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Gallery-templated Synthesis of Titanium/ Silicon -containing Mesoporous Montmorillonite-based Catalytic Materials

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Abstract: A mesoporous **t**itanium/silicon -containing montmorillonite-based catalytic materials has been synthesized by novel gallery-templated techniques. XRD, SEM, framework IR, and N_2 adsorption–desorption isotherms provided evidence of the formation of Si/Ti pillars. The synthetic materials show potential catalytic application for hydroxylation of phenol with peroxide.

Keywords: Mesoporous materials, montmorillonite, pillared clay, hydroxylation of phenol.

Titanium-containing molecular sieves have been regarded as promising catalytic materials for the selective partial oxidation of organic substrates with hydrogen peroxide since the invention of TS-1 and TS-2 [1,2]. However, their relative small pore size (about 0.6 nm) in the framework greatly limited their application. The preparation of titanium-containing porous solids with larger pore is of great significance [3]. An alternative approach to create mesoporous titanium-containing structure has been reported by Yamanaka *et al.* through preparation of porous clays pillared with SiO_2-TiO_2 [4]. But titanium/silicon-pillared clay is usually synthesized by intercalation of Ti and Si oxide sol particles which have to be prepared under non-environmentally friendly strong acidic condition and suffer from problems of nonuniform gallery heights due to the nonuniform size and shape of the sol particles [5]. Recently Pinnavaia *et al.* [6,7] invented silica porous clay heterostructures (PCHs) with narrow pore size distribution formed by gallery-templated synthesis starting from Li-hectorite and saponite. By utilizing double function of template and solvation of organic amine for organic Ti and Si compound, in the present work a novel synthesis method for Ti/Si-containing mesoporous montmorillonite (mmt) heterostructure with narrow pore size distribution was developed directly using $Si(OC_2H_5)_4$ and $Ti(OC_4H_9)_4$, instead of pre-preparation of acidic Ti and Si sol.

Na-mmt ($Na^+_{0.66}[Al_{2.97}Fe_{0.37}Mg_{0.66}](Si_{8.00})O_{20}(OH)_4$)[8] was firstly converted to a quaternary ammonium exchanged form by ion-exchange with twofold excess of aqueous octadecyltrimethylammonium chloride (OTMA). After adding 25 g of DDA to 5 g of organo-mmt and stirring for 30 min, $Ti(OC_4H_9)_4$ and $Si(OC_2H_5)_4$ at a molar ratio of 3:100 were added to the above suspension and reacted for 24 h at room temperature. The resulting intercalates were centrifuged, aged and slowly dried in air. Finally the organic

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Figure 1 XRD patterns of the samples

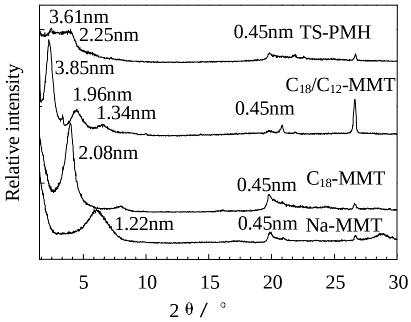


Figure 2 SEM photograph of the sample TS-PMH

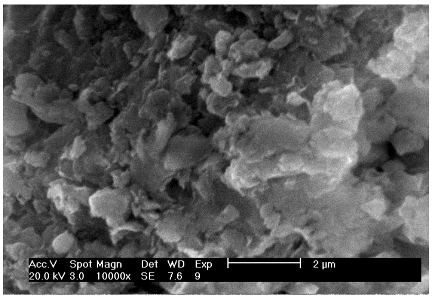


Figure 3 N_2 adsorption-desorption isotherms for TS-PMH (Insert: the corresponding pore size distribution curve)

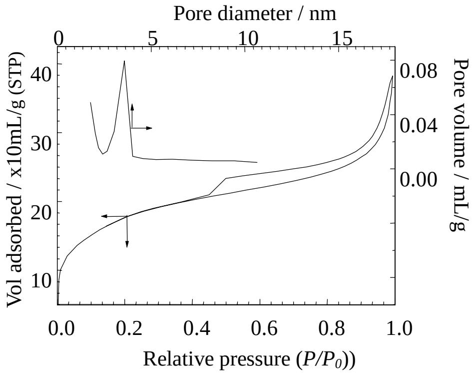
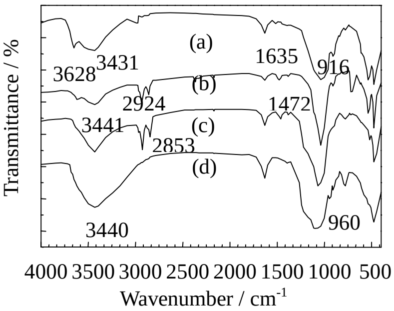


Figure 4 IR spectra of synthetic samples (a) Na-mmt; (b) C_{18}-mmt; (c) C_{18}/C_{12}-mmt; (d) TS-PMH



template was removed by ethanol extraction as reported by Pinnavaia *et al.* and Benjelloun *et al.*[9,10] and the solids were dried at 200 ℃ in air to yield Ti/Si-containing porous mmt heterostructure sample (denoted TS-PMH).

Figure 1 illustrates the X-ray powder diffraction patterns (Philips X'pert with CuKα radiation) for the sample at different stage. OTMA readily intercalates mmt and increase interlayer distance d_{001} to 2.08 nm (2θ = 4.24°) which is higher than that of starting Na-mmt (d_{001}=1.22 nm, 2θ =7.24°). Organic compound with long chain not only changed the characteristics of interlamellar surface from hydrophilic to hydrophobic, but also expanded the gallery to facilitate the accessibility of amine (d_{001}=3.86 nm, 2θ =2.28 °). Under template solvation and ion exchange, the organic Si and Ti precursors can intercalate the gallery. The intragallery hydrolysis and assembly promoted by water and amine-based catalysis resulted in the formation of Si/Ti pillars . The d_{001} diffraction line of the resulting TS-PMH provided further evidence of the presence of pillars with high basal space value (2θ =2.44° , d_{001}=3.61 nm). No anatase TiO_2 and SiO_2 has been observed in the XRD patterns. As shown in **Figure 2** (Philips XL30ESEM), there is no amorphous matter outside the gallery of TS-PMH.

The BET specific surface area of the material reaches 636 m^2/g, with a BJH average pore diameter of 3.6 nm and BJH desorption cumulated pore volume 0.49 mL/g. If a dense silica/titania phase completely filled the interlayer region, the materials would not yield the observed high surface areas. The shape of nitrogen adsorption-desorption isotherms for synthetic samples have a hysteresis loop which has the characteristic of mesoporous structure which belong to type-Ⅳ isotherms (Micromeritics ASAP 2000 at 77 K) (see **Figure 3**). The results are also in good agreement with the specific surface areas measurements.

In IR framework spectra (Bruker Vector 22) of TS-PMH samples, an additional band at 960 cm^{-1} has been observed, which is absent in the IR spectra of original mmt as well as organoclay (**Figure 4**). The disappearance of bands at 2853 cm^{-1}, 2924 cm^{-1} confirms the elimination of organic template, indicating the higher gallery and larger pore was yielded by Ti and Si, instead of larger organic molecules. Scarano *et al.* [11,12] reported that the IR adsorption at 960 cm^{-1} was attributed to the presence of titanium in the tetrahedral Si－O－Ti linkages. Thus, the band at 960 cm^{-1} appeared in the IR spectra of the sample TS-PMH can be possibly ascribed to the presence of in the tetrahedral Si-O-Ti linkages, which form the pillars in the galleries of clay.

Table 1 Catalytic hydroxylation of phenol with peroxide over synthetic materials

Catalyst	Reaction solvent	Conversion of phenol /(%)	Conversion of H_2O_2 (%)	Selectivity of hydroquinone (%)
TS-PMH	Acetone	14.5	87.4	25.0
TS-PMH	*m*-xylene	24.8	95.6	36.7
TS-PMH	Ethanol	29.5	80.3	11.3
TS-PMH	Toluene	31.7	93.2	25.7
TS-PMH	Water	17.6	84.2	11.0

Reaction condition: 300 mg catalyst, 5 g phenol, 1.8 g H_2O_2, 5 mL solvent, 100 ℃, 30 min.

The catalytic activity of synthesized TS-PMH was evaluated in the hydroxylation of phenol by hydrogen peroxide in a batch reactor under different solvents. The samples TS-PMH showed relative catalytic partial oxidative activity and selectivity, as shown in **Table 1**. The highest phenol conversion can reach 29.5% and the best selectivity of hydroquinone can also reach 36.7%. On the other hand, the catalytic activity and selectivity were highly dependent upon the solvent in the reaction. In contrary, the sample mmt, TiO_2, SiO_2, mechanical mixture of Mont-SiO_2, and SiO_2-TiO_2 showed complete inactivity for the yield of partial oxidation products. Thus, it can be suggested that only when the silicon and titanium ions were incorporated galleries of clay layers and presented in the form of Si-O-Ti bond, TS-PMH are active in partial oxidation catalysis.

As showed above, this novel synthetic strategy for TS-PMH avoided the use of concentrated acid and preparation of Si and Ti mixed oxide sol precursor by utilization of double function of organic surfactants. In the meantime, the addition of a non-ionic surfactant produces more ordered pillared porous clay materials with partial oxidation catalysis.

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