

Propionylation of anisole to 4-methoxypropiophenone over zeolite H-beta

S Sugunan*, Bindhu Jacob & Binoy Jose

Department of Applied Chemistry, Cochin University of Science and Technology, Cochin 682 022, India

Received 11 May 1999; accepted (revised) 18 August 1999

The results of a detailed study of the propionylation of anisole over various medium and large pore zeolites such as H-ZSM-5, H-beta, H-Na-beta, H-mordenite, H-Y and H-RE-Y are presented and discussed. In addition, homogenous catalysts and amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$ are also included for comparison. The catalyst and process parameters are optimised to enhance the conversion of propionyl chloride(PC) and selectivity to 4-methoxypropiophenone(4-MOPP).

Methoxy propiophenones are found to have wide applications in the area of fine chemical synthesis. They are usually prepared by the Friedel-Crafts acylation of anisole with propionyl chloride/propionic anhydride using AlCl_3 catalyst^{1,2,3}. The use of various types of catalysts like ZnCl_2 , FeCl_3 ^{4,5}, H_3PO_4 ⁶, and cobalt (II) chloride⁷ have been reported recently in the liquid phase propionylation of anisole. Zeolites due to their shape-selectivity, thermostability, ease of separation from the products and the regeneration of the deactivated catalysts, have been widely used in the field of petrochemistry. However, the use of zeolite catalysts in fine organic synthesis and particularly in the acylation and alkylation reactions of aromatics is limited.

Herein we report the results obtained in the propionylation of anisole under various reaction conditions and on the effects of some catalyst variables on catalyst performance. The results obtained over zeolite H-beta are also compared with the Lewis acid catalyst, AlCl_3 .

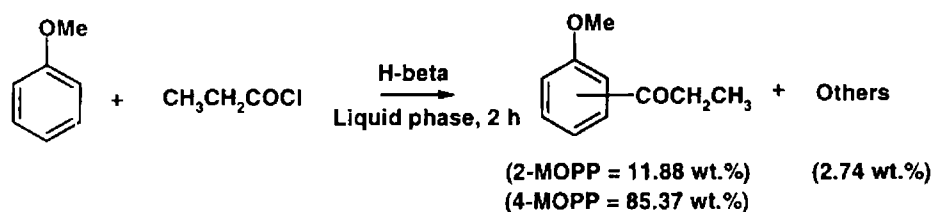
Experimental Section

Zeolites Na-Y and H-mordenite were obtained from Laporte Inorganics, Cheshire, UK. Zeolites ZSM-5 and beta were prepared using the methods described in the literature^{8,9}. The synthesized zeolites were washed with deionised water, dried and calcined at 813 K for 16 hr in the presence of air to eliminate the organic templates from the zeolite channels. The resultant samples were NH_4^+ -exchanged three times using the following conditions: 10 mL NH_4NO_3 (1M)/g zeolite, 353 K, 8 hr exchanged run, pH 7-8. The NH_4^+ -exchanged samples were again calcined at

823 K for 8 hr to get their protonic forms. Na-exchanged beta samples were prepared by treating fresh H-beta with 100 mL aliquots of 0.1M and 1M aqueous solutions of NaNO_3 by following the above exchange conditions. The H.RE(42.2)Y and H.RE(70.6)Y were prepared by treating $\text{NH}_4\text{-Y}$ with 5% rare earth chloride solution.

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). The surface area of the catalysts was measured by the nitrogen BET method using an Omnisorb 100 CX apparatus. X-ray powder diffraction (XRD) was carried out on a Rigaku, D-Max/III-VC model using the CuK_α radiation and was used to evaluate the peak positions of various zeolite samples. The acidity of the various zeolites were determined using temperature programmed desorption of ammonia¹⁰⁻¹². The size and morphology of the zeolite catalysts were estimated by scanning electron microscope (Cambridge Stereoscan 400).

The acylation of anisole was carried out in liquid phase at 343 K under atmospheric pressure. In a typical run, appropriate amounts of anisole and propionyl chloride (5:1) molar ratio was charged in the batch reactor along with 0.3 g catalyst. Samples were withdrawn periodically and analyzed with a gas chromatograph. The percentage conversion (wt.%) of propionyl chloride (PC) is defined as the total percentage of PC transformed. The main products obtained were 4-methoxypropiophenone(4-MOPP) and 2-methoxypropiophenone(2-MOPP) along with some amount of other consecutive products (Scheme I).



Scheme I

Table I—Propionylation of anisole^a

Catalyst	Reaction time (h)	Conversion ^b of PC (wt%)	Rate of ^c PC conversion (mmol g ⁻¹ h ⁻¹)	Product distribution (wt.%) ^d		
				4-MOPP	2-MOPP	Others
H-ZSM-5	2	62.02	19.10	83.45	15.55	0.99
H-beta	2	69.76	21.48	85.37	11.88	2.74
H-Na (13.6) beta ^e	2	63.64	19.60	75.07	17.27	7.65
H-Na (37.3) beta ^e	2	48.39	14.90	55.73	30.48	13.78
H-mordenite	2	57.15	17.60	78.20	20.02	1.78
H-Y	2	58.66	18.07	67.56	24.76	7.58
H-RE (42.2)Y ^f	2	59.81	18.42	68.21	26.62	5.27
H-RE (70.6)Y ^f	2	65.32	20.11	58.03	30.70	11.27
AlCl ₃	2	82.93	25.54	59.7	22.07	18.23
SiO ₂ -Al ₂ O ₃ (amorphous)	2	47.47	14.62	64.88	31.35	3.76

^a Reaction conditions: catalyst (g) = 0.3; catalyst / C₂H₅COCl (wt./wt.) = 0.17; anisole / C₂H₅COCl (molar ratio) = 5; reaction temperature (K) = 343

^b PC = propionyl chloride (C₂H₅COCl)

^c Rate of PC conversion (mmol g⁻¹h⁻¹) = (amount of PC reacted)/(weight of catalyst × reaction time)

^d 4-MOPP = 4-methoxypropiofenone; 2-MOPP = 2-methoxypropiofenone others = consecutive products

^e Values in parenthesis represents the percentage of Na exchanged in the H-beta

^f Values in parenthesis represents the percentage of RE³⁺-exchanged in zeolite H-Y

The rate of PC conversion (mmol g⁻¹h⁻¹) was calculated as the amount of PC (m mole) converted per hour per g of the catalyst. The selectivity for a product is expressed as the % of the particular product formed.

Results and Discussion

The conversion of PC (wt.%), rate of PC conversion (mmol g⁻¹h⁻¹) and the product distribution (wt.%) of the products, 4-methoxypropiofenone and 2-methoxypropiofenone obtained over various zeolite catalysts are listed in Table I. Among various zeolite catalysts, H-beta catalyzes the reaction efficiently and selectively to 4-MOPP and it is found to be superior to other zeolite catalysts and AlCl₃. The conversion of PC, rate of PC conversion and selectivity for the major product, 4-MOPP over zeolite H-beta after 2 hr

of reaction time were found to be 69.76 wt.%, 21.48 mmol g⁻¹h⁻¹, 85.37 wt.% respectively. The highest activity of H-beta may be attributed to its stronger acid sites and the space available in the 12-membered three dimensional pore system (5.4×5.6 and 5.1×5.5). AlCl₃ gave higher amounts of consecutive products due to its non-shape selective character.

The conversion of PC over H-Y, H-RE(42.2)-Y and H-RE(70.6)-Y are found to be 58.66 wt.%, 59.81 wt.% and 65.32 wt.% respectively. The enhancement in catalytic activity may be due to the increase in strength of acid sites due to RE-cation exchange¹¹. The activity of zeolite H-beta in the propionylation reaction decreases drastically with the increase in Na⁺ content in H-beta. This may be due to the removal of some amount of stronger Brönsted acid sites by Na⁺ exchange in H-beta. A blank run carried out at the

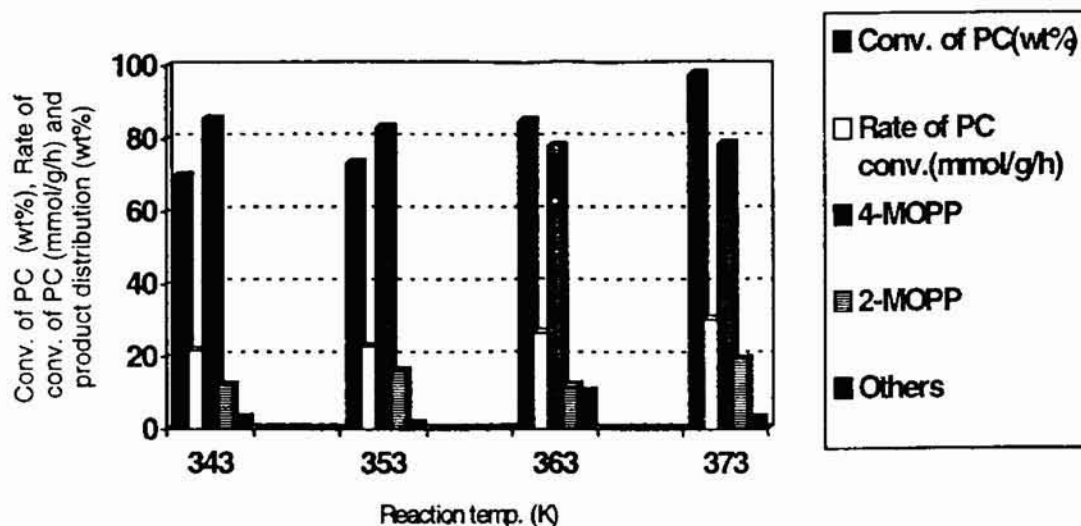


Figure 1—Influence of reaction temperature on the conversion of PC (wt. %); rate of PC conversion (m mols $g^{-1} h^{-1}$) and product distribution (over H-beta)

Table II—Influence of SiO_2/Al_2O_3 ratio of zeolite H-beta^a

	SiO_2/Al_2O_3 (molar ratio)		
	26	50	80
Reaction time (hr)	2	2	2
Conversion of PC (wt.%) ^b	69.76	23.25	18.11
Rate of PC conversion ($mmol g^{-1} h^{-1}$) ^c	21.48	7.16	5.57
Product distribution (wt.%)			
4-MOPP	85.37	82.07	84.93
2-MOPP	11.88	12.95	6.98
Others	2.74	4.98	8.09

a,b,c & d see footnotes to Table I

same reaction conditions in the absence of any catalyst gave a PC conversion of 19.65 wt. %.

A significant increase in the rate of PC conversion is achieved with the increase in the reaction temperature from 343 K to 373 K. However, the product distribution is not significantly influenced. The selectivity towards 4-MOPP remains more or less constant in the range of temperature studied (Figure I).

Table II shows the effect of SiO_2/Al_2O_3 molar ratio of zeolite H-beta in the propionylation of anisole. The conversion of PC is found to decrease from 69.76 wt. % to 18.11 wt. % with increase in SiO_2/Al_2O_3 molar ratio from 26 to 80.

The effect of catalyst concentration (cat/PC ratio) in the range of 0.05 to 0.41 g/mole of PC on the conversion of PC is studied at 343 K for 2 hr of reaction over zeolite H-beta catalyst. When the

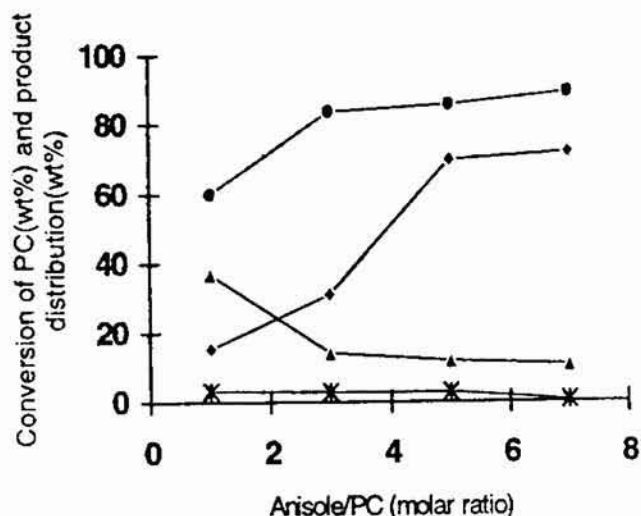


Figure 2—Effect of anisole/PC molar ratio on the conversion of PC (♦) and product distribution (Over zeolite H-beta). 4-MOPP (●), 2-MOPP(▲) and others (*); Reaction conditions: See footnotes to Table I; Reaction time = 2 hr

catalyst to PC ratio is increased from 0.05 to 0.41, the conversion of PC is also found to increase from 50.20 wt. % to 64.15 wt. % (Table III). Furthermore, it is observed that, the selectivity of the major product, 4-MOPP is found to be relatively little affected by the increase in catalyst concentration. The increase in selectivity of 2-MOPP can be explained on the basis of shape selective behaviour of H-beta.

Figure II shows the effect of varying the anisole/PC molar ratio in the reaction mixture on the activity of H-beta and product distribution at a fixed anisole concentration. An increase in both the

Table III—Effect of catalyst (H-beta) concentration^a

Catalyst/PC (wt./wt.)	Conversion ^b of PC (wt %)	Rate of PC conversion (mmol g ⁻¹ h ⁻¹)	Product distribution(wt%) ^d		
			4-MOPP	2-MOPP	others
0.05	50.20	46.38	87.23	8.13	4.64
0.17	69.76	21.48	85.37	11.88	2.74
0.29	65.32	12.07	76.05	13.48	10.46
0.41	64.15	8.46	74.80	19.12	6.08

a,b,c & d see foot notes to **Table I**; reaction time = 2 hr

Table IV—Recycling of H-beta^a

Run	Change in SiO ₂ /Al ₂ O ₃ (molar ratio)	Conversion ^b of PC (wt. %)	Rate of PC ^c conv. (mmol g ⁻¹ h ⁻¹)	Product distribution (wt%) ^d			% crystallinity of H-beta
				4-MOPP	2-MOPP	Others	
1 (parent catalyst)	26.0	68.73	21.16	68.85	23.58	7.57	100
2	29.56	41.32	12.72	61.03	29.51	9.46	79.1
3	31.38	29.89	9.2	58.72	31.43	9.85	75.3

a,b,c & d see foot notes to **Table I**; reaction time (hr) = 2

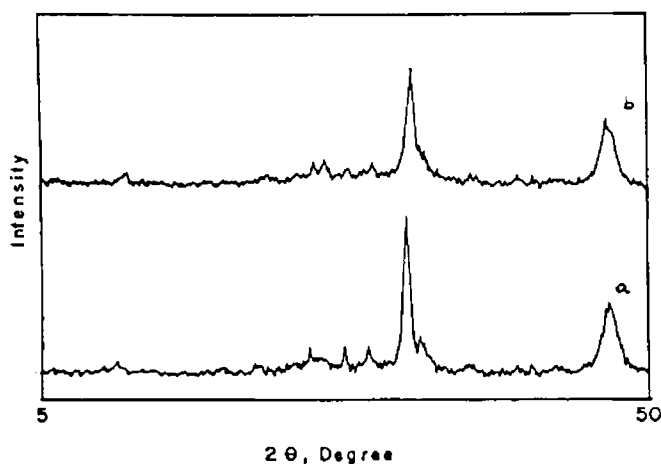


Figure 3—X-ray diffraction patterns of (a) fresh H-beta and (b) H-beta after recycling

conversion of PC and selectivity of 4-MOPP is observed with increase in anisole/PC molar ratio. The conversion of PC at 1, 3, 5 and 7 molar ratios of anisole to PC was found to be 15.50 wt.%, 31.14 wt.%, 69.76 wt.% and 71.66 wt.% respectively.

Table IV depicts the recycling of zeolite H-beta in the propionylation of anisole. The used catalyst is activated each time at 773 K in the presence of air and characterized for its chemical composition and crystallinity (**Figure III**). A decline in the propionyl chloride conversion was observed after each reuse. It has been presumed that the decrease in catalytic

activity is probably due to the dealumination of the zeolite framework by HCl, which is formed as a by-product during the reaction.

The formation of methoxypropionophenone is explained by an electrophilic attack of the propionyl cation (C₂H₅CO⁺) on the anisole ring whose formation is facilitated by the stronger acid sites of the catalyst¹³.

In summary, zeolite catalysts can catalyze the propionylation of anisole to methoxy propionophenones. H-beta is found to be a more active catalyst than the other zeolites and it showed a better selectivity in the reaction than the conventional Lewis acid catalyst AlCl₃. The catalysts used in this study could be arranged in the decreasing order of PC conversion (mmol g⁻¹h⁻¹) as follows:

AlCl₃ > H-beta > H-RE(70.6)-Y > H-Na(13.6)-beta > H-ZSM-5 > H-RE(42.2)-Y > H-Y > H-mordenite > H-Na(37.3)-beta > SiO₂-Al₂O₃(amorphous).

The yield of the product decreases with an increase in SiO₂-Al₂O₃ ratio of H-beta. A higher yield of methoxypropionophenone is obtained by increasing the reaction temperature, catalyst concentration and molar ratios of anisole to propionyl chloride.

References

- 1 Bindhu Jacob, Sugunan S & Anand P Singh, *J Mol Catal A Chemical*, 139, 1999, 43 and references cited therein.
- 2 Singh A P, Jacob B, Jacob Bindhu & Sugunan S, *J Appl Catal, A General*, 174, 1998, 51 and references cited therein.

- 3 Johnson K M & Shotter R G, *Tetrahedron*, 30, 1974, 4059.
- 4 Platova A I, Denisenkova V Ya Svadkovskaya G A & Kheifits, L A, *Maso-Zhir Prom-st*, 9, 1976, 29; *Chem Abstr*, 86, 1977, 72099n.
- 5 Yuldasev Kh Yu, *Zh Org Khim*, 14, 1978, 2088; *Chem Abstr*, 90, 1979, 86932y.
- 6 Bauer Kurt: Moellenken Reiner, *Ger*, 2, 1974, 418.
- 7 Iqbal, Javed Khan, Nayyar M A & Naresh K, *Tetrahedron Lett*, 32, 1991, 5179.
- 8 Argauer R J & Landolt G R, *U S Pat*, 3 702 886, 1972.
- 9 Cambor M A & Perez Pariente J, *Zeolites*, 11, 1991, 202.
- 10 Singh A P, Bhattacharya D & Sharma S, *J Mol Catal*, 102, 1995, 139.
- 11 Choudhary V R & Pataskar S G, *Zeolites*, 6, 1986, 307.
- 12 Chamoumi M, Brunel D, Fajula F, Geneste P, Moreau P & Solof J, *Zeolites*, 14, 1994, 283.
- 13 Arata K, Yabe K & Toyoshima I, *J Catal*, 44, 1995, 409.