

Liquid phase bromination of phenols using potassium bromide and hydrogen peroxide over zeolites[☆]

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Abstract

An efficient, simple, mild and regioselective method for oxybromination of phenols catalyzed by CrZSM-5(30) is reported. The electrophilic substitution of bromine generated in situ from KBr as a bromine source and hydrogen peroxide as an oxidant. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zeolites; Oxybromination; Potassium bromide; Hydrogen peroxide; *Para*-selectivity

1. Introduction

In recent years considerable emphasis has been placed on improvement in the environmental impact of industrial chemical processes [1]. It is well recognized that solid catalysts can play a significant role in the development of cleaner technologies through their abilities to act as catalysts, support reagents, entrain by-products, avoid aqueous work ups and influence product selectivities, and several books on the applications of solids in organic synthesis have appeared [2]. Advances are particularly needed in the area of electrophilic aromatic substitutions [3], where traditional Lewis acid catalysts are a cause of considerable concern and where reactions are frequently unselective. Bromination which is of considerable industrial importance, is a case in point.

Halogenated aromatic compounds are a useful class of intermediates as they are precursors to a number of organometallic species useful in the synthesis of natural products and pharmaceutically important compounds [4]. Brominated arenes are versatile intermediates in the synthesis of a wide variety of biologically active compounds. Consequently, a variety of methods for the bromination of aromatics have been reported in the literature [4–14].

Traditional methods of aromatic bromination involve the use of non-selective hazardous acidic reagents such as mineral acids and metal halides, which can lead to separation difficulties and unacceptable levels of toxic and corrosive and waste materials.

The classical direct bromination of aromatic compounds suffers from being wasteful in the bromine employed, one half ends up as hydrogen bromide. In large scale operations this is an environmental as well as an economic problem. Oxybromination [15–18] using HBr as a bromine source, H₂O₂ as an oxidant which was thought to be possible solution to overcome these said difficulties met with partial success,

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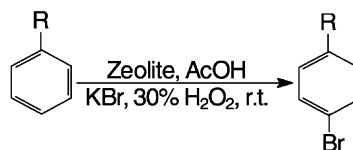
since the HBr is highly toxic and corrosive as harmful as molecular bromine to the environment. The replacement of such reagents by non-toxic and more selective reagents is very desirable and represents an important goal in the context of clean synthesis. We have designed a novel heterogeneous catalytic system to generate electrophilic bromine in situ from easily available KBr as a bromine source and H₂O₂ as an oxidant for the oxybromination as a possible alternative to solve the disadvantages described in the earlier methods. Herein we report a new method for the *para* selective oxybromination of phenols using CrZSM-5(SiO₂/Al₂O₃ = 30) as a catalyst, H₂O₂ as an oxidant and KBr as a bromine source.

2. Experimental

HY zeolite was obtained from Zeolyst Corporation, USA, TS1 was obtained from NCL, Pune and HZSM-5(30) was obtained from Conteka, Sweden. HZSM-5 was further modified by Cr, Mo, Cu, and Fe (5 wt.%) using conventional impregnation methods, using nitrates as their corresponding precursors.

2.1. General procedure for the bromination of phenols

A 50 ml two-necked round bottomed flask was charged with 200 mg of zeolite, the substrate (2 mmol) and KBr (2.2 mmol) in acetic acid (4 ml). Thirty percent H₂O₂ (2.2 mmol) was then, added dropwise to the reaction mixture and the contents allowed to stir at



Scheme 1.

room temperature (Scheme 1). The reaction mixture was monitored by thin layer chromatography (TLC). After the completion of the reaction, the catalyst was filtered and solid was washed with ether. The combined filtrates were washed with saturated sodium bicarbonate solution. The organic extract was dried over anhydrous sodium sulfate and solvent evaporated under reduced pressure. The products were purified by column chromatography and confirmed by ¹HNMR and mass spectra.

3. Results and discussion

We have investigated the use of various zeolites as catalysts in the reaction of phenol with KBr and H₂O₂ at room temperature in acetic acid. The results (Table 1) showed that all catalysts were capable of catalyzing the reaction. The yields of *p*-bromo phenol, *o*-bromo phenol and dibromo phenol obtained are shown in Table 1. The conversion was higher when MoZSM-5(30) was used as a catalyst, but the *para* selectivity was higher when CrZSM-5(30) was the catalyst. The reaction over MoZSM-5(30) gave 36% yield of *p*-bromo phenol within 5 h, whereas

Table 1
Oxybromination of phenol using KBr and H₂O₂:variation of catalyst^a

Entry	Catalyst	T (h)	Conversion (%)	Yield (%) ^b		
				<i>Para</i>	<i>Ortho</i>	Di
1	HZSM-5(30)	5	73	31	24	18
2	CrZSM-5(30) (5 wt.% Cr)	5	83	58	25	–
3	MoZSM-5(30) (5 wt.% Mo)	5	89	36	31	22
4	CuZSM-5(30) (5 wt.% Cu)	5	73	19	42	12
5	FeZSM-5(30) (5 wt.% Fe)	5	78	31	25	22
6	HY	5	75	45	30	–
7	TS1	5	75	28	33	14
8	–	5	68	28	29	11

^a Phenol (2 mmol), KBr (2.2 mmol), H₂O₂ (2.2 mmol), zeolite (200 mg), and acetic acid (4 ml).

^b The products were characterized by NMR, mass spectra and quantified by GC.

Table 2
Bromination of phenols using KBr/H₂O₂ over CrZSM-5(30) catalyst^a


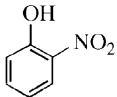
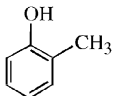
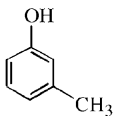
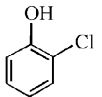
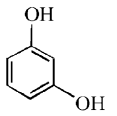
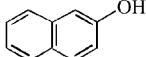
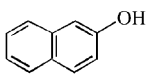
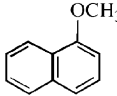
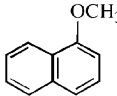
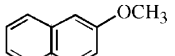
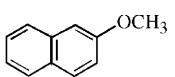

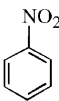
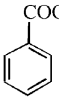
Entry	Substrate	T (h)	Conversion (%)	Yield (%) ^b		
				Para	Ortho	Di
1		5	83	58	25	–
2		5	48	38	10	–
3		5	86	73	13	–
4		5	96	50	22	24
5		5	76	76	–	–
6		5	95	95	–	–
7		5	45	–	45	–
8		5	<5 ^c	–	<5	–
9		5	72	72	–	–
10		5	<8 ^c	8	–	–
11		5	99	–	99	–
12		5	10 ^c	–	10	–
13		5	–	–	–	–

Table 2 (Continued)

Entry	Substrate	T (h)	Conversion (%)	Yield (%) ^b		
				Para	Ortho	Di
14		24	–	–	–	–
15		24	–	–	–	–

^a Substrate (2 mmol), KBr (2.2 mmol), H₂O₂ (2.2 mmol), CrZSM-5(30) (200 mg), and acetic acid (4 ml).

^b The Products were characterized by NMR, mass spectra and quantified by GC.

^c Reaction was carried out in absence of catalyst.

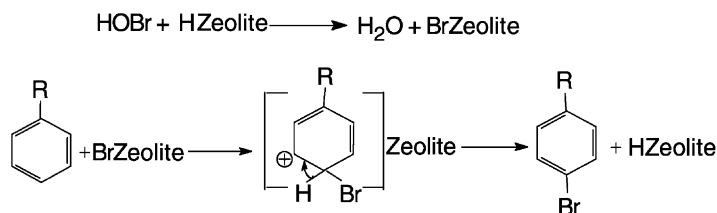
CrZSM-5(30) gave *p*-bromo phenol in yield of 58% (Table 1).

Efficient bromination of phenols with good yields and regioselectivity observed with KBr and H₂O₂ over CrZSM-5(30) presented in Table 2. A number of different phenolic compounds were subjected to the bromination to test the generality of this method and the results are summarized in Table 2. Table 2 shows that the reaction gives high yields and para selectivity for a range of substituted phenols. The results in Table 2 indicate that introduction of an electron-withdrawing group on the aromatic ring substantially decreases the rate of ring bromination (Table 2, column 2) while an electron donating group increases it. 2-Methoxy naphthalene gives 1-bromo-2-methoxynaphthalene. In the case of naphthalene derivatives the yield of brominated product under the same experimental conditions without catalyst was ≤10% and in presence of CrZSM-5 the reaction probably occurs only on the external surface or on the external acidic sites. When less reactive aromatics such as nitrobenzene, toluene, benzoic acid

failed to undergo bromination under the same reaction conditions.

A wide range of solvents have been employed in these reaction including, carbon tetrachloride, hexane, dichloromethane, methanol, acetonitrile and acetic acid. The best results were obtained when acetic acid was used as a solvent compared to others. Using acetic acid as a solvent, the conversion in the reaction of oxybromination of phenol was 83 and 58%, and 25% *para* and *ortho* isomers were obtained, respectively. In case of other solvents the conversion was negligibly small. In the presence of H₂O₂ the acetic acid forms peracetic acid which is stronger oxidant than H₂O₂ and efficiently oxidizes the Br[−] to Br⁺. This may be the reason for acetic acid has given better results compared to other solvents.

It is assumed that CrZSM-5(30) with H₂O₂ forms a peroxo species [19]. The formed peroxo metal species then catalyzes the oxidation of Br[−] (KBr) to Br⁺(HOBr) which reacts in presence of Bronsted acidic centres of zeolite with organic substrates to give brominated compounds (Scheme 2).



Scheme 2.

The zeolite (CrZSM-5(30)) easily recovered and reused after the reaction by simple filtration. Further, CrZSM-5(30) was reused in the bromination of phenol. The recovered catalyst showed consistent activity. The high catalytic activity and selectivity maintained even after third reuse. The catalyst was highly crystalline before and after the reaction which was confirmed by XRD. There is small amount (2.67%) of Cr leaching from CrZSM-5 zeolite observed by elemental analysis.

4. Conclusion

In conclusion, we have developed an efficient new method for the bromination of phenols. The present catalytic method which is more attractive than the earlier methods, offers the additional advantages such as the commercial availability of the reagents, simple reaction conditions, no evolution of hydrogen bromide, high yield, economical, easy set-up and work-up, selective mono bromination with high *para* selectivity, inexpensive and environmentally friendly catalysts make our method valuable from a preparative point of view.

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