

Mechanistic Aspects of Friedel-Crafts Alkylation over FeY Zeolite

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Foram estudados os efeitos da razão molar aromático/cloreto de alquila, adição de base, solvente e agente alquilante, na alquilação do etilbenzeno catalisada pela zeólita FeY. Ficou caracterizada a alquilação ocorrendo no interior dos poros da zeólita, uma vez que ela é pouco afetada pela razão molar dos reagentes. A adição de bases e solventes oxigenados, capazes de complexar com o sítio ativo, inibe a reação. Foi proposto um mecanismo envolvendo transferência de um elétron entre as espécies de ferro ativas e o cloreto de alquila, para explicar os resultados.

The effect of aromatic/alkylchloride molar ratio, base addition, solvent and alkylating agent on the ethylbenzene alkylation over FeY zeolite was investigated. It was shown that alkylation occurs inside the pores and it is little affected by the reactants molar ratio. On the other hand, addition of bases or oxygenated compounds, capable of complexing with the active site, blocks the reaction. A mechanism involving single electron transfer between the active iron species and the alkylchloride was proposed to account for the results.

Keywords: zeolite, Friedel-Crafts alkylation, *tert*-butylchloride, green chemistry

Introduction

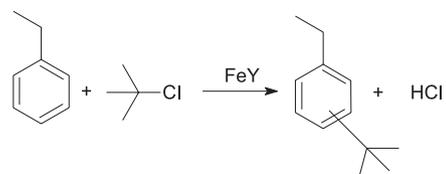
Friedel-Crafts alkylation is probably one of the most important classes of reactions in organic chemistry.¹ It usually involves the electrophilic attack of an aromatic ring by an alkylating agent, such as alkyl halides, olefins or alcohols.² Lewis acids, such as AlCl₃, are the most traditional catalysts for Friedel-Crafts alkylations. It is generally assumed that the Lewis acid interacts with the alkyl halide, forming a complex, which can either directly attack the aromatic ring, or decompose to a carbocation, which in turn acts as the alkylating species.

Some traditional catalysts, especially AlCl₃, FeCl₃, ZnCl₂, HF and H₂SO₄ 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. Thus, formation of polyalkylated products is normally observed in Friedel-Crafts alkylation, leading to decreased yields and laborious separation procedures. 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}

In recent years the use of cleaner catalysts for the chemical industry has grown in importance.⁵ Hence, the use of clays,⁶ resins^{7,8} and zeolite⁹⁻¹¹ catalysts in Friedel-Crafts alkylations has been studied. Iron-exchanged zeolites have been reported^{12,13} to be good catalysts for benzylation of aromatic hydrocarbons. We have also shown¹⁴ that FeY is an active catalyst for *tert*-butylation of ethylbenzene with *tert*-butylchloride, yielding a selectivity of 98% to monoalkylation with 96% conversion (scheme 1).

Bachari *et al.*¹⁵ have recently revisited the mechanism of benzylation over iron-exchanged materials. They found



Scheme 1. Friedel-Crafts alkylation catalyzed by FeY zeolite.

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no correlation between the rate of the reaction with several substituted benzene derivatives and the σ^+ constant. Except for chlorine, they found a good correlation between the rate and the substituent ionization potential, suggesting a radical mechanism for initiation. These results prompted us to present some recent data on the use of FeY zeolite in Friedel-Crafts alkylation.

Experimental

The iron-exchanged zeolite was prepared by cation exchange of NaY (unit cell composition: $\text{Na}_{51}\text{Al}_{51}\text{Si}_{141}\text{O}_{384}$; BET area of $728 \text{ m}^2 \text{ g}^{-1}$) obtained from Petrobras, using 1.0 mol L^{-1} aqueous solution of iron (III) sulfate at ambient temperature for 15 h. The weight percent of iron in the sample was 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, 82 mmol of ethylbenzene, used as solvent as well, and 140 μL of *n*-nonane as internal standard. The catalyst was activated by calcination in an oven at $400 \text{ }^\circ\text{C}$ for 2 h in the reaction flask. Lower activation temperatures did not impair the reaction, but slow down the rate. After activation, the catalyst was cooled to room temperature, under controlled atmosphere, and the reactants were introduced in the flask. The system was heated to the reaction temperature (45 or $60 \text{ }^\circ\text{C}$) and, unless otherwise stated, stirred with a magnetic bar for 180 min. The products were quantitatively analyzed by gas chromatography and their identity confirmed by gas chromatography coupled with mass spectrum (GC/MS). Typically, a sample of 0.3 mL was carefully withdrew at the end of the reaction, and transferred to a vial with 200 mg of Amberlyst-21 to neutralize any residual HCl, before gas chromatography analysis. For any kinetic determination, the procedure was the same, except for the time intervals.

To study the effect of base addition it was used 9 mmol of the base (triethylamine, 2,6-dimethyl-pyridine, Amberlyst-21 and Na_2CO_3). The procedure was the same, with introduction of the base together with the aromatic and the alkylhalide. To study the effect of solvent, the reaction was carried out with alkylchloride/ethylbenzene molar ratio of 1, using 9 mL of the 1,2-dichloroethane, acetone, THF or ethylacetate as solvent.

Results and Discussion

Effect of the aromatic/RCl ratio

To prove that the reaction is occurring inside the pores we firstly checked the effect of the aromatic/RCl ratio in the reaction. Table 1 shows the results for ethylbenzene

Table 1. Effect of the aromatic/alkylchloride ratio on the conversion and selectivity for the Friedel-Crafts alkylation on FeY at $60 \text{ }^\circ\text{C}$ and 180 min

RCl	Ph-Et/RCl molar ratio	Conversion (%)	Selectivity		
			mono	di	tri
<i>tert</i> -butylchloride	9	99	97	3	
<i>tert</i> -butylchloride	1 ^a	98	96	3	1
<i>sec</i> -butylchloride	9	99	97	3	
<i>sec</i> -butylchloride	1 ^a	99	61	38	1

^aCyclohexane as solvent (9 mL).

alkylation with *tert*-butylchloride and *sec*-butylchloride on FeY at different stoichiometric ratio. One can see that no significant difference could be observed in the selectivity for monoalkylation with the *tert*-butylchloride, indicating that reaction is mostly occurring inside the pores and that the external zeolite surface has little influence on the reaction. For the *sec*-butylchloride the selectivity for monoalkylation, although higher than for di and trialkylation, was inferior to the results when using a large excess of aromatic. This suggests that shape selectivity is playing a role, preventing the formation of bulky transition state. Hence, the zeolite environment might affect the reactivity of the aromatic system. In the case of the *tert*-butyl-ethylbenzenes, formed in the monoalkylation, a second *tert*-butylation inside the pores seems to proceed with a bulky transition state and then, it is not favored.

Effect of base addition

We noticed that during the reaction there was formation of HCl, which might alter the isomer distribution and, in an ultimate case, destroy the crystalline structure. Therefore, we decided to add a base to react with the forming HCl. Table 2 shows the results of addition of different bases to the reaction system. It can be seen that, except for the Amberlyst-21 and Na_2CO_3 , the other bases impaired the reaction. This might be attributed to the fact that the amines might coordinate with the active iron species, thus virtually blocking the reaction with the

Table 2. Effect of the base addition on the conversion and selectivity for alkylation of ethylbenzene with *tert*-butylchloride at $60 \text{ }^\circ\text{C}$ and 180 min

Base ^a	Conversion (%)	Selectivity to Monoalkylation (%)	Isomer Distribution ^b		
			<i>o</i>	<i>m</i>	<i>p</i>
Triethylamine	0	0			
2,6-Dimethylpyridine	0	0			
Amberlyst-21 ^c	99	98	-	17	83
Na_2CO_3 ^d	99	98	-	17	83
None	99	97	-	23	77

^aRCl/Base molar ratio of 1. ^bDistribution of the *tert*-butylethylbenzene isomers formed (%). ^cDried overnight at $80 \text{ }^\circ\text{C}$ before use. ^dDried at $400 \text{ }^\circ\text{C}$ for 2 h before use.

alkylchloride. For Amberlyst-21, a base resin that cannot enter the pores, and Na_2CO_3 , which is not soluble in the reaction medium, there was no effect in the conversion and selectivity. This is an additional proof that the reaction occurs inside the pores.

Effect of oxygenated compounds

In order to explore the limitations of FeY in Friedel-Crafts alkylations, we decided to investigate the use of oxygenated substrates and solvents on the reaction. Table 3 shows that acetone, ethyl acetate and THF, all oxygenated solvents, impair the reaction, while 1,2-dichloroethane has no appreciable effect on the conversion and selectivity. The probable explanation is the same as in the case of the amines. Hence, the oxygenated solvents interact with the iron active species, preventing them to react with the alkylchloride.

Table 3. Effect of oxygenated solvents on the conversion and selectivity for alkylation of ethylbenzene with *tert*-butylchloride at 60 °C and 180 min

Solvent ^a	Conversion (%)	Selectivity to monoalkylation (%)
1,2-Dichloroethane	98	97
Acetone	0	0
THF	0	0
Ethylacetate	0	0
None ^b	99	97

^aPh-Et/RCl molar ratio of 1. ^bExcess ethylbenzene as solvent.

We also decided to investigate the effect of oxygenated substrates. Table 4 reports the conversion and selectivity for ethylbenzene alkylation with *tert*-butanol and *tert*-butanol/*tert*-butylchloride mixtures. One can see that the use of the alcohol as alkylating agent gives low conversion to the products. *tert*-Butanol is probably acting as poison, preventing the adsorption of the *tert*-butylchloride on the active site.

The reactivity of the aromatic substrate was investigated in the benzylation with benzylchloride at

Table 4. Effect of oxygenated alkylating agent on the conversion and selectivity for alkylation of ethylbenzene at 60 °C and 180 min

Alkylating agent	Conversion (%)	Selectivity to monoalkylation (%)
<i>tert</i> -butyl alcohol	5	93
<i>tert</i> -butyl alcohol and <i>tert</i> -butylchloride ^a	7	99
<i>tert</i> -butyl alcohol and <i>tert</i> -butylchloride ^b	47	99
<i>tert</i> -butylchloride	99	97

^a*tert*-BuOH/*t*-BuCl (1:1 molar ratio) added at the beginning of the reaction. ^b*tert*-BuOH added after 10 minutes of reaction.

30 °C on FeY. Toluene and ethylbenzene were three fold more reactive than benzene, whereas anisole showed a reactivity 24.5 times higher than benzene. One can see that substitution of a methoxy group greatly enhances the reactivity, while methyl and ethyl groups increase the reactivity almost to the same extent.

The variation of the aromatic/RCl molar ratio indicated that most of the alkylation occurs inside the pores. Then, the high selectivity toward monoalkylation in the *tert*-butylation of ethylbenzene is due to limitations for the formation of bulky transition states that leads to di and tri alkylations. This is an important result, because one can just adjust the pore size of the zeolite to the size of the aromatic and alkylating agent used in the reaction. The zeolite Y cavity seems to be perfectly adjusted for the monoalkylation of ethylbenzene with *tert*-butylchloride. On the other hand, for *sec*-butylchloride the selectivity to dialkylation increases as the amount of aromatic diminishes. This indicates that formation of the transition state for a second alkylation in this system is not totally prevented by the pore size of the zeolite Y.

The use of bases, to trap the HCl formed, showed to strongly inhibit the reaction. It is worth to mention that no significant reaction of the alkylchloride with the base (elimination or nucleophilic substitution) was detected under the reaction conditions used in the experiments. Apparently, the role of the base is to strongly coordinate with the active iron sites, impairing the interaction with the alkylchloride. Thus, the active sites become blocked and inaccessible to the alkylhalide. Neither the use of Amberlyst-21, a resin base not capable of entering inside the pore system of the zeolite Y, nor the addition of sodium carbonate, which is not soluble in the organic medium system, altered the conversion and selectivity to monoalkylation. This is an additional proof that the reaction occurs inside the zeolite cavity. It is interesting to note that the *tert*-butylethylbenzene isomer distribution showed a slight change with the use of these bases. The meta isomer was in higher percentage when no base was present. This indicates that, at least part of the isomerization is catalyzed by the HCl formed, and occurs outside the zeolite pore system. Once this HCl is trapped by the Amberlyst-21 or the sodium carbonate, the distribution of the meta isomer decreases. Additional evidence for this hypothesis comes from a study of toluene alkylation with *tert*-butylbromide over FeY at 25 °C. Figure 1 shows that the isomer distribution varies significantly with the reaction time, achieving the thermodynamic equilibrium after 80 minutes. On the other hand, when the reaction was carried out in the presence of Amberlyst-21, the isomer distribution does not alter

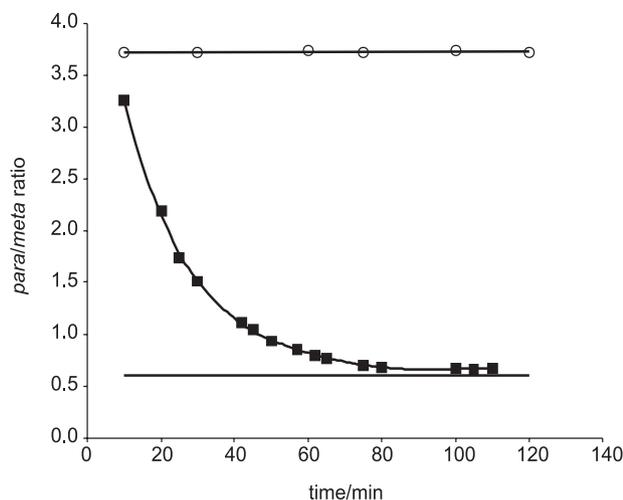


Figure 1. *para/meta* ratio in the alkylation of toluene with *tert*-butylbromide over FeY. (O) reaction at 25 °C. (■) reaction at 25 °C in the presence of Amberlyst-21 resin (—) Thermodynamic distribution.

with reaction time, indicating that isomerization occurs outside the zeolite pores and it is catalyzed by the HBr formed upon alkylation. Once the HBr is neutralized by the basic resin, the isomer distribution reflects the kinetics control.

The results showed in Table 4 are in agreement with the data obtained with addition of base. The role of the oxygenated solvents seems to be similar to the role of the bases, coordinating with the iron active species and thus, impairing the reaction with the alkylchloride. A less nucleophilic solvent, such as 1,2-dichloroethane, has no apparent role in the catalyst reactivity. This effect is also revealed when *tert*-butanol was used as alkylating agent. Low conversions were observed when the alcohol alone, or mixed with the *tert*-butylchloride was introduced in the beginning of the reaction. Addition of the alcohol during the course of the reaction with *tert*-butylchloride virtually stopped the alkylation, indicating that oxygenated compounds act as poisons of the active sites. A similar situation was reported^{16,17} to explain the preferential adsorption of benzyl ether and benzyl alcohol over clay catalysts, impairing the conversion of benzyl chloride in the Friedel-Crafts alkylation of toluene

Recently, it was reported¹⁵ that the presence of water leads to significant drop in the benzylation of benzene catalyzed by iron mesoporous molecular sieve. In fact, it has been reported that other Lewis acid catalysts¹⁸ are also affected by the presence of water in the reaction medium. Hence, amines and oxygenated compounds have a similar effect of the water addition, strongly coordinating with the Lewis acid sites, thus impairing alkylation.

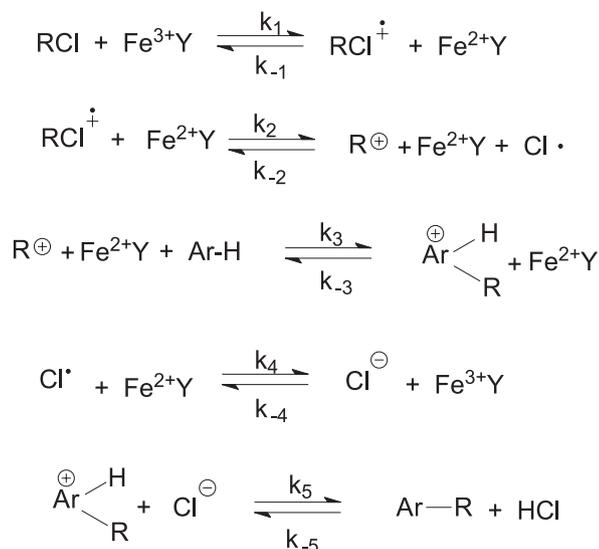
The reactivity experiments with benzene, toluene, ethylbenzene and anisole showed that electron-releasing

groups accelerated the reaction, indicating a carbocationic mechanism for the attack to the aromatic ring. It is interesting to note that no reduction in activity was observed when anisole was used, in spite of the fact of the presence of an oxygen atom. This might be explained in terms of resonance structures of the anisole molecule, delocalizing the electrons into the aromatic ring, thus reducing the coordination capability of the oxygen atoms.

Bachari *et al.*¹⁵ found no correlation of the rate of benzylation of toluene, over iron mesoporous molecular sieve, with σ or σ^+ constants. In fact, they showed that there exists some correlation with the ionization potential of the aromatic substrate, interpreting these results in terms of one electron transfer mechanism. However, it was not clear in their mechanistic proposal, how the aromatic participates in the ionization step. It has been normally proposed^{6,18} that Friedel-Crafts alkylation catalyzed by iron containing clays takes place through a mechanism involving single electron transfer. An ionic mechanism has already been proposed in the literature to account for the activity of iron containing graphite in Friedel-Crafts alkylation.¹⁹ Of course the nature of iron active species has a great influence on the mechanism. XPS analysis of the FeY zeolite showed evidences for the presence of iron-oxygen species, besides the Fe^{3+} , stressing the complexity of the catalytic system.

It is worth to mention that in control experiments using the parent NaY zeolite as catalyst we observed a conversion of 18% on the reaction of ethylbenzene with *tert*-butylchloride. The selectivity to monoalkylation was about 93%. Since the Na^+ reduction potential is very low (highly negative), one should not expect a mechanism involving ion radicals on this catalyst. In fact, we have shown that alkoxides and carbocationic reactions can be observed upon the interaction of alkylchlorides and NaY zeolite,^{20,21} explaining the catalytic behavior of this material. On the other hand, the lower conversion compared with FeY suggests that formation of the adsorbed carbocation involves a higher energy transition state on NaY than on FeY.

Scheme 2 shows a possible mechanistic picture for the Friedel-Crafts alkylation over iron containing zeolites. The first step might involve a single electron transfer between the RCl and the active iron species to form a cation radical. Then, the cation radical can interact with the reduced iron species, represented as Fe^{2+} in the scheme, forming a chlorine atom and a carbocation (free or bonded to the zeolite framework), which alkylate the aromatic compound. The nature of the active iron species will influence the kinetics of the reactions and therefore, may change the mechanism (the rate determining step). In an



Scheme 2. Mechanistic view of the Friedel-Crafts alkylation over FeY zeolite.

experiment of toluene alkylation with *tert*-butyliodide over FeY, we were able to isolate molecular iodine from the reaction mixture, supporting the mechanistic scheme involving single electron transfer. If one assumes a mechanism depicted in Scheme 2, then regeneration of the active iron species would take place together with the reduction of the halogen atom to the halide ion. In the case of alkyl iodides, the reduction of the iodine atom might be considerably slower compared to the chlorine atom, giving rise to formation of molecular iodine. In fact, the conversion of *tert*-butyliodide into alkylated products was about 40%, whereas *tert*-butylchloride was practically 100% consumed in the same reaction period.

Conclusions

Friedel-Crafts alkylations over FeY zeolite occurs inside the pore cavity system. Depending on the structure of the aromatic and the alkylhalide, high selectivity for monoalkylation could be achieved, using stoichiometric amounts of reagents. Use of bases and oxygenated solvents impair the reaction, probably due to strongly coordination with the active iron species.

The results suggest a single electron transfer mechanism, forming a cation radical which decompose to the carbocation.

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