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A novel single step selective synthesis of 4-hydroxybenzophenone (4-HBP) using zeolite H-beta

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The single step selective synthesis of 4-hydroxybenzophenone (4-HBP/2-HBP = 2.1, selectivity for 4-HBP among 2- and 4-HBP = 67.7 wt%) at 95.3 wt% conversion level of benzoic anhydride has been investigated for the first time by the benzoylation of phenol using benzoic anhydride as benzoylating agent and zeolite H-beta as catalyst at 493 K in a Parr autoclave at autogenous pressure.

KEY WORDS: benzoylation of phenol; benzoic anhydride; zeolite H-beta; 4-hydroxybenzophenone; 2-hydroxybenzophenone.

1. Introduction

The preparation of 4-hydroxybenzophenone (4-HBP), which is an intermediate for dyes, polymers, drugs and perfumeries [1], is accomplished industrially using Friedel—Crafts homogeneous Lewis acid catalyst such as $AlCl_3$ and $FeCl_3$. In one industrial process, the 4-HBP is prepared in high yield by the treatment of phenol with anhydrous $AlCl_3$, then treatment of the resulting Al dichloride phenoxide with CCl_4, further treatment of the resulting benzotrichlorides with benzene in the presence of $AlCl_3$ and then hydrolysis of the resulting product giving 50% 4-HBP [2]. Another important process for the manufacture of hydroxybenzophenones begins with the treatment of phenols with aromatic carboxylic acids in the presence of strongly acidic ion exchangers (Amberlyst-15) [1]. Hydroxybenzophenones are also prepared through reaction of benzoic acids with phenols in the presence of nitrobenzene using BF_3 as catalyst [3]. Hydroxyketones such as hydroxyacetophenones and hydroxypropiophenones can be obtained through catalytic rearrangement of phenylesters or direct acetylation or propionylation of phenol with acylating agents on acid zeolites [4–10]. However, due to the difference in the rates of catalyst deactivation and lower yield of para-product in the Fries rearrangement of phenylesters, direct acetylation or propionylation of phenol (in single step) is preferred [4,10]. The mechanism of formation of 4-HBPs in higher yield (in the direct benzoylation of phenol) and 2-hydroxybenzophenone (2-HBP) is also discussed in this paper. The traditional procedures using acyl halides as acylating agent and soluble Lewis acids as catalyst have drawbacks in these reaction systems. In general, they are pollutant, non-shape-selective, difficult to work with, and more than the stoichiometric amount of catalyst is required which ends up as waste. This may pose increasing problems due to environmental considerations. In addition, unwanted heavier (consecutive) products in the Friedel–Crafts reaction with Lewis acids complicate the separation process. In order to diminish the waste problem and to increase the yield of para-product, there is a need to develop a solid recyclable catalyst for the synthesis of 4-HBP in a single step. The use of zeolites in the field of fine chemical synthesis has grown continuously in recent years. In addition, zeolites meet the essential requirements for industrial processing of organic chemicals taking into account their environmental advantages. Zeolites have been used in the acylation of aromatics [11–23] and Fries rearrangement of phenylesters [4,9,24–26]. However, there is no report of the direct benzoylation of phenol using zeolites as catalyst. Hence in the continuation of our studies on the catalytic activities of zeolites in acylation reactions, the present paper is concerned with obtaining a higher yield of 4-HBP in the direct benzoylation of phenol using zeolite H-beta as catalyst and benzoic anhydride as benzoylating agent. The influence of various catalysts, duration of the run, SiO_2/Al_2O_3 of H-beta and molar ratio of phenol/benzoic anhydride (Ph/BA) is investigated on the conversion of phenol to the ring products and mainly to the 4-HBP. The results obtained in the benzoylation of phenol over H-beta are compared with the conventional catalyst, $AlCl_3$.

2. Experimental

Phenol and benzoic anhydride (99% purity) were purchased from S.D. Fine Chemicals and Aldrich,

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Table 1
Benzoylation of phenol[a]

Catalyst[b]	SiO_2/ Al_2O_3	NH_3 desorbed at different temperature (K) (mmol g^{-1})					NH_3 chemisorbed at 303 K (mmol g^{-1})	Conv.[c] BA (wt%)	Product yields (wt%)[d]				4-/2-[e]
		303–353	353–433	433–513	513–653	653–773			PB	2-HBP	4-HBP	Others	
H-beta	26.0	0.14	0.24	0.05	0.16	0.16	0.75	95.9	61.2	11.4	23.3	–	2.1
H-Y	4.1	0.29	0.55	0.49	0.11	0.01	1.45	97.6	55.0	25.7	16.9	–	0.6
RE-Y	4.1	0.17	0.10	0.26	0.11	0.10	0.74	89.5	56.5	16.5	16.5	–	1.1
H-mordenite	22.0	0.20	0.17	0.15	0.12	0.07	0.71	87.7	87.0	0.7	–	–	–
H-ZSM-5	41.0	0.55	0.16	0.05	0.26	0.21	1.21	86.1	86.1	–	–	–	–
$AlCl_3$	–	–	–	–	–	–	–	91.4	70.8	5.4	3.3	11.9	0.6

[a] Reaction conditions: catalyst = 0.5 g; phenol = 0.21 mol; BA = 0.01 mol; phenol/BA = 20 (molar ratio); reaction temperature = 493 K; reaction time = 20 h.

[b] Surface area (m^2/g), degree of ion exchange (%) and crystal size (μm) = H-beta = 745, 98, 0.5; H-Y = 615, 98, 1.0; RE-Y = 659, RE-exchange (%) = 70.6; 1.0; H-mordenite = 552, 98, 1.0; H-ZSM-5 = 413, 98, 0.4, repectively.

[c] BA = benzoic anhydride.

[d] PB = phenylbenzoate; 4-HBP = 4-hydroxybenzophenone; 2-HBP = 2-hydroxybenzophenone; Others = consecutive products.

[e] 4-/2- = 4-HBP/2-HBP ratio.

respectively, and used without further purification. The reactants were dried over 4 Å molecular sieves.

Zeolite H-ZSM-5 and beta were prepared according to published procedures [27,28]. Zeolite H-Y and H-mordenite were obtained from Laporte Inorganics, Cheshire, U.K. 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 zeolites channels. Thus zeolites obtained were pre-treated with 1 M NH_4NO_3 solution to get their protonic forms. Zeolite NH_4-Y was exchanged with 5% rare earth chloride solution at 353 K to gets its RE-Y form.

The chemical compositions of the zeolites were estimated by the combination of wet and atomic absorption (Hitachi 800) methods. The X-ray powder diffraction patterns of various zeolites samples were recorded on an X-ray diffractometer. The surface area of the catalyst was measured by the nitrogen BET method using an area meter. The size and morphology of the zeolite catalysts were estimated by scanning electron microscope (SEM). The acidity of the zeolites was evaluated using the procedure described in the literature [29]. Typical characteristic data are reported in table 1.

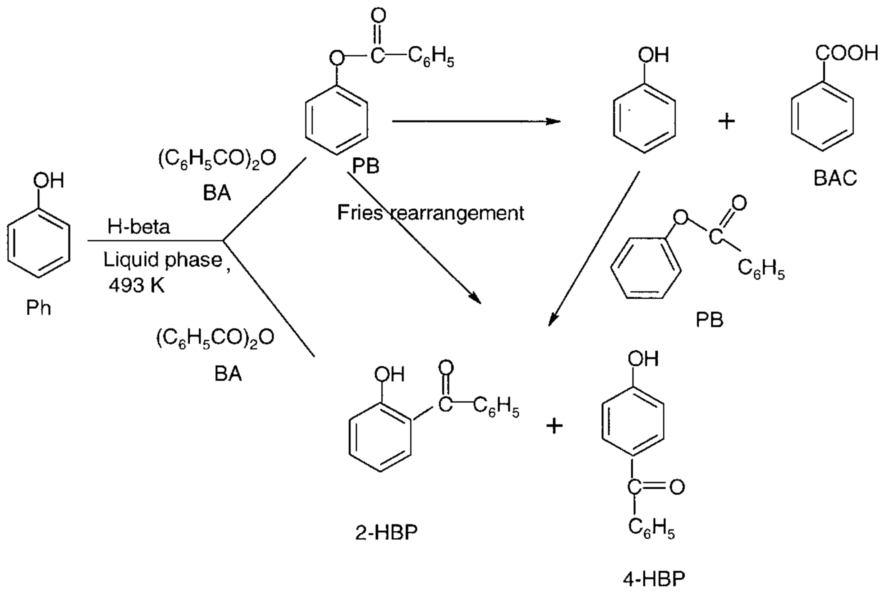
Anhydrous AR grade chemicals were used without further purification and the reaction was carried out in a Parr reactor. A mixture of 0.21 moles of phenol, 0.01 moles BA and 0.5 g of catalyst were taken in a Parr reactor and heated to 493 K for 20 h under autogeneous pressure. The product was analysed with gas chromatograph (HP 6890) equipped with flame ionization detector and capillary column (50 m × 0.2 mm) of methylsilicone gum. The samples were also identified by injecting the authentic samples and GC/MS.

3. Results and discussion

Table 1 lists the SiO_2/Al_2O_3 ratios, acid strength distributions (mmol/g), H^+ or Na^+ exchange (%), crystal size and surface area of zeolites used in this work. These data reveal that zeolite samples are highly crystalline and in protonic forms. No reflections of a dense phase or any other zeolite phase are found.

3.1. *Activity of various catalysts*

The catalytic activities of different catalysts such as H-beta, H-Y, RE-Y, H-ZSM-5, H-mordinite and conventional catalyst, $AlCl_3$, in the benzoylation of phenol at 493 K are summarized in table 1. It is seen that all catalysts readily form the phenyl benzoate (PB) as a major product by the O-acylation of phenol (scheme 1). Further, reaction mechanisms have been proposed for the formation of nuclear products such as 2-HBP and 4-HBP (scheme 1). Zeolite H-beta, H-Y and RE-Y were found to be the most active catalysts for the formation of nuclear products whereas the selectivity of H-beta was much higher (4-/2- = 2.1) than those of H-Y (4-/2- = 0.6) and RE-Y (4-/2- = 1.1). The most attractive shape-selectivity of H-beta among the zeolites and conventional catalyst, $AlCl_3$, is attributed to the three dimensional pore system with straight channels of *ca.* 7.3 × 6.5 Å and tortuous channel of 5.5 × 5.5 Å of H-beta [30,31]. Very small amount of 2-HBP was formed over H-mordenite. In addition, the inactivity of H-ZSM-5 might be explained on the basis of its smaller pore size (5.4 × 5.6 and 5.1 × 5.5 Å) compared with the bulkier size of the products. For comparison, the results over conventional Lewis acid catalyst, $AlCl_3$, are also obtained in the benzoylation of phenol. Obviously the $AlCl_3$ catalyst demonstrates the reasonable activity for nuclear products (lower than H-Y, RE-Y and H-beta) but lower selectivity for 4-HBP (4-/2- = 0.6) than H-beta (4-/2- = 2.1). The activity of various catalysts in the formation of 2-HBP and 4-HBP and others (consecutive products in the case of $AlCl_3$) decreases in the sequence: H-Y > H-beta > RE-Y > $AlCl_3$ > H-mordenite



Scheme 1.

whereas the selectivity for 4-HBP (4-/2- ratio) decreases in the following order: H-beta > RE-Y > H-Y ≈ $AlCl_3$.

The effect of the number and strength of acid sites (represented for instance by NH_3 desorption at different temperature (mmol g^{-1})) on the various reaction steps (scheme 1) in the benzoylation of phenol is shown in table 1. The formation of 2-HBP and 4-HBP is considered to be dependent on the number and strength of acid sites. The formation of 2-HBP and 4-HBP by the Fries rearrangement of PB and the reaction of phenol with PB seems to be dependent not only on the number of acid sites but also on their strength [10]. The H-beta offers acidic centres with higher acid strength that is very well suited for the transformation of PB into 2-HBP and 4-HBP by the Fries rearrangement and benzoylation of phenol with PB into 2-HBP and 4-HBP [4–6]. The higher values of 4-HBP/2-HBP found with the H-beta in the benzoylation of phenol could be related to the presence of very strong acidic sites and its pore structure (table 1).

The phenol benzoylation may occur through different reaction pathways. The formation of PB occurs rapidly *via* O-acylation of phenol with benzoic anhydride (BA) [10]. Further, the debenzoylation of PB leads to the formation of phenol, and benzoic acid (BAC). Phenol, which again reacts by an intermolecular reaction with PB, results in the formation of 2-HBP and 4-HBP [4–6]. In addition, 2-HBP and 4-HBP would be produced through different reaction pathways: *via* C-acylation of phenol with BA and also by the intramolecular rearrangement (Fries rearrangement) of phenyl benzoate over zeolite H-beta (scheme 1) [4,10].

3.2. Duration of the run

In order to investigate the effect of duration of run on the 4-HBP/2-HBP ratios and the yield of 2-HBP and 4-HBP obtained by different reaction pathways (scheme 1), the reaction was performed for 20 h over zeolite H-beta at 493 K. The results are presented in figure 1. The yield of 4-HBP slowly but steadily increases from 11.1 wt% to 23.0 wt% and simultaneously the yield of PB decreases from 79.0 wt% to 63.6 wt% when reaction time was increased from 4 h to 20 h, respectively. The results suggest that mostly increase in the yield of 4-HBP with reaction time takes place by the transformation (intramolecular reaction) of PB into 4-HBP and the reaction of phenol with PB (intermolecular reaction). However, a small increase in the yield of 2-HBP (from 8.5 wt% to 10.2 wt%) could not be avoided when the reaction time was increased from 4 h to 20 h, respectively. In addition an increase in the ratio of 4-HBP/2-HBP with the increase in the reaction time may be attributed to the transformation of higher amount of PB into 4-HBP.

3.3 Influence of the SiO_2/Al_2O_3 ratio

Figure 2 shows the influence of SiO_2/Al_2O_3 ratio of H-beta on the yield of 2-HBP, 4-HBP and 4-/2- ratio in the benzoylation of phenol as a function of aluminium content of the H-beta. Increasing the SiO_2/Al_2O_3 ratio from 30 to 60 decreases the yield of 2-HBP and 4-HBP formations. In addition, the yield of 4-HBP decreases at a faster rate compared with the yield of 2-HBP and, as a result, the 4-HBP/2-HBP ratio in the product mixture is significantly decreased from 2.1 to 1.1 when SiO_2/Al_2O_3 ratio of H-beta is increased from 30 to 80, respectively. It seems that the transformation of phenol is catalysed by both weak and stronger acid sites, so the higher the acid site density (lower SiO_2/Al_2O_3 ratio), the higher the catalytic activity of H-beta.

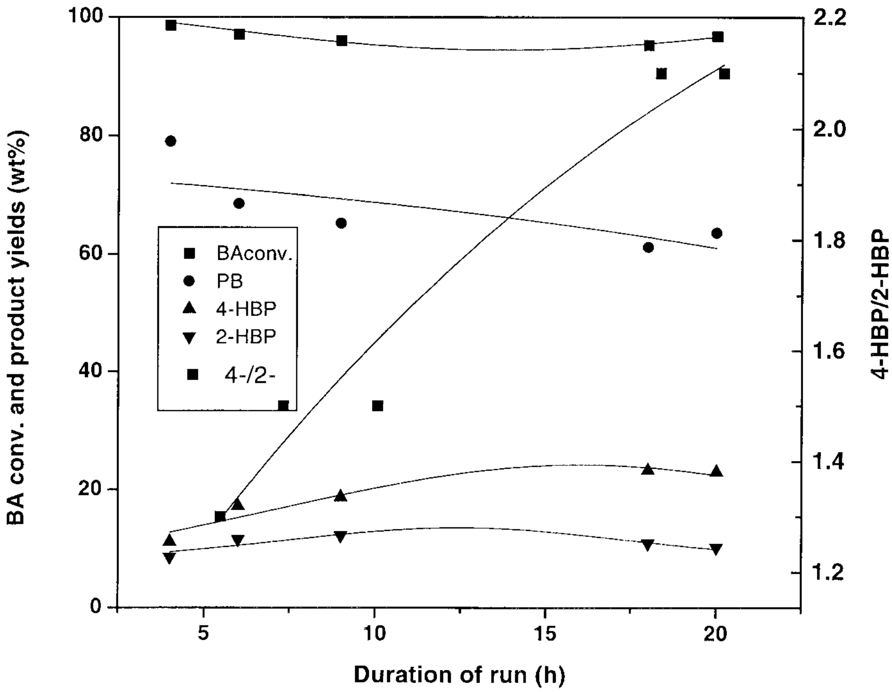


Figure 1. Conversion of BA and product yields as a function of reaction time. Reaction conditions: catalyst = 0.5 g; phenol = 0.21 mol; BA = 0.01 mol; phenol/BA = 20 (molar ratio); reaction temperature = 493 K; reaction time = 20 h.

3.4. *Influence of phenol/BA molar ratio*

A series of catalytic activity tests were performed to investigate the effect of Ph/BA ratio on the 2-HBP and 4-HBP formations. The Ph/BA ratio was varied (by keeping the amount of phenol constant) in the range 10 to 20. Figure 3 clearly shows that the gradual increase in the Ph/BA molar ratio causes a progressive but small increase in the 2-HBP and 4-HBP formation and the PB transformation. The 4-HBP/2-HBP ratios are not significantly affected by the increase in the Ph/BA molar ratio from 10 to 20.

3.5. *Recycle*

In order to check the stability and reusability of the catalyst, two reaction cycles were carried out using the same catalyst. After completion of the reaction on

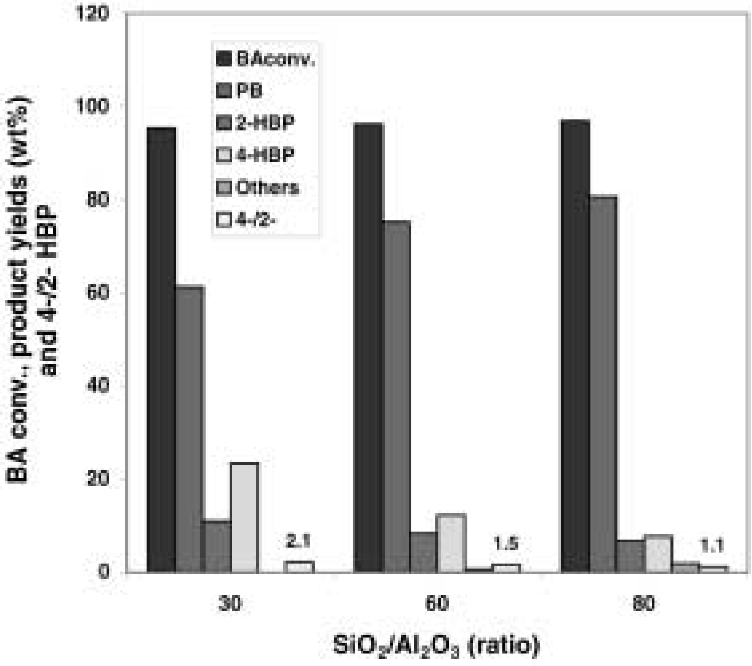


Figure 2. Influence of SiO_2/Al_2O_3 ratio of H-beta on the conversion of BA, product yields and 4-/2- isomer ratio. Reaction conditions: see figure 1 legend.

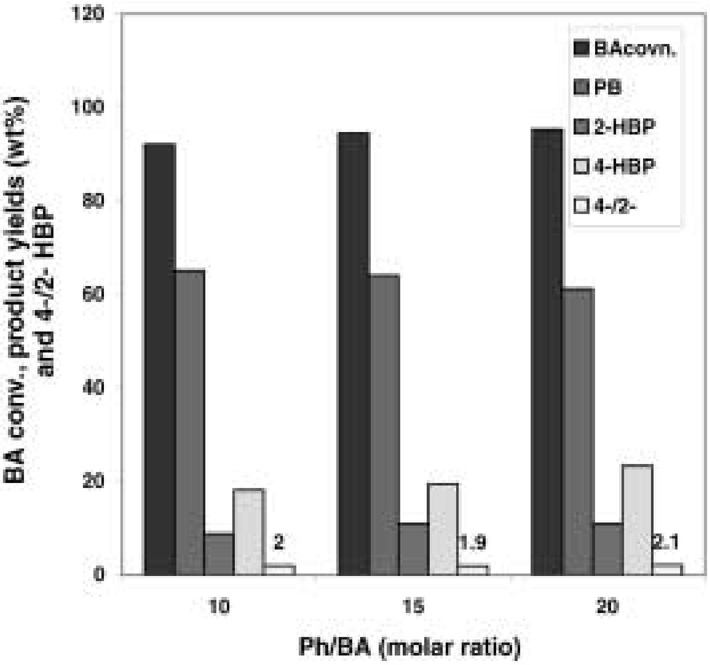


Figure 3. Influence of Ph/BA molar ratio on the conversion of BA, product yields and 4-/2- isomer ratio. Reaction conditions: see figure 1 legend.

fresh catalyst, it was separated from the reaction mixture via sedimentation, filtration and subsequent washing with the acetone; further, the catalyst was dried at 383 K for 2 h and calcined in air at 773 K for 16 h then the next run was carried out. The reaction was performed for 20 h at 493 K. The results are given in figure 4. It was found that the activity of the catalyst in the formation of 2-HBP and 4-HBP does not distinctly decrease when catalyst was used from fresh to first recycle, and the product selectivity (4-HBP/2-HBP) seemed to remain unchanged. In order to study the structure change of the catalyst after reactions, X-ray powder diffraction patterns were recorded after the last run, and XRD measurement indicated that the catalyst retained its structure, which suggests that the catalyst was stable in structure.

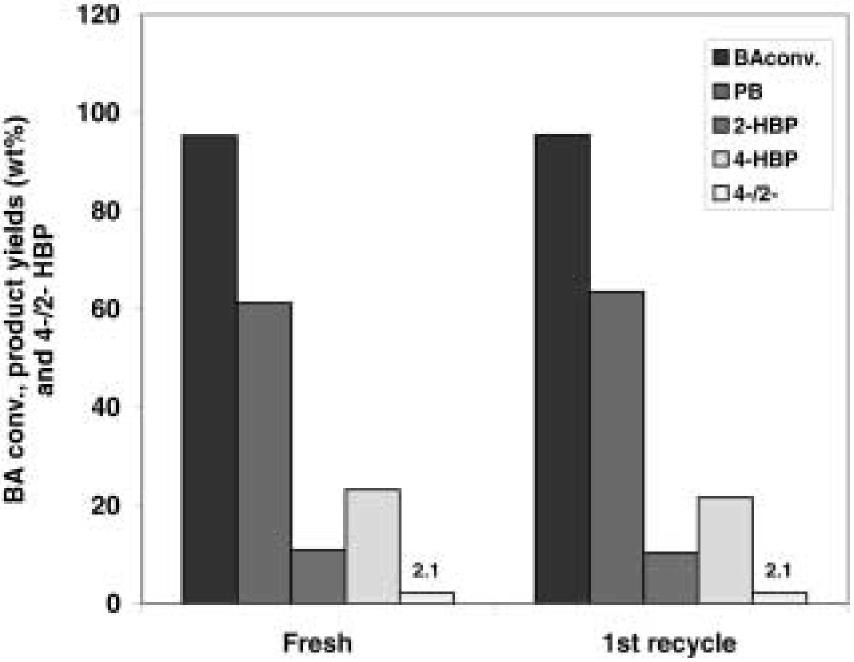


Figure 4. Influence of recycle of catalyst H-beta on the conversion of BA, product yields and 4-/2- isomer ratio. Reaction conditions: see figure 1 legend.

4. Conclusions

Catalytic behaviour of the zeolite catalysts in the benzoylation of phenol was studied. Results showed that only H-beta has higher selectivity (4-HBP/2-HBP = 2.1) and reasonably stable catalytic performance for the formation of 2-HBP and 4-HBP in the reaction. The activity of the catalyst increases with the increase in the number of acid site, whereas the selectivity for 4-HBP (4-HBP/2-HBP) was found to increase with the increase in acid strength of acid sites. The yields of 2-HBP and 4-HBP are mainly dependent on the duration of the run, SiO_2/Al_2O_3 ratio of H-beta and phenol to BA molar ratio. The yields of 2-HBP and 4-HBP increases with the increase in the number of acid sites, duration of run and phenol to BA molar ratio whereas it decreases with the increase of SiO_2/Al_2O_3 ratio of H-beta. Recycle of H-beta does not appreciably decreases its activity and selectivity in the benzoylation of phenol. Phenol debenzoylation to 2-HBP and 4-HBP can occurs through several pathways: the reaction of phenol with BA rapidly forms the PB through O-acylation. The benzoylation of PB leads to the formation of phenol, which further reacts with PB by an intermolecular reaction and produces 2-HBP and 4-HBP. Direct C-acylation of phenol with BA and Fries rearrangement of PB also results in the formation 2-HBP and 4-HBP.

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References

[1] T. Abe, T. Kimura, Y. Ayabe and T. Shiomi, Japanese Patent 85-123831 (1985).
[2] N. Fukuoka and M. Suzuki, Japanese Patent 87-228021 (1987).
[3] U. Eichenauerand and P. Neumann, German Patent 3831092 (1988).
[4] M. Guisnet, D.B. Lukyanov, F. Jayat, P. Magnoux and I. Neves, Ind. Eng. Chem. Res. 34 (1995) 1624.
[5] I. Neves, F. Jayat, P. Magnoux, G. Perot, F.R. Ribeiro, M. Gubelmann and M. Guisnet, J. Mol. Catal. 93 (1994) 169.
[6] Y.V. Subba Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, Appl. Catal. A 33 (1995) L1.
[7] A. Heidekum, M.A. Harmer and W.F. Hoelderich, J. Catal. 176 (1998) 260.
[8] F. Jayat, M.J. Sabater Picot and M. Guisnet, Catal. Lett. 41 (1996) 181.
[9] B.B.G. Gupta, U.S. Patent 4,668,826 (1987).
[10] V.D. Chaube, P. Moreau, A. Finiel, A.V. Ramaswamy and A.P.Singh, J. Mol. Catal. A 174(1–2), (2001) 255.
[11] B. Chiche, A. Finiels, C. Gauthier and P. Geneste, J. Org. Chem. 51 (1986) 2128.
[12] A. Corma, M.J. Climent, H. Garcia and P. Primo, Appl. Catal. 49 (1989) 109.
[13] I. Neves, F. Jayat, P. Magnoux, G. Perot, F.R. Ribeiro, M. Gubelman and M. Guisnet, J. Chem. Soc. Chem. Commun. (1994) 717.
[14] F. Richard, H. Carreyre and G. Perot, J. Catal. 159 (1996) 427.
[15] R. Fang, H.W. Kouwenhoven and R. Prins, Stud. Surf. Sci. Catal. 83 (1994) 1441.
[16] H. Van Bekkum, A.J. Hoefnagel, M.A.Vankoten, E.A.Gunnewegh, A.H.G.Vog and H.W. Kouwenhoven, Stud. Surf. Sci. Catal. 83 (1994) 379.
[17] E.A. Gunnewegh, S.S. Gopie and H. Van Bekkum, J. Mol. Catal. A 106 (1996) 5.
[18] A.P. Singh, D. Bhattacharya and S. Sharma, J. Mol. Catal. A 102 (1996) 139.
[19] A.P. Singh and D. Bhattacharya, Catal. Lett. 32 (1995) 327.
[20] A.K. Pandey and A.P. Singh, Catal. Lett. 44 (1997) 129.
[21] A.P. Singh and A.K. Pandey, J. Mol. Catal. 123 (1997) 141.
[22] A.P. Singh, D. Bhattacharya and S. Sharma, Appl. Catal. A 150 (1997) 53.
[23] B. Jacob, S. Sugunan and A.P. Singh, J. Mol. Catal. A 139 (1999) 43.
[24] I. Nicolau and A. Aguilo, U.S. Patent 4,652,683 (1987).
[25] I. Neves, F. Jayat, P. Magnoux, G. Perot, F.R. Ribeiro, M. Gubelman and M. Guisnet, J. Mol. Catal. 93 (1994) 169.
[26] I. Neves, F. Jayat, P. Magnoux, G. Perot, F.R. Ribeiro, M. Gubelman and M. Guisnet, J. Chem. Soc., Chem. Commun. (1994) 717.
[27] R.J. Argaurer and G R. Landolt, U.S. Patent 3,702,886 (1972).
[28] M.A. Chambler and J. Perze Pariente, Zeolites 11 (1991) 202.
[29] M. Chamumi, D. Brunel, F. Fajula, P. Geneste, P. Moreau and J. Solof, Zeolites 14 (1994) 283.
[30] J.M. Newsam, M.M.J. Teracy, W.T. Koestier and C.B. DeGruyter, Proc. E. Soc. London A 420 (1988) 375.
[31] M.M.J. Treacy and J.M. Newsam, Nature 332 (1988) 249.