites within the porous structure [5]. Generally speaking, in titanium silicate and mesoporous Fe-HMS [6], water is a better solvent. Furthermore, from catalyst stability viewpoint, the loss of Ti through leaching during oxidation using peroxide is of great concern particularly Ti-beta [7]. Some catalysts such as Ti-beta [8,9] and Fe-HMS [6] have different hydrophilic/hydrophobic properties and thus different product distribution from TS-1.

While TS-1 is limited to the application of those substrates and oxidants smaller than its pore opening of 5.4 Å, many new types of catalysts were studied in the catalysis for large molecules such as mesoporous Fe-HMS [6], superconductor mixed oxides Cu-Bi-V-O complex [10], mesoporous titanosilicates [11], vanadium-substituted phosphomolybdate [12], Fe-containing pillared clays [13], Fe/KIT-polystyrene composite [14], and metalloporphyrin complexes [15].

Although titanium silicates with periodic mesoporous structure can possess improved accessibility of active sites and the diffusion of substrate molecules inside the pore system, mesoporous titanium silicates were found to exhibit much lower intrinsic activity than TS-1 [16].

Introducing mesoporosity into zeolite can improve the diffusivity of zeolite [17]. Cejka and Mintova recently reviewed the preparation and catalysis of micro/mesoporous composite and hierarchical material [18,19]. Hierarchical material can be prepared either by direct synthesis, post-chemical treatment or formation of zeolite monoliths [20,21]. Among various post-treatment methods, Groen

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et al. reported that desilication of MFI zeolite by alkaline post-treatment can create mesopores more effectively than dealumination procedure does [22]. Tuel and coworkers reported that TS-1 catalytic activity can be improved by TPAOH post-treatment [23]. Recently, we found that the catalytic performance of TPAOH treated TS-1 can be significantly improved by alkaline post-treatment [24]. The present paper studies the effect of different post-treatments on the pore structure of TS-1 and its catalytic performance in phenol hydroxylation.

2. Experimental

Nanometer sized TS-1, denoted as nmTS1, was synthesized hydrothermally at 443 K for 12–24 h from a gel mixture of SiO_2 : TiO_2 :TPAOH:IPA:H₂O = 1:0.02:0.20–0.35:1.0:25–50 using TEOS as silica precursor and *t*-butyl orthotitanate as titanium precursor following the procedure reported by Guo et al. [25–27]. On the other hand, micrometer sized TS-1, denoted as umTS1, was synthesized from the gel at the composition the same gel composition as nmTS1 but using tetrapropylammonium bromide (TPABr) as template and triethylamine as organic base, colloidal silica as silica source and TiCl_4 as titanium precursor. Those TS-1 samples were calcined in flowing air stream at 813 K for 8 h to remove organic template.

The parent umTS1 sample was post-treated with TPAOH solution of 0.15 mol/L hydrothermally at 443 K for 48 h, which was denoted as MT-umTS1; or with NaOH solution of various concentrations, represented as solution A (2×10^{-2} mol/L), B (4×10^{-4} mol/L) and C (2×10^{-3} mol/L), at 353 K for *x* minutes, denoted as Na*Xx*-umTS1. Successive post-treatment was also conducted by treating first with TPAOH and then with NaOH solution, denoted as Na*Xx*-MT-umTS1. Similarly, parent nmTS1 sample was post-treated to prepare MT-nmTS1, Na*Xx*-nmTS1 and Na*Xx*-MT-nmTS1. The NaOH treated samples were then ion exchanged with 1 mol/L NH_4NO_3 solution at 353 K for 6 h and finally calcined in air at 813 K for 8 h.

The structures of various TS-1 samples were determined with a Rigaku Multiflex X-ray diffractometer using $\text{Cu K}\alpha$ radiation and their compositions were analyzed by PerkinElmer Optima 2100 DV inductive coupling plasma (ICP-AES) spectrometer. The surface area was determined by BET method using Micromeritics ASAP2020. Prior to the measurements, samples were degassed at 373 K for 1 h and at 623 K for 4 h at a pressure less than 1.4 Pa. Nitrogen adsorption was conducted at 77 K. The pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method using the desorption branch of the isotherm. A temperature programmed desorption (TPD) of hexane isomers [28] was devised to determine the micropore structures of the parent and post treated TS-1 samples. The experimental setup was a gas chromatography (GC) equipped with a flame ion detector (FID). A stainless steel (ss) tube packing with zeolite sample of 25 mg is used as the column of the GC. The column is heated to 573 K in nitrogen carrier gas flow for 3 h to desorb any adsorbed substances particularly water. Adsorption measurement was conducted in nitrogen flow by pulse injecting one hexane isomer at 308 K and atmospheric pressure until breakthrough as on-line observed with GC FID signal. Desorption was conducted first at 308 K for 30 min and then by raising oven temperature at a heating rate of 5 °C/min up to 573 K. The desorption capacity was measured from the FID peak area calibrated with a known volume of the hexane isomer.

Phenol hydroxylation reaction was conducted in a rotary reactor in batch mode using a reaction mixture with the composition of phenol:H₂O₂ = 3:1. Oxidation products were analyzed by an Agilent 5890 Gas Chromatography equipped with a FID detector using an OV-101 column. The molecular formula of reaction products were determined using Varian Star 3380 GC/MASS spectrometer equipped with TR-5MS column.

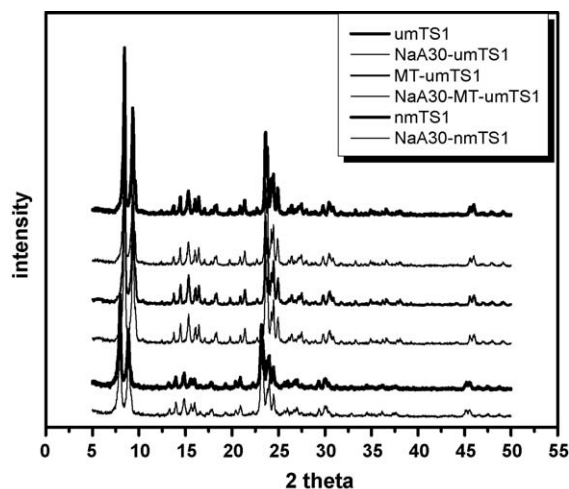


Fig. 1. X-ray diffraction patterns of the parent TS-1 and post-treated TS-1 sample.

3. Results and discussion

As shown in Fig. 1, all the X-ray diffraction patterns of the tested samples, including micrometer sized umTS1 and nanometer sized nmTS1 as well as the post-treated samples, possessed pure TS-1 phase. Therefore, post-treatment with TPAOH or NaOH at the stated conditions do not destroy MFI framework structure. The crystal size of the TS-1 sample determined with transmission electromicroscopy (TEM) was about 5 μm for the umTS1 sample and 50 nm for the nmTS1 sample. Micrometer sized TS-1 can be prepared with conventional method using TPABr as template and triethylamine as organic base [29]. On the other hand, nmTS-1 be prepared using organic base TPAOH as template [30].

The umTS1 and nmTS1 sample subject to TPAOH treatment kept the same crystal size but turned into hollow crystal in TPA-umTS1 sample. On the other hand, NaOH treatment form aggregates of nano-crystals. Cundy et al. reported that morphology of MFI crystal changes with NaOH solution treatment [31]. As shown in Table 1, both the parent umTS1 and MT-umTS1 have Ti content determined with ICP-AES as 4.0 wt.%. Similar effect was observed on the post-treated nmTS1 sample, showing unchanged Ti content of 3.5 and 3.7 wt.% in nmTS1 and MT-nmTS1, respectively. In contrast, NaOH post-treatment raises titanium content. The titanium content increases up to 5.2 and 4.2 wt.% respectively in the NaOH treated NaA30-umTS1 and NaA30-nmTS1 sample. On the other hand, the titanium content increases slightly in the successive treated sample first with TPAOH following with NaOH up to 4.2% in the NaA30-MT-umTS1 and 4.0 wt.% in the NaA30-MT-nmTS1. Therefore, TPAOH post-treatment can generate holes inside crystal without changing crystal composition. In contrast, alkaline treatment can dissolve silica and disintegrate crystal agglomerates.

Table 1

Textural properties of various TS-1 samples determined with nitrogen adsorption isotherm.

Sample	Ti (wt.%)	S_{BET} (m^2/g^{-1})	S_{meso} (m^2/g^{-1})	S_{micro} (m^2/g^{-1})	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)	Mesopore size (\AA)
umTS1	4.0	404.5	131.4	273.1	0.10	47.2
MT-umTS1	4.0	425.2	150.9	274.2	0.13	44.9
NaA30-umTS1	5.2	346.6	110.5	236.1	0.19	22.4
NaA30-MT-umTS1	4.2	416.9	148.8	268.1	0.23	22.9
nmTS1	3.5	546.2	341.0	205.1	0.50	74.8
MT-nmTS1	3.7	423.8	261.1	162.7	0.31	69.6
NaA30-nmTS1	4.2	507.2	230.8	276.4	0.41	98.3
NaA30-MT-nmTS1	4.0	428.4	275.3	153.2	0.33	75.0

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