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Synthesis and characterization of VOx/LUS-1 nanoporous silica and application for direct oxidation of benzene to phenol

JavadGholami[1], Alireza Badiei[1]*, Alireza Abbasi[1], Ghodsi Mohammadi Ziarani[2]

[1]School of chemistry university college of science, University of Tehran, Tehran, Iran
[2]Department of Chemistry, Alzahra University, Tehran, Iran

Corres. Author: badiei@khayam.ut.ac.ir

Abstract: The VOx/LUS-1 nanoporous silica synthesis and characterized by XRD, Nitrogen adsorption–desorption isotherms and UV-visible spectrophotometer. Direct oxidation of benzene to phenol in liquid phase by H_2O_2 peroxide were examined by using various (methanol, acetone, acetic acid, acetonitryl) solvents.

Key words: VOx/LUS-1 nanoporous silica, direct oxidation, benzene, phenol.

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 chemicals . These highly ordered nanoporous silica such as MCM-41[1] LUS-1[2,3] , and SBA-15[4] with very high surface area, uniform open form structure and extremely narrow pore size distribution has great potential for application in many fields such as catalysts. All reactions and conversions are based on the acid and redox properties and shape-selective behavior of nanoporous materials. The redox properties of these materials achieve by incorporation of transition metals into the framework of silicate.

Recently, the liquid phase direct oxidation to phenol using hydrogen peroxide studied over Ti, V, Mg, Fe, Co, and Cu containing nanoporous catalysts[5] . Only vanadium catalysts showed both high selectivity and sufficient activity.

However, the yield for hydroxylation of benzene to give phenol, reported in literature, was relatively low. This motivated us to investigate the reaction by new support and reaction conditions to improve the yield and selectivity of phenol.

In the present study, vanadium catalysts containing VO_x species on high surface area supports of LUS-1 were synthesized and characterized. The hydroxylation of benzene was studied by hydrogen peroxide in various solvents. The objective of this study was a significant improvement of catalytic performance compared to the best results referred in the literature.

Experimental

Materials

Silica gel (60), Sodium hydroxide, n-decane, ammonium monovanadate, benzene, hydrogen peroxide (30%) and cetyltrimethylamoniumbromid (Merck) and P-toluenesulfonic acid monohydrate (Aldrich), of analytical grade were used without further purification.

Preparation of Catalysts

The preparation methods of the following nanoporous silica LUS-1 were described in our previous reports[6,7] . Deposition of NH_4VO_3 complex on to the LUS-1 surface was carried out by the liquid-phase immobilizes method. About 3 g of uncalcined LUS-1 was stirred in 100ml of H_2O solution containing 0.14g of NH_4VO_3 complexes for 3 h at room temperature. The solids were then filtered and washed with H_2O to remove the excess metal complexes. The filtered samples were dried under vacuum follwed by heating at 120 °C for 2h. After the dried, sample calcined in 600 °C for 5 h.

Spectrophotometric measurements

The electronic absorption spectra of solids were measured by adding the materials to spectral grade n-decane using a quartz window with about 0.5 mm path length. Very low light scattering was obtained from clear solid in n-decane. Since the reflective index of n-decane is very close to that of silica LUS-1, therefore good quality spectra were obtained.

Catalytic tests in the liquid-phase hydroxylation

The catalytic activities were evaluated by the reaction of benzene and hydrogen peroxide 30% using various compounds (acetone, acetonitryl, methanol, acetic acid) 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 1ml of benzene in 11 mL of solvent solution was added. The mix was stirred for 5 min, then 2ml of H_2O_2 (30% in aqueous solution) were added. After 23 h reflux and analyzed by a GC.

Characterization techniques

UV-visible spectra were taken on a Ray Leigh UV-1600 spectrophotometer. Nitrogen adsorption and desorption isotherms were measured at -196 °C using a Belsorp II system after the samples were vacuum dried at 150°C overnight. Powder X-ray diffractograms was recorded by bruker axs D8 diffractometer with nickel filtered Cu-Kα (λ= 1.5418 °A) where the x-ray tube was operated at 40KV and 30mA, the spectra were scanned at 0.02 step size. The reaction product was analyzed by a Perkin-Elmer 8500 Gas chromatography with FID detector.

Results and Discussion

Figure 1 shows the XRD patterns of VOx/ LUS-1 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.

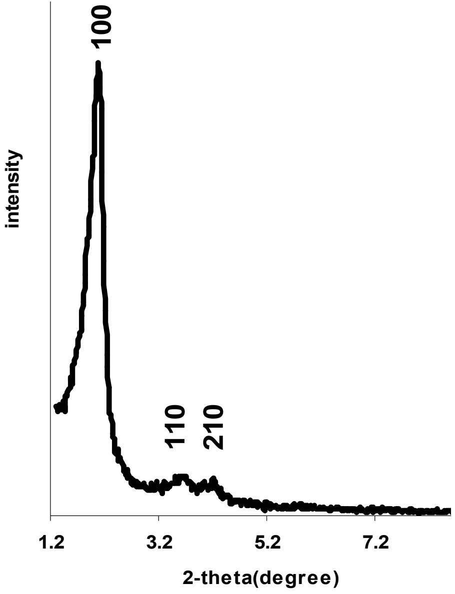

Figure.1. XRD patterns of the VO_x/LUS-1.

The nitrogen adsorption–desorption isotherms for VO_x/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. The surface area, average pore diameter calculated by the BET method and pore volume of VOx/LUS-1 is 440 m^2g^{-1}, 4.21 nm and 0.4267 cm^3g^{-1}, respectively.

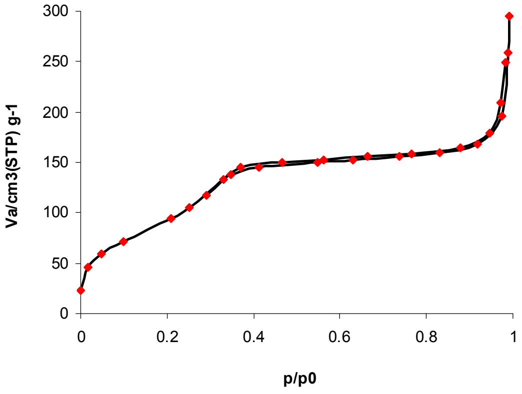

Figure.2. Nitrogen adsorption-desorption isotherms of VOx/LUS-1

The nature of vanadium species on the VO_x/LUS-1 was studied by UV-vis spectroscopy (Fig.3). It generally provides valuable information about the coordination environments and oxidation states of vanadium[8,9] . The UV-vis shows three bands at *ca.* 240, 315, 430 nm. The band at 240 and 315 nm can be attributed to charge transfer (CT) between O^{2-} and a center V^{5+} ion, as already observed for centers in zeolitic structures[10] .The CT band at higher energy (lower wavelength) can be ascribed to isolated monomeric tetrahedral vanadium species (scheme 1). The presence of one-dimensional oligomeric units connected by V-O-V bands up to distorted tetrahedral coordination can be observed at the strong band at 315 nm. The third band at lower energy (430 nm) can be ascribed to distorted octahedral V^{5+} species. Similar UV-vis spectra have been previously reported for V-MCM-41, V-MCM-48, V-HMS, and V-SiO_2[11-14]. Furthermore, the semi-quantitative calculations of the peak fitting values shows that vanadium species in VO_x/ LUS-1 exist mostly in tetrahedral VO*x* and much less in octahedral . The texture results and UV-vis indicated that vanadium species are easily accessible to organic molecules.

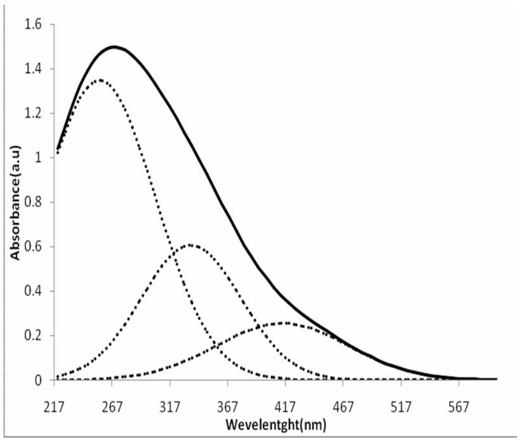

Figure. 3. UV-vis spectra of VO_x/ LUS-1.

Catalytic Activities

Table 1 presents the results of the influence of the various solvents on the catalytic hydroxylation of benzene by VO_x -LUS-1. All reactions were accomplished in the reflux condition for 23 h. It is noteworthy here that the reaction yielded and selectivity was strongly affected by the nature of the 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 radically mechanism for this reaction. We can suggest that acetic acid interaction by hydrogen peroxide over VOx/LUS-1 and produced acetoxy radicals. These radicals may attacked of the benzene and output benzyl radicals in the next section reaction by hydroxyl radicals genesis of decomposition of hydrogen peroxide over vanadium segment and produced phenol[15,16].

Table 1. Effect of the solvent direct oxidation of benzene to phenol in liquid phase by H_2O_2 over VOx/LUS-1

solvent	PHE (%)	BEN (%)	HYD (%)	BIP (%)	BEN O cov (%)	SEL (%)
Acetic acid	10.1	2.0	0.5	0.5	13.5	74.8
methanol	8.0	0.2	1.1	1.8	10.5	76.2
acetone	3.2	0.2	0.5	0.7	4.8	66.7
Acetonitryl	3.9	0.9	0.1	0.5	5.6	69.7

a: phenol; b: 1,4-benzoquinone; c: 1,4-hydroquinone; d: biphenyl; e: benzene conversion = mmol product/mmol initial benzene; f: selectivity= mmol phenol /mmol product

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