



Direct Oxidation of Benzene to Phenol in Liquid Phase over Nanoporous Silica of Chromium-LUS-1

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(Received: May 18, 2012; Accepted in Revised Form: February 4, 2013)

Abstract: Direct oxidation of benzene to phenol in liquid phase in the medium of methanol, acetone, acetic acid and acetonitrile as a solvent over chromium catalyst supported on highly ordered nanoporous silica (Cr-LUS-1) by H₂O₂ were examined. The best results obtained from methanol solvent with 20% yield and selectivity of 90%. Cr-LUS-1 characterized by XRD, nitrogen adsorption-desorption isotherms and visible spectrophotometer.

Key words: Benzene • Oxidation • Phenol • Chromium • Nanoporous Silica • LUS-1

INTRODUCTION

Phenol is an important intermediate in the manufacture of petrochemicals products, which it is mainly produced by the three-step Cumene process that marketability of this process depends on acetone as a byproduct because this process has low yield and energy consuming [1].

One step production of phenol from benzene over catalyst with high yield and selectivity could be a proper idea for replacement of cumene process that attracted more attention in recent research [2-4]. The first direct oxidation of benzene to phenol has been previously reported using Fenton reagent (ferrous sulfate-hydrogen peroxide) [5]. After that the direct oxidation of benzene to phenol in liquid phase using hydrogen peroxide studied over Ti-[3], V [6], Al-, Fe-, Co- and Cu-containing catalysts [7-10].

These highly ordered nanoporous silica such as MCM-41 [11], LUS-1 [12,13] and SBA-15 [14] with very high surface area, uniform open form structure and extremely narrow pore size distribution has great potential as a supporter for application in many fields such as catalysts. In the previous studies, we used LUS-1 as a supporter of vanadium oxide and titanium oxide for direct oxidation of benzene to phenol in liquid phase [15-16].

K₂Cr₂O₇ over SiO₂ has been tested for direct oxidation of benzene to phenol by H₂O₂ in the medium of acetonitrile [17]. In the present study, catalysts containing chromium ion on high surface area supports of LUS-1 were synthesized and examined in benzene hydroxylation with hydrogen peroxide, using various (methanol, acetone, acetic acid, acetonitrile) solvents. The purpose of this study is a significant improvement of catalytic performance. A phenol selectivity of at 90% at a phenol yielding of more than 20% was aspired.

MATERIALS AND METHODS

Experimental

Materials: Silica gel (60), Sodium hydroxide, n-decane, potassium dichromate, benzene, hydrogen peroxide (30%) and cetyltrimethylammoniumbromid (Merck, Germany) and P-toluenesulfonic acid monohydrate (Aldrich, USA), of analytical grad were used without further purification.

Preparation of Catalysts: The preparation methods of the following nanoporous silica LUS-1 were described in our previous reports [12-13]. Deposition of chromium ion 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 H₂O solution containing 2.94 g of

$K_2Cr_2O_7$ 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 by heating in oven at 70-75°C for 3h. The obtained material was so called Cr-LUS-1.

Spectrophotometric Measurements: The electronic absorption spectra of Cr-LUS-1 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: Hydroxylation of benzene over Cr-LUS-1 with hydrogen peroxide 30% using various solvent was done 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 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 a GC.

Characterization Techniques: Chromium contents of the samples were analyzed with simultaneous inductively coupled plasma (ICP) allied analytical system (Jarrel-Ash, Model ICAP 9000). 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-K α ($\epsilon = 1.5418 \text{ \AA}$) 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 GC with FID detector.

RESULT AND DISCUSSION

Powder X-Ray Diffraction (XRD): Figure 1 shows the XRD patterns of LUS-1 samples before and after the loading of $K_2Cr_2O_7$ complexes. The chromium containing LUS-1 samples will exhibit their characteristic peaks assignable to hexagonal $P6mm$ symmetry for LUS-1 sample. The diffractograms display the hexagonal symmetry with (100), (110) and (200) diffraction peaks. The XRD diffraction intensity is reduced after the loading of $K_2Cr_2O_7$ complexes in LUS-1. The XRD patterns show that

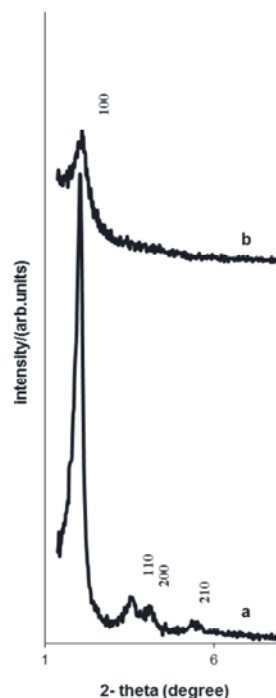


Fig. 1: XRD patterns of a) LUS-1 samples b) Cr/LUS-1.

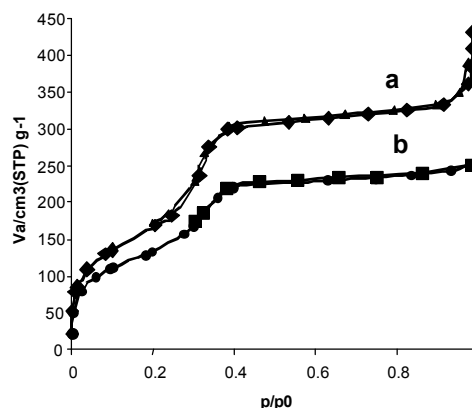


Fig. 2: Nitrogen adsorption-desorption isotherms of a) LUS-1, b) Cr-LUS-1

the loading of $K_2Cr_2O_7$ complexes in LUS-1 in solution decrease the integrity of the well-defined mesostructure of solid supports. The decrease of intensity may be arising from attacking of K^+ to pores silica walls (LUS-1) and destroying it.

Nitrogen Adsorption-Desorption Isotherm (BET): The nitrogen adsorption-desorption isotherms for LUS-1 and Cr/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.

Table 1: Surface area, pore size and pore volume of $K_2Cr_2O_7$ complexes incorporated in the uncalcined samples of LUS-1 before and after the loading.

| Name | Mmol of Cr/100g of sample | Surface area (m^2/g) | Pore volume (cm^3/g) | Average pore diameter (nm) |
|----------|---------------------------|--------------------------|--------------------------|----------------------------|
| LUS-1 | - | 620 | 0.67 | 3.1 |
| Cr/LUS-1 | 45 | 410 | 0.39 | 2.5 |

Table 2: Effect of the solvent direct oxidation of benzene to phenol in liquid phase by H_2O_2 over Cr/LUS-1

| Solvent | PHE ^a (%) | BEN ^b (%) | HYD ^c (%) | BIP ^d (%) | Ben ^e CONV (%) | SEL ^f (%) |
|--------------|----------------------|----------------------|----------------------|----------------------|---------------------------|----------------------|
| Acetic acid | 6.2 | 4.3 | 3.8 | 15 | 29 | 21 |
| Methanol | 20.0 | 0.0 | 1.0 | 1.2 | 22 | 90 |
| Acetone | 5.8 | 0.1 | 2.0 | 0.4 | 6.8 | 85 |
| Acetonitrile | 6.6 | 0.1 | 0.8 | 0.6 | 7.5 | 88 |

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

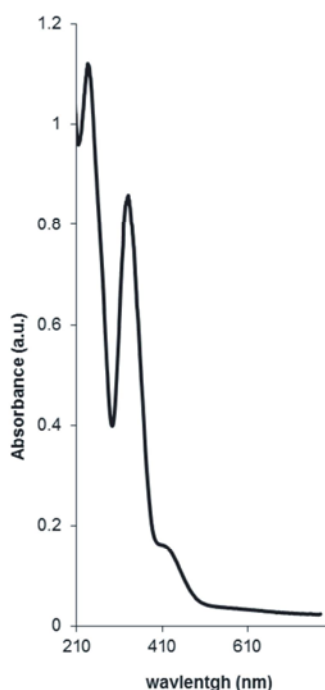


Fig. 3: UV-vis spectrum of Cr- LUS-1.

The surface area, average pore diameter calculated by the BET method and pore volume of Cr/LUS-1 are $410 m^2g^{-1}$, 2.5 nm and $0.39 cm^3g^{-1}$, respectively, which are smaller than those of LUS-1 due to the deposition of chromate into the pores.

UV-Visible Spectroscopy: The nature of chromium species on the Cr/LUS-1 was studied by UV-vis spectroscopy (Figure 3). The UV-vis shows three bands at *ca.* 280, 367, 440 nm. The band at 280 nm can be attributed to charge transfer (CT) between O^{-2} and a center Cr^{+6} ions, as already observed for centers in tetrahedral structures. The CT band at higher energy (367 nm) can be ascribed to isolated monomeric tetrahedral chromate species. The third band at lower

energy (440 nm) can be ascribed to poly chromate species [18-20].

Catalytic Activities: Table 2 presents the results of the influence of the various solvents on the catalytic hydroxylation of benzene by Cr-LUS-1. All reactions were accomplished in the reflux condition for 24 h. It is noteworthy here that the reaction yielded and selectivity was strongly affected by the nature of the solvent. The maximum yield (20%) and selectivity (90%) of the phenol produced was obtained in the presence of methanol. It can be attributed the existence hydrogen bonding in methanol and raise interaction of hydrogen peroxide and center of catalyst therefore produced much radical hydroxyl for attack to benzene. It seem 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 Cr/LUS-1 and produced acetoxy radicals [21]. These radicals may attack of the benzene and output benzyl radicals in the next section reaction produced biphenyl (yield=15%). In acetone and acetonitrile not existent hydrogen bonding follow the yield is low.

CONCLUSION

In conclusion, chromium supported on highly ordered nanoporous silica (Cr-LUS-1) was synthesized and characterized of showed ordered structural patterns for the catalyst prepared. Direct oxidation of benzene to phenol in liquid phase by H_2O_2 peroxide were examined over this catalyst by using various (methanol, acetone, acetic acid, acetonitrile) solvents. The maximum yield and selectivity of the phenol produced was obtained in the presence of methanol. It can be attributed the existence hydrogen bonding in methanol and raise interaction of hydrogen peroxide and center of catalyst therefore produced much radical hydroxyl for attack to benzene.

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