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Hydroxylation of phenol with hydrogen peroxide catalyzed by Ti-SBA-12 and Ti-SBA-16

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ABSTRACT

We report here, for the first time, the application of ordered, three-dimensional, mesoporous titanosilicates, Ti-SBA-12 and Ti-SBA-16, as reusable solid catalysts, for hydroxylation of phenol, an industrially important organic transformation. The reactions were conducted using 30% aqueous H_2O_2 as oxidant. The catalysts of this work are more efficient than the hitherto known mesoporous Ti-silicates. They are more *para*-product selective than TS-1 and other titanosilicates. Ti-SBA-12 exhibited higher activity and hydroquinone/catechol selectivity (by nearly two times) than Ti-SBA-16. H_2O_2 efficiency of ~90 mol% was obtained. Our study reveals that framework substituted Ti with pseudo-tetrahedral geometry, three-dimensional mesoporosity as well as surface structure are the unique features responsible for the high catalytic activity and selectivity of these titanosilicate catalysts.

1. Introduction

Hydroxylation of phenol is an industrially important reaction as the product diphenols, *viz.*, catechol and hydroquinone (Scheme 1), are widely used as photography chemicals, antioxidants, polymerization inhibitors, flavoring agents and drug intermediates [1]. Since 1970, phenol hydroxylation has been widely investigated using various homogeneous and heterogeneous catalysts. In the *Brichima process* (now Enichem, Italy) [2,3], the salts of Fe^{2+} and Co^{2+} are used as catalysts for phenol hydroxylation by using 60% aqueous H_2O_2 as oxidizing agent. In the *Rhône-Poulenc process* [4,5], strong mineral acids such as phosphoric acid and catalytic amount of perchloric acid are employed with 70% aqueous H_2O_2. In the *Hamilton process* [6], Fenton reagent is used as a catalyst. In the *Ube-Rhone-Poulenc process* [7], this reaction is carried out with ketone peroxides (α-hydroxy hydroperoxides) formed *in situ* from a ketone and 60% aqueous H_2O_2 in the presence of an acid catalyst (sulphuric or sulphonic acid). But these homogeneous catalysts are difficult to recover from the reaction mixture. Heterogeneous catalysts are particularly attractive for hydroxylation of phenol due to their engineering and catalyst reusability advantages.

Titanosilicates have been widely investigated due to their remarkable catalytic activity for oxidation reactions at mild conditions using aqueous hydrogen peroxide as oxidant [8–10]. Hydroxylation of phenol catalyzed by microporous titanosilicates (TS-1 or TS-2) created an environmentally benign route for the production of catechol and hydroquinone [11–15]. The process has been commercialized by Enichem, Italy in 1986. However, the application of TS-1 and TS-2 catalysts is limited to molecules with smaller dimensions due to inherent constraints on pore size (0.54 nm). Mesoporous M41S-type titanosilicates are less stable and show lower intrinsic catalytic activity and selectivity toward the use of H_2O_2 in phenol hydroxylation [10]. Ti-MCM-68 showed superior activity to TS-1 but a decrease in product yield after some duration of the reaction due to tar formation was noted [16]. Hence, there is a need to develop more efficient and stable, ordered mesoporous silica materials with Ti substituted in their framework for transformation of bulky organic molecules of pharmaceutical interest.

Among SBA-type mesoporous silica, SBA-12 and SBA-16 attract much attention due to their outstanding stability and three-dimensional mesopore architecture [17,18]. We have recently reported a method for direct synthesis of framework-substituted Ti in Ti-SBA-12 and Ti-SBA-16 [19–21]. These materials exhibited high catalytic activities for epoxidation of cyclic olefins and for the synthesis of β-amino alcohols through ring-opening of epoxides with amines [19–21]. We, now, extend their application, for the first time, for the liquid-phase hydroxylation of phenol with

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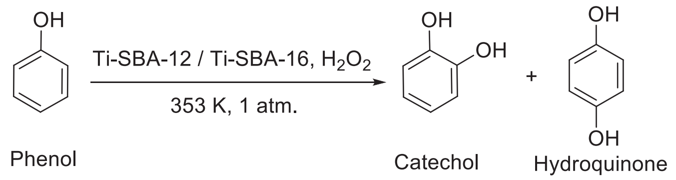

Scheme 1. Hydroxylation of phenol.

30% aqueous H_2O_2. These catalysts showed remarkably high catalytic activity than the hitherto known mesoporous titanosilicate catalysts.

2. Experimental

Ti-SBA-12 and Ti-SBA-16 with Si/Ti input molar ratios of 80, 50, 40, 30 and 20 were prepared and characterized as described by us earlier (Supplementary information, S1) [19–21]. The Si/Ti output molar ratios of the catalysts are listed in Table 1.

Liquid-phase hydroxylation of phenol was carried out in a 50 ml glass round-bottom flask, fitted with a water-cooled condenser and placed in a temperature-controlled oil bath. In a typical reaction, 10 mmol of phenol (0.94 g), 10 ml of distilled water and 0.1 g of catalyst were taken in the glass reactor. To it, a known quantity of 30% aqueous H_2O_2 was added in one lot. Temperature of the reaction mixture was raised to a specific value and the reaction was conducted while stirring for a desired period of time. The progress of the reaction was monitored by gas chromatographic technique (GC – Varian 3400; CP-SIL8CB column; 30 m-long and 0.53 mm-i.d.). Prior to GC analysis, solid catalyst, present if any in the aliquot was removed by centrifugation followed by filtration. Solvent (water) was separated by treating the liquid portion of the reaction mixture with diethyl ether. Unreacted phenol and the oxidation products which remained in the ether layer were then separated. Ether was distilled out under reduced pressure using a rotavapor. The reaction mixture thus recovered was diluted with a known quantity of methanol and analyzed by GC. Identification of the products was done by GC–MS (Varian CP-3800; 30 m-long, 0.25 mm-i.d., and 0.25 μm-thick CP-Sil8CB capillary column) and by comparing with the standard samples. A typical mass balance greater than 98% was obtained.

3. Results and discussion

3.1. Structural and spectroscopic properties

We present here, in brevity, the salient features of Ti-SBA-12 and Ti-SBA-16. Detailed characterization of these catalysts could be found elsewhere [19–21]. Fig. 1 shows the X-ray powder diffraction (XRD) patterns of the catalysts in the low-angle region ($2\theta = 0.5–5°$). SBA-12 shows an intense main peak at 1.68° corresponding to (0 0 2) reflection and two well-resolved, weak peaks at 2.90° and 3.28° attributable to (1 1 2) and (3 0 0) reflections, respectively (Fig. 1(a)). A weak shoulder (to the main peak) at 1.47° due to (1 0 0) reflection is also observed. These characteristic features of SBA-12 are consistent with the ordered, three-dimensional, hexagonal mesoporous structure with a space group of $p6_3/mmc$ [17]. SBA-16 shows a strong peak at 0.92° attributable to (1 1 0) reflection and two poorly-resolved, weak peaks at 1.2° and 1.9° due to (2 0 0) and (2 1 1) reflections, respectively (Fig. 1(b)). The diffraction patterns of SBA-16 can be indexed to an ordered, three-dimensional, mesoporous, cubic structure with a space group of $Im\bar{3}m$ [17,22–26]. In the case of Ti containing samples (Ti-SBA-12 and Ti-SBA-16), these peaks shifted to lower 2θ values evidencing an increase in the unit cell parameters (a and c for the hexagonal Ti-SBA-12 and a for the

Table 1
Composition, structural and textural properties of Ti-SBA-12 and Ti-SBA-16.

Catalyst	Si/Ti molar ratio		Unit cell parameter (nm; XRD)		Textural properties (N_2 physisorption)				Average pore diameter (nm)	Wall thickness (XRD and N_2 physisorption)
					S_{BET} (m^2/g)	Pore volume (cm^3/g)				
	Input	Output (ICP–OES)	a	c		Micro	Meso	Total		
SBA-12	∞	∞	6.93	10.56	672	0.01	0.63	0.64	3.8 (5.4)	6.76
Ti-SBA-12 (80)	80	146.0	7.02	10.64	767	0	0.96	0.96	5.0	5.64
Ti-SBA-12 (50)	50	80.2	7.02	10.64	857	0	1.20	1.20	5.6	5.04
Ti-SBA-12 (40)	40	68.7	7.08	10.80	460	0.02	0.62	0.64	5.5	5.30
Ti-SBA-12 (30)	30	61.4	7.08	10.80	765	0.03	0.98	1.01	5.3 (5.8)	5.50
Ti-SBA-12 (20)	20	45.7	7.20	10.90	500	0.02	0.61	0.63	5.0	5.90
SBA-16	∞	∞	13.57	–	800	0.16	0.51	0.67	3.4 (3.6)	8.35
Ti-SBA-16 (80)	80	150.2	13.57	–	886	0.15	0.64	0.79	3.6	8.15
Ti-SBA-16 (50)	50	80.5	13.72	–	910	0.11	0.75	0.86	3.8	8.08
Ti-SBA-16 (40)	40	70.6	13.88	–	709	0.10	0.60	0.70	4.0	8.02
Ti-SBA-16 (30)	30	53.8	14.18	–	765	0.15	0.52	0.67	3.5 (3.4)	8.78
Ti-SBA-16 (20)	20	40.6	14.87	–	780	0.18	0.49	0.67	3.4	9.47

[a] SBA-12 and Ti-SBA-12 are described by a hexagonal system with space group of $p6_3/mmc$. SBA-16 and Ti-SBA-16 are defined by a cubic system with space group of $Im\bar{3}m$. Unit cell parameter $a = 2d_{100}/\sqrt{3}$ and $c = 2d_{002}$ (for SBA-12 and Ti-SBA-12) and $a = \sqrt{2} \times d_{110}$ (for SBA-16 and Ti-SBA-16).

[b] Values in parentheses are those obtained from HRTEM measurements.

[c] Wall thickness = c – average pore diameter (for SBA-12 and Ti-SBA-12) and $\sqrt{3}/2\,a$–average pore diameter (for SBA-16 and Ti-SBA-16).