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A novel and direct selective iodination of toluene to para-iodotoluene using zeolite catalysts

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A new and direct procedure for the selective formation of para-iodotoluene from toluene is demonstrated for the first time using iodine monochloride (ICl) as the iodinating agent and zeolite H-beta as the catalyst. Zeolite H-beta and H.K-L are found to be more para-selective compared to other zeolite catalysts and the conventional catalysts, H_2SO_4 and SiO_2. In the presence of a solvent (nitrobenzene) the conversion of ICl increases and the formation of side products (chlorotoluenes) decreases. The probable mechanism for the formation of iodotoluenes and some amount of chlorotoluenes involves the electrophilic attack of toluene by I^+ and Cl^+, respectively.

Keywords: iodination of toluene; para-iodotoluene; iodination over zeolites

1. Introduction

Iodoaromatic compounds are important in metabolism and radiolabeling studies. Thyroid hormones, amphetamines and corticosteroids have been investigated using radio-iodine derivatives [1]. Direct chlorination and bromination of aromatic compounds are well known. However, the direct and selective iodination of aromatic compounds with molecular iodine is much more difficult owing to the lower electrophilic strength of the iodine molecule. Conventionally, the iodination of toluene by molecular iodine is carried out using oxidising agents such as nitric acid, sulphur trioxide, sulphuric acid, iodic acid and hydrogen peroxide to oxidize the iodine molecule to an electrophile [2–7]. In addition, iodotoluenes are also prepared using molecular iodine in the presence of $AlCl_3$, $CuCl_2$ or peracetic acid [8–10]. The use of mineral acids and metal halides in the iodination reactions poses some major problems like the use of a stoichiometric amount of catalyst, lower para-selectivity, hazardous reaction conditions and difficulty in separation of catalyst from the final product. ICl, without involving a Friedel–Crafts catalyst, has also been used as an iodinating agent but its applicability so far is limited as the reaction is not para-selective [11–15]. Recently, zeolite catalysts have been found to catalyze the selective chlorination [16–23] and bromination [24–25] of a variety of aromatic substrates. However, there is no report on the selective iodination of aromatic compounds using zeolite catalysts. In this paper, we report for the first time interesting findings for the selective formation of para-iodotoluene over various zeolites, showing that it is formed by an electrophilic process in high selectivity, especially in the case of H-beta and H.K-L zeolites. The influence of nitrobenzene (solvent) on the product formation is also studied.

2. Experimental

Zeolites Na-Y and H-mordenite were provided by Laporte Inorganics, Cheshire, UK ZSM-5, beta and K-L were synthesized hydrothermally according to the procedure described elsewhere [26–28]. The synthesized zeolites were calcined at 823 K in an air stream and changed into their H^+- and K^+-forms [29]. The chemical analyses of the zeolites were carried out by a combination of wet chemical and atomic absorption (Hitachi Z-800) methods. The crystallinity and phase purity of the zeolites were known from X-ray diffractograms obtained using Cu Kα radiation. The catalysts were further characterised by SEM and N_2 adsorption techniques. The physico-chemical properties of the samples are given in table 1. Before reaction, the zeolite samples were dehydrated at 473 K under N_2 for 6 h.

In a typical reaction, 10 g (0.11 mol) of toluene, 3.52 g (0.022 mol) of ICl and 0.53 g activated catalyst were mixed in a small glass flask and heated with stirring at 363 K. After the reaction, the reaction mixture was separated from the catalyst and analysed by a gas-chromatograph (Blue Star, India model 421) equipped with a FID detector and a 50 mm × 0.2 mm capillary column with methyl silicone gum. The products were identified by GC-MS (Shimadzu, QP 2000 A), ^{1}H NMR and compared with authentic samples.

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Table 1
Physico-chemical properties of catalysts

Catalyst [a]	SiO_2/Al_2O_3	Cation composition [b] (%)			Surface area [c] (m^2/g)	Crystal size (μm)
		H^+-	Na^+-	K^+-		
H-ZSM-5	41.0	98.1	1.9	–	413	0.5
K-ZSM-5	41.0	2.5	1.4	96.1	404	0.5
H-mordenite	22.0	98.0	2.0	–	552	1.0
H-beta	26.0	98.7	1.3	–	745	1.0
K-beta	26.0	3.2	3.4	93.4	731	1.0
H-Y	4.1	98.2	1.8	–	615	1.0
K-Y	4.1	–	7.2	92.8	603	1.0
H.K-L	6.8	75.6	0.9	23.5	227	1.0
K-L	6.8	–	1.4	98.6	215	1.0

[a] %crystallinity of zeolites > 98.

[b] H^+ was obtained by the difference between the Al content and the sum of the alkali metal values. Values are reported as percent of the total cation sites, with aluminium content taken as 100%.

[c] N_2 adsorption.

3. Results and discussion

Table 2 lists typical values of the iodination of toluene by ICl over various acidic and basic zeolites. In all reactions, the iodination of toluene is accompanied to some extent by simultaneous chlorination (scheme 1) [11–15]. The main products of the reaction are para-iodotoluene (PIT), ortho-iodotoluene (OIT), para-chlorotoluene (PCT) and ortho-chlorotoluene (OCT). The formation of minor quantities of consecutive reaction products (others) is also observed. The absence of side chain products (benzyl iodide and benzyl chloride) suggests that halogenation of toluene by ICl occurs by a heterolytic rather than a homolytic process. The results show a strong influence of different catalysts on the para-selectivity (PIT/OIT). Acidic H-beta and H.K-L are far more selective with PIT/OIT ratio 2.88 and 2.58, respectively, compared to other acidic and basic zeolites. The conversion of ICl over acidic H-beta and H.K-L was found to be 51.5 and 52.0%, respectively. Table 2 shows that the selectivity for PIT is not only determined by the pore structure of the zeolite but also, probably, by the acid strength of the catalyst, electrostatic forces produced

Table 2
Iodination of toluene with ICl [a]

Catalyst	ICl conv. (wt%)	Products [b] (wt%)					PIT/OIT [c]	CT/IT [d]
		PCT	OCT	PIT	OIT	others		
no catalyst	37.5	9.4	14.1	40.0	31.8	4.7	1.26	0.33
SiO_2 [e]	56.5	10.6	18.6	38.1	28.3	4.4	1.35	0.43
H-ZSM-5	53.5	7.5	15.0	42.1	29.9	5.5	1.41	0.31
K-ZSM-5	63.0	8.7	15.9	37.3	30.0	8.1	1.24	0.40
H-mordenite	68.5	9.6	17.5	37.9	29.2	5.8	1.30	0.40
H-beta	51.5	6.9	10.7	59.6	20.7	2.1	2.88	0.22
H-beta [f]	97.5	4.4	8.8	47.9	36.8	2.1	1.30	0.15
K-beta	57.0	8.8	14.9	46.5	27.2	2.6	1.71	0.32
H-Y	41.5	8.4	13.3	49.4	24.1	4.8	2.05	0.30
K-Y	56.5	8.8	15.9	42.5	25.7	7.1	1.65	0.36
H.K.-L	52.0	5.8	12.6	55.3	21.4	4.9	2.58	0.24
K-L	55.0	9.1	15.4	40.9	29.1	5.5	1.41	0.35
H_2SO_4	72.5	7.7	12.0	43.4	34.3	2.6	1.27	0.25

[a] Reaction conditions: catalyst = 4.9 g/mol toluene; reaction temperature (K) = 363; toluene/ICl (molar ratio) = 5; toluene (mol) = 0.11; reaction time (h) = 0.25.

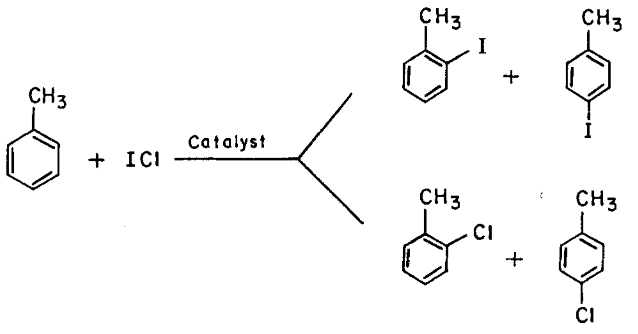
[b] PCT = para-chlorotoluene; OCT = ortho-chlorotoluene; PIT = para-iodotoluene; OIT = ortho-iodotoluene; others = dichloro- and diiodotoluenes.

[c] PIT/OIT = isomer ratio.

[d] CT/IT = ratio of chlorotoluenes/iodotoluenes.

[e] Fumed silica.

[f] Reaction conditions: solvent (nitrobenzene) = 5 ml; catalyst = 4.9 g/mol toluene; reaction temp. (K) = 363; toluene/ICL (molar ratio) = 5; toluene (mol) = 0.055; reaction time (h) = 0.25.



Scheme 1.

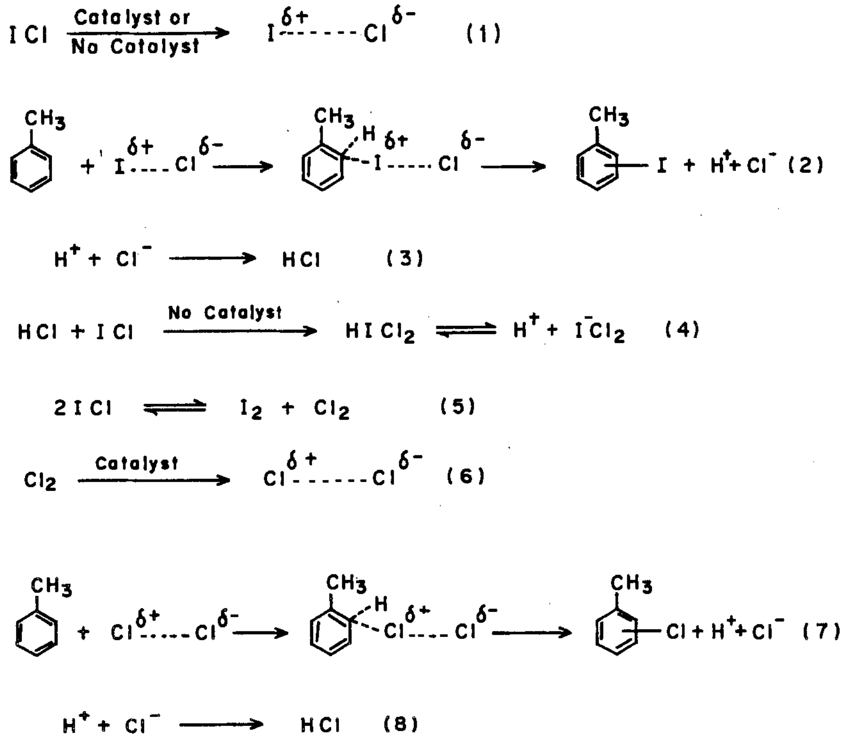
in the zeolite channels and restricted orientation of the adsorbed molecule in the pores of the zeolites [18–25]. There was no selective formation of PIT over H_2SO_4 and SiO_2 even though the ICl conversion was higher (72.5 and 56.5%, respectively). The lower conversion of ICl (37.5%) in the absence of any catalyst may be attributed to the presence of unreactive I^-Cl_2 (or $HICl_2$) species in the reaction mixture produced by the combination of iodine monochloride and liberated hydrogen chloride during the course of the reaction (eq. (4) of scheme 2) [11–15].

Mechanistically, it is assumed that the formation of iodotoluenes (IT) and little amount of chlorotoluenes (CT) proceeds through electrophilic attack on the aromatic ring. Presumably, the iodinating species is an electrophile (I^+) which is produced by the ionization of ICl (eqs. (1)–(3)) [11–15]. Similarly, it is believed that the chlorination of toluene also proceeds by electrophilic substitution. The fact that ICl dissociates into the elements ($I_2 + Cl_2$) to a little extent, favourably in non-polar medium (eq. (5)) [11–15], suggests that zeolite catalysts or other ICl molecules (Lewis acid) polarize the Cl_2 into an electrophile (Cl^+) which then attacks the aromatic ring resulting in the formation of chlorotoluenes (eqs. (6)–(8)) [11–15].

In addition, the formation of chlorotoluenes was suppressed to some extent (CT/IT ratio = 0.15) when reaction was carried out in the presence of nitrobenzene (as solvent). Also, the conversion of ICl increased in this case but selectivity for PIT markedly decreased (table 2). It is believed that nitrobenzene prevents the dissociation of ICl into I_2 and Cl_2 and subsequently the formation of chlorotoluenes [11–15].

4. Conclusions

In summary, the results described herein demonstrate the novelty of zeolites, H-beta and H.K-L in enhancing the selectivity for PIT in the catalytic iodination of toluene by ICl. Nitrobenzene (polar solvent) prevents the formation of chlorotoluenes. The reaction proceeds readily with ICl under mild conditions.



Scheme 2.

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