

Efficient acylation of phenol with acetic anhydride using nanocrystalline hierarchical ZSM-5 catalyst

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The current paper reports the activity of hierarchical ZSM-5 (Si/Al = 100) in the vapour phase acylation of phenol with acetic anhydride. The catalyst was characterized for its structural features by using X-ray diffraction, SEM, TEM and FT-IR techniques. The reaction parameters, such as reaction temperature, phenol: acetic anhydride molar ratio and catalyst quantity were optimized. XRD analysis confirmed the formation of indicated that highly crystallized ZSM-5 zeolite without any impurities. The sample has a structure characteristic of MFI. The hierarchical nature of the catalyst sample was confirmed by SEM and TEM analysis. The average particle size was found to be around 40 to 50 nm and the nanocrystals were more or less spherical in shape. Catalytic activity of this catalyst showed that the phenol: acetic anhydride molar ratio had a remarkable influence on the acylation of phenol. Under the optimum reaction conditions (275°C, a Phenol: Acetic anhydride mole ratio of 1, and reaction time for 2 h), the hierarchical ZSM-5 catalyst showed high selectivity towards the formation of O-hydroxyacetophenone (o-HAP). The results show that the hierarchical ZSM-5 catalysts are very efficient and environmentally benign system for the acylation of phenol.

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1. Introduction

Hydroxyacetophenone are very useful intermediates for the manufacture of agrochemicals and pharmaceuticals, and are generally synthesized by the very popular Fries rearrangement or direct acylation of phenol (1-2). Conventional acylation of phenol have been carried out by using homogeneous acid catalysts such as AlCl_3 , FeCl_3 , ZnCl_2 , HF, etc [3]. The use of these catalysts leads to many problems such as more stoichiometric quantities of catalyst, homogeneous catalysts for acylation of phenol can be eliminated by a more effective handling, safety, corrosion of equipment and waste disposal. The heterogeneous catalytic method from the environmental viewpoint (4). A number of solid acids have great ability to take account instead of Friedel-Crafts catalysts. Among the solid acid catalysts, zeolites are attractive as catalysts for the acylation reactions due to their acidity, shape selectivity and regenerability properties, etc [5-7]. Unfortunately, slow diffusion of reactants through commercial micro-porous zeolites makes them relatively poor catalysts. Nevertheless, nanocrystalline zeolite particles provide large external surface areas and shortening of the diffusion distances in the channels of the particles, thereby exposing the active surface for reaction and reducing deactivation. However, the nanocrystals often easily aggregate without leaving transport pores, and pore enlargement is the prominent target of zeolitic chemistry of research To overcome this problem, some recent research efforts have been concentrated on

introducing meso- and even macropores into the zeolitic materials using different strategies (8-18).

The aim of the present study deals with the vapour phase acylation of phenol using hierarchical ZSM-5 crystals under atmospheric pressure. The reaction parameters such as, reaction temperature, phenol:acetic anhydride molar ratio and catalyst quantity were optimized.

2. Experimental

2.1 Synthesis of nanocrystalline hierarchical ZSM-5

The hierarchical ZSM-5 (Si/Al = 100) material was prepared using dual template approach under controlled steaming at 150°C. Tetrapropylammoniumhydroxide (TPAOH) was used as a structure directing agent and natural rubber (NR) latex particles was used as macro pore template.

2.2 Characterization of nanocrystalline hierarchical ZSM-5

Powder X-ray diffraction patterns were recorded on a Regaku 2000 diffractometer using $\text{Cu-K}\alpha$ radiation from $2\theta = 2$ to 30° at a scan rate of $2^\circ/\text{min}$. FT-IR spectra were recorded using the KBr wafer technique

(1.2% w/w) on a Jasco-410 FT-IR instrument. The spectra were recorded with a resolution of 2 cm^{-1} from 400 to 1800 cm^{-1} after performing a correction measurement for the background. Morphology and particle size of the zeolite nanocrystals were examined with SEM (JEOL JSM-6500f) and TEM (JEM-2010, 200 kV) analyses. For TEM analysis, a drop of the diluted solution (0.0005 wt % g/water) was placed (placed a drop of ethanol and dried before placing sample) on carbon coated copper grid for TEM examination.

2.3 Acylation of phenol

The acylation of phenol was carried out using a tubular down-flow reactor at atmospheric pressure. About 1 g of catalyst was charged to the reactor, packed in a layer of ceramic wool and supported by glass beads. The reactor was heated to the reaction temperature with the help of a tubular furnace controlled by a digital temperature controller. The catalyst was activated at $400\text{ }^{\circ}\text{C}$ for 5 hrs prior to the catalytic runs. Reactants were fed into the reactor using a syringe infusion pump. A solution of phenol and acetic anhydride was vaporized and fed through the reactor. The products were collected at the bottom by circulating cold water. The reaction products were analysed using a China gas chromatograph (8990) with a capillary column of SE30 30 % and a flame ionization detector (FID). The reaction products were confirmed by GC-MS.

3. Results and discussion

3.1 XRD analysis

The XRD pattern of hierarchical ZSM-5 zeolite (Fig. 1) indicated that highly crystallized ZSM-5 zeolite formed without any impurities. The characteristic peaks showed typical MFI-type structure.

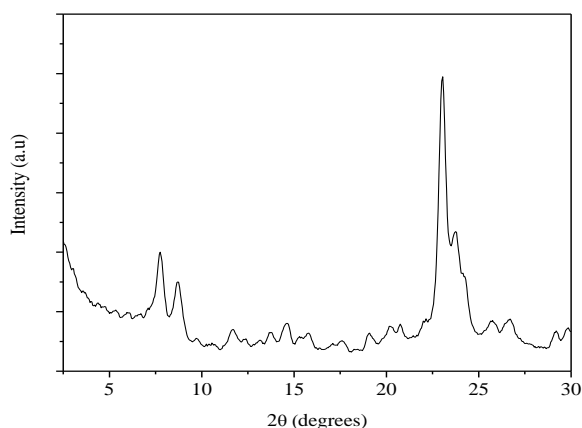


Fig. 1. XRD pattern of the hierarchical ZSM-5 zeolite.

3.2 FT-IR analysis

FT-IR spectra of the hierarchical ZSM-5 zeolite is shown in Fig. 2. The band at 950 cm^{-1} can be attributed

to localized Si-OH stretching mode. The regions $750\text{--}850\text{ cm}^{-1}$ and $500\text{--}650\text{ cm}^{-1}$ can be attributed to the ring structure of silica. The band observed at $\sim 540\text{ cm}^{-1}$ is assigned to the double 5-rings of crystalline ZSM-5. (For nano-sized ZSM-5, a doublet at 542 and 556 cm^{-1} is observed). The broad band around 550 cm^{-1} is due to the small ring structure of silica, although its intensity is not strong. (In fully crystalline ZSM-5, the 550 cm^{-1} band is about 70% of the Si-O bending region at 450 cm^{-1}). This reveals that the sample has a structure characteristic of MFI (strong 550 cm^{-1}).

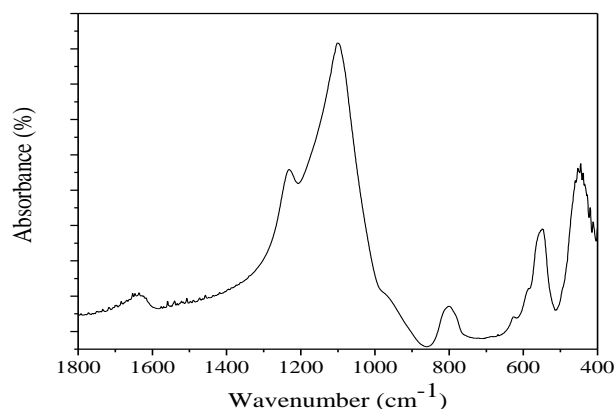


Fig. 2. FTIR spectra of the hierarchical ZSM-5 zeolite.

3.3 SEM and TEM analysis

The morphology of the sample clearly shows the interconnected structure, where macropores are continuous and open at the external surface in the range of $0.5\text{--}1.5\text{ }\mu\text{m}$ (Figure 3). The average particle size was found to be around 40 to 50 nm and the nanocrystals were more or less spherical in shape.

3.4 Catalytic activity

Acylation of phenol with acetic anhydride was studied systematically using hierarchical ZSM-5 as a catalyst. The catalyst was activated at $350\text{ }^{\circ}\text{C}$ in air for 4 h before the reaction. The results are very promising and the major product is o-HAP. The high ortho selectivity is due to the reactive intermediate for the ortho-isomer being more stable. In all the reactions the major side product is phenyl acetate (PA) resulting from the facile O-acylation of phenol. In the first step the influence of reaction parameters such as, phenol/acetic anhydride molar ratio and catalyst quantity were optimized and are 1:1 and 1 g respectively.

The effect of the phenol to Ac2O ratio in acylation was studied (Table 1) in detail. The experimental results reveal that the selectivity was governed by the molar ratio of acetic anhydride. The ratio of o-HAP to p-HAP decreases with increase of acetic anhydride. Therefore, all reactions were studied by using a phenol:acetic anhydride mole ratio of 1:1.

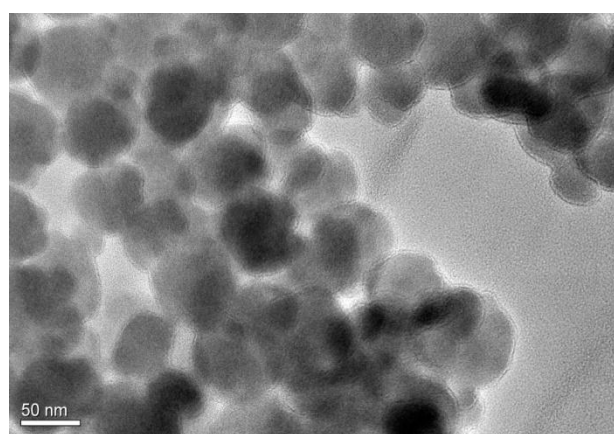
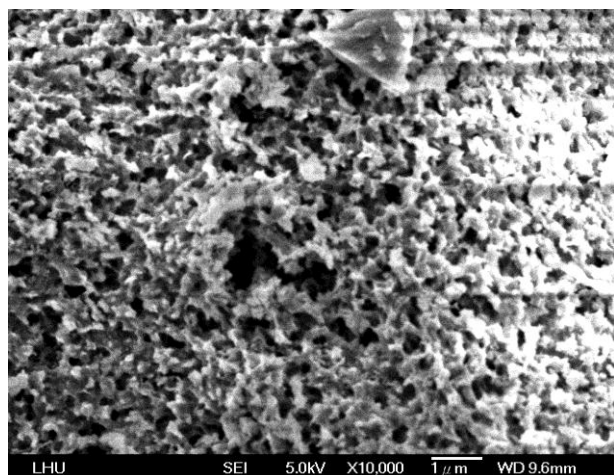


Fig. 3. SEM (a) and TEM (b) images of hierarchical porous ZSM-5.

The effect of temperature on the conversion of acetic anhydride was studied over a range of 175–375 °C (Table.2). At lower temperature, 175°C, the major product is phenyl acetate resulting from O-acylation. The suitable temperature for C-acylation of phenol is 275°C.

Table 1. Effect of mole ratio on the conversion of phenol (TOS, 120 min; catalyst, 1 g of hierarchical ZSM-5; temperature: 275 C).

S.No.	Phenol: Ac ₂ O mole ratio	Conversion of Phenol (%)	PA	p-HAP	o-HAP
1	1:0.5	70.5	30.1	3.7	66.2
2	1:1	75.1	23	2.6	74.4
3	1:1.5	82.9	31.4	6.0	62.6
4	1:2	91.9	39	7.9	53.1

Table 2. Effect of temperature on the conversion of phenol (TOS, 120 min; catalyst, 1 g of hierarchical ZSM-5; molar ratio of phenol: Ac₂O, 1 : 1).

S.No.	Temp. (C)	Conversion of Phenol (%)	PA	p-HAP	o-HAP
1	175	89.8	45	2.8	52.2
2	225	76	30.6	2.7	66.7
3	275	75.1	23	2.6	74.4
4	325	61.9	20.1	6.9	73.0
5	375	58	18.1	7.1	74.8

4. Conclusions

Hierarchical ZSM-5 is a very efficient and environmentally benign heterogeneous catalyst for the vapour-phase acylation of phenol. Acylation of phenol by acetic anhydride was studied systematically using hierarchical ZSM-5 as a catalyst. The catalyst was fully characterized. This catalyst was found to be very active and also stable without any deactivation. The reaction has been performed in at 275 °C using a phenol:acetic anhydride mole ratio of 1:1. An increased molar ratio of acetic anhydride to phenol leads to more para isomer formation. The best temperature for acylation of phenol was 275°C. These solid acid catalysts are potential substitutes for the homogeneous catalyst at the industrial level for the above reaction.

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