

Acetylation of benzene to acetophenone over zeolite catalysts

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Abstract

The vapour phase acetylation of benzene has been investigated over various zeolite catalysts using acetic acid as acetylating agent in a tubular reactor and at atmospheric pressure. The rate of acetic acid conversion ($\text{TOF} = \text{m mol s}^{-1} \text{ mol}^{-1} \text{ Al} \times 10^{-3}$) is found to be about eleven times higher over H-ZSM-5 ($\text{TOF} = 46.2$) compared to the H-mordenite ($\text{TOF} = 4.3$). HY and REY do not catalyze the reaction. The acidity of the catalysts is evaluated by the temperature programmed desorption of ammonia. NH_3 -TPD results show that the presence of strong Brønsted acid sites are desired for the acetylation of benzene by acetic acid. The effects of time on stream (TOS), degree of Na-exchange, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios, reaction temperature, weight hourly space velocity (WHSV h^{-1}) and molar ratios of benzene/ CH_3COOH upon the conversion of acetic acid and product yields are investigated in the acetylation of benzene using H-ZSM-5 zeolite. H-ZSM-5 is partially deactivated under these reaction conditions. Acetic acid conversion increased with reaction temperature and benzene/ CH_3COOH molar ratios, whereas it decreased with the increase in reaction time, degree of Na-exchange, WHSV h^{-1} and $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio. Presumably, the acetylation proceeds by the attack of an electrophile (CH_3CO^+) on the benzene ring resulting in the formation of acetophenone. © 1997 Published by Elsevier Science B.V.

Keywords: Acetylation of benzene; Zeolite catalysts; Acetophenone

1. Introduction

Acetophenone can react with formaldehyde to yield light resistant resins which are used as additives in nitrocellulose paints [1]. It is also used as a photoinitiator and in the pharmaceuticals, perfumery and pesticide industries [2]. It can be hydrogenated to 1-phenylethanol which is used for the production of aromatic ester fragrances [3]. Industrially, acetophenone is produced in the Hock process by decomposition of hydroperoxide. A more selective synthesis of

acetophenone by cleavage of cumene hydroperoxide over a cupric catalyst, has been patented [4]. Acetophenone can also be produced by oxidizing the methyl phenyl carbinol intermediate which is found in styrene production processes [5,6]. Conventionally, it was prepared by the Friedel–Crafts reaction of acetyl chloride with benzene in the presence of homogeneous catalyst, AlCl_3 . However, the homogeneous catalysts have several disadvantages if applied to industrial processes such as wasting large amounts of catalysts, corrosion of reactors, water pollution by acidic waste water and difficulty of catalyst recovery [7]. In order to overcome the difficulties of the homogeneous sys-

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tems, the development and utilization of a solid zeolite catalyst is important. Zeolites are attractive as catalysts for the acetylation reactions due to their acidity, shape selectivity and regenerability properties [8–17]. The objective of the present work is to develop a zeolite catalyst for the acetylation of benzene to acetophenone and to replace acetyl chloride (used in the conventional methods) by acetic acid. Acetyl chloride produces HCl during the reaction, which is environmentally hazardous. The catalyst and process parameters are optimised to enhance the conversion of acetic acid and selectivity to acetophenone. The reaction using zeolite as a catalyst and acetic acid as an acetylating agent has not been reported before.

2. Experimental

ZSM-5 zeolites were synthesized using the literature procedure [18]. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the final product was varied by adjusting the amount of Al source added in the synthesis mixture. As synthesized ZSM-5 samples were calcined in air at 773 K for 16 h to remove the occluded structure-directing agent. The calcined samples were then refluxed thrice with a 1 M NH_4NO_3 solution for 8 h at 353 K followed by calcination at 773 K for 16 h in order to ensure that the samples were in their complete protonic forms. Modified forms of H-ZSM-5 such as H-Na(28.9)ZSM-5, H-Na(34.1)ZSM-5 and H-Na(37.3)ZSM-5 were prepared by an exchange with 0.3, 0.5 and 1.0 M solutions of NaNO_3 , respectively, for 24 h at room temperature. Zeolites H-mordenite and Na-Y were obtained from Laporte Inorganics, Cheshire, UK. 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 $\text{NH}_4\text{-Y}$ was treated with 5% rare earth chloride solution by following the analogous method employed for $\text{NH}_4\text{-Y}$ exchange.

The X-ray powder diffraction patterns of all samples were recorded on a Rigaku (D-

Max/III-VCmodel, Cu K α radiation) X-ray diffractometer. Chemical analysis was performed by a combination of wet chemical and atomic absorption spectroscopy (Hitachi 800). The nitrogen BET surface areas were measured using an Omnisorb 100 CX apparatus. Scanning electron microscope (Shimadzu, Model UV-2101 PC) was used to determine the average crystal size of the zeolites. Typical characteristic data of the zeolites are listed in Table 1.

Temperature programmed desorption (TPD) of ammonia was recorded on a fixed bed flow type apparatus attached to a HCl solution trap [9,19]. Approximately 1.0 g of sample was activated in flowing N_2 at 773 K for 4 h, then ammonia was passed over the sample at 303 K for 30 min. The sample was subsequently kept in the flow of N_2 (50 ml min^{-1}) at 303 K for 15 h in order to eliminate the physisorbed ammonia. Acid-strength distribution and NH_3 chemisorbed at 303 K were obtained by raising the temperature, with a ramping rate of $10^\circ\text{C min}^{-1}$, from 303 to 773 K in a number of steps in a flow of nitrogen (10 ml min^{-1}), Table 1. The NH_3 evolved was trapped in a HCl solution and titrated with a standard NaOH solution.

The gas-phase acetylation of benzene with acetic acid was carried out in a fixed bed type reactor with a continuous flow system at atmospheric pressure. The zeolite catalyst (2.0 g, mesh size 15–30 mesh range) was packed in a glass reactor (1.4 cm I.D) and placed in a vertical furnace. Pretreatment of the catalyst consisted of heating in a stream of nitrogen ($50 \text{ cm}^3 \text{ min}^{-1}$) for 2 h. Then a predetermined mixture of benzene and acetic acid was passed through the catalytic bed by a syringe pump. The product mixture was condensed at the reactor outlet and the samples were analyzed periodically by a gas-chromatograph (Blue Star Model 421) equipped with a flame ionization detector and a capillary column (5 μm thick crosslinked methyl silicone gum, 0.2 mm \times 50 m long). The products were also identified by injecting an authentic sample and GC/MS (Shimadzu, QP 2000A) analysis.

Table 1
Acetylation of benzene^a

Catalyst	SiO ₂ /Al ₂ O ₃ (molar ratio)	NH ₃ desorbed (m mol/g) at different temperatures (K)				NH ₃ Chemisorbed at 303 K (m mol/g)	Conv. of acetic acid (wt%)	TOF ^b (m mol s ⁻¹ mol ⁻¹ Al × 10 ⁻³)	Product distri- bution (wt%) ^c	
		303–353	353–433	433–513	513–653				653–773	ACP
H-ZSM-5 ^d	41.0	0.55	0.16	0.05	0.26	0.21	1.23	46.2	91.1	8.9
H-mordenite ^e	22.0	0.20	0.17	0.15	0.12	0.07	0.71	4.3	31.4	68.6

^a Reaction conditions: Catalyst weight = 2.0 g; benzene/acetic acid (molar ratio) = 2; feed rate = 2 ml/h; reaction temperature = 523 K.

^b Turnover rates are expressed as turnover frequencies (TOF, mol of CH₃COOH converted per s per mol of aluminium).

^c ACP = acetophenone, others = di- and triacetyl products.

^d H-ZSM-5 (degree of H⁺-exchange (%)) = > 98; crystal size (μm) = 0.4–0.6; surface area (m²/g) = 413.

^e H-mordenite (degree of H⁺-exchange (%)) = > 98; Crystal size (μm) = 1.0; Surface area (m²/g) = 552.

Finally, the percentage conversion (wt%) is defined as the total percentage of CH_3COOH transformed and the selectivity (wt%) for a product is expressed as the amount of the particular product divided by the amount of total products and multiplied by 100. The turnover frequency (TOF = $\text{m mol s}^{-1} \text{ mol}^{-1} \text{ Al}$) is determined as the number of CH_3COOH mol transformed per s per mol of aluminium of the catalyst.

3. Results and discussion

3.1. Catalyst characterization

Table 1 lists the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, H^+ -exchange (%), crystal size and surface areas of H-ZSM-5 and H-mordenite zeolites used in this work. These data reveal that zeolite samples are highly crystalline and in the protonic forms. No reflections of a dense phase or any other zeolite phase are found. Table 1 also illustrates the amount of NH_3 desorbed from zeolites in different temperature steps.

3.2. Catalytic activity

The results of the catalytic activities in the acetylation of benzene with acetic acid using H-ZSM-5 and H-mordenite catalysts are shown in Table 1. The main product of the reaction is acetophenone. Small amounts of diacetylbenzenes (others) are also detected in the reaction. The activities of H-ZSM-5 and H-mordenite are compared using data after the initial 2 h of the run under similar reaction conditions. H-ZSM-5 exhibits the higher catalytic activity and the rate of acetic acid conversion (TOF) is found to be several times higher over H-ZSM-5 than that of the H-mordenite. Zeolites H-Y and RE-Y are ineffective for the acetylation of benzene to acetophenone at our reaction conditions. The conversion of acetic acid over H-ZSM-5 and H-mordenite are found to be 42.6 and 7.2 wt%, respectively. The corresponding TOF are 46.2

and 4.3, respectively. In addition, the results show that the selectivity for acetophenone over H-ZSM-5 is greater (91.1 wt. %) than that of H-mordenite (31.4 wt%). From the data in Table 1, it is clear that the performance of the catalyst is governed by the acidity and structure of the zeolites. The higher conversion of acetic acid over H-ZSM-5 seems to be due the fact that the H-ZSM-5 exhibits the three dimensional channel systems and stronger Brønsted acid sites compared to the H-mordenite (Table 1). These results indicate that acid strength is the most important factor for the polarization of CH_3COOH into an electrophile (CH_3CO^+) which attacks the benzene ring and produces the acetophenone [9,12,14,20]. The higher selectivity for acetophenone over H-ZSM-5 might be attributed to its smaller pore openings ($0.51 \times 0.55 \text{ nm}$ and $0.54 \times 0.56 \text{ nm}$) than H-mordenite ($0.65 \times 0.7 \text{ nm}$) which prevent the secondary reactions in the zeolite channels and consequently the formation of diacetyl benzene.

3.3. Time on stream

The conversion of acetic acid and product distribution for acetophenone and diacetyl ben-

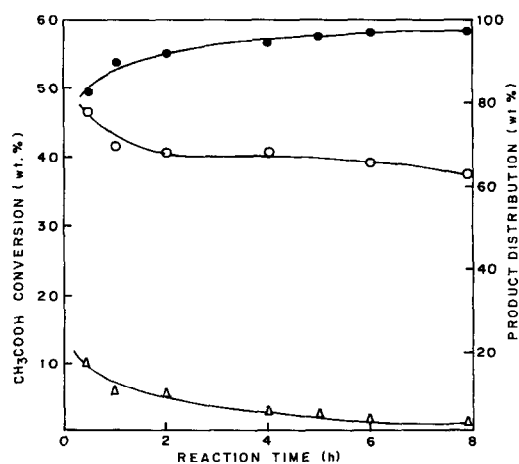


Fig. 1. Effect of time on stream in the conversion of CH_3COOH (○) and product distribution; ACP (●) and others (△). Reaction conditions; H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 41$) = 2 g; benzene/acetic acid (molar ratio) = 2; feed rate (ml/h) = 2; reaction temperature = 523 K.

zenes (others) over H-ZSM-5 are presented as a function of time on stream in Fig. 1. No substantial change in the conversion of acetic acid is observed after 2 h time on stream study, however, slight deactivation of the catalyst is noticed in the beginning of the reaction. A marginal increase in the selectivity for acetophenone is noticed with the reaction time. The increase in selectivity for acetophenone with time on stream may be attributed to the deactivation of the outer surface of H-ZSM-5 which inhibits the formation of unwanted products.

3.4. Effect of Na-exchange

The conversion of acetic acid to the products in the acetylation of benzene was measured over a series of Na⁺-exchange H-ZSM-5 zeolites at a constant temperature (523 K) with benzene/acetic acid molar ratio of two. The data presented in Table 2 show that the rate of acetic acid conversion decreases in the following order: H-ZSM-5 > H-Na(28.9)-ZSM-5 > H-Na(34.1)-ZSM-5 > H-Na(37.3)-ZSM-5. H-ZSM-5 zeolite is much more active than Na⁺-exchanged zeolite [12] but is less selective for acetophenone formation. In addition, there is more diacetyl benzenes produced over H-ZSM-5 than over Na⁺-exchanged H-ZSM-5. These data suggest that the stronger Brønsted acid sites of H-ZSM-5 are capable of facilitating reaction between acetophenone and acetic acid (to a little extent) to the formation of diacetyl benzenes. Thus removal of little amount of stronger Brønsted acid sites by Na⁺-ion exchange in

Table 3
Effect of SiO₂/Al₂O₃ molar ratio of H-ZSM-5^a

	SiO ₂ /Al ₂ O ₃ molar ratio			
	41	80	102	160
Conversion of acetic acid (wt%)	42.6	38.8	15.4	14.1
Product distribution (wt%)				
Acetophenone (ACP)	91.1	86.1	91.9	88.4
Others	8.9	13.9	8.1	11.6

^a Reaction conditions: see footnotes to Table 1.

H-ZSM-5 results in slightly lower activity but improves selectivity up to 100 wt% for acetophenone (Table 1).

3.5. Effect of SiO₂/Al₂O₃ ratio

Table 3 depicts a comparison of the performance of H-ZSM-5 zeolite having SiO₂/Al₂O₃ molar ratios of 41, 80, 102 and 160 in the acetylation of benzene at 523 K. Acetic acid conversion decreased with the increase in SiO₂/Al₂O₃ molar ratio without a significant change in the product distribution.

3.6. Effect of reaction temperature

The temperature of the reaction has a determining influence on the rate of acetic acid conversion and product distribution (Fig. 2). The initial rate of CH₃COOH conversion (TOF) over H-ZSM-5 increases linearly with the increase in reaction temperature but selectivity towards acetophenone decreases as shown in Fig. 2. A maximum in acetophenone selectivity (100%) over this catalyst is observed at 503 K

Table 2
Effect of Na-exchange^a

Catalyst	Conv. of acetic acid (wt%)	TOF (M mol s ⁻¹ mol ⁻¹ Al × 10 ⁻³) ^b	Product distribution ^c (wt%)	
			ACP	others
H-ZSM-5 ^d	42.6	38.5	91.1	8.9
H-Na(28.9)ZSM-5 ^e	39.3	35.5	93.7	6.3
H-Na(34.1)ZSM-5 ^e	31.1	28.1	100.0	—
H-Na(37.3)ZSM-5 ^e	30.2	27.3	100.0	—

^{a,b,c,d} See Table 1.

^e Values in parenthesis represent the Na-exchange (%) in H-ZSM-5.

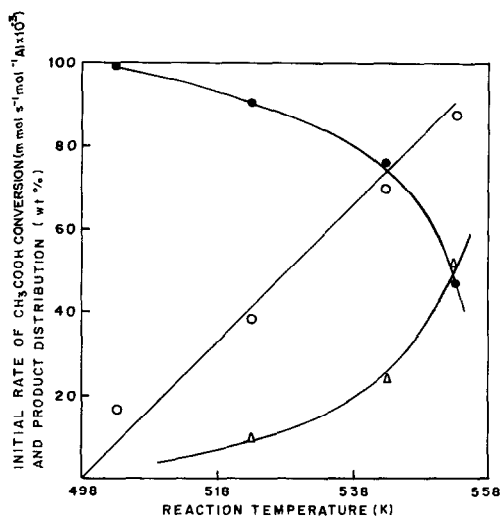


Fig. 2. Effect of reaction temperature on the initial rate of CH₃COOH conversion (m mol s⁻¹ mol⁻¹ Al × 10⁻³) (○) and product distribution, ACP (●) and others (Δ); Reaction conditions, H-ZSM-5 (SiO₂/Al₂O₃ = 41) = 2 g; benzene/acetic acid (molar ratio) = 2; feed rate (ml/h) = 2.

but the rate of acetic acid conversion is found to be very low (TOF = 16). The selectivity for acetophenone drops sharply above 523 K, whereas a higher temperature favours the formation of consecutive products (others) and the concentration of acetophenone and consecutive products becomes nearly equal at 553 K.

3.7. Effect of weight hourly space velocity h^{-1} (WHSV h^{-1})

The influence of WHSV h^{-1} on the activity and selectivity of the H-ZSM-5 catalyst is studied at 523 K and a benzene/acetic acid molar ratio of 2. Fig. 3 shows the conversion of acetic acid and product distribution for the reaction at WHSV h^{-1} ranging between 0.44 and 1.76. As expected, the conversion of acetic acid decreased from 60.5 to 12.5 wt% with increasing space velocity from 0.44 to 1.76 h^{-1} , respectively. However, the selectivity for acetophenone increased with the increase in space velocity.

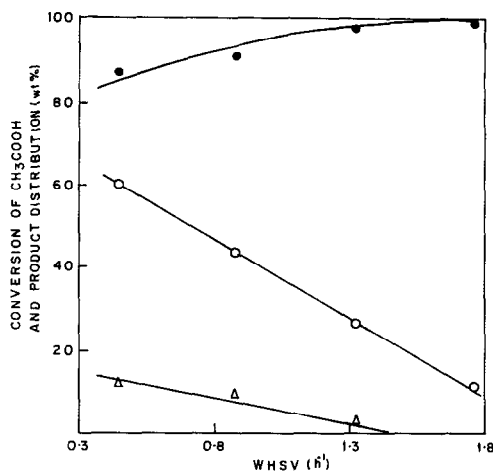


Fig. 3. Effect of WHSV (h^{-1}) on the conversion of CH₃COOH (○) and product distribution, ACP (●) and others (Δ); Reaction conditions; H-ZSM-5 (SiO₂/Al₂O₃ = 41) = 2 g; benzene/acetic acid (molar ratio) = 2; reaction temperature = 523 K.

3.8. Effect of benzene / acetic acid molar ratio

The effect of varying the benzene/acetic acid molar ratio in the reaction mixture on the activity and selectivity of the H-ZSM-5 at a fixed benzene concentration is shown in Fig. 4. The results at 523 K show that conversion of acetic acid and selectivity to acetophenone increased with increasing benzene to acetic acid molar

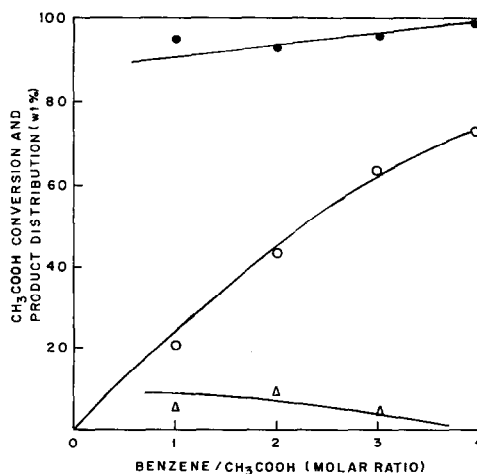
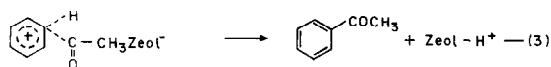
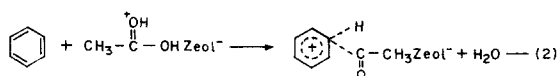
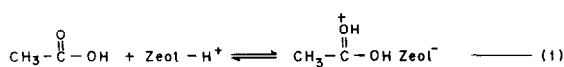


Fig. 4. Effect of benzene/acetic acid molar ratios on the conversion of CH₃COOH (○) and product distribution, ACP (●) and others (Δ). Reaction conditions; H-ZSM-5 (SiO₂/Al₂O₃ = 41) = 2 g; feed rate (ml/h) = 2; reaction temperature = 523 K.

ratio. In addition, the formation of diacetyl benzenes decreased significantly with the increase of molar ratio.

3.9. Mechanism

The classical Friedel–Crafts acylation is an electrophilic aromatic substitution in which an electron-deficient species (electrophile) is generated by the activation of acetic acid on the protonic sites of the zeolite which attacks the benzene ring resulting in the formation of acetophenone according to the following equations (Eqs. (1)–(3)) [9,12,14,20].



4. Conclusions

As a result of this work, it has been demonstrated that H-ZSM-5 showed higher catalytic activity and selectivity than that of H-mordenite for the vapour phase acetylation of benzene by acetic acid. The present study reveals that the excellent activity and selectivity of H-ZSM-5 compared to the H-mordenite are due to both the stronger acid sites and to its narrow pore structure. Increased reaction temperature and molar ratios of benzene/acetic acid lead to increase in acetic acid conversion whereas it decreased with the increase in reaction time, degree of Na⁺-exchange in H-ZSM-5, SiO₂/Al₂O₃ ratio and WHSV h⁻¹. Further, it is concluded that the presence of stronger

Brønsted acid sites in zeolite catalysts appears to be very important for the polarization of acetic acid into an electrophile (CH₃CO⁺) which then attacks the benzene ring resulting in the formation of acetophenone.

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