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Acylation of aromatic compounds on H-Beta zeolites

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Abstract

Friedel–Crafts acylation of anisole by acetic anhydride and the Fries rearrangement of phenyl acetate were investigated in the liquid phase using the H-form of various zeolites. Zeolite Beta was found to be the most active catalyst for acylation reactions compared to Y- and ZSM-5 zeolites. The reactions were found to be controlled by mass transfer limitations caused by coke deposition. Two types of coke (extractable and non-extractable) were identified. Combining liquid phase reaction with continuous extraction of the catalyst with refluxing reaction mixture in a Soxhlet-like reactor led to a higher conversion of phenyl acetate in the Fries rearrangement. The ratio of protonated to acylated surface centres strongly determines the selectivity. The formation of *o*-hydroxyacetophenone proceeds both via intramolecular rearrangement and intermolecular acylation. On the other hand, *p*-hydroxyacetophenone is formed entirely by intermolecular acylation. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: H-Beta zeolite; Friedel–Crafts acylation; Fries rearrangement

1. Introduction

Aromatic acylation is of importance in various areas of the fine chemical industry. The synthesis of substituted acetophenones is an essential step in the production of paint additives [1], photoinitiators [2], pharmaceuticals, e.g. 4-acetaminophenol [3] and ester fragrances [4].

Present industrial practice involves over-stochiometric amounts of metal halides (e.g. $AlCl_3$, $FeCl_3$) as catalysts and acyl chlorides, which results in a substantial amount of by-products and corrosion problems as well. The high amount of catalyst is related to the stronger coordination of the formed ketone to the catalyst compared with the acid chloride. Thus the association constant of $FeCl_3$ was found to be 100 times larger for ketone than for the corresponding chloride [5]. Alternatively, strong mineral acids, e.g. hydrogen flouride, are used in the industrial practice. Therefore, the application of heterogeneous catalysts becomes very attractive due to the simple separation of the products and the possibility to regenerate the catalyst.

The alternative use of zeolites which are reusable and very easily tailored to fit the desired reaction is very promising. It can be expected that the combination of strong acidity with shape selectivity favours the regioselective formation of the preferentially required *para*-products.

The successful application of zeolite catalysts to the Friedel–Crafts acylation of aromatics has already been described in the literature.

The earliest results were published by Chiche et al. [6], who studied the acylation of toluene and *p*-xylene

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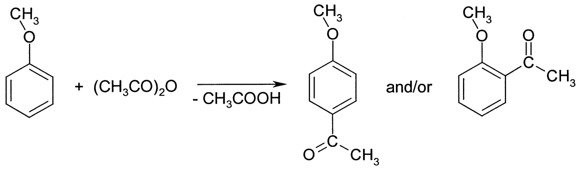
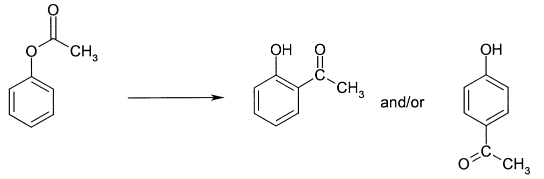


Scheme 1. Acylation of anisole with acetic anhydride.



Scheme 2. Fries rearrangement of phenyl acetate.

with straight-chain carboxylic acids catalysed by CeNa–Y zeolites in liquid phase. They observed a yield of the *para* isomer of at least 94% with all acids studied. For acids of carbon numbers C_{12} to C_{20}, the maximum yield of acylated *p*-xylene was found to be dependant on the chain length.

The electrophilic acylation of methoxybenzene (anisole) was studied using phenylacetyl chloride [7,8], phenylpropionyl chloride [7], acetyl chloride [9], acetic anhydride [8–10] (Scheme 1), and phenylacetic and phenylpropionic acids [7].

Recently, Singh and Pandey [11] reported on zeolite catalysed formation of acetophenone by the reaction of benzene with acetic acid.

The transformation of arylesters into aromatic ketones, known as the Fries rearrangement, may be regarded as an intramolecular migration of the acyl group to the *ortho*- or *para*- position of the aromatic ring (Scheme 2).

The Fries rearrangement of phenyl acetate was extensively studied in gas phase using shape selective zeolites (e.g. zeolite Beta [8,12], Y [13,14] and ZSM-5 [13,15–17]) to improve the yield of *p*-hydroxyacetophenone. In general, the expected hydroxyacetophenones were minor components and phenol was the main product. The rapid deactivation was explained by the condensation of formed ketene [14,18].

In the liquid phase, under less drastic conditions at 450–480 K using a batch reactor, the activity of zeolites is less pronounced [8,12,15]. Moreover, in continuous liquid phase experiments, the conversion of phenyl acetate did not exceed 20% [8].

Contradictory results were published on the influence of the Si/Al ratio of the zeolites on the catalytic activity. Corma et al. [7] reported that the turnover numbers varied only slightly in dependence on the Si/Al ratio. These results were confirmed by Harvey et al. [8] who reported that the conversion observed for acylation of anisole by acetic anhydride as well as the Fries rearrangement of phenyl acetate was constant despite varied Si/Al ratio of zeolite Beta. In addition, the activity per Al site of ZSM-5 zeolite in this reaction was independent of the Si/Al ratio [19]. In contrast, Gaare and Akporiaye [9] detected an almost linear increase in the yield of *p*-methoxyacetophenone with decreasing aluminium fraction. However, in the liquid phase, zeolites deactivate rapidly.

The aim of this work is to study the Friedel–Crafts acylation of methoxybenzene with acetic anhydride and the Fries rearrangement of phenyl acetate on H-Beta zeolite in liquid phase. In order to avoid fast deactivation, the reaction was combined with a continuous extraction in a trickle bed reactor.

2. Experimental

H-Beta (Si/Al=12), dealuminated H-Beta (Si/Al=90), NH_4-Y, and H-ZSM-5 zeolites were supplied by Süd Chemie (Munich, Germany).

For Friedel–Crafts acylation of anisole, H-zeolites were used without pretreatment. Preliminary experiments had shown that water could be removed by thermal activation at 673 K as well as by reaction with acetic anhydride at reaction temperature. The H-form of Y zeolite was obtained by calcination of NH_4-Y zeolite at 723 K for 6 h. The batch experiments were performed at 388 K (in toluene) and at 403 K without solvent in reflux. The mass ratio of anisole to acetic anhydride was 1:1.

For Fries rearrangement, about 2 g of fresh catalyst, activated at 623 K for 2 h, was added to 0.35 mol of phenyl acetate. Additionally, both reactions were also carried out at 469 K in a trickle bed reactor (Fig. 1), which represents a combination of catalytic reaction with continuous extraction (Soxhlet-like). In doing so, the zeolite was placed in the reflux of the condensing reaction mixture. All reactions were carried out in dry nitrogen atmosphere.

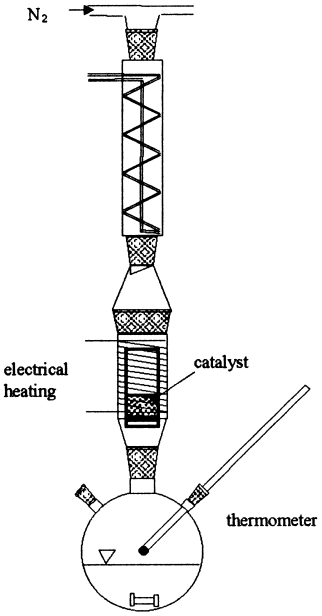


Fig. 1. Trickle bed reactor.

3. Results and discussion

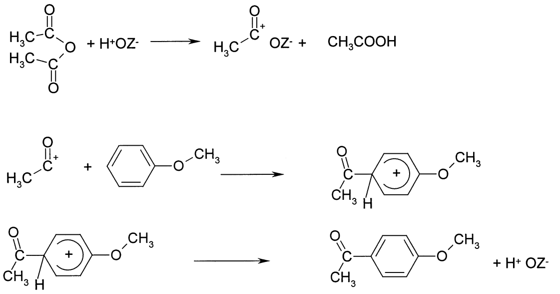
3.1. Intermolecular acylation

A comparison of the catalytic activity and the selectivity of H-Beta, H-Y, NH_4-Y, and H-ZSM-5 zeolites is presented in Table 1. The 10-ring pores of H-ZSM-5 (t=240 min, $X_{anisole}$=14.2 wt%) are probably too small for penetration of the aromatic compounds or the intersections of the channels limit the formation of the transition state. The 12-ring pores of both H-Y and H-Beta zeolites should have similar activities. H-Beta was found to be the most active catalyst in all the reactions. The selectivity of *p*-methoxyacetophenone (MAP) was higher than 99%, which underlines the shape selectivity of the H-Beta zeolite. Only trace amounts of the *ortho*-isomers could be detected. By-products, indicating a scission of C–O bond of anisole like methanol and phenol, were not observed.

Table 1
Liquid phase Friedel–Crafts acylation of anisole with acetic anhydride

Zeolite	Conversion (mol%)	Selectivity[a] (mol%)	
		o-MAP	*p*-MAP
NH_4-Y	3.6	3.7	96.3
H-Y	16.4	3.3	96.7
H-ZSM-5	14.2	1.3	98.7
H-Beta	67.9	0.5	99.5
H-Beta (dealuminated)	68.3	1.5	98.5

Conditions: 1.5 g zeolite, T=388 K, t=240 min, solvent: 30 ml toluene, 0.1 mol anisole, and 0.1 mol acetic anhydride.
[a] *o*-, *p*-MAP: *ortho*- and *para*-methoxyacetophenone, respectively.



Scheme 3. Reaction mechanism of MAP formation on zeolite. OZ^- – zeolite lattice.

The acylation reaction should proceed through an acylium intermediate which is formed via an attack of the proton of the Brönsted acid site to the nucleophilic carbonyl group of acetic anhydride. The acylium ion reacts with anisole giving a Wheland type intermediate. The size of the intermediate is about 290 Å^3 [10], which is larger than the intersection of the channels in ZSM-5 type zeolites (150 Å^3 [10]). The constraint environment should also determine the preferential formation of *p*-MAP. In the final step MAP desorbs and the zeolitic acidic site is restored (Scheme 3).

In a typical run, using toluene as a solvent, the activity of zeolite H-Beta depends strongly on the reaction time. In the initial period (t<100 min), the conversion was about 60 wt%, following this the rate declined and after 300 min the conversion degree remained constant at about 68 wt% (e.g. Fig. 2). The observed results were in agreement with the results in the literature [8,10].

Comparing the activity of NH_4-Y with those of the H-Y zeolite it seems that the presence of Brönsted acidic sites is a necessary prerequisite for the catalytic activity. On the other hand, dealumination of H-Beta zeolite, i.e. reduction of the number of Brönsted acidic sites, accompanied with an increase in the acidic strength, did not favour a further increase in catalytic

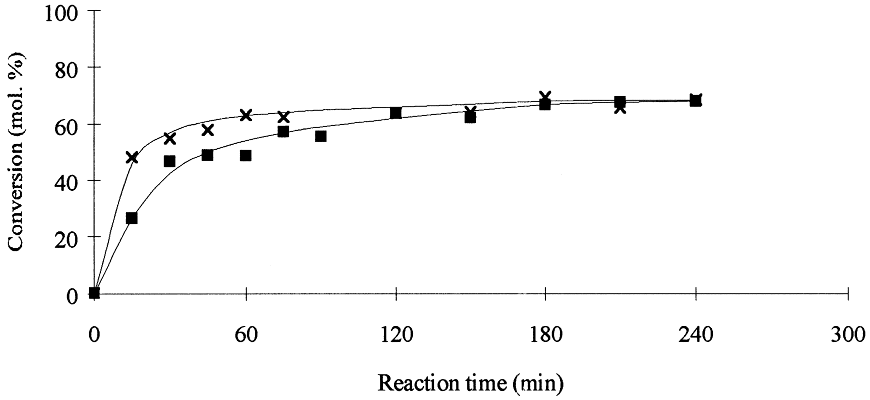


Fig. 2. Acylation of anisole with acetic anhydride on (■) H-Beta and (×) dealuminated H-Beta zeolite.

activity. These results are in agreement with data published by Harvey et al. [8], who studied the same reaction on several zeolites.

However, H-Beta and H-Beta (dealuminated) zeolites differ in their kinetic behaviour (Fig. 2). The dealuminated H-Beta zeolite (t=15 min, X_{anisole}=48.1 mol%) shows a higher activity in the initial period compared to the H-Beta zeolite (t=15 min, X_{anisole}=26.4 mol%), whereas at longer reaction times both curves only slightly differ and the slopes approach zero.

This behaviour could be explained by different factors. Besides changes in acidity, dealumination is accompanied by changes in pore distribution. The improved diffusion in the initial period could be due to a higher activity until coking reactions dominate. Furthermore, the shape of the curve indicates the equilibrium nature of the acylation reaction. However, using p-methoxyacetophenone as a substrate, no conversion was observed at the same reaction conditions. Moreover, without any solvent the conversion of anisole with acetic anhydride was nearly complete. This result correlates with data already published in the literature [8].

Consequently, the decrease in activity should be attributed either to coke deposition or mass transfer limitations. The latter was proved using different types of mixers, but no differences in catalytic behaviour was observed.

The change of catalyst's colour from white to dark brown was also an indication of coking. When studying the influence of coke formation, the spent catalyst was exposed to fresh reaction mixture (Fig. 3). Surprisingly, the catalyst was still active, i.e. the loss in

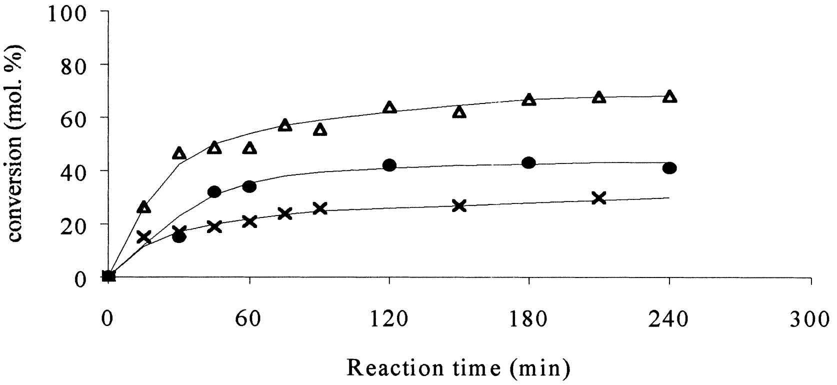


Fig. 3. Acylation of anisole with acetic anhydride on H-Beta zeolite: (△) activated zeolite; (×) used zeolite with fresh reaction mixture; (●) used zeolite, extracted with CH_2Cl_2, with fresh reaction mixture. Conditions: batch reactor; solvent: toluene; T=388 K, 1.5 g zeolite, 0.1 mol anisole, and 0.1 mol acetic anhydride.

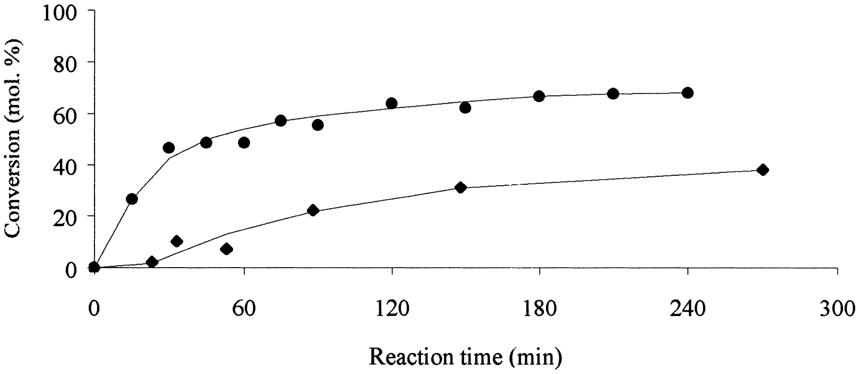


Fig. 4. Comparison of acylation of anisole with acetic anhydride in batch (●) and trickle bed reactor (◆), respectively. Conditions: T=388 K, solvent: toluene, 1.5 g H-Beta, 0.1 mol anisole, and 0.1 mol acetic anhydride.

activity of the activated H-Beta zeolite was probably caused by the deposition of higher molecular compounds ("coke"). The fresh reaction mixture added was able to extract those compounds, the desorption of which was hindered. Additionally, after a typical run, the coked catalyst was ex situ extracted with dichloromethane and used in a second run, demonstrating that the activity was further improved. When used catalyst was regenerated in air at 770 K for 4 h, the initial activity was completely restored, i.e. the non-extractable coke forming compounds were removed by oxidation. Therefore, two types of coke exist in the channel system and/or on the external surface: (i) extractable ("reversible"), and (ii) non-extractable ("irreversible") coke.

In order to proof this hypothesis, a further increase in activity should be expected, if the zeolite was continuously extracted. In a Soxhlet-like extractor (Fig. 1), the zeolite was placed in the reflux of the condensing reaction mixture. However, the conversion was lower compared to the batch experiment (Fig. 4). This is probably caused by the different vapour pressures of both reactants at the boiling temperature of the reaction medium (T=388 K). Therefore, the composition of the reflux differed from those of the liquid phase.

In studying an intramolecular reaction, e.g. Fries rearrangement, this obstacle should be overcome.

3.2. Intramolecular Fries rearrangement

Fig. 5 depicts the conversion of phenyl acetate in dependence on the amount of zeolite used and the type of reactor applied. In the initial period, the conversion in the batch reactor is higher than in the trickle bed reactor, which is caused by the higher heat capacity of the latter. After 15 min, the reactor reached steady state and the conversion exceeded those in the batch reactor, i.e. the concept of combination of reaction and extraction could successfully be applied to the rearrangement reaction. Furthermore, the higher the catalyst to reactant ratio the higher the conversion. When comparing the results with literature data for liquid phase Fries rearrangement of phenyl acetate, the high conversion in trickle bed reactor was realised in a shorter time at significantly higher reactant to catalyst ratio. Harvey et al. [8] reported that under batch conditions, a conversion degree of 50% was obtained on H-Beta zeolite only after 24 h. Similar results were published by Vogt et al. [16]. Therefore, the permanent treatment of the zeolite with condensed reaction mixture improves the mass transfer. Since the linear flow rate relative to the fixed zeolite is very low, the internal mass transport is probably improved by extracting higher molecular coke precursors. The expected effect of the continuous extraction should be improved by using different solvents. However, as shown in Table 2, the addition of solvents was accompanied by the change of reaction temperature, i.e. the influence of the solvent could not be separated.

3.2.1. Reaction scheme

The initial selectivities of phenol, p-acetoxyacetophenone and o-hydroxyacetophenone are different from zero, meaning that they are primary products

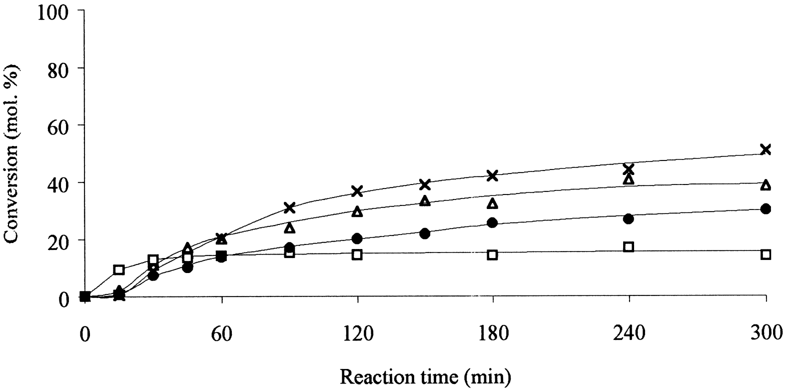


Fig. 5. Influence of the type of reactor (batch (□) and trickle bed (●), and the amount of H-Beta zeolite (□), (●) 2.0 g; (△) 4.0 g; (×) 6.0 g) on its activity in the Fries rearrangement of phenyl acetate at 469 K.

Table 2
Fries rearrangement of phenyl acetate over H-Beta in a trickle bed reactor in different solvents

Solvent	Temperature (K)	Conversion (mol%)	Selectivity[a] (mol%)			
			Phenol	*p*-AAP	*p*-HAP	*o*-HAP
Chlorobenzene	428	1.5[b]	53.0	33.0	0.0	15.0
Decane	444	16.6	35.4	32.9	6.0	25.0
Without	469	30.0	26.2	33.9	18.4	19.4
Sulpholane	491	44.0	29.3	38.0	22.0	10.0

Conditions: 2.0 g zeolite, 40 ml solvent, 0.35 mol phenyl acetate, reaction time: 300 min.
[a] *p*-AAP: *p*-acetoxyacetophenone; *p*-HAP: *p*-hydroxyacetophenone; *o*-HAP: *o*-hydroxyacetophenone.
[b] t=120 min.

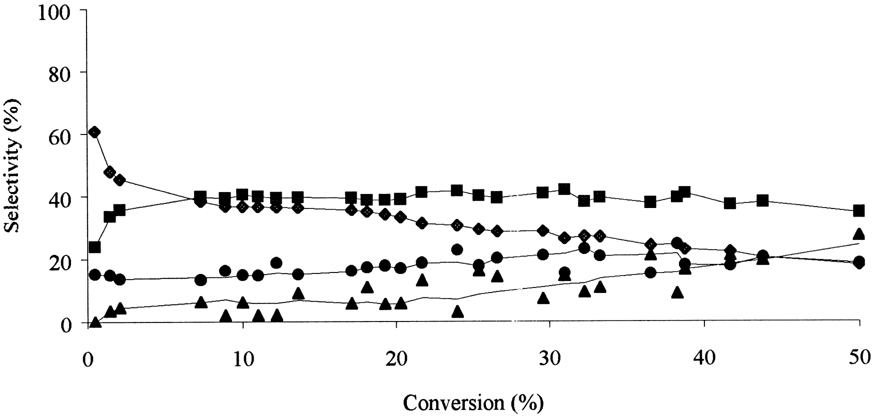
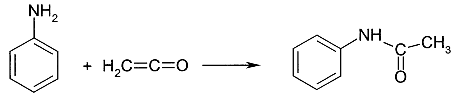


Fig. 6. Selectivity vs. conversion of phenyl acetate at 471 K: (◆) phenol, (■) *p*-acetoxyacetophenone, (●) *o*-hydroxyacetophenone, (▲) *p*-hydroxyacetophenone.

of a Fries rearrangement of phenyl acetate (Fig. 6), while *p*-HAP is a secondary one. *o*-HAP can result from an intramolecular rearrangement of phenyl acetate on a Brönsted acidic site of the zeolite. The acidic centre will be restored after the desorption of *o*-HAP.

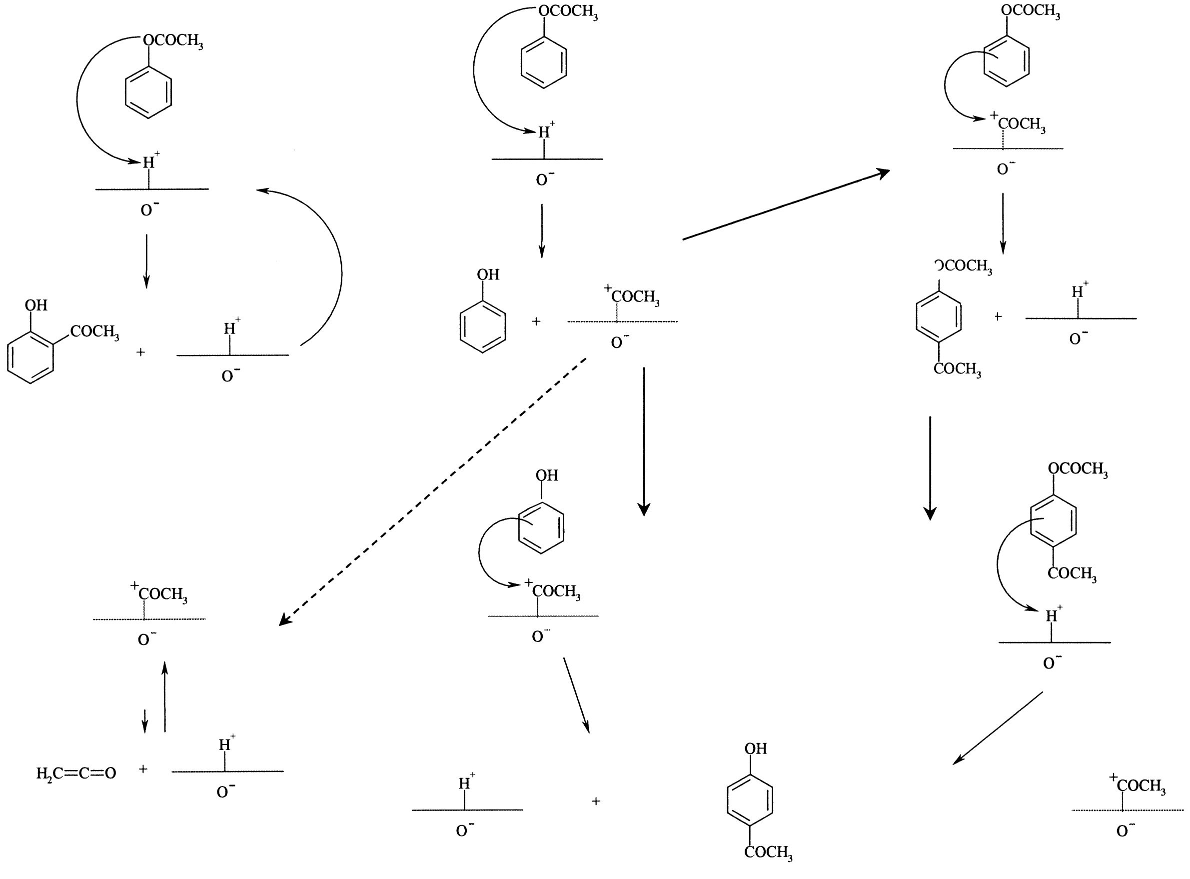


Scheme 4. Proposed reaction mechanism for the conversion of phenyl acetate on H-Beta zeolite.

On the other hand, the acidic hydroxyl group catalyses the scission of the ester bond (Scheme 5). Phenol desorbs and an acylium ion remains on the surface. The acylium ion is able to form HAP through direct C-acylation of phenol [17]. The proposed mechanism suggests that the phenol to acetoxyacetophenone ratio should be close to one. During the initial period it is greater than one. This means that phenyl acetate decomposes into phenol plus acetic acid (which would require moisture) or more likely into phenol plus ketene. Indeed, when traces of water were excluded, the ratio was close to one. With increasing conversion, the ratio becomes lower than one. This could be an indication that phenol could be involved in the coke formation. An interesting feature is that the addition of small amounts of phenol had no accelerating influence on the formation of HAP.

In the case of reaction with phenyl acetate, AAP is formed. The *ortho* to *para* ratio should depend on the spatial constraints in the intersection of the zeolitic channels. In the absence of water, the acidic attack of the zeolitic proton to the ester bond of AAP leads to HAP and to a new acylium ion on the surface.

At higher temperature, the acylium ion decomposes giving ketene which plays an important role in gas phase reaction [18,20]. At moderate temperature of liquid phase conditions, this reaction is not favoured. When the nitrogen flow was passed through the trickle bed reactor, trace amounts of ketene were confirmed



Scheme 5. Formation of acetanilide.

by its reaction with aniline (Scheme 4). Thus, we conclude that under the present reaction conditions, ketene is only present in the adsorbed state.

Summarising the proposed mechanism, the following model can be drawn. The formation of *p*-HAP requires a well-balanced coverage of the zeolitic surface with protons and acylium ions. Brönsted sites catalyse the ester scission of phenyl acetate and acetoxyacetophenone to phenol and HAP, respectively, and an acylium ion (adsorbed ketene). The acylated surface centres act as C-acylating agent for phenol (to HAP) and phenyl acetate (to AAP) restoring Brönsted acidic sites. Therefore, only *o*-HAP is produced by intramolecular Fries rearrangement. The intermolecular transacylation gives *o*-HAP, *p*-HAP and *p*-AAP. However, the *o*- to *p*-HAP ratio should depend on the steric constraints of zeolitic channels, which also explains the absence of *o*-acetoxyacetophenone.

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