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Shape-selective *para*-chlorination of phenol using sulfuryl chloride with the aid of microporous catalysts

Jallal M. Gnaim[a,*] and Roger A. Sheldon[b]

[a]*Department of Chemistry, The Triangle Regional R&D Center, PO Box 2167, Kfar-Qari 30075, Israel*
[b]*Department of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands*

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Abstract—Aluminum-pillared montmorillonite clay, and partially cation-exchanged L type zeolites, efficiently catalyze the selective *para*-chlorination of phenol using SO_2Cl_2 in 2,2,4-trimethylpentane at 25 °C. A conversion of ~96%, a *para*-selectivity of ~89%, and a *para*/*ortho* ratio of 8.0, were achieved with H^+, Al^{3+}, Na^+, and K^+-L zeolite. This heterogeneous zeolite-catalyzed process is the first example, which shows a pronounced shape-selectivity in the chlorination of phenol.

Chlorophenols[1] are mainly applied as intermediates in pharmaceutical and agricultural chemistry as well as in the dye industry.[2,3] The most common monochlorophenol, *para*-chlorophenol (PCP), is used as an intermediate in the synthesis of dyes and drugs, and especially, in the production of the herbicide dichlorophenoxybutyric acid, and the germicide 4-chloro-2-methylphenol.[4]

Phenols are commonly chlorinated in the liquid phase, using Cl_2 in the presence of Lewis acid catalysts. A mixture of isomeric mono-, and polychlorinated phenols is obtained,[5] from which the desired isomer can be isolated by laborious procedures. Furthermore, the Lewis acid catalyst is often toxic,[6] and cannot be recycled due to its dissolution in the reaction mixture, and thus it may cause environmental pollution.[7] Therefore, attempts have been made to overcome these disadvantages, by employing recyclable heterogeneous catalysts with a wide variety of reagents and conditions.[4]

Much attention has been paid to the use of molecular sieves and other microporous catalysts, in the halogenation of aromatic compounds.[8–20] While, many successful shape-selective catalysts were recorded for the halogenation of halo- and alkyl-benzenes, little was achieved with anisoles and phenols. Very recently,[21] we reported an efficient process for *ortho*-chlorination of phenol using a recyclable solid amine catalyst. However, to the best of our knowledge, no shape selective microporous catalyst has been reported for the *para*-isomer.

In this communication, we wish to present our results on the chlorination of phenol using SO_2Cl_2 and various microporous catalysts, in a nonpolar medium. The stability of these microporous catalysts under the reaction conditions is also discussed.

Phenol reacts with most chlorinating reagents, even in the absence of a catalyst, because of its high reactivity toward electrophilic substitution. In the early stages of our study, we discovered that, in order for a microporous catalyst to have any influence on the chlorination selectivity, a suitable chlorinating system must be used, that is, a weak chlorinating agent, a nonpolar solvent, and low temperatures. For example, phenol reacts very slowly with SO_2Cl_2 using 2,2,4-trimethylpentane (TMP) at 25 °C giving after a 26 h reaction, only an ~8% yield of chlorophenols (Table 1, run 1).

More than 30 commercial microporous catalysts and some of their cation-exchanged analogs, were investigated in the chlorination of phenol using SO_2Cl_2 in TMP at 25 °C. The addition of a microporous catalyst, such as, acidic silica gel, neutral alumina, ZrO_2–SiO_2, active montmorillonite clay, montmorillonite KSF,

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* Corresponding author. Tel./fax: +972 4 638 4650; e-mail: jallal_g@zahav.net.il

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Table 1. Chlorination of phenol with SO_2Cl_2 in the presence of microporous catalysts[a]

Run No.	Catalyst	Reaction time, h	Yield, mol%			*p*/*o* ratio
			Phenol	OCP[b]	PCP[c]	
1	None	26	91.9	3.0	5.1	1.7
2	Zn-pillared hectorite	20	77.9	3.6	18.5	5.1
3	Al-pillared montmorillonite	42	10.9	13.4	75.7	5.7
4	Al^{3+}, Na^{+}, K^{+}-L zeolite	22	4.2	12.8	83.0	6.5
5	H^{+}, Al^{3+}, Na^{+}, K^{+}-L zeolite	22	4.0	10.7	85.3	8.0

[a] Chlorination procedure: to a mixture of phenol (9.4 g, 0.10 mol), 2,2,4-trimethylpentane (120 mL), and the appropriate solid catalyst (10.0 g) gently stirred in a 250 mL three-necked round-bottom flask, was added SO_2Cl_2 (8.0 mL, 0.10 mol) dropwise at 25 °C. The reaction mixture was stirred at this temperature for 20–42 h. The solid catalyst was filtered off, volatile solvents were removed under vacuum, and the residue was analyzed by GLC. The GLC analyses were performed with a Hewlett Packard instrument equipped with a F.I.D. coupled to a Perkin Elmer GP100 recorder. Yields, given in mol%, determined with 1,2-dichlorobenzene as an internal standard.

[b] OCP: *ortho*-chlorophenol.

[c] PCP: *para*-chlorophenol.

montmorillonite K10, Procter & Gamble clay, laponite B, surrey powder, fulacolor XW, fulmont premiere, fulcat 22A, fulcat 15, or laponite RD clay, resulted in some catalytic activity. Furthermore, by increasing the Brønsted acidity of the solid, an increased reaction rate was achieved. Although, these catalytic systems are highly specific for monochlorination, relatively poor regioselectivities were obtained, that is, the *para*/*ortho* ratios were in the range of 1.0–3.5.

At the edges of the crystalline clays, the sheet structure is broken and the crystal is terminated by OH groups. At high pH, they deprotonate, the edges become negatively charged, and have a cation exchange capacity. This interesting property allowed us to introduce mono-, di-, and trivalent cations into the structure of the clay, in order to enhance its Brønsted and Lewis acidity. Several Al^{3+}-, Fe^{3+}-, Cu^{2+}-, and H^{+}-exchanged montmorillonite clays were prepared by known techniques,[22] and tested in the chlorination of phenol, affording mixtures of monochlorophenols with conversions and selectivities very similar to that of the starting clay mineral (*para*/*ortho* ratios of 1.3–1.8). The poor shape-selectivity observed with the clays and their analogs, indicates that the chlorination is mainly occurring on the outer surface of the catalyst, rather than inside its interlamellar space.

In order to improve the shape-selective catalysis, a more highly organized, well-defined, and rigid molecular pore-size structure is called for. An example of such a class of materials is the pillared clays, which are microporous materials obtained by propping the silicate sheets of the clay apart with a chemical substance acting as a molecular prop, and creating a sort of 'mine shaft' between the layers.

As expected, improved selectivities were achieved for the *para*-isomer, using a laboratory synthesized Zn-pillared hectorite (~84%, *para*/*ortho* ratio of 5.1), and a commercial Al-pillared montmorillonite (~85%, *para*/*ortho* ratio of 5.7). These results show for the first time, a shape-selective effect of a solid microporous catalyst on the liquid phase chlorination of phenol (Table 1, runs 2 and 3).

However, the Zn-pillared hectorite catalyst was rapidly deactivated, and only a ~22% conversion was reached after a 20 h reaction. On the other hand, the Al-pillared montmorillonite, effectively catalyzed the chlorination of phenol affording a high conversion, ~89% (Table 1, run 3). Surprisingly, the *para*/*ortho* ratio increased during the course of the reaction, from 1.8 after 1 h to 5.7 after 42 h. We can only speculate regarding an explanation for this phenomenon. Possibly, dealumination of the catalyst by reaction of HCl produced in the system with the pillaring alumina may afford new aluminum species, which may enhance the Lewis acidity of the catalyst.[23,24]

Medium pore-size zeolites, such as, H-ZSM-5, TS-1, and Co-APO-11, and larger pore-size zeolites, such as, Na^{+}-X, Na^{+}-Y, Na^{+}-mordenite, and Na^{+}, K^{+}-L, were tested in the chlorination of phenol. These catalysts show low conversions and poor selectivities (*para*/*ortho* ratios of 1.0–2.6) for the *para*-isomer. The catalytic properties of several partially NH_4^{+}-, and H^{+}-exchanged zeolites were also examined. While, the NH_4^{+}-exchanged X, Y, mordenite and L zeolites gave low selectivities (*para*/*ortho* ratios of 1.1–1.4), the corresponding H^{+}-exchanged analogs showed relatively improved results (*para*/*ortho* ratios of 1.3–2.7).

By increasing the amount of the L-type zeolite catalyst, the selectivity was dramatically improved, yielding a *para*/*ortho* ratio of 5.5. This process demanded a relatively large quantity of catalyst. However, we note that the [catalyst (g)/substrate (mmol)] ratio in our study (0.1), is lower than those of previous works, for example, Onaka and Izumi[15] (1.5), Wortle et al.[20] (1.0), Smith et al.[16] (1.0), van Dijk et al.[8] (0.9), Smith et al.[10,18] (0.6–0.7), Smith and Bahzad[11] (0.6), de la Vega et al.[14] (0.3), Smith et al.[12] (0.3), de la Vega et al.[13,19] (0.3), Hojo and Masuda[17] (>0.1), and many others, who described the catalyzed nuclear halogenation of halo- and alkyl-aromatic compounds using microporous catalysts.

To study the effect of the cation type exchanged in the L zeolite and its catalytic activity on the chlorination of phenol, we prepared different partially cation-exchanged L zeolites starting from a commercial Na^{+}, K^{+}-L zeolite. The highest *para*/*ortho* ratios were achieved with Al^{3+}, Na^{+}, K^{+}-L zeolite, and H^{+}, Al^{3+}, Na^{+}, K^{+}-L zeolite (6.5 and 8.0, respectively; Table 1, runs 4 and 5). Thus, with H^+, Al^{3+}, Na^+, K^+-L catalyst, the selectivity for the *para*-isomer is ~89%. It can be concluded from this study, that the *para* selectivity in the chlorination of phenol catalyzed by zeolites depends strongly on the type of solvent, the catalyst, the exchanged-cation and the chlorinating reagent.

We have applied our Al-pillared montmorillonite catalytic system on the chlorination of *ortho*-cresol and anisole. The observed conversions were, ~98% and ~94%, respectively, and the corresponding *para*/*ortho* ratios were, 6.1 and 7.9, respectively. These results clearly demonstrate the generality of our heterogeneous catalytic system in the regioselective chlorination of phenol and related compounds.

Structural properties of the catalysts and their stability under the SO_2Cl_2 chlorination conditions, are under current investigation.

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