Iron-exchanged zeolite as effective catalysts for Friedel–Crafts alkylation with alkyl halides

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Friedel–Crafts alkylation of benzene and ethylbenzene with butyl halides has been investigated in the presence of iron-exchanged zeolites. The catalysts showed high conversions and selectivity for monoalkylated products with tertiary and secondary halides under mild reaction conditions (45–60 °C). Alkylation of ethylbenzene with 2-chlorobutane can be achieved in 99% yield and 100% selectivity to the monoalkylated product.

KEY WORDS: Friedel–Crafts alkylation; zeolites; ion exchange

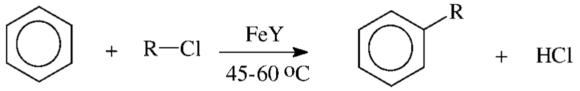
Friedel–Crafts alkylation is probably one of the most important classes of reactions in organic chemistry [1]. The traditional catalysts used in these reactions, such as aluminum chloride, aluminum bromide, iron(III) chloride, zinc chloride, HF and H_2SO_4 present several disadvantages. Among them are handling, storage and waste problems. Another difficulty to circumvent with these catalysts is polyalkylation. Alkyl groups normally activate the aromatic ring toward electrophilic substitution reactions and formation of polyalkylate products is always observed in Friedel–Crafts alkylation, leading to decreased yields and laborious separation procedures. Olah and collaborators showed [2] that by the action of $AlCl_3$, an equilibrium mixture of *meta* and *para t*-butyltoluene is achieved starting from any of the pure isomers. Yet, they found that disproportionation products (toluene and di-*t*-butylbenzene) accounts for about 50 mol% conversion. In order to reduce isomerization and disproportionation in aromatic alkylation catalyzed by aluminum chloride, the reactions were generally carried out at low temperature (below −10 °C) and in solvents, such as carbon disulfide and nitromethane, which present hazards [3,4]. The search for cleaner and more efficient catalysts led to the development of iron, aluminum, zinc and copper chlorides supported on silica, graphite, clays and ion exchange resins [5–8]. Zeolites are another class of materials tested for Friedel–Crafts alkylation. Due to its shape selective properties, easy separation from reaction medium and regeneration, zeolites can be promising catalysts for substituting $AlCl_3$ in industrial processes [7]. However, the majority of alkylation reactions with zeolites are carried out at high temperatures, in gas phase, generally using alkenes and alcohols as alkylating agents [7,9]. There are few works with benzyl chloride [10,11], but this methodology has not been explored as a general route to Friedel–Crafts alkylation with zeolites.

In this letter we wish to present preliminary results of alkylation of benzene and ethylbenzene with butyl halides, catalyzed by iron-exchanged zeolite Y, under mild reaction conditions. This procedure has a great potential for replacing the traditional and highly polluting $AlCl_3$ catalyst (scheme 1).

Benzene and ethylbenzene were treated with sulfuric acid, washed with 5% sodium carbonate solution and heated in reflux for 3 h over metallic sodium. Then, they were distilled and stored over molecular sieves. The alkyl halides were purchased from Aldrich and used without further purification.

The iron-exchanged zeolite was prepared by cation exchange of NaY (Si/Al 2.8; BET area of 728 m^2/g) obtained from PETROBRAS, using 1 M aqueous solution of iron(III) sulfate at ambient temperature for 15 h. The weight percent of iron in the sample was determined to be 7% by atomic absorption spectrometry.

The alkylations were carried out with 320 mg of zeolite (0.40 mmol of Fe), 9 mmol of alkyl chloride and 113 mmol of benzene or 82 mmol of ethylbenzene, used as solvent too. The catalyst was activated by calcination at 400 °C for 2 h in the reaction flask. The mixture was kept at reaction temperature (45 or 60 °C) and stirred with a magnetic bar. The products were quantitatively analyzed by gas chromatography (*n*-nonane used as internal standard) and confirmed by gas chromatography coupled with mass spectrum as well as ^1H and ^{13}C NMR. The NMR spectra



Scheme 1. Friedel–Crafts alkylation over FeY zeolite.

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of isolated products were run in $CDCl_3$ at 300 MHz, with TMS as internal standard. Two-dimensional NMR (^1H–^1H COSY and ^1H–^{13}C COSY) also confirmed the isomer distribution.

Tables 1 and 2 present the alkylation of benzene and ethylbenzene, respectively, with butyl halides. The yield and selectivity to monoalkylation is high with secondary and tertiary halides. Nevertheless, with *n*-butyl and isobutyl halides the yield is poor, although a still high selectivity to monoalkylation is achieved. The primary halides can also undergo rearrangement. For instance, 1-chlorobutane (entries 5 and 6) gave a significant amount of rearranged *sec*-butyl-ethylbenzenes. The increase in temperature has little effect on the yield and selectivity of the alkylation. For primary halides the increase in temperature did not significantly improve the yield. For secondary and tertiary halides a slight increase in yield and selectivity to monoalkylation was observed. Moreover, these reactions can be carried out with low amount of catalysts without decreasing the yield, but with some increase in the *para* selectivity (entry 12). When selectivity to monoalkylation was lower than 100%, the difference refers to dialkylated compounds. No other products were observed.

Table 1
Alkylation of benzene with butyl halides on FeY zeolite at 45 °C.

Halide	Entry	Time (min)	Conversion (mol%)	Selectivity monoalkylate (%)
1-chlorobutane	1	300	3.4	100
Isobutyl chloride	2	300	2.5	100
2-chlorobutane	3	210	71	90
t-butyl chloride	4	320	86	81

Entry 13 shows the results of ethylbenzene alkylation with *t*-butyl chloride and a previously used, regenerated, FeY catalyst. It can be seen that yield and selectivity are little affected by regeneration of the zeolite, indicating its potential industrial application in environmentally friendly processes.

Figure 1 shows a kinetic study for alkylation of ethylbenzene with 2-bromobutane and *t*-butyl chloride. It can be seen that maximum yield is achieved within 30 min. Longer reaction times alter the isomer distribution, favoring the thermodynamic more stable *meta* isomer, as shown in figure 2, suggesting that acid-catalyzed isomerization of the alkylaromatics formed, may occur with longer reaction time.

Concerning the reaction mechanism, other studies using ion-exchanged zeolites and clay catalysts, have proposed a

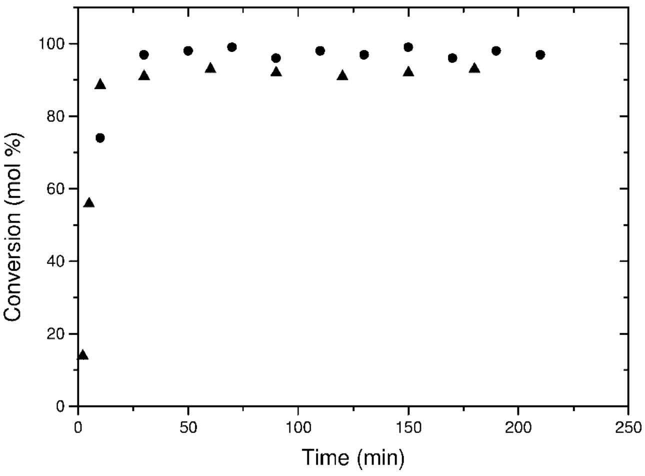

Figure 1. Kinetics of ethylbenzene alkylation on FeY at 60 °C. (▲) entry 15 and (●) entry 10.

Table 2
Alkylation of ethylbenzene with butyl halides on FeY at 60 °C.

Halide	Entry	Time (min)	Conversion (mol%)	Selectivity monoalkylate (%)	Monoalkylate isomers (%)		
					m	*o*	*p*
1-chlorobutane	5	120	4.3	100	19^{d} 11^{e}	14^{d} 10^{e}	34^{d} 12^{e}
1-chlorobutane[a]	6	240	4.0	100	23^{d} 9^{e}	15^{d} 9^{e}	34^{d} 10^{e}
Isobutyl chloride	7	330	2.7	100	n.a.	n.a.	n.a.
2-chlorobutane	8	260	99	100	25	26	49
2-chlorobutane[a]	9	180	85	89	23	26	51
t-butyl chloride	10	200	96	97	21	–	79
t-butyl chloride[a]	11	240	96	93	24	–	76
t-butyl chloride[b]	12	180	96	99	13	–	87
t-butyl chloride[c]	13	180	93	98	21	–	79
1-bromobutane	14	300	3	92	19^{d} 11^{e}	16^{d} 12^{e}	30^{d} 12^{e}
2-bromobutane	15	240	93	90	31	16	53

[a] Alkylation at 45 °C.
[b] FeY: 50 mg (0.063 mmol of Fe).
[c] Regenerated: the zeolite was filtered from the reaction mixture, washed with ethyl ether (12 ml), methyl alcohol (12 ml) and dried at 100 °C. The catalyst was calcined for 2 h at 400 °C before reusing in another alkylation experiment.
[d] *Sec*-butyl-ethylbenzene isomers.
[e] *n*-butyl-ethylbenzene isomers.

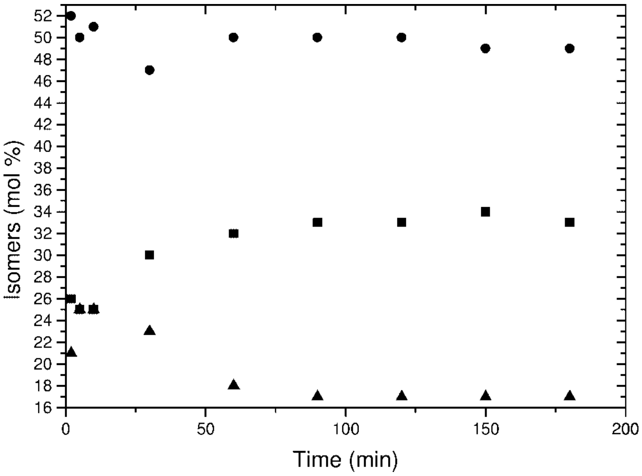

Figure 2. Isomer distribution as a function of time in the alkylation of ethylbenzene on FeY zeolite at 60 °C (entry 15): (▲) *ortho*, (■) *meta* and (●) *para*.

radical pathway when benzyl chloride was the alkylation agent [8,10]. However, since we were able to observe rearranged products, it seems to us that under our reaction conditions the classic electrophilic mechanism of Friedel–Crafts alkylation is taking place. We are presently investigating this point and the scope of the methodology.

In summary, iron-exchanged zeolites showed a good performance as catalysts for Friedel–Crafts alkylation with tertiary and secondary halides. High yields and selectivity for the monoalkylated products could be achieved under mild conditions and short reaction times. Hence, it can be a viable alternative for substituting the traditional $AlCl_3$ catalyst.

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