

Selective propionylation of veratrole to 3,4-dimethoxypropiophenone using zeolite H-beta catalysts

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Abstract

The catalytic liquid phase propionylation of veratrole (VT) (1,2-dimethoxybenzene, 1,2-DMB) is investigated over a number of zeolite catalysts. Zeolite H-beta is found to be an effective catalyst for the selective conversion of VT to 3,4-dimethoxypropiophenone (3,4-DMPP). The SiO₂/Al₂O₃ ratio of zeolite H-beta is higher (SiO₂/Al₂O₃ = 26) than the H-Y and RE (70.6)-Y (SiO₂/Al₂O₃ = 4.1). The performance of zeolite H-beta is compared with that of conventional catalyst, AlCl₃. The conversion of VT, the rate (turn over frequency, TOF) of VT conversion (10⁻⁴ s⁻¹ mol⁻¹ Al), turnover number (TON) (mol of VT converted per mol Al in the catalyst) and the selectivity to 3,4-DMPP over H-beta after 1 h reaction time and at 403 K are found to be 40.8 wt.%, 18.8 × 10⁻⁴ s⁻¹ mol⁻¹ Al, 67.8 and 89 wt.%, respectively. For comparison, the conversion of VT, TOF, TON and selectivity to 3,4-DMPP over AlCl₃ under identical reaction conditions are estimated to be 48.5 wt.%, 3.6 × 10⁻⁴ s⁻¹ mol⁻¹ Al, 1.3 and 68.9 wt.%, respectively. The acidity of the zeolite catalysts is measured by the temperature programmed desorption (TPD) of ammonia. The effects of acidity of the zeolite catalysts, reaction time, catalyst concentration, reaction temperature and VT to propionyl chloride (PC) molar ratio on the catalyst performance are examined in order to optimise the conversion of VT and selectivity to 3,4-DMPP. The conversion of VT increases with the increase in reaction time, catalyst concentration and reaction temperature, whereas it decreases with the increase VT/PC molar ratio. The propionylation of 1,3-dimethoxybenzene (1,3-DMB) and 1,4-dimethoxybenzene (1,4-DMB) is also investigated over zeolite H-beta catalyst. The zeolite H-beta was recycled two times with a marginal decrease in catalytic activity, but without the loss of 3,4-DMPP selectivity and crystallinity of H-beta. Mechanistically, the PC is first polarised (CH₃CH₂CO^{δ+}, Cl^{δ-}) by the zeolite catalyst. The generated electrophile (CH₃CH₂CO⁺) attacks the ring of VT, resulting in the formation of 3,4-DMPP. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Propionylation of veratrole; Zeolite H-beta; 3,4-Dimethoxypropiophenones

1. Introduction

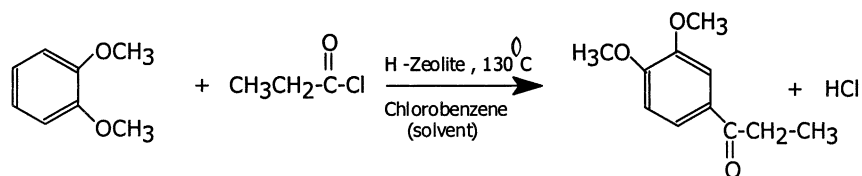
Selective propionylation of veratrole (VT) to 3,4-dimethoxypropiophenone (3,4-DMPP) is of con-

siderable interest due to its commercial importance in several organic intermediates for the production of fine chemicals (Scheme 1). Several homogeneous acid catalysts (AlCl₃, TiCl₄, FeCl₃, SnCl₄, CF₃SO₃H, FSO₃H and H₂SO₄) have been widely used for the acylation reactions [1,2]. Recently, the uses of solid catalysts, such as Nafion-H [3], clay [4], heteropoly acids [5] and metal oxides promoted by sulphate ions

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Scheme 1.

($\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$), $\text{SO}_4^{2-}/\text{ZrO}_2$, $\text{SO}_4^{2-}/\text{TiO}_2$, FeSO_4 and $\text{Fe}(\text{SO}_4)_3$ have been reported for the acylation of aromatics [5–7]. In addition, 3,4-DMPP is also prepared in 70–76% yield by the acylation of VT with propionyl chloride (PC) in the presence of polyphosphoric acid [8]. Lewis acid catalysts pose some major problems, such as the formation of consecutive reaction products in substantial amounts, lower regio-selectivity, difficulty in separation of catalyst from the final product and requirement of stoichiometric amounts of catalyst. In order to overcome the difficulties of the homogeneous systems, the development and utilisation of a solid catalyst are important. Zeolites are well-defined microporous crystalline materials and have been investigated extensively and applied as solid catalysts in the field of petrochemistry [9,10]. Zeolite catalysts are also known to catalyze various synthetic organic transformations much more effectively and selectively than the Lewis acid catalysts. Zeolites are also attractive as catalysts for the acylation reactions due to their acidity, shape-selectivity and regenerability [11–23]. In addition, VT can be efficiently acetylated to 3,4-dimethoxyacetophenone in liquid phase by acetic anhydride with zeolite catalysts under mild reaction conditions [24–26]. However, there is no report to date in the open literature on the propionylation of VT using zeolite catalysts. The objective of the present work is to develop a selective zeolite catalyst for the propionylation of VT to 3,4-DMPP and to replace the environmentally unfriendly homogeneous catalyst, AlCl_3 . The present paper describes a new catalytic method for the selective propionylation of VT to 3,4-DMPP using zeolite H-beta as catalyst and PC as propionylating agent (Scheme 1). The effects of various catalysts and reaction conditions on catalytic activity and selectivity are also investigated to ascertain the activity and selectivity trends. The results obtained over zeolite catalysts are compared

with those obtained over the conventional catalyst, AlCl_3 .

2. Experimental

2.1. Materials

ZSM-5 and zeolite beta were prepared using the methods described in the literature [27,28]. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the final product of beta was varied by adjusting the amount of Al source added in the synthesis mixture. Zeolites, H-Y and H-mordenite were obtained from Laporte Inorganics, Cheshire, UK. The as-synthesized zeolites were washed with deionised water, dried and calcined at 813 K for 16 h in the presence of air to eliminate the organic templates from the zeolite channel. The resultant samples were thrice NH_4^+ -exchanged using the following conditions: 10 ml NH_4NO_3 (1 M) g^{-1} zeolite, 353 K, 8 h exchanged run, pH 7–8. The NH_4^+ -exchanged samples were again calcined at 823 K for 8 h to get their protonic forms. The RE (70.6)-Y was prepared by treating NH_4 -Y with 5% rare earth chloride solutions by following the above exchange procedure [18,22].

2.2. Characterisation

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of various zeolites and the degree of ion-exchange were estimated by a combination of wet and atomic absorption methods (Hitachi 800). X-ray powder diffraction (XRD) analysis was carried out on a Rigaku, D-Max/III-VC model using the $\text{Cu K}\alpha$ radiation. The surface areas of the catalysts were estimated by the BET method using nitrogen as adsorbed at liquid nitrogen temperature. The particle size and morphology of the zeolite catalysts were estimated by scanning electron microscopy (SEM, Cambridge Stereoscan 400).

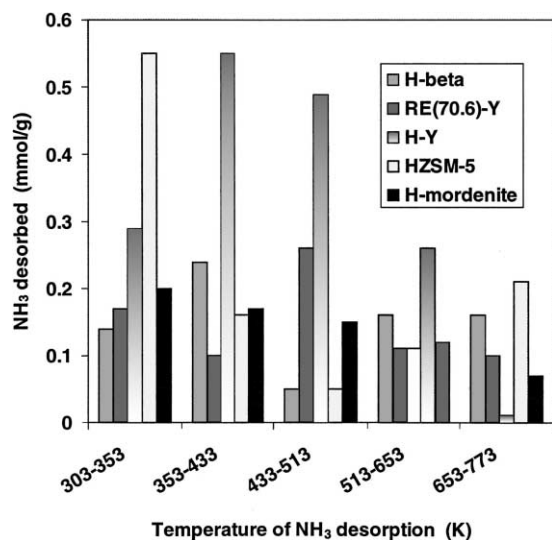


Fig. 1. Acid strength distribution of various zeolites.

2.3. Acidity of zeolites

Temperature programmed desorption (TPD) of ammonia was carried out to evaluate acidic properties of the zeolites using NH₃ as an adsorbate (Fig. 1) [18,29]. In a typical run, 1 g of a calcined sample was placed in a quartz tubular reactor and heated at 773 K under a N₂ flow of 50 ml min⁻¹ for 4 h. The reactor was cooled to 303 K; thereafter, NH₃ was passed over the sample for 30 min. The sample was subsequently kept in the flow of N₂ (50 ml min⁻¹) at 303 K for 15 h in order to eliminate the physisorbed ammonia. The desorption of NH₃ and the acid strength distribution of samples were obtained by raising the temperature at a ramp rate of 10°C min⁻¹ in N₂ flows. The NH₃ evolved was trapped in an HCl solution and titrated with a standard NaOH solution (Fig. 1).

2.4. Catalytic reaction experiments

Anhydrous AR grade chemicals were used without further purification. The liquid phase propionylation of VT with PC was carried out in a 100 ml two-necked flask attached to a condenser and septum (used to sample the reaction mixture). The temperature of the reaction vessel was maintained using an oil bath. In a typical run, VT (10 mmol), PC (10 mmol) and chlorobenzene (20 ml) of solvent were added to

the activated (0.5 g) catalyst. However, in case of recycling experiments, higher amounts of VT (50 mmol), PC (50 mmol) and chlorobenzene (50 ml) were taken. The reaction mixture was magnetically stirred and heated to the required temperature at atmospheric pressure. The product samples were analysed periodically by a gas-chromatograph (HP 6890) equipped with a flame ionisation detector and a capillary column (5 μm thick cross-linked methyl silicone gum, 0.2 mm × 50 m long). The products were also identified by GC/MS (Shimadzu, QP 2000 A) analysis.

Finally, the percentage conversion (wt.%) of VT is defined as the total percentage of VT transformed. The rate of VT conversion (turn over frequency, TOF) was calculated as the amount of VT (mol) converted per mol of Al (in the catalyst) per second. Turnover number (TON) is defined as the mol of VT converted per mol Al (in the catalyst). The selectivity to a product is expressed as the amount of the particular product divided by the total amount of products and multiplied by 100.

3. Results and discussion

3.1. Catalyst characterisation

The zeolites used in this study and their physico-chemical properties are presented in Table 1. The crystallinity and phase purity of the zeolite samples as well as the absence of amorphous matter within their pore structure were first ensured. The X-ray pattern of all zeolites matched with those in the literature. The surface areas and scanning electron micrographs showed the absence of amorphous matter inside the channels as well as on the external surface of the zeolites. All the samples consisted of particles of about 0.5–1.0 μm. Table 1 also lists the chemical composition of the zeolites used in the present study. Fig. 1 illustrates the amount of NH₃ desorbed from zeolites in different temperature steps.

3.2. Influence of various catalysts on the catalytic activity

Fig. 2 shows the activities and selectivities of various catalysts in the propionylation of VT. The results with Lewis acid catalyst, AlCl₃, are compared under

Table 1
Physico-chemical properties of zeolite catalysts

Sl. No.	Catalyst	SiO ₂ /Al ₂ O ₃ (molar ratio)	Degree of H ⁺ -exchange ^a	Crystal size (μm)	Surface area ^b (m ² g ⁻¹)
1	H-beta	26.0	>98	0.5	745
2	H-Y	4.1	>98	1.0	615
3	Re (70.6)-Y	4.1	>70.6	1.0	659
4	H-ZSM-5	41.0	>98	0.4	413
5	H-mordenite	22.0	>98	1.0	552

^a Values reported as percent of the total cation sites, aluminium content being taken as 100%.

^b Measured by N₂ adsorption.

identical reaction conditions. The main product of the reaction is 3,4-DMPP. Small amounts of others (consecutive products) are also observed. However, the concentration of consecutive products depends upon the reaction conditions and the type of catalyst used in the study. The activities of various catalysts are compared using data after an initial 1 h run.

As can be seen from Fig. 2, zeolite H-beta catalyses the reaction more efficiently than other zeolite catalysts. However, the selectivity for 3,4-DMPP was found to be nearly the same except in the case of AlCl₃. It should be noted that SiO₂/Al₂O₃ ratio of H-beta is higher (SiO₂/Al₂O₃ = 26) than that of H-Y (SiO₂/Al₂O₃ = 4.1).

In order to gain an understanding of acidity affecting the catalytic activity of the reaction, the desorption of NH₃ was carried out in five steps (303–353,

353–433, 433–513, 513–653 and 653–773 K). The results of the NH₃ desorption are listed in Fig. 1. It can be seen that the higher the desorption temperature of NH₃, the stronger the acid sites. With the increase of NH₃ desorption temperature, the conversion of VT enhances, which means that the reaction was promoted by medium and strong acid sites. Strong acid sites are necessary to get higher conversion of VT and hence H-beta and RE (70.6)-Y are found to be active catalysts in the propionylation of VT to 3,4-DMPP.

The conversion of VT, rate of VT conversion (TOF) TON and selectivity for 3,4-DMPP over zeolite H-beta after 1 h reaction time are found to be 40.8 wt.%, $18.8 \times 10^{-4} \text{ s}^{-1} \text{ mol}^{-1} \text{ Al}$, 67.8 and 89 wt.%, respectively. Under identical reaction conditions, conversion of VT, rate of VT conversion, TON and selectivity for 3,4-DMPP over AlCl₃ are found to be 48.5 wt.%,

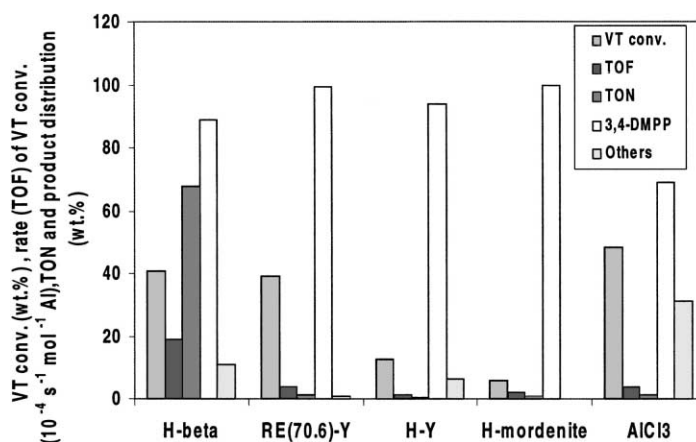


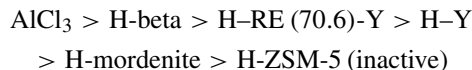
Fig. 2. Propionylation of VT over various catalysts. Reaction conditions: catalyst (g) = 0.5; catalyst/PC (wt. wt.⁻¹) = 0.53; VT/PC (molar ratio) = 1; VT (mol) = 0.01; chlorobenzene (ml) = 20; reaction temperature (K) = 403 K; reaction time (h) = 1. TOF ($10^{-4} \text{ s}^{-1} \text{ mol}^{-1} \text{ Al}$) is the rate of VT conversion (TOF) expressed as the amount of VT (mol) converted per mol of Al (in the catalyst) per second; TON is mol of VT converted per mol of Al (in the catalyst); 3,4-DMPP is 3,4-dimethoxypropionophenone and others are demethoxylated products. RE (70.6)-Y are values in the parenthesis represent the percentages of RE⁺³-exchanged in zeolite H-Y.

$3.6 \times 10^{-4} \text{ s}^{-1} \text{ mol}^{-1} \text{ Al}$, 1.3 and 68.9 wt.%, respectively. Presumably, the higher activity of H-beta may be attributed to its acid sites being stronger than those of other zeolite catalysts (Fig. 1) [12,18,19,22]. The lower activity of H-ZSM-5 (<1 wt.% conversion of VT) compared with the activities of other zeolite catalysts may be attributed to its small pore openings (5.4×5.6 and $5.1 \times 5.5 \text{ \AA}$) which are smaller than the size of VT and the reaction products. When H-Y is exchanged to H-RE (70.6)-Y, the catalytic activity is enhanced considerably. This may be due to the higher strength of acid sites generated by RE^{3+} -cations [18,22]. Compared with AlCl_3 catalyst, all zeolite catalysts show higher selectivity for 3,4-DMPP (Fig. 2).

3.3. Duration of the run

Fig. 3 compares the rates of VT conversion as a function of reaction time over various catalysts in the propionylation of VT. Reaction conditions are those detailed in Fig. 2. AlCl_3 gave higher conversion of VT compared with other catalysts, but it is a poor catalyst in terms of selectivity. The conversion of VT over zeolite H-beta is found to increase with the increase in reaction time and reaches to about $\cong 50$ wt.% conversion in a 2 h run. Zeolites H-mordenite, H-Y and H-RE (70.6)-Y exhibit comparatively lower activities, whereas H-ZSM-5 is found to be inactive in this reaction. From the result (Fig. 3) at 4 h stream, it can

be seen that activities increase with the acid strength of the catalyst, being very low for H-mordenite and H-Y and higher for H-beta and RE (70.6)-Y. Based on the conversion of VT after 2 h of reaction time, the trend in activities for the catalysts studied is as follows.



Such results have revealed that zeolite H-beta and RE (70.6)-Y are the best catalysts for the propionylation of VT to 3,4-DMPP. The influence of various parameters on the conversion of VT, rate of VT conversion and product distribution over H-beta is reported in the following sections.

3.4. Influence of catalyst concentration

Fig. 4 represents the conversion of VT, rate of VT conversion, TON and product distribution as a function of catalyst loading. The different H-beta/VT (wt. wt.⁻¹) ratios are obtained by varying the amount of the H-beta zeolite and keeping the concentration of VT constant. It can be seen that the addition of a small amount of catalyst (H-beta/VT = 0.05 ratio), the conversion of VT increases sharply from 3 (no catalyst) to 20 wt.%. Beyond this level, the conversion of VT becomes slower. However, the TOF of VT conversion decreases and TON of VT increases

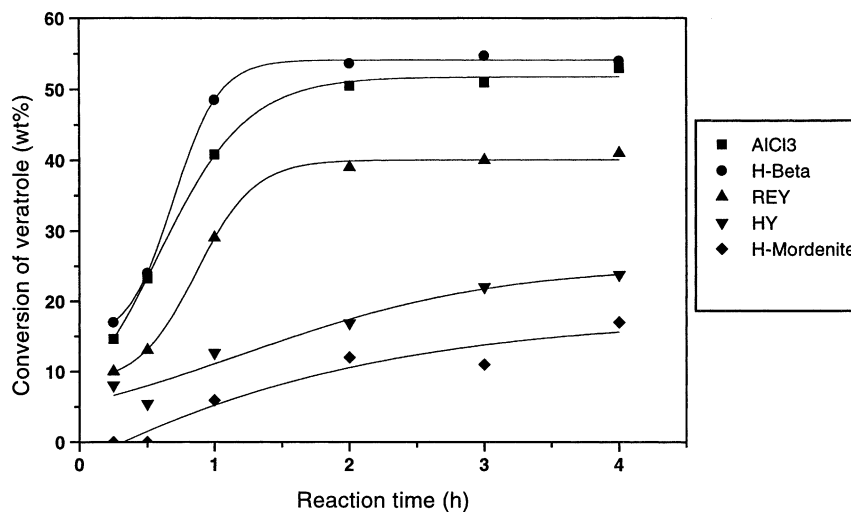


Fig. 3. Conversion of VT vs. reaction time over various catalysts; for reaction conditions, see notes to Fig. 2.

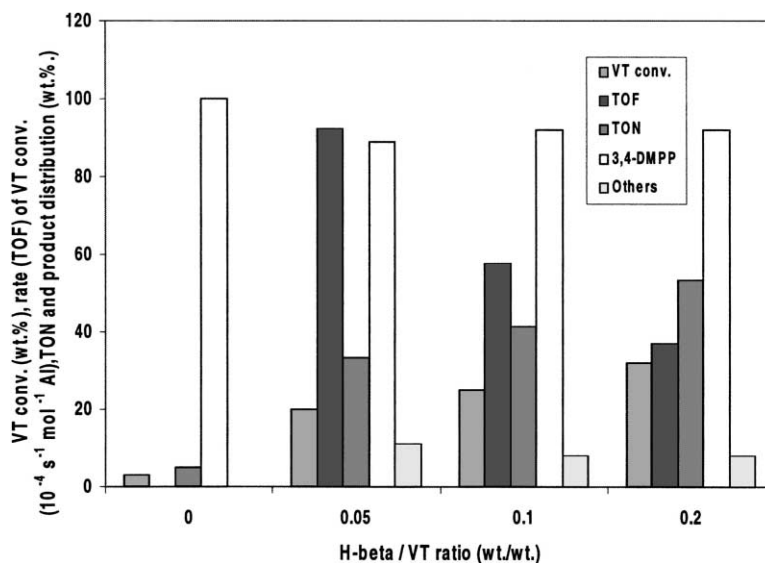


Fig. 4. Influence of H-beta/VT ratio (wt. wt.⁻¹) on the VT conversion, TOF and product distribution. Reaction conditions: H-beta (g) = 0.1; for other conditions, see Fig. 2.

continuously with the increase in catalyst concentration. In addition, the concentration of other by-products also decreases to some extent with the increase in the catalyst concentration, due to the increase of mol of Al in the total number of zeolite H-beta.

The conversion of VT as a function of reaction time for the propenylation of VT using different concentrations of H-beta (ratio of H-beta/VT = 0.05–0.5) is displayed in Fig. 5. The reaction conditions are detailed in Fig. 4. It is noted that the conversion of

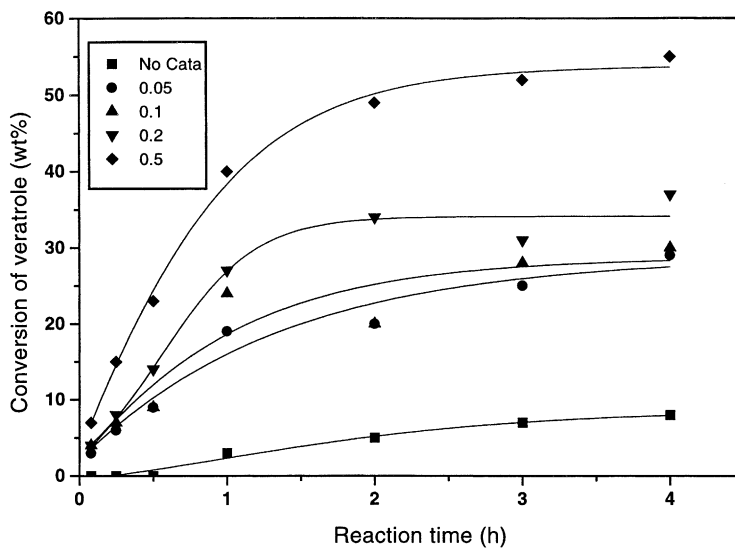


Fig. 5. Influence of different catalyst (H-beta) concentrations on the conversion of VT (wt.%) vs. reaction time (h). The values in the figure represent the H-beta/VT (wt. wt.⁻¹) ratio; for reaction conditions, see notes to Fig. 4.

VT increases with the increase in catalyst concentration sharply up to 1 h of reaction time and then a slower increase in the conversion of VT is observed with reaction time at all H-beta to VT ratios studied. An increase in the conversion of VT versus reaction time is also observed in the absence of any catalyst.

3.5. Influence of reaction temperature

The dependence of the VT conversion, rate of VT conversion (TOF), TON and product distribution (wt.%) on the reaction temperature is investigated in the temperature range of 383–403 K using the H-beta as catalyst (Fig. 6). The conversion and rate of VT conversion and TON are found to increase with increase in reaction temperature. The conversion and rate of VT conversion and TON increase from 4.1 to 25 wt.%, 9.5 to $57.7 \times 10^{-4} \text{ s}^{-1} \text{ mol}^{-1} \text{ Al}$ and 6.8 to 41.6 wt.%, respectively, when the temperature was raised from 383 to 403 K. However, the selectivity for 3,4-DMPP decreases with the increase in reaction temperature, as shown in Fig. 6. At a higher temperature (403 K), selectivity to 3,4-DMPP decreases due to the formation of other products. The apparent activation energy of VT conversion over H-beta is estimated to be 117 kJ mol^{-1} (Fig. 7) in the temperature range 383–403 K.

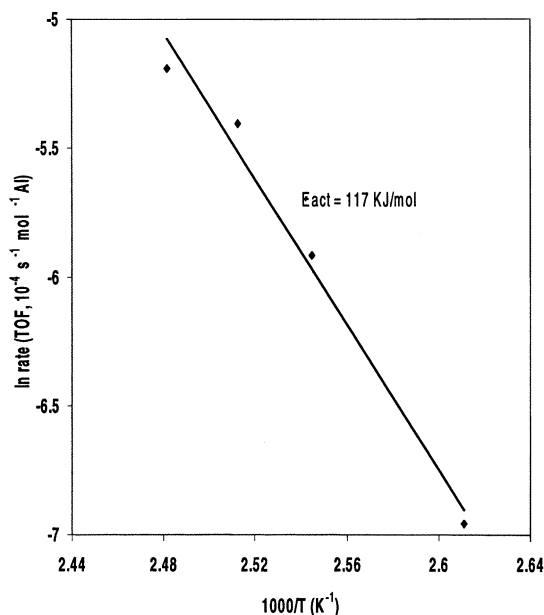


Fig. 7. Arrhenius plot for the propionylation of VT by PC over zeolite H-beta.

3.6. Influence of reactants molar ratio

The results of the influence of VT/PC ratios on the conversion of VT (wt.%), rate of VT conversion

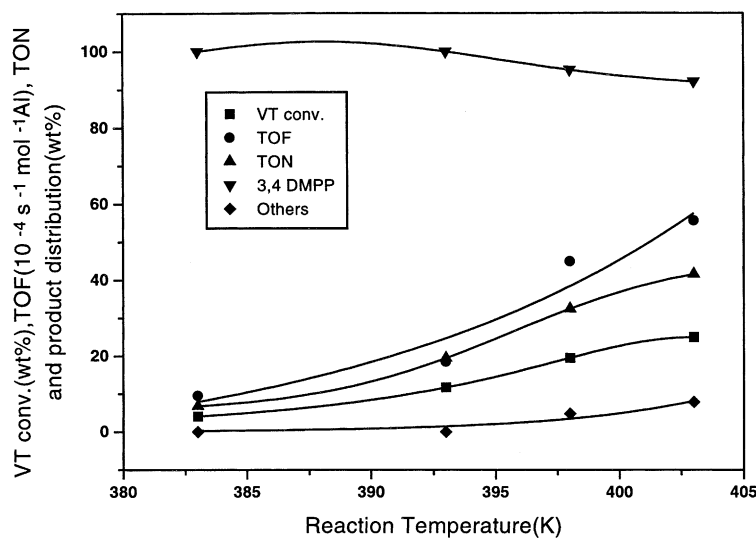


Fig. 6. Influence of reaction temperature on the conversion of VT (wt.%), TOF ($10^{-4} \text{ s}^{-1} \text{ mol}^{-1} \text{ Al}$) and product distribution; for reaction conditions, see notes to Fig. 4.

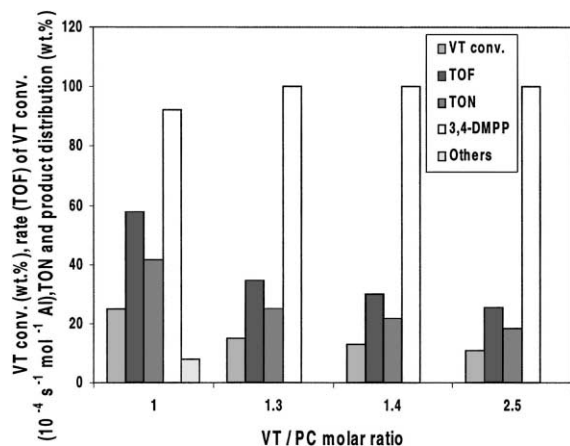


Fig. 8. Influence of VT/PC molar ratio on the conversion of VT (wt.%), TOF ($10^{-4} \text{ s}^{-1} \text{ mol}^{-1} \text{ Al}$) and product distribution; for reaction conditions, see notes to Fig. 4.

(TOF) and TON product distribution are summarised in Fig. 8. The ratios were changed by keeping the amount of VT constant. An increase in the VT/PC molar ratio from 1 to 2.5, the conversion of VT, TOF and TON of VT conversion decreases from 25 to 11 wt.%, 57.7 to $25.3 \times 10^{-4} \text{ s}^{-1} \text{ mol}^{-1} \text{ Al}$ and 18.3 to 24.9 wt.%, respectively. The selectivity for 3,4-DMPP remains nearly constant in all experiments.

3.7. Recycling

The results of the catalyst recycling experiments using zeolite H-beta in the propionylation of VT are shown in Table 2. After completion of the reaction of each cycle for 1 h, the catalyst was removed by filtration from the reaction solution, washed thoroughly with acetone, calcined at 773 K for 16 h in the

presence of air and characterised for its crystallinity. The activity of the catalyst decreases progressively to a small extent on recycling, but the selectivity for 3,4-DMPP remains nearly unaffected (Table 2). In order to check the structure and the crystallinity of the catalyst after reaction, XRD patterns were recorded. XRD measurements indicated that the catalyst retains the structure and the degree of crystallinity was 100% even after second recycle. The results reported here are in good agreement with the earlier reported data for the acylation of aromatics using zeolite catalysts [18].

3.8. Propionylation of dimethoxybenzenes (*o*-, *m*-, *p*-isomers)

To study the comparative reactivities and generality of the *o*-, *m*- and *p*-isomers of dimethoxybenzenes, the propionylation of these isomers was carried out over zeolite H-beta at 403 K using PC as propionylating agent under identical reaction conditions (Table 3). The position of methoxy groups on the benzene ring plays an important role in defining the type of products and reactivities of the isomers. The propionylation of VT leads to the formation of 3,4-DMPP in 92.1 wt.% selectivity, whereas *m*- and *p*-dimethoxybenzenes produce 2,4-dimethoxypropiophenone (2,4-DMPP) and 2,5-dimethoxypropiophenone (2,5-DMPP) in 100% selectivity, respectively. The conversion and rate of 1,2-DMB (VT), 1,3-dimethoxybenzene (1,3-DMB) and 1,4-dimethoxybenzene (1,4-DMB) conversion are found to be 25.0, 20.9, 6.8 wt.% and 57.7, 48.3, $15.8 \times 10^{-4} \text{ s}^{-1} \text{ mol}^{-1} \text{ Al}$, respectively. The reactivities of these isomers in this reaction are found to be in the following order.

1, 2-DMB (VT) > 1, 3-DMB > 1, 4-DMB

Table 2
Recycling^a

Recycle	Conversion of VT (wt.%)	Product distribution (wt.%) ^b		Crystallinity (%)
		3,4-DMPP	Others	
Fresh	42.6	93.4	6.6	100
First	40.4	96.3	3.7	100
Second	37.5	95.8	4.2	100

^a Reaction condition: catalyst = 0.5 g; VT/PC (molar ratio) = 1; VT (mol) = 0.01; chlorobenzene (ml) = 50; reaction temperature (K) = 403; reaction time (h) = 1.

^b 3,4-DMPP = 3,4-dimethoxypropiophenone and others.

Table 3
Propionylation of dimethoxybenzenes (*o*-, *m*-, *p*-isomers)^a

DMB ^b	Conversion of VT (wt.%)	TOF (10 ⁻⁴ s ⁻¹ mol ⁻¹ Al)	TON	Product distribution (wt.%)			
				3,4-DMPP	2,4-DMPP	2,5-DMPP	Others
VT (1,2-DMB)	25.0	57.7	41.5	92.1	–	–	7.9
1,3-DMB	20.9	48.3	34.7	–	100	–	–
1,4-DMB	6.8	15.8	11.3	–	–	100	–

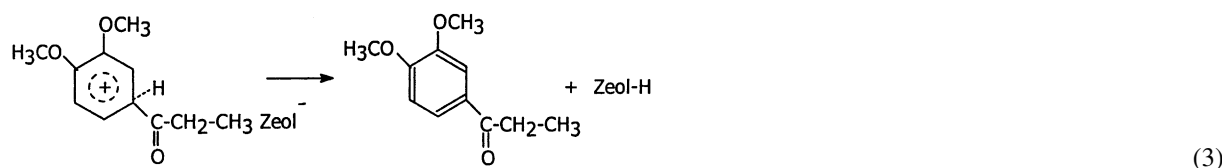
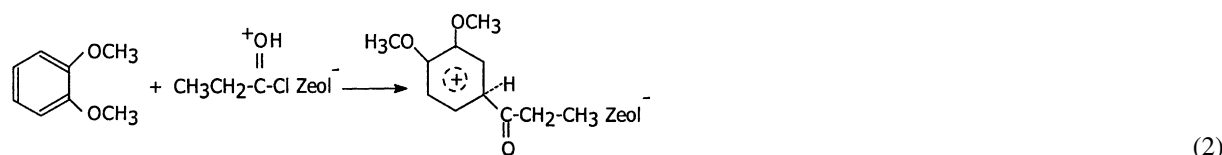
^a Reaction conditions: H-beta (g) = 0.1; for other conditions, see notes to Fig. 2.

^b 1,2-DMB = 1,2-dimethoxybenzene (VT); 1,3-DMB = 1,3-dimethoxybenzene; 1,4-DMB = 1,4-dimethoxybenzene.

From this study it can be concluded that all isomers of dimethoxybenzenes may be propionylated to the corresponding propiophenones.

3.9. Mechanism

The classical Friedel-Crafts propionylation is an electrophilic aromatic substitution in which an electron-deficient species (electrophile) is generated by the activation of PC on the protonic sites of the zeolite, which then attacks the dimethoxybenzene ring, resulting in the formation of propiophenones according to the following equations (Eqs. (1)–(3)) [12,14,18,30].



4. Conclusions

Several zeolite catalysts are studied in this work for the propionylation of VT to 3,4-DMPP. Zeolite H-beta and RE (70.6)-Y showed higher propionylation activity than H-Y, H-mordenite and H-ZSM-5.

The Bronsted acid sites of the zeolite catalysts favour the formation of 3,4-DMPP and hence H-beta and RE (70.6)-Y are found to be better active catalysts for the selective propionylation of VT to 3,4-DMPP. The conventional Lewis acid catalyst AlCl₃ is found to be active but non-selective and higher amounts of consecutive products are obtained in the reaction mixture due to its strong Lewis acid sites and non-shape-selective character. The conversion of VT increases with increase in duration of run, catalyst concentration and reaction temperature, whereas it decreases with an increase in SiO₂/Al₂O₃ ratio and VT/PC molar ratio. However, the TOF of VT conversion decreases continuously with the increase in catalyst concentration. The selective propionylation of *o*-, *m*- and *p*-isomers of dimethoxybenzenes proves the generality of the reactions. Recycling of H-beta

progressively decreases the conversion of VT due to the extraction of minor amounts of aluminium from the framework of H-beta by the HCl which is produced during the reaction. However, the selectivity for 3,4-DMPP remains roughly constant during recycling. The presence of strong Bronsted acid sites in the zeolite catalysts thus appears to be very

important for the polarisation of PC into an electrophile ($\text{CH}_3\text{CH}_2\text{CO}^+$), which then attacks the VT ring, resulting in the formation of dimethoxypropio-phenone.

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