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Bromination of phenol with NBSac over synthesized zeolite as a heterogeneous recyclable catalyst

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Abstract: ZSM-5 zeolite in acidic form was synthesized with a common laboratory instrument and careful procedure of heating and crystallization. Zeolite identification and characterization were performed by FT-IR, XRD and SEM techniques. Bromination of phenol was catalyzed using ZSM-5 zeolite as a catalyst and *N*-bromosacharin (NBSac) as a brominating agent. The nuclear as well as side-chain bromination of phenol has been achieved in high yield and substantial regioselectivity with *N*-Bromosacharin (NBSac) over synthesized zeolite.

Keywords: Zeolite; Bromination; Catalyst; *N*-Bromosacharin; Phenol.

Introduction

The manufacture of a number of bulk and fine chemicals such as flame retardants, pharmaceuticals, dyes and agrochemicals, involves bromination reactions [1].

Bromination of aromatic compounds has been developed by several methods using variety of brominating agents under different conditions. Conventional bromination methods involve the use of molecular bromine and metal bromide, generating toxic and corrosive hydrogen bromide, leading to environmental pollution. Examples of traditional and conventional methods include: Br_2–Lewis acids, NBS–PTSA, NBS–NaOH, NBS–SiO_2, Br_2–Zeolite, NBS–Amberlyst, NBS-HZSM-5, tert-BuOOH– or H_2O_2–HBr, Tungstated zirconia/ NH_4Br/ H_2O_2 [2-9].

Today solid acidic catalysts in their H-form have attracted intense attention due to important advantages related to soluble mineral acids because their separation from the products should be facile [10, 11]. Many researchers on ZSM-5 zeolites have been conducted due to its unique structural and physical-chemical performance, selectivity and stability. ZSM-5 zeolites show excellent catalytically performance in many organic transformation reactions. The activity of zeolite is associated to the shape selectivity effects due to the molecular sieving properties and a strong Brønsted acidity of bridging Si–(OH)–Al sites generated by the presence of aluminum inside the silicate framework [12-14].

However, in terms of ease of handling and availability, NBSac is a superior brominating agent and nuclear bromination of phenol using NBSac over synthesized HZSM-5 has not been studied so far. The present paper reports the synthesis of ZSM-5 with Si/Al ratio of 14.5 in the initial synthesis mixture and its catalytic performances for bromination of phenol. The resulted zeolite was modified to HZSM-5 using NH_4NO_3 solution.

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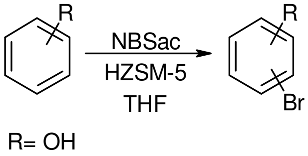
In continuation of our work on the application of heterogeneous catalysts for the development of useful synthetic methodologies, Optimization of the reaction conditions for the bromination of phenol with NBSac was investigated as a model transformation (Scheme 1).



Scheme1. Model transformation for bromination of phenol with NBSac over ZSM-5 zeolite at 0°C.

Results and discussion

Characterization of synthesized zeolite

The FT-IR spectrum of the synthesized zeolite was recorded in the range 400-1700 cm^{-1} and shown in Figure 1. Bands around 790, 1080 and 1219 cm^{-1} are characteristic of SiO_4 tetrahedron units and one near 542 cm^{-1} is attributed to a structure-sensitive vibration caused by the double five-membered rings of the external linkages. The absorption band near 450 cm^{-1} is due to the T-O bending vibrations of SiO_4 and AlO_4 internal tetrahedral. The presence of absorption bands around 542 and 450 are characteristic of the ZSM-5 crystalline structure. X-ray diffractogram of as-synthesized zeolite is given in Figure 3, which confirms the MFI type zeolite [15].

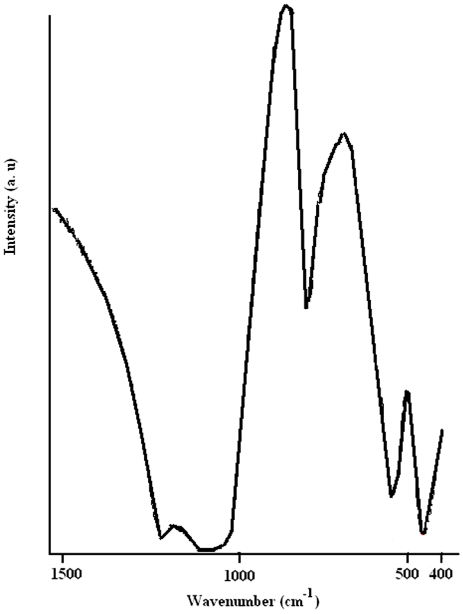


Figure 2, FT-IR spectra of calcinated ZSM-5 zeolite

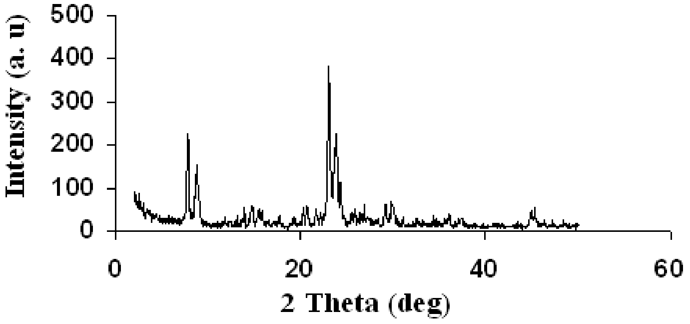


Figure 3. X- ray diffractogram of the as-synthesized ZSM-5 zeolite.

Scanning electron microscopy

The scanning electron micrograph of the calcinated form of synthesized zeolite is shown in Figure 4, and shows that this zeolite crystallized in cubical shape crystals.

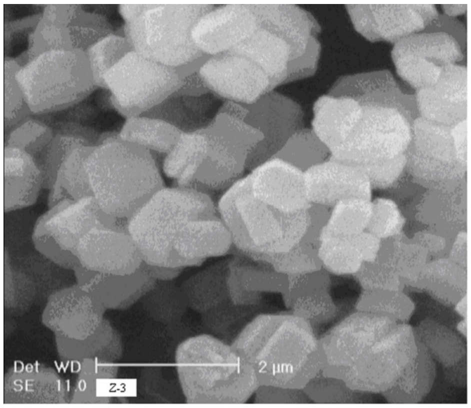


Figure 4. SEM image of the synthesized ZSM-5 crystallites

Catalytic evaluation of synthesized zeolites

Table 1, shows that the reaction was complete within 7 min with ZSM-5 catalyst, in acetonitrile and THF, with 95% conversion, to give *para*-bromophenol regioselectively in 90% yield. However, in dichloromethane and diethylether, the reaction was slower and less selective towards *para*-bromophenol (40-50%), also yielding *ortho*-bromophenol and 2,6-dibromophenol. The extent of conversion of phenol was in the order, THF~CH_3CN>$CHCl_3$>Et_2O>EtOH which followed by TLC, and then the overall yield was determined after extraction of reaction mixture then obtained product was subjected to column chromatography (silica gel, *n*-hexane:EtOAc 4:1) to obtain pure *para* brominated phenol. This observation suggests that more polar or more ionizing solvents enhance the reactivity of NBSac and favor nuclear bromination. Due to safety of THF related to CH_3CN, THF was selected as a solvent in this study.

Table 1. Effect of solvents on the bromination of phenol over modified zeolite

Entry	Solvent	Time(min)	Conversion (%)	Yield (%)
1	THF	7	95	90
2	CH_3CN	7	95	90
3	CH_2Cl_2	60	40	20
4	Et_2O	60	50	25
5	EtOH	60	0	0

The obtained results for *para* bromination of phenol at 0°C over various amount of modified ZSM zeolite are listed in Table 2. As one can see the amount of zeolite is an effective parameter on the overall yield and reaction time of bromination reaction. The further amount of zeolite have not better yield and do not reduced the reaction time under mentioned condition, then the amount of 0.007 g was optimum amount for used zeolite.

Table 2. The results for bromination of 4-bromo phenol using NBSac over modified ZSM-5 zeolite

Entry	Zeolite (g)	Conversion (%)	Yield (%)	Reaction time (min)
1	0.005	95	79	14
2	0.006	95	89	6
3	0.007	100	90	7

Experimental

Synthesis of ZSM-5 zeolite

The reaction mixture used for synthesis of zeolite was silicic acid, tetrapropylamounium hydroxide (TPAOH, 20% aqueoes solution), sodium aluminate and sodium hydroxide. All chemicals were purchase from Merk Company. Seeding gel was prepared by mixing appropriate amount of water, sodium hydroxide, TPAOH and silicic acid. The resulting mixture was aged at 100°C for 16 hours. In the second step, a mixture of sodium hydroxide and sodium aluminate were dissolved in water and mixed thoroughly. Then silicic acid was added in portions under stirring and the synthesized gel was shaked at ambient temperature. After that 2.10 g of seeding gel was added and shaked. The molar ratio of the resulting mixture was 3.25 Na_2O: Al_2O_3: 30 SiO_2: 958 H_2O (exclusive of seeding gel). The synthesis gel was exposed to microwave radiation at low power for 30 min. There after the hydrogel was transferred to the PTFE-lined stainless steel autoclave for further heating by conventional method.

Characterization of synthesized zeolite

The X-ray diffractogram of synthesized ZSM-5 was measured using an X-ray diffractometer (XRD, GBC MMA Instrument). Which was run with Ni filtered Cu K_α radiation (λ= 1.5418 Angestroem) at 35.4 KV and 28 mA with a scanning speed of 2θ= 10° min^{-1}. FT-IR spectrum was recorded at room temperature using FT-IR spectrometer (Vector 22-Bruker), in the range of 400- 1700 cm^{-1} with a resolution of 2 cm^{-1} on KBr pellet. Scanning electron microscopy was done to determine the crystallite size and morphology using a JEOL JXA-840 SEM.

Bromination reaction procedure

General procedure for bromination of phenol: To a mixture of phenol (0.047 g; 0.5 mmol) and ZSM-5 (0.005-0.007 g) in THF (5ml), NBSac (0.150 g; 0.5 mmol) was added. The mixture was stirred at ice bath and the reaction was followed by TLC and GC. After completion (monitored by TLC and GC) the reaction, the mixture was filtered. The filtrated was concentrated and the residue was subjected to column chromatography (silica gel, *n*-hexane:EtOAc 4:1) to obtain pure brominated phenol. The product was analyzed by ^{1}HNMR. After filtration, the zeolite can be washed and used for several times.

Conclusion

ZSM-5 zeolite with Si/Al molar ratio of 14.5 and high purity was synthesized under microwave-assisted hydrothermal condition. The zeolitic sample was modified with HCl solution to HZSM-5 and used as an inorganic catalyst. We have developed an efficient and versatile method for the nuclear monobromination of phenol (4-bromo phenol) using NBSac in the presence of HZSM-5 as a heterogeneous catalyst. The mild reaction conditions, simple experimental procedure, rapid conversion, excellent yields and reusability of the catalyst are notable advantages of the method.

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