

Synthesis and Characterization of Titanium Supported on High Order Nanoporous Silica and Application for Direct Oxidation of Benzene to Phenol

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Abstract: Direct oxidation of benzene to phenol in liquid phase by H₂O₂ peroxide was examined over Ti/ LUS-1 catalyst in methanol and acetic acid as solvents. The maximum yield and selectivity of the phenol produced was obtained in the presence of acetic acid. It can be attributed to the stabilization of H₂O₂ as peroxy acetic acid species in the radical mechanism for this reaction. Acetic acid interacts with hydrogen peroxide over Ti/LUS-1 and produces acetoxy radicals.

Keywords: Nanoporous silica, LUS-1, Titanium, Oxidation catalyst.

Introduction

Nanoporous materials nowadays cover a broad range of economically very important processes related to the upgrading of crude oil and natural gas as well as the profitable production of fine chemicals¹. All reactions and conversions are based on the acid and redox properties and shape-selective behavior of nanoporous materials. The most common reactions, where nanoporous catalysts are involved, are fluid catalytic cracking, hydrocracking, aliphatic alkylation, isomerisation, oligometisation, transformation of aromatics, alcohols and amines since these reactions can be performed under mild condition in the liquid phase.

The field of porous titanium silicates is one of the fastest developing areas of porous materials². The materials possess remarkable catalytic activity in selective oxidation of organic compounds. Microporous titanium silicates such as zeolites Ti-silicalite-1 and Ti-Beta are extremely efficient catalysts for epoxidation of alkenes in the presence of aqueous H₂O₂ and *tert*-butyl hydroperoxide as oxidants, which is attributed to the unique architecture of titanium centres that are isolated in the silicate framework³. The dimensions of micropores within zeolitic structures limit the application of these catalysts to catalytic reactions with small molecules. Larger reactants could in principle be processed by using mesoporous titanium silicates such as Ti-MCM-41 or Ti-SBA-15⁴.

In the present study, hydroxylation of benzene to phenol with hydrogen peroxide has been carried out using titanium supported on LUS-1 nanoporous silica. Phenol is an important intermediate for the manufacture of petrochemicals, agrochemicals and plastics which is currently carried out through the Cumene process or toluene oxidation. The economics of this process has a large extent dependent on the marketability of acetone (as a byproduct)⁵. In the first step of the study, titanium catalysts containing TiO₂ species on high surface area supports of LUS-1 were synthesis and characterized and in second step using of for direct oxidation of benzene to phenol with hydrogen peroxide in the liquid phase.

Experimental

Silica gel(60) , sodium hydroxide, *n*-decane, titanium trichloride, carbon tetrachloride, benzene, hydrogen peroxide(30%) and the quaternary ammonium surfactant *N*-acetyl-*n,n,n*-trimethylammoniumbromid were obtained from Merck Chemicals, co surfactant *p*-toluenesulfonic acid monohydrate were obtained from Aldrich. All chemicals were used as received.

Synthesis

The preparation methods of the following nanoporous silica LUS-1 were described in previous report⁶. About 3 g of uncalcined LUS-1 was stirred in 60 mL of carbon tetrachloride solution containing TiCl₃ for 24 h in atmosphere of argon and temperature of 70 °C. Then the product was filtered and washed with carbon tetrachloride to remove the excess metal complexes. The filtered samples were dried under vacuum and these final products were denoted.

Results and Discussion

Figure 1 shows the XRD patterns of LUS-1 samples before and after loading of TiO₂. The TiO₂ contained LUS-1 samples will exhibit their characteristic peaks assignable to hexagonal *P6mm* symmetry for LUS-1 sample. The spectra display the hexagonal symmetry with (100), (110) and (200) diffraction peaks. The (100) diffraction peak indicates well-defined mesostructure (pore diameter 2-50 nm) solid supports and the XRD patterns show that the loading of TiO₂ on LUS-1 in solution do not affect the ordered of mesostructure.

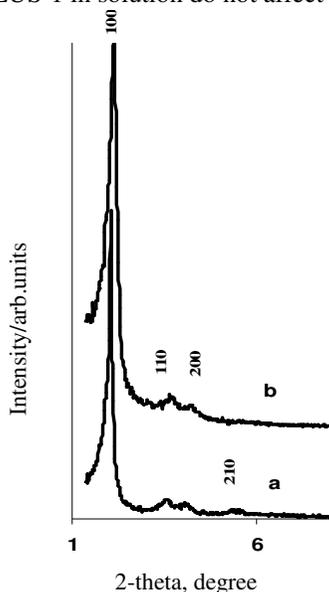


Figure 1. XRD patterns of a) LUS-1 b)Ti /LUS-1.

The nitrogen adsorption-desorption isotherms for LUS-1 and Ti/LUS-1 are shown in Figure 2. Both materials show type-IV adsorption behavior with the hysteresis loops appearing at relatively high pressure, suggesting that the prepared samples have regular mesoporous framework structures. Their texture properties are given in Table 1. The surface area, average pore diameter calculated by the BET method and pore volume of Ti/LUS-1 are $800 \text{ m}^2\text{g}^{-1}$, 4.21 nm and $0.4267 \text{ cm}^3\text{g}^{-1}$, respectively, which are smaller than those of LUS-1 due to the deposition of titanium oxide into the pores.

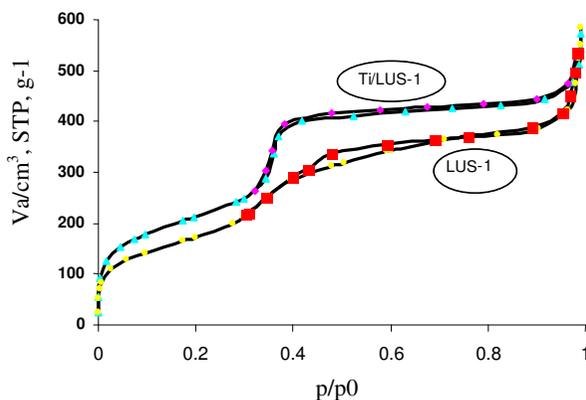


Figure 2. Nitrogen adsorption-desorption isotherms of LUS-1 and Ti/LUS-1.

Table 1. Surface area, pore size, and pore volume of Ti incorporated in the uncalcined samples of LUS-1 before and after the loading.

Name	Surface area, m^2/g	Pore volume, cm^3/g	Average pore diameter, nm
LUS-1	900	0.85	4.3
Ti/LUS-1	800	0.80	4.2

The nature of titanium species on the Ti/LUS-1 was studied by UV-vis spectroscopy (Figure 3). It generally provides valuable information about the coordination environments and oxidation states of titanium. The UV-vis shows three bands at *ca.* 220 and 282 nm. The band at 220 nm can be attributed to charge transfer (CT) between O^{2-} and a center Ti^{4+} ion, as already observed for centers in zeolitic structures. The band at lower energy (282 nm) can be ascribed to distorted octahedral Ti^{4+} species. Furthermore, the semi-quantitative calculations of the peak fitting values shows that titanium species in Ti/LUS-1 exist mostly in tetrahedral Ti and much less in octahedral^{7,8}. The texture results and UV-Vis indicated that titanium species are easily accessible to organic molecules. Thus, Ti/LUS-1 with high oxidation state of titanium can be a good candidate for redox catalytic reaction.

Catalytic activities

The catalytic activities were evaluated by the reaction of benzene and hydrogen peroxide 30% using various compounds as a solvent under reflux. A typical catalytic condition is the following: 0.1 g of catalyst was placed in a 50 mL round bottom flask with a condenser, and then 1 mL of benzene in 11 mL of solvent was added. The mixture was stirred for 5 min, then 2 mL of H_2O_2 (30% in aqueous solution) were added. After one day heated in 60°C , the solid was filtered and analyzed by GC.

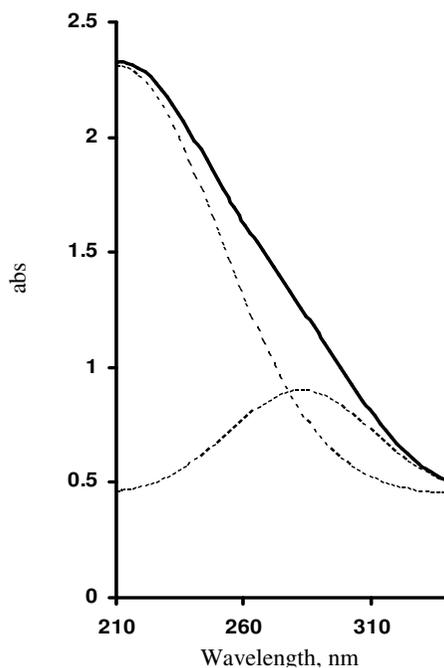


Figure 3. UV-vis spectra of Ti/LUS-1.

Catalytic hydroxylation of benzene over TiO_2 species supported on LUS-1 samples by hydrogen peroxide (30%) in acetic acid and methanol was investigated. The oxidation yield of benzene is 5% and 1% in acetic acid and methanol, respectively. Selectivity for phenol production is around 90%.

The yield and selectivity of the phenol in the presence of acetic acid was higher than the methanol. It can be attributed to the stabilization of H_2O_2 as peroxy acetic acid species in the radical mechanism. We can suggest that acetic acid interacts with hydrogen peroxide over Ti/LUS-1 and produces acetoxy radicals. These radicals may attack benzene and output benzyl radicals in the next reaction step by hydroxyl radical's genesis of decomposition of hydrogen peroxide over titanium segment and produced phenol⁹⁻¹⁰.

Conclusion

Ti-LUS-1 was synthesized and characterized and showed ordered structural patterns for the catalyst prepared. Direct oxidation of benzene to phenol in liquid phase by H_2O_2 peroxide was examined over this catalyst in methanol and acetic acid as solvent. The maximum yield and selectivity of the phenol produced was obtained in the presence of acetic acid. It can be attributed to the stabilization of H_2O_2 as peroxy acetic acid species in the radical mechanism for this reaction. We suggest that acetic acid and hydrogen peroxide interaction over Ti/LUS-1 leads to acetoxy radicals.

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