Origin of catalyst deactivation in Fries rearrangement of phenyl acetate over zeolite H-Beta

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Abstract

The catalytic activity of zeolite H-Beta during the Fries rearrangement of phenyl acetate (PA) was investigated. Experiments were carried out in a batch reactor. It is shown that the decline of activity of the catalyst is associated with inhibition by the phenolic product compounds (phenol and hydroxyacetophenons). The long-term deactivation is caused by coking.
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Keywords: Phenyl acetate; Zeolite; Deactivation; Adsorption

1. Introduction

The Fries rearrangement of aryl esters is an important Friedel–Crafts acylation reaction yielding aromatic ketones [1], which are valuable intermediates in the synthesis of pharmaceuticals (e.g. paracetamol) [2], perfumes (e.g. musk) [3], acetophenone resins [4], etc. Commercially, Fries rearrangement reactions are carried out homogeneously catalysed using either an over-stoichiometric amount of metal halides (e.g. aluminium chloride) or mineral acids such as hydrofluoric acid. This results in substantial amounts of by-products such as acid sludge, which is expensive to dispose off, undesired co-product salts from hydrolysis of the product: metal halide complexes, safety problems handling the highly toxic hydrofluoric acid as well as corrosion problems.

Acid zeolites may become an alternative to homogeneous catalysts for the Fries rearrangement with the additional advantages of easy separation and regeneration of the catalyst. The acid zeolite catalysed Fries rearrangement of phenyl acetate (PA) yielding phenol, *ortho*-hydroxyacetophenone (*o*-HAP), *para*-hydroxyacetophenone (*p*-HAP) and *para*-acetoxyacetophenone (*p*-AAP) has been studied in quite a detail [5–7]. Scheme 1 shows the proposed reaction pathway

[6–8]. *o*-HAP can be formed via an intra-molecular rearrangement of phenyl acetate. In a parallel reaction, the acid catalysed ester cleavage of phenyl acetate yielding phenol and a surface bound acylium ion takes place. The reaction of the phenol with the acylium ion leads to the formation of *p*-HAP and *o*-HAP. The reaction of phenyl acetate with the acylium ion leads selectively to the formation of *p*-AAP. The latter can decompose yielding *p*-HAP and an acylium ion.

A major problem with the zeolite catalysed Fries rearrangement is rapid catalyst deactivation. This has been attributed either to the formation of high-molecular by-products ("coke") [9–11] or accumulation of phenol in the zeolite pore system [12].

The formation of coke was suggested to occur through the irreversible polymerisation of highly reactive ketene [13], which would be formed by the decomposition of the adsorbed acylium ion (Scheme 2) [7]. Rohan et al. [12] investigated the origin of the deactivation in the Fries rearrangement of phenyl acetate on zeolite H-Beta extracting the deactivated catalyst with methylene chloride and dissolving it in concentrated hydrofluoric acid. The extract consisted mainly of phenol and only small amounts of high-molecular by-products, such as bisphenol A and substituted phenyl benzoates. Thus, it was concluded that the access of phenyl acetate to the internal acid sites is limited by filling the pores with phenol, which finally results in the deactivation of the catalyst.

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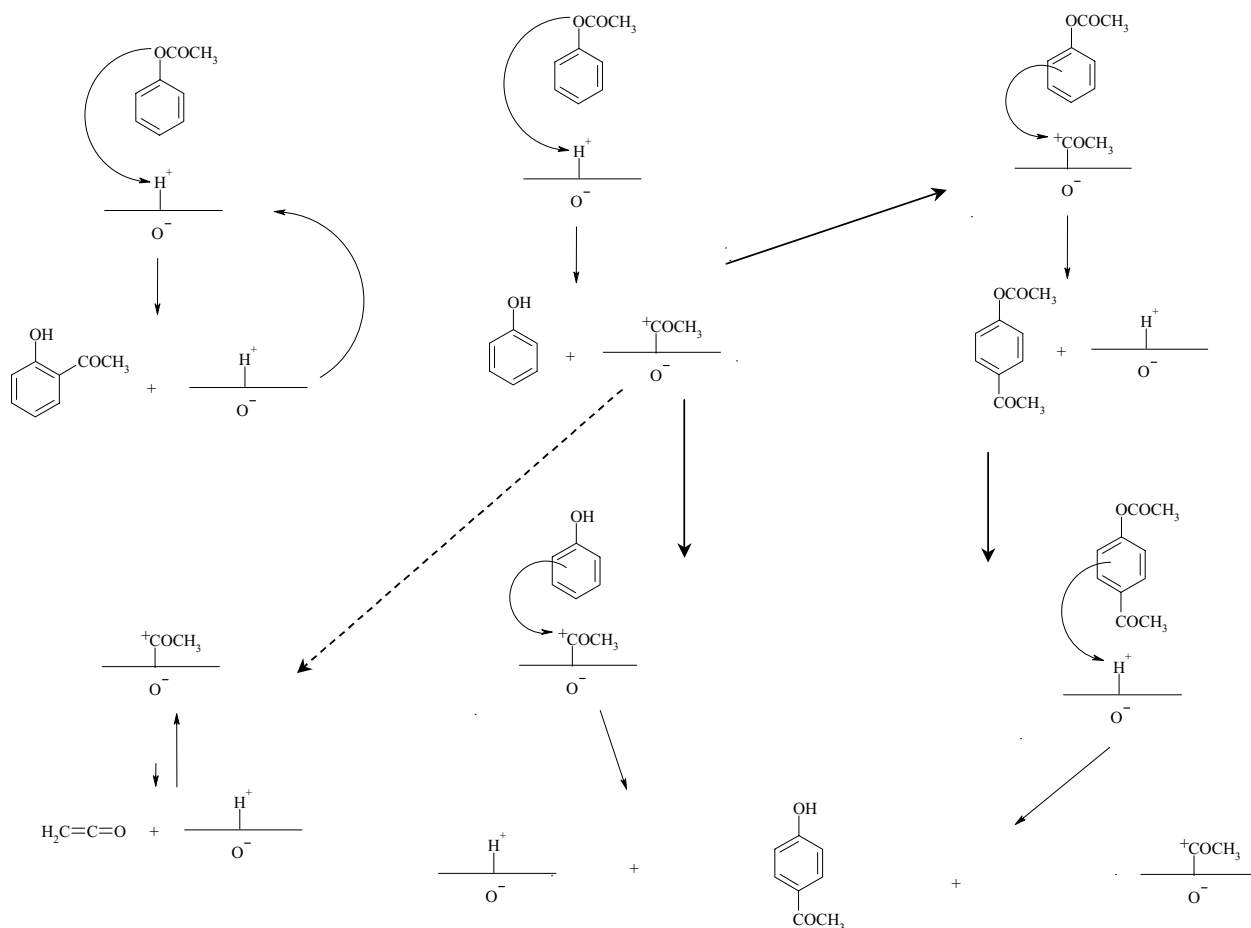
Scheme 1. Proposed reaction mechanism for the Fries rearrangement of phenyl acetate on H-Beta zeolite.
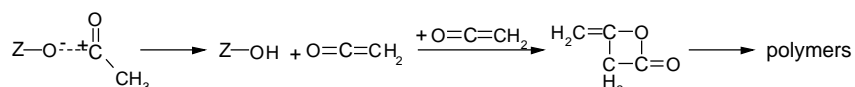
Scheme 2. Formation of ketene via an acylium ion with following dimerisation giving diketene and polymers.

This study focuses on identifying the origin of catalyst deactivation testing the two hypotheses presented in literature up to date, viz. "coke" formation via ketene and phenol blockage, utilising reaction data and investigating the influence of phenol and other product compounds on the Fries rearrangement of phenyl acetate.

2. Experimental

Fries rearrangement of phenyl acetate was investigated using zeolite H-Beta (Süd-Chemie AG; Si/Al = 12.5). Two grams of fresh zeolite were activated in flowing nitrogen at 623 K for 2 h. Subsequently, the catalyst was cooled down to 473 K and rapidly transferred into the reactor under nitrogen.

Phenyl acetate (0.35 mol (47.65 g)) were loaded to the reactor. The reaction was performed at 452 K in a jacketed vessel using boiling 1,2-dichlorobenzene boiling under re-

flux as the heat transfer medium, guaranteeing invariant reaction temperature independent of the composition of the reaction mixture. All reactions were performed under nitrogen atmosphere at ambient pressure.

Samples ($\sim$150 µl) were withdrawn from the reaction mixture at regular intervals and analysed using a Perkin-Elmer Autosystem gas chromatograph with flame ionisation detector. Compounds were separated on a HP-5 MS capillary column (length 30 m, internal diameter 0.25 mm, film thickness 0.25 µm). Conversion and selectivities were calculated using response factors of all detected compounds.

3. Results and discussion

Fig. 1A shows conversion in the Fries rearrangement of phenyl acetate as a function of reaction time. Selectivity to the major products as a function of phenyl acetate conver-
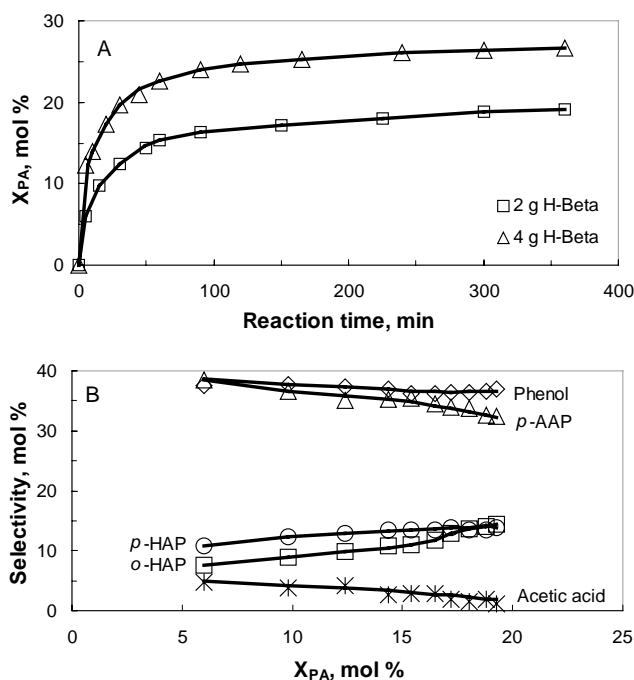
Fig. 1. Activity (A) and selectivity (B) in Fries rearrangement of phenyl acetate over zeolite H-Beta (Si/Al = 12.5) at 452 K as a function of reaction time and conversion, respectively.

Fig. 2. Molar ratio of p-AAP plus acetic acid relative to phenol in Fries rearrangement of phenyl acetate over zeolite H-Beta (Si/Al = 12.5) at 452 K as a function of reaction time.

sion (X_{PA}) is displayed in Fig. 1B. The selectivity to phenol and p-AAP is high and decreases with increasing conversion. Acetic acid is formed in appreciable amounts but constant yield over reaction time. Acetic acid can be formed via hydrolysis of the phenyl acetate with traces of water present in the reaction system.

The phenyl acetate conversion does not exceed 20% after 360 min. This low level cannot be due to thermodynamic limitations, since the gas phase equilibrium constant for the conversion of phenyl acetate to p- and o-HAP is higher than 70 (with p-HAP/o-HAP ≈ 2) [14]. In addition, when applying a higher catalyst to feed ratio the final conversion is higher (Fig. 1A). Hence, the limited conversion in the base experiment must be ascribed to catalyst deactivation. Catalyst deactivation can further be seen by the change in the slope of the conversion-time plot during the first 50 min indicating a strong decrease in the rate of reaction with increasing reaction time. This strong decrease cannot be explained by the change in the concentration of phenyl acetate.

In gas phase experiments [10,15], the deactivation of the zeolite is explained in terms of ketene formation from the decomposition of surface acylium ions (see Scheme 2). Ketene represents a very active molecule, which can dimerise to diketene [16] and further polymerise to high molecular weight compounds [15,17], which block the active sites.

Therefore, the analysis of the acylium ion balance during the course of the reaction should provide information on the acylium ion consumption for polymeric products.

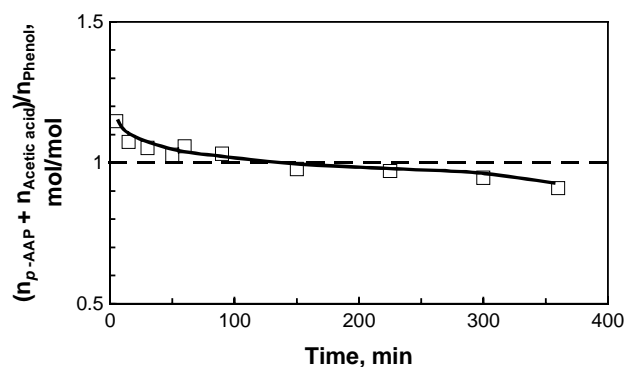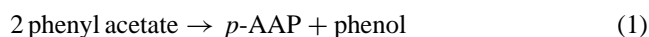According to Scheme 1 cleavage of phenyl acetate leads to phenol and an acylium ion. The acylium ion can then react with another phenyl acetate molecule to yield p-AAP (Eq. (1)). Additionally, phenol can be formed by hydrolysis of phenyl acetate with acetic acid as co-product (Eq. (2)).

$$2 \text{ phenyl acetate} \rightarrow p\text{-AAP} + \text{phenol} \qquad (1)$$

$$\text{phenyl acetate} + H_2O \rightarrow \text{acetic acid} + \text{phenol} \qquad (2)$$

For stoichiometric reasons the molar ratio of p-AAP plus acetic acid to phenol must be equal to one, if the acylium ion only yields p-AAP or acetic acid. If the molar ratio of p-AAP plus acetic acid to phenol is lower than one, the acylium ion has reacted to other products, e.g. higher molecular weight products ("coke"). If the ratio is higher than one, the deficit of phenol can be explained by its adsorption on the zeolite. Fig. 2 demonstrates the change of this ratio as a function of reaction time.

It appears that initially a larger amount of p-AAP and acetic acid is present in the reaction mixture than expected based on reaction stoichiometry. This higher initial ratio indicates adsorption of phenol. The ratio decreases with increasing reaction time and increasing conversion, respectively. After 150 min the ratio equals one. By then the rate of phenyl acetate consumption has already slowed down significantly (compare Fig. 1A) indicating that the formation of higher molecular weight compounds from acylium ions (via ketene) does not contribute significantly to the initial deactivation. Hence, it is concluded that the initial, major decline in activity is due to adsorption of phenol and other initially formed products.

After ca. 150 min the ratio falls below one indicating that from then onwards it is the acylium ion which is consumed with preference forming high molecular compounds which do not desorb under reaction conditions.

The general trend of the molar ratio of p-AAP plus acetic acid relative to phenol as a function of reaction time has been confirmed for the Fries rearrangement applying zeolite H-Beta with different Si/Al ratios [18].

In order to test the hypothesis of inhibition through adsorption of phenol [12], Fries rearrangement of phenyl acetate was performed adding 0.35 mol of phenol to the fresh
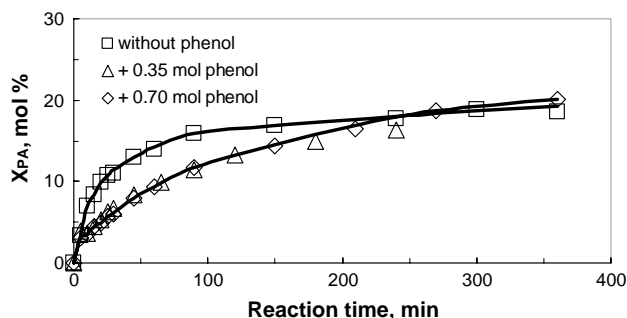
Fig. 3. Influence of phenol on conversion in the Fries rearrangement of phenyl acetate on zeolite H-Beta (Si/Al = 12.5) at 452 K as a function of reaction time.
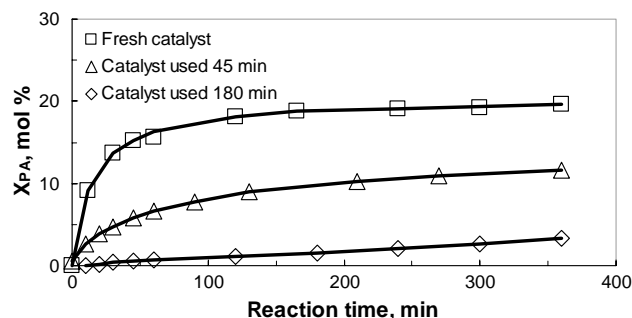

Fig. 4. Activity of fresh and used zeolite H-Beta (Si/Al = 12.5) in the Fries rearrangement of phenyl acetate at 452 K as a function of reaction time.

reaction mixture (see Fig. 3). The presence of phenol right at the beginning of the reaction reduces the reaction rate. In order to check the influence of dilution, the amount of added phenol was doubled from 0.35 to 0.70 mol (thereby reducing the initial concentration of phenyl acetate from 4.4 to 2.9 mol/l). However, adding more phenol did not affect the conversion-time profile and thus the rate of reaction. Thus, it is concluded that phenol slows down the rate of reaction (probably either by competitive adsorption or by retarding the intracrystalline diffusion of phenyl acetate in the highly occupied pore system). However, this effect does not result in an ultimate deactivation of the catalyst.

Experiments were conducted in order to find out if the deactivation of the catalyst in the Fries rearrangement of phenyl acetate is caused by non-identified reaction products. After the first experiment the reaction product was separated from the spent catalyst (see Table 1, row 1 for the composition of the starting mixture, conversion and phenol selectivity) and added to a fresh batch of catalyst and phenyl acetate (Table 1, starting mixture, row 2). After 360 min reaction time, conversion in this batch was marginal (ca. 4%, Table 1, row 2), i.e. far lower than would result from dilution effects only. For the third experiment, a "synthetic" reaction mixture was prepared (Table 1, row 3) and fresh catalyst was added. After 360 min conversion was low again (ca. 3%). This strongly suggests that one or more of the reaction products considered in the "synthetic mixture" are responsible for the strong deactivation. Since phenol was found just to slightly retard conversion of the phenyl acetate, the acylated

products must be responsible for most of the initial deactivation of the zeolite.

p-AAP is one of the bulky product compounds, which may block the pores or active sites of H-Beta. In order to investigate whether this compound may cause the strong slow-down of the reaction rate, the conversion of *p*-AAP with phenol (Eq. (3)) was investigated (Table 1, row 4).

$$\text{phenol} + p\text{-AAP} \rightarrow p\text{-HAP} + \text{phenyl acetate} \qquad (3)$$
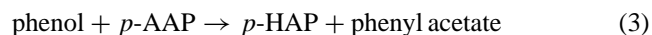
This is in fact the reverse of the phenyl acetate disproportionation step and appears to be an easy reaction, since a conversion of 84% of *p*-AAP was achieved only after 45 min ($S_{p\text{-HAP}} = 48$ mol%; $S_{\text{PA}} = 43$ mol%; $S_{\text{acetic acid}} = 9$ mol%). The high rate of *p*-AAP conversion suggests that the strong slow-down of the rate of conversion of phenyl acetate in the Fries rearrangement is caused by the strong adsorption of one of the other product compounds.

The strong adsorption of a product compound is not the only mechanism of deactivation taking place in the Fries rearrangement of phenyl acetate. As shown above in the discussion of the ratio of *p*-AAP and acetic acid to phenol (see Fig. 2) the formation of higher molecular weight compounds could also contribute to deactivation. This is corroborated by the use of spent catalyst for the Fries rearrangement (Fig. 4). For this purpose, the reaction was stopped after 45 min ($X_{\text{PA}} = 15\%$). The reaction mixture was decanted and fresh phenyl acetate (0.35 mol, as loaded initially) was added. In this run, a conversion of 12% instead of 19% as in the base case was obtained after 360 min. This indicates

Table 1
Fries rearrangement of phenyl acetate and disproportionation of *p*-AAP with phenol over zeolite H-Beta (2.0 g) at 452 K after 360 min

Starting mixture (mol)						X_{PA} (%)	S_{phenol} (mol%)
Phenyl acetate	Phenol	*p*-AAP	*p*-HAP	*o*-HAP	Acetic acid		
0.35	–	–	–	–	–	39.6[a]	27
0.56	0.020	0.020	0.013	0.010	0.001	4.3	66
0.35	0.060	0.070	0.050	0.040	0.006	3.1	74
–	0.350	0.350	–	–	–	84.0[b]	–

[a] The reaction was carried out in a modified reactor (for details see [19]).
[b] Conversion of *p*-AAP after a reaction time of 45 min, after which the conversion did not increase significantly.

that the catalyst was partially deactivated. When a catalyst was used which had been operated for 180 min, a conversion of fresh phenyl acetate of only 3% was observed, i.e. this catalyst was almost completely deactivated.

Despite the marginal change in conversion in the runs with reduced reaction time ($t = 45$ min: $X_{PA} = 15\%$ versus $t = 180$ min: $X_{PA} = 18\%$) reduced catalyst activities in the subsequent runs are clearly pronounced. Under the reaction conditions applied structural changes of the zeolite Beta can be excluded. Therefore, the different activities have to be explained by the formation of different reaction products. It is concluded that during the initial period of reaction catalyst deactivation can be ascribed to the strong adsorption of one or more product compounds (product inhibition), most likely the phenolic compounds (vide supra). When adding fresh phenyl acetate they are extracted from the catalyst so that the catalyst activity is mostly regained. After longer reaction times, higher molecular weight compounds may form (via ketene) as can be deduced from the ratio of *p*-AAP plus acetic acid to phenol (see Fig. 2). These compounds cannot be extracted and thus a permanent deactivation is observed.

4. Conclusions

It was demonstrated that different deactivation processes affect the activity of zeolite H-Beta applied in liquid phase Fries rearrangement of phenyl acetate.

It was found that the phenolic products (phenol, *p*-HAP and *o*-HAP) are strong inhibitors of phenyl acetate conversion (product inhibition). While all the phenolic compounds contribute to reaction inhibition during the initial reaction period, phenol is replaced by competitive adsorption of *p*-HAP and *o*-HAP after a longer reaction time, when they have been formed to a greater extent. This is indicated by the ratio of *p*-AAP plus acetic acid to phenol initially being higher than one and its constant decline with increasing duration of the reaction. This conclusion is supported by the effect of addition of a "synthetic" product mixture to the reaction system. Acetates (phenyl acetate and *p*-AAP) were found not to contribute relevantly to this inhibition.

The deactivation by higher molecular weight products ("coke") formed via ketene only plays a role after prolonged reaction time and leads to irreversible deactivation of the catalyst as indicated by the decline of the ratio of *p*-AAP plus acetic acid to phenol below one and the reduced activity of used catalysts.

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