

Propionylation of phenol to 4-hydroxypropiophenone over zeolite H-beta

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Abstract

The liquid phase propionylation of phenol (Ph) with propionyl chloride (PC) has been studied over zeolite H-beta, Re-Y, H-Y, mordenite, H-ZSM-5 and AlCl₃ at 413 K. H-beta catalyzes the reaction to 4-hydroxypropiophenone (4-HPP), 2-hydroxypropiophenone (2-HPP) and phenylpropionate (PP) as major products. H-beta is found to be superior to other zeolite catalysts and AlCl₃. The product distribution largely depends upon the reaction conditions and acidity of the zeolite catalysts. The acidity of the zeolite catalysts was measured by the temperature programmed desorption of ammonia. The conversion of phenol remains nearly constant due to the rapid formation of PP. The yield of the 2-HPP and 4-HPP increases with the increase in reaction time, H-beta to Ph (w/w) ratio, reaction temperature and phenol:PC molar ratio. The H-beta was recycled two times and a decrease in the yield of 2-HPP and 4-HPP was observed after each recycle. Plausible reaction pathways are proposed for the formation of PP, 2-HPP, 4-HPP and 4-propionyloxypropiophenone (4-PXPP) using zeolite as catalyst. Mostly, the reaction pathways are found to be similar to that of acetylation of phenol. The *O*-propionylation of phenol is much faster than the *C*-propionylation. The PP results from the rapid *O*-propionylation of phenol with PC. 2-HPP is produced through the Fries rearrangement of PP, propionylation of phenol with PP and direct *C*-propionylation of phenol with PC. 4-HPP is produced by the reaction of 4-PXPP with zeolite hydroxyl groups, small amount of 4-HPP is also produced through the direct propionylation phenol with PC and propionylation of phenol with PP, whereas formation of 4-PXPP takes place by the bimolecular reaction of two PP molecules. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Propionylation of phenol; Zeolite H-beta; 4-Hydroxypropiophenone

1. Introduction

4-Hydroxypropiophenone (4-HPP) and 2-hydroxypropiophenone (2-HPP) are used as intermediate for the manufacture of perfumes, pharmaceuticals and as UV adsorbent [1]. The *o*- and *p*-acylated products of phenol have been made from the direct reaction

of phenol with acylating agent or by the Fries rearrangement of aryl esters using Lewis acid catalyst, AlCl₃ [2–4]. The use of conventional catalyst, AlCl₃, causes important environmental problems and involves a tedious work up procedure. Zeolites have been used in the acylation of aromatics [5–17] due to their activity, shape selectivity, reusability, and easy separation from the reaction products. Recently, few studies have been reported on the direct acetylation of phenol over zeolite H-ZSM-5 [18–20] and Fries rearrangement of phenyl acetate over zeolite H-beta

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[21,22]. However, there is no report yet on the direct propionylation of phenol using zeolite catalysts and particularly H-beta. It is reported that Fries rearrangement of phenylacetate on H-ZSM-5 produces lower yield of smaller *p*-isomer than the *o*-isomer [18,23–26] and hence the second route (direct acylation of phenol) is preferable to achieve the higher yield for *p*-isomer. A reaction scheme is proposed for the propionylation of phenol with propionyl chloride using zeolite H-beta as catalyst which explain the formation of the main reaction products, e.g. PP, 4-HPP, 2-HPP and 4-propionyloxypropiofenone (4-PXPP) including the difference in the formation of 4-HPP and 2-HPP. In order to confirm the reaction pathways, additional experiments such as Fries rearrangement of PP and propionylation of phenol with equimolar quantity of PP were carried out at 413 K using zeolite H-beta. The objective of the present work is to replace the conventional Lewis acid catalyst AlCl_3 , with the solid zeolite catalyst and to achieve the 4-HPP in one step by the propionylation of phenol over solid zeolite H-beta catalyst. In addition, we report the results of the effect of various zeolite catalysts, duration of the run using zeolite H-beta, acidity of the zeolite catalysts, $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio, catalyst concentration, reaction temperature, molar ratio of the reactants and reuse of the zeolite H-beta on the formation of 4-HPP. The results obtained over various zeolites are compared with the conventional catalyst, AlCl_3 .

2. Experimental

2.1. Materials

Zeolites Na-Y and H-mordenite were obtained from Laporte Inorganics, Cheshire, UK. Zeolites ZSM-5 and H-beta were prepared using the methods described in the literature [27,28]. The synthesized zeolites were washed with deionized water, dried and calcined at 813 K for 16 h in the presence of air to eliminate the organic templates from the zeolite channels. The resultant samples were thrice NH_4^+ -exchanged for 8 h at 353 K. The NH_4^+ -exchanged samples were again calcined at 823 K for 8 h to get their protonic forms. Re-Y was prepared from Na-Y by exchange with 1 M NH_4NO_3 (three exchanges, 353 K, 8 h) and thus the resulting NH_4 -Y was treated with 5% rare earth

chloride solution by following the analogous method employed for other zeolites to get their protonic forms.

2.2. Characterization

The $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of various zeolites and degree of ion-exchange were carried out by a combination of wet and atomic absorption methods (Hitachi 800). X-ray powder diffraction (XRD) was carried out on a Rigaku, D-Max/III-VC model using the $\text{Cu K}\alpha$ radiation and was used to evaluate the peak positions of various zeolite samples. The surface area of the catalysts was measured by nitrogen BET method using an area meter. The size and morphology of the zeolite catalysts were estimated by scanning electron microscope (Cambridge Stereoscan 400).

2.3. Acidity measurements

Temperature programmed desorption measurements were carried out to measure the acid strength of the zeolite catalysts using ammonia as an adsorbate (Table 1) [29,30]. In a typical run, 1.0 g of a calcined sample was placed in a quartz tubular reactor and heated at 773 K under a nitrogen flow of 50 ml/min for 4 h. The reactor was then cooled to 303 K and adsorption conducted at that temperature by exposing the sample to ammonia for 30 min. Physically adsorbed ammonia was removed by purging the sample with a nitrogen stream flowing at 50 ml/min for 15 h at 303 K. Acid strength distribution was obtained by raising the catalyst temperature ($10^\circ\text{C}/\text{min}$) from 303 to 773 K in a number of steps in a flow of nitrogen (10 ml/min). The NH_3 evolved was trapped in an HCl solution and titrated with a standard NaOH solution (Table 1).

2.4. Catalytic reactions

The propionylation reactions were carried out batchwise in a glass reactor. Typically, 0.5 g of catalyst, 0.106 mol of phenol and 0.035 mol of PC were introduced. The reaction was continued for 4 h at 413 K. Product samples were analysed by a gas chromatograph (HP 6890) equipped with a flame ionisation detector and capillary column (50 m \times 0.2 mm) of methyl silicone gum. The products were

Table 1
Properties and acid strength distribution of zeolite catalysts

| Catalysts | SiO ₂ :Al ₂ O ₃ molar ratio (mol) | Degree of H ⁺ or Re ³⁺ exchange (%) ^a | Crystal size (μm) | Surface area (m ² /g) ^b | NH ₃ desorbed (m mol g ⁻¹ h ⁻¹) in various steps | | | | | NH ₃ chemisorbed at 303 K (m mol g ⁻¹) ^c |
|---------------------|--|--|----------------------|--|--|-----------|-----------|-----------|-----------|---|
| | | | | | 303–353 K | 353–433 K | 433–513 K | 513–653 K | 653–773 K | |
| H-beta | 26.0 | >98 | 0.5 | 745 | 0.14 | 0.24 | 0.05 | 0.16 | 0.16 | 0.75 |
| H-ZSM-5 | 41.0 | >98 | 0.4 | 413 | 0.55 | 0.16 | 0.05 | 0.26 | 0.21 | 1.21 |
| H-mordenite | 22.0 | >98 | 1.0 | 552 | 0.20 | 0.17 | 0.15 | 0.12 | 0.07 | 0.71 |
| H-Y | 4.1 | >98 | 1.0 | 615 | 0.29 | 0.55 | 0.49 | 0.11 | 0.01 | 1.45 |
| H-Re-Y ^d | 4.1 | >70.6 | 1.0 | 659 | 0.17 | 0.10 | 0.26 | 0.11 | 0.10 | 0.74 |

^a Cation-exchange (H⁺- or Re³⁺)-values reported as percent of the total cation sites, taken as the aluminium content 100%.

^b Measured by N₂ adsorption.

^c NH₃ chemisorbed at 303 K (m mol g⁻¹).

^d 70.6% Re³⁺-exchange in NH₄-Y-zeolite.

characterized by GC–MS and compared with authentic samples.

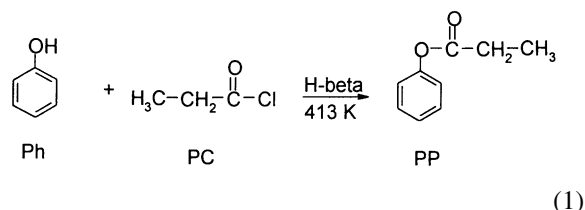
3. Results and discussion

The properties of zeolite catalysts are given in Table 1. The X-ray diffraction pattern of the zeolites match well with the literature values and are found to be highly crystalline. The scanning electron microscopy and surface area show that there is no pore blocking or amorphous material inside the channels and on the external surface of the zeolites.

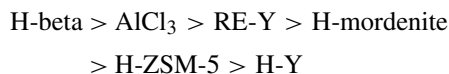
3.1. Activity of various catalysts

The propionylation of phenol with PC over H-beta, Re-Y, H-Y, H-mordenite, H-ZSM-5 and conventional catalyst AlCl_3 is investigated under atmospheric pressure at 413 K. The results of 4 h reaction time are summarized in Fig. 1. As is evident from the Fig. 1, the conversion of phenol remains nearly constant due the rapid formation of primary product phenylpropionate

(PP) (Eq. (1)).



The formation of various products (2-HPP, 4-HPP and 4-PXPP) is established by different reaction pathways (Eqs. (1)–(7)) [18–20]. Zeolite H-beta is found to be the most active in the formation of ring products and selective for 4-HPP among 4-HPP and 2-HPP (4-HPP:2-HPP = 1.9) catalyst to achieve higher yields of 2-HPP (2.8 wt.%) and 4-HPP (5.3 wt.%) compared to the other zeolite catalysts. The conventional catalyst, AlCl_3 , is less active and selective (4-HPP:2-HPP = 0.9) than H-beta and a higher yield of others (3.6 wt.%) is obtained over AlCl_3 due to its non-shape selective character. Re-Y sample produced lower yields of 2-HPP (1.0 wt.%) and 4-HPP (0.8 wt.%) than H-beta. However, Re-Y was found to be more active than H-Y, H-mordenite and H-ZSM-5. The higher activity of Re-Y in the formation of 2-HPP and 4-HPP compared to H-Y may be attributed to its higher strength of acid sites, which are generated by the exchange of Re^{3+} -cations in H-Y (Table 1) [12]. The lower activity of H-ZSM-5 (pore size = $6.0 \text{ \AA} \times 5.7 \text{ \AA}$ and $5.6 \text{ \AA} \times 5.4 \text{ \AA}$) in the formation of 2-HPP and 4-HPP may be due to its small pore openings than the size of the various reactants (intermediates), which are formed by different reaction pathways in the propionylation of phenol (Eqs. (1)–(7)). The catalysts used in the study show the following decreasing order of activity in the formation of hydroxypropionophenones (2-HPP and 4-HPP):



3.2. Acidity versus 2-HPP and 4-HPP formation

The effect of the number of acid sites and acid strength distribution of various catalysts on the formation of 2-HPP and 4-HPP in the propionylation of phenol are shown in Table 1 and Fig. 1. The formation of 2-HPP and 4-HPP over various catalysts not

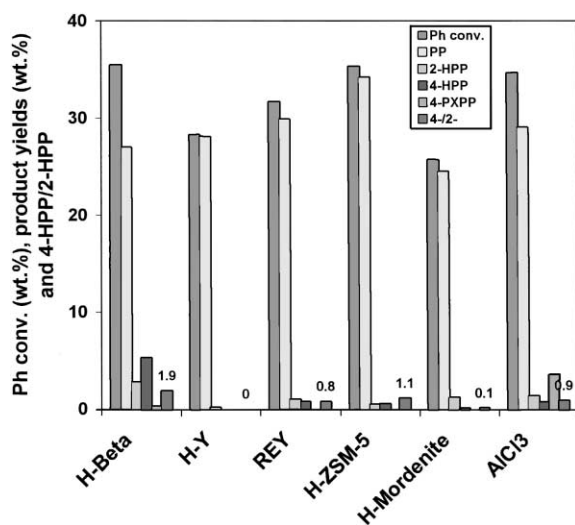


Fig. 1. Propionylation of phenol over various catalysts. Reaction conditions: catalyst = 0.5 g; phenol = 0.106 mol; PC = 0.035 mol; phenol:PC molar ratio = 3 mol; reaction temperature = 413 K; reaction time = 4 h. PP = phenylpropionate; Ph = phenol; 2-HPP = 2-hydroxypropionophenone; 4-HPP = 4-hydroxypropionophenone; 4-PXPP = 4-propionyloxypropionophenone; 4-/2- = isomer ratio of 4-HPP:2-HPP.

only seems to be dependent on the number of acid sites but also on their strength. On the very strong sites of the H-beta, the propionylation of phenol and intermediates produced during the propionylation such as PP and 4-PXPP transformed into the expected 2-HPP and 4-HPP (Eqs. (1)–(7)), which was not the case on the weak acid sites of the H-Y and H-mordenite (Table 1 and Fig. 1). The higher yields of 2-HPP and 4-HPP obtained over zeolite H-beta could be related to the presence of very strong acid sites compared to the other zeolite catalysts (Table 1 and Fig. 1).

The results indicate that the H-beta has high activity in the formation of 2-HPP and 4-HPP and selectivity for 4-HPP (4-HPP:2-HPP = 1.9) compared with other catalysts used in this reaction and hence further studies were carried out using zeolite H-beta to see the influence of various parameters on the yields of 2-HPP and 4-HPP and selectivity for 4-HPP in the propionylation of phenol.

3.3. Duration of the run

Fig. 2 shows the conversion of phenol, product yields and ratio of 4-HPP:2-HPP at 413 K using zeolite H-beta as a function of reaction time. It can be seen from the Fig. 2 that the conversion of phenol remains practically constant due to rapid for-

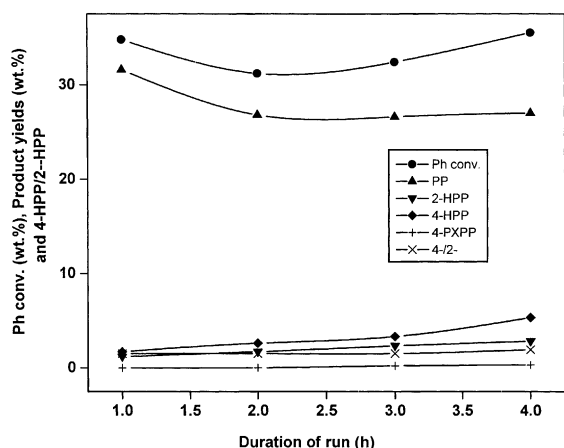


Fig. 2. Conversion of phenol and product yields as a function of reaction time. Reaction conditions: duration of run = 4 h; for other reaction conditions, see Fig. 1.

mation PP. However, the yield of 2-HPP, 4-HPP and 4-PXPP increases gradually but slowly with the progress of the reaction. The ratio of 4-HPP:2-HPP also increases from 1.5 to 1.9 when the reaction time was increased from 1 to 4 h, respectively. From the Fig. 2, it can be concluded that the *O*-acylation of phenol is much more rapid than the *C*-acylation [18–20]. Under the reaction conditions, PP was the predominant product along with 2-HPP, 4-HPP and 4-PXPP and the conversion of phenol was roughly proportional (32.4 wt.%) to the reactant molar ratio (Ph:PC = 3).

3.4. Influence of SiO₂:Al₂O₃ ratio of H-beta

H-beta used for the propionylation of phenol differs only in the SiO₂:Al₂O₃ that is in its acid strength. Increasing the SiO₂:Al₂O₃ ratio and thus decreasing the number of acid centers leads to a decrease in the yield of the ring products, i.e. the decrease in direct propionylation of phenol to ring products or transformation of *O*-acylated products to *C*-acylated products. The 4-HPP:2-HPP ratio also changes by varying the SiO₂:Al₂O₃ of H-beta (Fig. 3). The present study demonstrates that the conversion of phenol to the *C*-acylated products decreases as the SiO₂:Al₂O₃ ratio increases from 26 to 60 (Fig. 3).

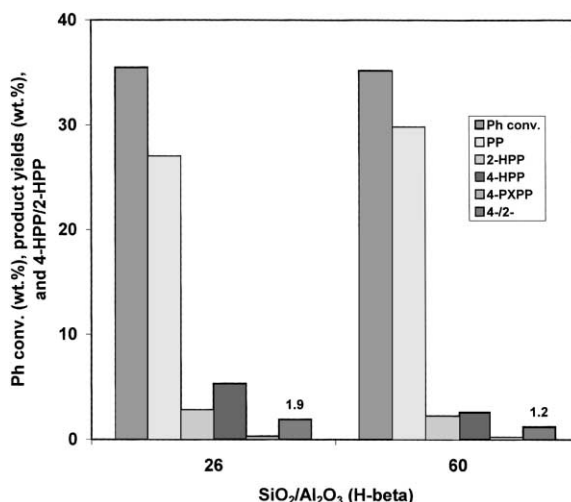


Fig. 3. Influence of SiO₂:Al₂O₃ ratio of H-beta on the conversion of Ph, product yields and 4-2-isomer ratio. Reaction conditions: reaction time = 4 h; for other reaction conditions, see Fig. 1.

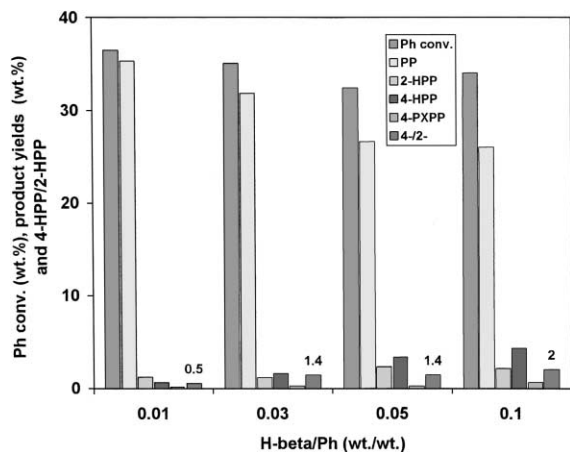


Fig. 4. Influence of H-beta:Ph (w/w) ratio on the Ph conversion, product yields and 4-:2-isomer ratio. Reaction conditions: reaction time = 3 h; for other reaction conditions, see Fig. 1.

3.5. Influence of catalyst concentration

Fig. 4 shows the conversion of phenol, yields of PP, 2-HPP, 4-HPP and 4-PXPP and 4-HPP:2-HPP ratio as a function of H-beta to phenol ratio (w/w) in the propionylation of phenol. The H-beta to phenol ratios are obtained by varying the amount of H-beta and keeping the constant concentration of phenol. The total surface area available for the reaction depends upon the loading of the catalyst. The conversion of phenol remains practically constant at all H-beta to phenol ratios. However, the yield of *O*-acylated product (PP) decreases from 35.3 to 26.0 wt.% with the increase in H-beta to phenol ratio (w/w) from 0.01 to 0.10. The decrease in the *O*-acylated product and simultaneously increase in the ring products with the increase in H-beta to phenol ratio may be due to the increase in medium and strong Brönsted acid sites which are available for the reaction. In the absence of catalyst mainly the *O*-acylated product is noticed. In addition, the 4-HPP:2-HPP ratio increases from 0.5 to 2.1 with the enhancement of H-beta to phenol ratio from 0.01 to 0.10, respectively. These results indicate that H-beta catalyzes directly the propionylation of phenol to some extent and mainly the transformation of *O*-acylated product to ring acylated products by various reactions (Eqs. (1)–(7)).

3.6. Influence of reaction temperature

Fig. 5 indicates the influence of reaction temperature on the product yields and ratio of 4-HPP:2-HPP in the propionylation of phenol using zeolite H-beta ($\text{SiO}_2:\text{Al}_2\text{O}_3 = 26$). As the temperature was increased from 403 to 443 K, the transformation of PP into 2-HPP, 4-HPP and 4-PXPP increased significantly by various reaction pathways (Eqs. (1)–(7)). However, the possibility of conversion of small amount of phenol into products cannot be ruled out. The PP yield (converted to products) decreased from 35.3 to 26.8 wt.% when temperature was raised from 403 to 443 K. The corresponding yields of 2-HPP, 4-HPP and 4-PXPP increased simultaneously from 0.6 to 2.4, 1.3 to 3.8 and 0.1 to 0.5 wt.%, respectively, which confirms the transformation of PP into products. The ratio of 4-HPP:2-HPP decreased from 2.0 to 1.5 with the increase in reaction temperature.

3.7. Influence of phenol:PC molar ratio

A series of catalytic experiments were performed to investigate the effect of the phenol:PC molar ratio on the yields of *O*-acylated (PP), *C*-acylated ring products (2-HPP, 4-HPP and 4-PXPP) and 4-HPP:2-HPP

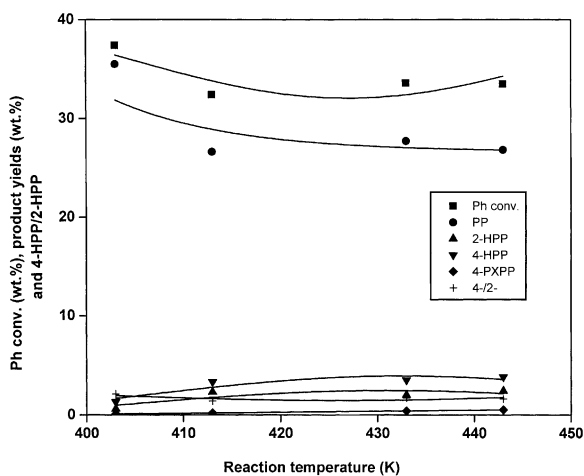


Fig. 5. Influence of reaction temperature on the conversion of Ph, product yields and 4-:2-isomer ratio. Reaction conditions: reaction time = 3 h; H-beta ($\text{SiO}_2:\text{Al}_2\text{O}_3 = 26$) = 0.5 g; phenol:PC molar ratio = 3 mol; for other reaction conditions, see Fig. 1.

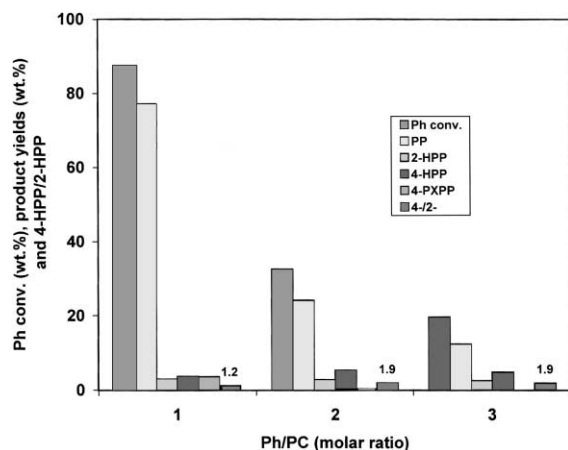


Fig. 6. Influence of Ph:PC molar ratio on the conversion of Ph, product yields and 4-:2-isomer ratio. Reaction conditions: reaction time = 4 h; for other reaction conditions, see Fig. 1.

ratio (Fig. 6). The phenol:PC molar ratio was varied in the range of 1–3 by keeping the constant concentration of phenol. It is evident that the proportion of PC in the reaction mixture greatly affects the conversion of phenol, product yields and ratio of 4-HPP:2-HPP. As the phenol:PC ratio increases from 1 to 5, the conversion of phenol decreases from 87.5 to 19.6 wt.%. Simultaneously, the transformation of PP into 4-PXPP is also affected greatly by the change in the phenol:PC ratio. The formation of 4-PXPP (by the autoacylation of PP) decreases from 3.6 to 0 wt.% and the 4-HPP:2-HPP ratio increases from 1.2 to 1.9 with the increase in phenol:PC molar ratio from 1 to 5, respectively. The formation of higher yield of 4-PXPP at lower ratio of phenol:PC may be attributed to the

presence of higher concentration of PP in the reaction mixture.

3.8. Recycling

To conclude this study, the H-beta was examined for recycling in the propionylation of phenol. After a first experiment, the zeolite was separated from the reaction mixture, washed with acetone, dried at 383 K for 4 h and regenerated by calcination in air at 773 K for 16 h. As can be seen in Table 2, the recycled material was less active in the formation of *C*-acylated products than the fresh sample. X-ray powder diffractometry shows that during the catalytic tests the structure of H-beta remains undamaged.

3.9. Reaction pathways

In order to clarify the reaction pathways for the formation of phenol, PP, 2-HPP, 4-HPP and 4-PXPP in the propionylation of phenol, additional experiments such as Fries rearrangements of PP (Fig. 7) and propionylation of phenol with PP (Fig. 8) were carried out at 413 K using zeolite H-beta as catalyst. Based on additional experimental results, various reaction schemes could be postulated as depicted in Eqs. (1)–(7).

The Fries rearrangements of PP (Fig. 7) and propionylation of phenol with PP (Fig. 8) show that 2-HPP and 4-HPP are formed through different reaction pathways which is also in agreement with the previous studies on the acylation of phenol [18–20]. The formation of 2-HPP may be attributed through direct *C*-propionylation of phenol with PC (Eq. (2)),

Table 2
Effect of recycling^a

| Catalyst (g) | Ph conversion (wt.%) ^b | Product yields (wt.%) ^c | | | | 4-HPP:2-HPP ^d | Crystallinity of catalyst |
|----------------|-----------------------------------|------------------------------------|-------|-------|--------|--------------------------|---------------------------|
| | | PP | 2-HPP | 4-HPP | 4-PXPP | | |
| Fresh | 35.5 | 27.1 | 2.8 | 5.4 | 0.3 | 1.9 | 100 |
| First recycle | 34.2 | 27.2 | 2.5 | 4.3 | 0.3 | 1.7 | 100 |
| Second recycle | 35.7 | 28.2 | 2.5 | 4.2 | 0.2 | 1.6 | 100 |

^a Reaction conditions: catalyst H-beta = 0.5 g; phenol = 0.106 mol; propionyl chloride = 0.032 mol; reaction time = 4 h.

^b Phenol conversion (wt.%).

^c PP = phenylpropionate; 2-HPP = 2-hydroxypropiofenone; 4-HPP = 4-hydroxypropiofenone; 4-PXPP = 4-propionyloxy-propiofenone.

^d 4-HPP:2-HPP = ratio of 4-hydroxypropiofenone:2-hydroxypropiofenone.

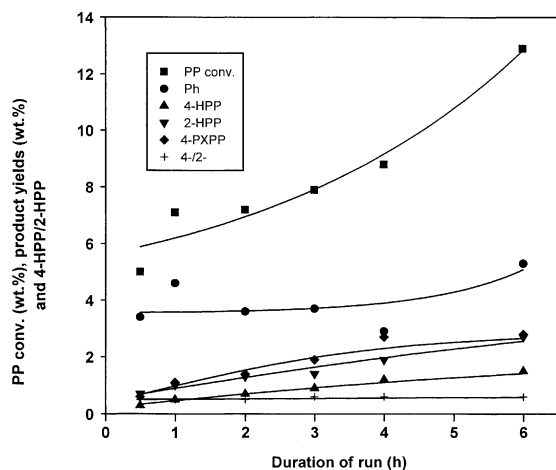


Fig. 7. Fries rearrangement of phenylpropionate over H-beta. Reaction conditions: H-beta = 0.5 g; PP = 0.075 mol; reaction temperature = 413 K; duration of run = 6 h. PP = phenyl-propionate; Ph = phenol; 2-HPP = 2-hydroxypropiofenone; 4-HPP = 4-hydroxypropiofenone; 4-PXPP = 4-propionyloxypropiofenone; 4-:2- = isomer ratio of 4-HPP:2-HPP.

as the ratio of 4-HPP:2-HPP were not affected significantly. In contrast to the Fries rearrangement results (discussed above) (Fig. 7), the formation of 2-HPP was lower and consequently the isomer ratio was found to

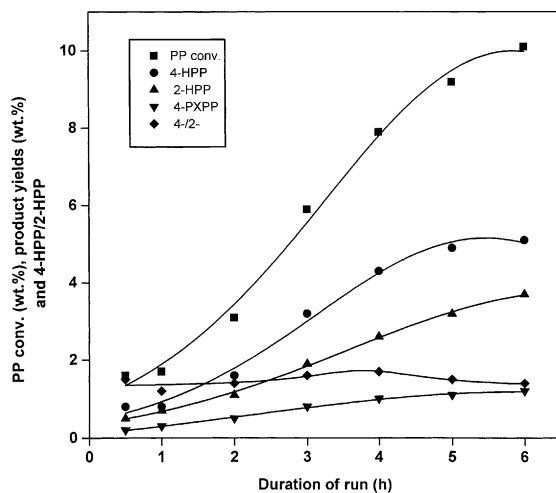
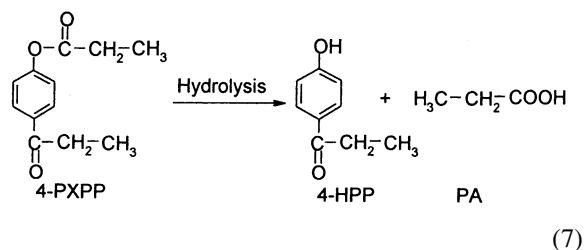


Fig. 8. Transformation of PP + Ph mixture on H-beta. Reaction conditions: H-beta = 0.5 g; PP = 0.059 mol; Ph = 0.059 mol; PP:Ph molar ratio = 1 mol; reaction temperature = 413 K; duration of run = 6 h; for abbreviation, see Fig. 7.

be higher (4-HPP:2-HPP = 1.5) in the propionylation of phenol with PP. These results further confirm that the formation of 2-HPP results from both the routes (Eqs. (3) and (4)).

A possible route for 4-HPP formation is through the reaction of 4-PXPP (produced from the bimolecular reaction of PP (Eq. (6)) with the zeolite hydroxyl groups or trace amount of water present in the reaction mixture (Eq. (7)) [22]. However, the formation of small amount of 4-HPP through the direct propionylation phenol with PC (Eq. (2)) and propionylation of phenol with PP (Eq. (3)) could not be ruled out [18].



The increase in the yields of 4-HPP and 4-PXPP with the reaction time in the Fries rearrangement of PP (Fig. 7) and propionylation of phenol with PP (Fig. 8) confirm this hypothesis.

4. Conclusions

In summary, zeolite H-beta catalyzes the propionylation of phenol with PC efficiently compared to other catalysts, which leads to the formation of 4-HPP selectively among 2-HPP and 4-HPP. The conventional catalyst, AlCl_3 , is less active and selective (4-HPP:2-HPP = 0.9) than H-beta (4-HPP:2-HPP = 1.9). The higher activity of H-beta in the formation of 2-HPP and 4-HPP could be related to the presence of very strong acid sites than other zeolite catalysts. The higher yields of hydroxypropiofenone (2-HPP and 4-HPP) could be achieved by increasing the values of reaction time, H-beta:PC ratio (w/w) and reaction temperature. The H-beta was recycled two times and a decrease in the yields of 2-HPP and 4-HPP was observed after each recycle in the propionylation of phenol. The plausible pathways for the formation of phenol, PP, 2-HPP, 4-HPP and 4-PXPP are confirmed by the additional experiments such as Fries rearrangement of PP and propionylation of phenol

with PP using zeolite H-beta as catalyst. The PP results from the rapid *O*-propionylation of phenol with PC. 2-HPP is produced through the intramolecular rearrangement of PP, propionylation of phenol with PP and direct *C*-propionylation of phenol with PC, 4-HPP is produced by the reaction of 4-PXPP with zeolite hydroxyl groups.

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