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Regioselective nitration of phenol over solid acid catalysts

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Abstract

Phenol is selectively nitrated in liquid phase to ortho-nitrophenol in high yield using dilute nitric acid over solid acid catalysts. Zeolite H-beta was found to be a very active catalyst for nitration of phenol to ortho-nitrophenol at room temperature in carbon tetrachloride as a solvent. Compared to the conventional process, phenol nitration over solid acid catalyst is a clean and environment friendly process with a simpler workup procedure for quantitative isolation of the products. © 2002 Published by Elsevier Science B.V.

Keywords: H-Beta; Solid acid catalysts; Nitrophenol; Nitration

1. Introduction

Nitrophenols are important intermediates for the manufacture of drugs and pharmaceuticals. Ortho-nitrophenol is an important starting material used in multiple step synthesis of valuable compounds [1]. Nitration of phenol using mixture of nitric acid and sulfuric acid gives 2-nitrophenol and 4-nitrophenol in a ratio 1.42 [2].

This process has limitations such as use of nitrating mixture, which in turn generates large quantity of dilute sulfuric acid as a waste posing its neutralization and disposal problems. Regioselective nitration of phenol to ortho-nitrophenol as a special case has been studied by various nitrating agents under different conditions.

Phenols are easily mononitrated at room temperature by $NaNO_3$ in a two phase system (water–ether) in the presence of HCl and a catalytic amount of $La(NO_3)_3$ with o/p ratio 2:1 [3]. Lazslo demonstrated that phenol can be nitrated in a system called claycop (trihydrated cupric nitrate supported on montmorillonite/acetic anhydride/CCl_4) in 92% yield with an o/p ratio 13.3 [4]. Very high regioselective nitration of phenol was achieved with a surfactant suspended in acetonitrile treated with nitronium tetrafluoroborate, which gave an o/p ratio of 19.0 [5].

Nitration of phenol has been performed by $AcONO_2/HNO_3/$ and aromatic solvents [6], N-nitropyrazole/$BF_3 \cdot Et_2O/CH_2Cl_2$ [7], via nitroso compounds and their subsequent oxidation to nitrocompounds with HNO_3 [8], metal nitrates [9], clay supported nitrates [10], impregnated alumina and silica with N_2O_4 [11], $AcONO_2$ [12] and $TfONO_2$ [13].

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Some of these methods that use less stable acetyl nitrate requires in situ generation of nitric acid using metal nitrates and organic acid which require tedious workup procedures. On the basis of the above facts, it is clear that there is a need for more regioselective control of nitration of phenol using nitric acid as a nitrating agent to obtain higher conversion and selectivity. To our understanding very little study has been done on the regioselective nitration of phenol using nitric acid as a nitrating agent over solid acid catalyst.

The nitration of phenol selectively to para-nitrophenol in high yields has been recently achieved by Tomasz et al. [14] over metal oxide solid acid catalysts and the selectivity for para-nitrophenol varied with the nature of the catalysts and the reaction conditions. However the microporous zeolites, well known for their shape selective behavior have not been studied as solid acid catalysts for phenol nitration. Here we report the nitration of phenol with dilute nitric acid over zeolite catalysts using various commonly used solvents.

2. Experimental

2.1. Catalyst preparation

Commercially available zeolite H-beta, H-Y, H-ZSM-5 in the powder form were procured from United Catalyst India. La-H-Beta was prepared by impregnation of lanthanum nitrate on H-beta. MoO_3/SiO_2(MoO_3: 15 mol%), $Fe_2O_3/MoO_3/SiO_2$ (Fe_2O_3: 0.7, MoO_3: 20 mol%) catalyst were pre-

pared for comparison by sol–gel method using ethyl silicate-40 (CAS Registry No. 18954-71-7) as silica source. Ferric nitrate solution in isopropyl alcohol was added to ethylsilicate-40 under constant stirring to which an aqueous solution of ammonium molybdate was added. A transparent gel was obtained which was air dried at ambient temperature and then heated in an oven at 110 °C for 12 h and further calcined at 450 °C for 12 h. Reaction was performed in the batch reactor. Two gram phenol was taken in a flask containing 3 ml solvent to which 1 g of catalyst and 4 ml of dilute nitric acid (30%) were added. The reaction mixture was stirred at room temperature for varying period of time to study the progress of the reaction. The maximum conversion of phenol to nitrophenol was reached before two hours of reaction time. The reaction product was extracted with diethyl ether, which was analyzed off-line by gas chromatography GC (HP6890, column: HP-1, 30 m length, 0.25 mm ID), GC/MS (SHIMADZU, column, DB-I). The catalyst was characterized before and after the reaction for its physical and chemical properties using various techniques such as XRD (Regaku, Miniflex), EDX (KEVEX 7000 system), and AAS (Perkin Elmer).

3. Result and discussion

The results of regioselective nitration of phenol using nitric acid over solid acid catalysts are given in Table 1. Among the catalysts studied, zeolite H-Beta (Si/Al = 30) showed highest conversion (96%)

Table 1
Effect of various solid acid catalysts on nitration of phenol[a]

| Catalyst	Conv. of phenol (%)	Selectivity[b] (%)			Total yield[c] (%)	o/p ratio
		ONP	PNP	Benzq.		
Mo/SiO$_2$	48	70	17	13	41.76	4.11
Fe/Mo/SiO$_2$	60	48	42	10	54.0	1.14
H-ZSM-5	60	55	37	8	55.2	1.48
H-Y	60	60	30	10	54.0	2.00
H-Beta	96	87	10	3	93.12	8.70
La-H-Beta	89	61	32	7	82.77	1.9

[a] Reaction conditions: Phenol/HNO$_3$ = 1; Catalyst = 50% w/w; Temperature = RT; HNO$_3$ = 30%, solvent = CCl$_4$, reaction time = 2 h.
[b] ONP = o-nitrophenol; PNP = p-nitrophenol.
[c] Total yield = yield of ONP + yield of PNP; Benzq. = Benzoquinone.

and selectivity (87%) for *o*-nitrophenol. The conversion as well as selectivity for *o*-nitrophenol was low for other catalyst under study showing the influence of acidity as well as porosity of the catalyst. The conversion was found to be decreased from 96% to 48% when the catalyst was changed from H-Beta to H-ZSM-5 and Mo/SiO_2 showing the influence of acidity of the catalyst on phenol nitration. Similarly the selectivity for *o*-nitrophenol also decreased from 87% in case of H-beta to 60% in the case of Y-zeolite. $Fe/Mo/SiO_2$ being dense solids having mesopores and micropores, ONP/PNP ratio was about 1:1 showing the selective nitration of phenol over zeolite catalysts. The highest conversion (96%) and selectivity (87%) in case of zeolite H-Beta may be because of preferred orientation of phenol inside the zeolite pores increasing the accessibility of ortho position to nitronium ion leading to selective formation of *o*-nitrophenol (Scheme 1). Lanthanum impregnated zeolite beta (La-H-Beta) showed lower conversion (90%) and selectivity (80%) may be because of pore blockage, reducing pore size affecting the selectivity. When the reaction was carried out using concentrated nitric acid (70%), formation of dinitrophenol (4–5%) was observed. With the use of dilute nitric acid (30%), there was no formation of dinitrophenol, which is an added advantage apart from its cheaper cost and ease of handling compared to concentrated nitric acid.

When the reaction was carried out without catalyst the conversion was low (49%) with nearly equal ortho- and para- isomers, suggesting the influence of solid acid catalyst on the conversion and selectivity.
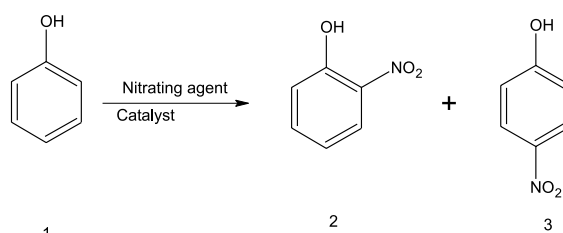
Scheme 1.

The zeolite beta showed the structural stability that was verified by XRD analysis after the reaction and catalyst could be used for five cycles without any appreciable reduction in the conversion and selectivity.

The nitration of phenol at room temperature was carried out using various common solvents such as acetone, CCl_4, MeOH, Et_2O, H_2O and hexane over H-beta zeolite and the results are given in Table 2. The highest conversion of 96% and selectivity for *o*-nitrophenol of 87% was obtained with CCl_4 indicating the influence of the solvents on the reaction.

The selectivity for ortho-nitrophenol is lower (*o/p* ratio 8.7) using zeolite catalyst as compared to reported method for nitration of phenol using acetyl nitrate preadsorbed on silica gel (*o/p* ratio of 13.3) described by Rodrigues et al. [6]. The acetyl nitrate used has drawbacks such as less stability of acyl nitrates and tedious workup procedures. The results of nitration of phenol over MoO_3/SiO_2 and $Fe/Mo/SiO_2$ are comparable to that of Tomasz et al. [14] over metal oxide solid acid catalysts using 100% nitric acid. When the reaction was carried out

Table 2
Effect of various solvents on nitration of phenol over zeolite H-beta[a]

Solvents	Conv. of phenol (%)	Selectivity[b] (%)			Total yield[c] (%)	*o/p* ratio
		ONP	PNP	Benzq.		
CCl_4	96	87	10	3	93.12	8.70
MeOH	11.5	39.67	–	60.24	45.60	–
Et_2O	88.7	49.24	47.83	2.92	86.10	1.03
2-butanone	75.2	67.78	24.73	7.42	69.56	2.74
H_2O	63.9	58	27.36	14.63	54.5	2.12
Hexane	81.4	57.88	34.15	7.96	74.9	1.69

[a] Reaction conditions: Phenol/HNO_3 = 1; Catalyst = 50% w/w; Temperature = RT; HNO_3 = 30%, reaction time = 2 h.
[b] ONP = *o*-nitrophenol; PNP = *p*-nitrophenol; Benzq. = Benzoquinone.
[c] Total yield = yield of ONP + yield of PNP.

using concentrated nitric acid (70%) over MoO$_3$/SiO$_2$ the ortho selectivity was decreased from 70% to 51% suggesting the influence of water on the selectivity of phenol nitration.

4. Conclusion

Phenol is selectively nitrated to ortho-nitrophenol in high yields with dilute nitric acid in carbon tetrachloride solvent over zeolite H-beta catalyst. The zeolite catalysts could be easily separated from the reaction mixture by filtration for recycle and the workup procedure for isolation reaction products is simpler as compared to the conventional process. The regioselective nitration of phenol using dilute nitric acid over solid acid catalyst without any use of acetic anhydride/acyl nitrate, metal nitrates or sulfuric acid is a comparatively clean and environmental friendly process.

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