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Vapor-phase synthesis of acetophenone in benzene acylation over CeHZSM-5(30) zeolite *

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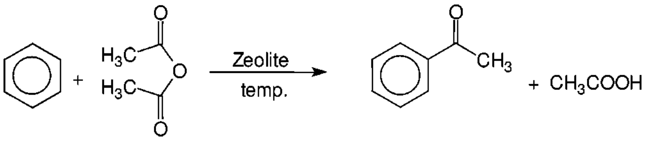
The benzene acylation was carried out with acetic anhydride as an acylating agent in vapor phase over HZSM-5, Si/Al = 30 and 280, HY and Ce-, V-modified HZSM-5(30) zeolite catalysts at atmospheric pressure. The yield of acylated product acetophenone was found to be 82.1 wt% with 95.0% selectivity at 86.4 wt% conversion of acetic anhydride over Ce-modified HZSM-5(30) where Brønsted acidic sites are active for this reaction.

Keywords: zeolite, benzene, acetic anhydride, acylation, acetophenone

1. Introduction

Acetophenone is prepared by Friedel–Crafts reaction of acetyl chloride with benzene in the presence of a homogeneous catalyst $AlCl_3$ [1]. However, the homogeneous catalysts have several disadvantages in industrial processes such as large amount of catalyst wastage, corrosion of reactors, water pollution by effluents in the processes and difficulty of catalyst recovery, etc. In order to overcome these difficulties, the development and utilization of a solid zeolite catalyst has taken a major lead. Zeolites are attractive as catalysts for the acylation reactions due to their acidity, shape selectivity and regenerability properties, etc. [2–10]. Acetophenone has many applications in organic reactions. It can react with formaldehyde to yield light-resistant resins, which are used as additives in nitrocellulose [11]. It is also used as a photoinitiator, in pharmaceutical, perfumery and pesticide industries [12]. It can be hydrogenated to 1-phenylethanol, which is used for the production of aromatic ester fragrance [13]. Industrially, the Hock process yields acetophenone by decomposition of hydroperoxide. A more selective synthesis of acetophenone by cleavage of cumene hydroperoxide over a cupric catalyst has been patented [14]. Oxidizing the methyl phenyl carbinol intermediate which is found in styrene production processes [15,16] can also produce acetophenone.

Recently, the benzene acylation with acetic acid is reported with no detailed study over HZSM-5(41) with 88.1% selectivity of acetophenone at 76.0 wt% conversion of acetic acid. The same group in another report mentioned that the work of benzene acylation over the same catalyst, 91.1% selectivity of acetophenone at 42.6 wt% conversion of acetic acid. The reaction conditions are more or less the same in both studies of acylation [17,18].



Scheme 1.

We are reporting here the benzene acylation (scheme 1) in vapor phase over HZSM-5(30), HZSM-5(280), HY and V-, Ce-modified HZSM-5(30) zeolite systems with acetic anhydride as an acylating agent. We obtain 82.1 wt% yield of acetophenone at 95.0% selectivity and 86.4 wt% conversion of acetic anhydride over the Ce-modified HZSM-5(30) zeolite catalyst.

2. Experimental

The commercial zeolites HY and HZSM-5 supplied by PQ Corporation of USA and Conteka of Sweden are modified by an impregnation method with Ce and V cations. The required quantities of cerium nitrate and vanadium acetylacetonate were used as precursor salts. The required amounts were dissolved in distilled water to which the zeolite was added and kept for soaking for 5–6 h. After that it was left overnight in an oven at 70–80 °C to evaporate the residual water. The thus obtained material was calcined between 400 and 420 °C to obtain the finished catalyst.

The vapor-phase alkylation reaction was carried out using a fixed-bed tubular down flow glass reactor with 20 mm internal diameter at atmospheric pressure. 4 g of the catalyst (18–30 mesh size) was placed in the reactor. The reaction mixture was fed from the top of the reactor by using a syringe pump (Perfusor, B. Braun). The bottom of the reactor was connected to a condenser to collect the product. Blank experiments were performed at the reaction temperature of study. The product was analyzed by using a gas chromatograph (Chemito 3865) with a flame ionization

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detector and SE-30 column (30%, 2 m) and was identified by the GC-MS technique.

3. Results and discussion

3.1. Catalyst characterization

Stepwise temperature-programmed desorption (STPD) of ammonia was measured, as reported in the literature [19], for the zeolite systems used in the benzene acylation reaction. It was observed that the zeolite HZSM-5(30) modified by the rare earth metal Ce cation increased the acidity and it decreases when it was modified with the transition metal V cation. The results were given in our previous reports [7–9]. The X-ray diffraction of all the modified zeolites was measured and from that it is inferred that the crystallinity was not changed as compared with the fresh catalyst even after calcining at various temperatures (figure 1). The surface area of the zeolite samples was measured by the BET unit. The modified zeolite surface area decreases compared to unmodified zeolites and the values are shown in table 1.

The vapor-phase acylation reaction of benzene with acetic anhydride was carried out over HZSM-5(30), HZSM-5(280), CeHZSM-5(30), VHZSM-5(30) and HY zeolite catalysts. The results on time-on-stream product distributions correspond to the second and fifth hour collected samples shown in table 2. The conversions were given with respect to the acylating agent, i.e., acetic anhydride.

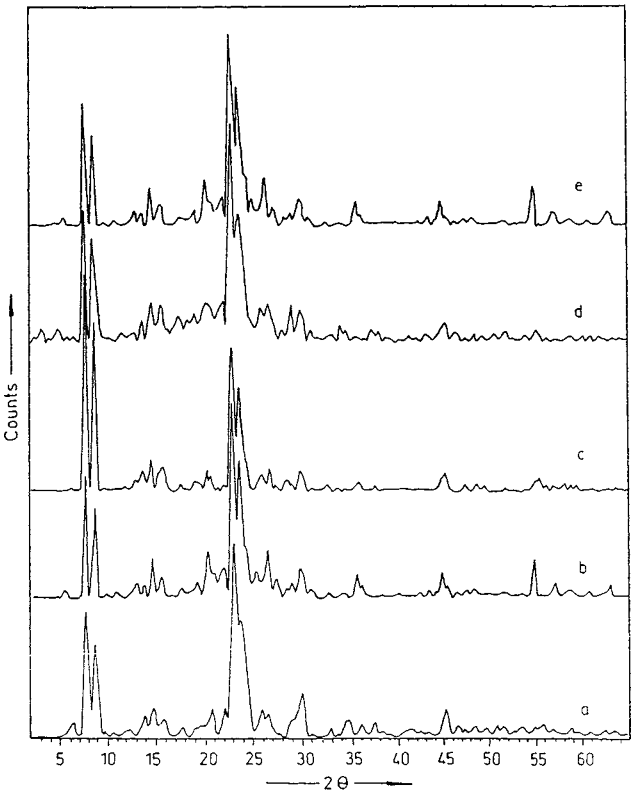


Figure 1. XRD patterns of (a) HZSM-5(30), (b) HZSM-5(280), (c) 3 wt% CeHZSM-5(30), (d) 5 wt% CeHZSM-5(30), (e) VHZSM-5(30) zeolite catalysts.

From the data presented in table 2 we can say that the activity depends on the size and acidity of the zeolite catalyst. The high yield of acetophenone over the HZSM-5 system as compared to HY zeolite is due to its small pore size. HZSM-5(280) exhibits a little lower activity than HZSM-5(30) and this may be due to its low acidity. The maximum yield of acetophenone was obtained on the Ce-HZSM-5(30) zeolite catalyst. The high activity with Ce-modified zeolite is due to the Ce^{3+} ions and the Brønsted acid centers (H^+) of the zeolite. The Brønsted acid centers of the zeolite were developed by dissociation of water molecules and by Ce modification, as is shown in equation (1) [20]:

$$Ce^{3+} + H_2O \rightarrow [Ce(OH)]^{2+} + H^+ \qquad (1)$$

The cerium cation on zeolite thus increases its acidity [20–23] and reduces the coke formation, furthermore it acts as a promoter [6]. The decreasing selectivity over HY is because of its larger pore size than that of HZSM-5(30) zeolite and there are possibilities of formation of diacetylbenzene. Even though HY zeolite is more acidic than HZSM-5(30) [7,8], it is not suitable for this reaction under the conditions tested, because benzene easily undergoes cracking over HY zeolite and forms aliphatic hydrocarbons which, in turn, block the zeolite channels. Modified zeolites with transition metals are not suitable for Friedel–Crafts reactions, as is reported in the literature [4,8,9]. This may be the reason for the low yields that were obtained on the VHZSM-5(30) system. Furthermore, it is mentioned in the literature that zeolites modified by rare earth cations such as Ce and La are effective catalysts for Friedel–Crafts reac-

Table 1
Surface areas of the zeolite catalysts used for benzene acylation.

Catalyst	Surface area (m^2/g)	Catalyst	Surface area (m^2/g)
HZSM-5(30)	427.3	3 wt% CeHZSM-(30)	219.3
HZSM-5(280)	307.4	5 wt% CeHZSM-(30)	202.1
HY	409	3 wt% VHZSM-(30)	210.4

Table 2
Effect of variation of catalyst on benzene acylation.[a]

Catalyst	TOS (h)	Conversion of AC_2O[b] (wt%)	Yield of Acph[c] (wt%)	Selectivity of Acph (%)
HZSM-5(30)	2	70.6	61.0	86.4
	5	53.3	43.0	80.6
HZSM-5(280)	2	64	54.2	80.7
	5	57.4	46.0	80.1
3 wt% CeHZSM-5(30)	**2**	**86.4**	**82.1**	**95.0**
	5	74.1	68.9	93.0
3 wt% VHZSM-5(30)	2	40.3	35.7	88.5
	5	29.1	22.6	77.6
HY	2	42.3	26.7	63.1
	5	29	18.8	64.8

[a] Reaction temperature = 250 °C; molar ratio benzene : acetic anhydride = 2 : 1; WHSV = 0.5 h^{-1}.
[b] AC_2O = acetic anhydride.
[c] Acph = acetophenone.

Table 3
Effect of variation of Ce promoter loading on HZSM-5(30) in benzene acylation.[a]

Ce on HZSM-5(30) (%)	TOS (h)	Conversion of AC_2O (wt%)	Yield of Acph (wt%)	Selectivity of Acph (%)
2	2	72.1	63.0	87.3
	5	62.4	54.2	86.8
3	**2**	**86.4**	**82.1**	**95.0**
	5	74.1	68.9	93.0
3[b]	2	47.8	41.6	87.0
	5	42.7	35.2	82.4
4	2	75.3	67.2	89.2
	5	63.4	55.7	87.8
5	2	68.9	59.0	85.6
	5	61.4	50.7	82.5

[a] Molar ratio benzene : acetic anhydride = 2 : 1; $T_R = 250\,^\circ C$.
[b] Acetic acid as an acylating agent.

tions [21–24]. Consequently, the reaction was carried out on Ce-modified HZSM-5(30) and the maximum yield of 82.1 wt% acetophenone with 95% selectivity was obtained at 3 wt% Ce on HZSM-5(30). Also it is reported in the literature that zeolite exchanged with Ce exhibits the highest activity for Friedel–Crafts acylation reactions among all the zeolite catalysts [22,25,26]. The present results are very much in agreement with the earlier reported trends. In view of this, an activity study with respect to the loading of Ce was made.

3.2. Variation of Ce loading on HZSM-5(30)

The reaction of benzene acylation was carried at 2–5 wt% loading of Ce promoter on HZSM-5(30), as shown in table 3. The maximum yield of acetophenone was obtained at 3 wt% and, above this loading, there was no improvement of the product yield. The reason may be the increase in acidity of the HZSM-5(30) catalyst by the modification with Ce cation and also the decrease of available active site centers due to the increased promoter concentration. Thus the 3 wt% Ce loading was obtained as optimum for HZSM-5(30).

3.3. Effect of acylating agent

Using acetic acid as an acylating agent the benzene acylation was also carried out but the yield of acetophenone, the acylated product, was found to be 41.6 wt% with 87% selectivity at 47.8 wt% conversion of acetic acid. In contrast, with acetic anhydride as an acylating agent, the yield of acetophenone was found to be increased to 82.1 wt% with 95% selectivity at 86.4 wt% conversion of acetic anhydride (figure 2). Therefore, we can say that acetic anhydride is an effective acylating agent for the Friedel–Crafts acylation reactions here, and this data is also supported by the results of our previous work in furan and pyrrole acylation [8].

The other reaction parameters such as temperature, molar ratio of benzene to acetic anhydride, weight hour space velocity (WHSV) and activity data with time-on-stream were varied to get optimum conditions for this benzene acylation.

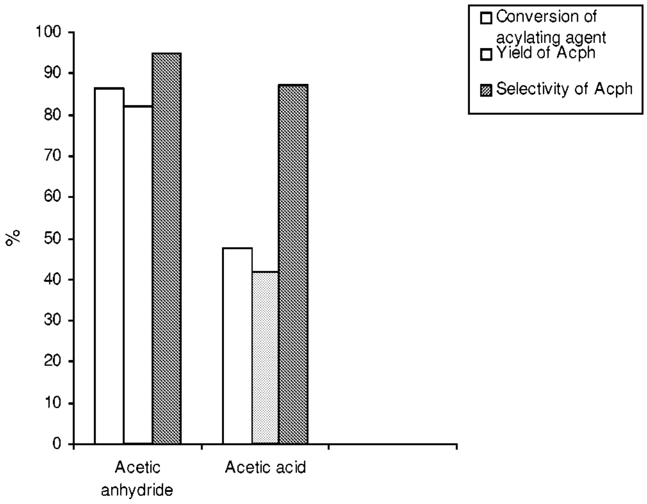


Figure 2. Effect of acylating agent in benzene acylation over CeHZSM-5(30) zeolite at 250 °C reaction temperature.

Table 4
Effect of temperature on benzene acylation over CeHZSM-5(30).[a]

T_R (°C)	TOS (h)	Conversion of AC_2O (wt%)	Yield of Acph (wt%)	Selectivity of Acph (%)
150	2	36.4	31.5	86.5
	5	30.1	24.2	80.3
200	2	66.2	56.1	84.7
	5	58.4	50.2	85.9
250	**2**	**86.4**	**82.1**	**95.0**
	5	74.1	68.9	93.0
300	2	81	61.2	75.5
	5	62	47.8	77.0

[a] Molar ratio benzene : acetic anhydride = 2 : 1; WHSV = $0.5\ h^{-1}$.

3.4. Effect of temperature on benzene acylation

The acylation of benzene with acetic anhydride was carried out at different temperatures and the results are shown in table 4. Conversion of acetic anhydride was low at temperature below 200 °C and the acid sites required may not be active for this benzene acylation under the reaction conditions used. The yield of acylated product is good at 300 °C, but with time-on-stream, the catalytic activity decreases. The catalytic activity decrease above 300 °C may be due to the transformation of Brønsted acid sites into Lewis acid sites at high temperatures which are not suitable for the present acylation reaction [4,7]. The formation of aliphatic hydrocarbons is developed by acetic acid, formed through acetic anhydride decomposition. Also, the catalytic cracking of substrate benzene causes coke formation which leads to deactivation of the catalyst [3,27]. The maximum yield of acetophenone is obtained at 250 °C. At this temperature, the Brønsted acid sites, which are found to be responsible for this acylation reaction [4,18], are more in number.

3.5. Variation of feed molar ratio and weight hour space velocity (WHSV)

The molar ratio of benzene to acetic anhydride was varied from 1 : 2 to 3 : 1. The values are shown in tables 5 and 6. At higher concentrations of acetic anhydride the selectivity was seen to be little decreased, and acetic acid was produced as the by-product. At higher concentration of benzene, i.e., at 3 : 1, the benzene deactivates the zeolite. Therefore, the optimum molar ratio was chosen as 2 : 1, and at this molar ratio, the reaction temperature used was 250 °C over CeHZSM-5(30). The maximum yield of acetophenone was 82.1 wt%. Similarly, the optimum weight hour space velocity (WHSV) was 0.5 h^{-1}.

3.6. Effect of time-on-stream

The reaction was carried out for nearly 9 h on CeHZSM-(30) under optimum conditions of reaction temperature 250 °C, 2 : 1 feed molar ratio and 0.5 h^{-1} WHSV to check the life of the catalyst. It has been observed that the conversion of acetic anhydride and yield of acetophenone gradually decrease over a period of time, as shown in figure 3. The decrease in selectivity is less and this may be absence of by-products, such as diacetylbenzene over Ce-modified HZSM-5(30) zeolite catalyst.

3.7. Reaction mechanism

It is known that the classical Friedel–Crafts acylation is an electrophilic substitution in which an electron-

Table 5
Variation of feed molar ratio on benzene acylation over CeHZSM-5(30).[a]

Molar ratio	TOS (h)	Conversion of AC_2O (wt%)	Yield of Acph (wt%)	Selectivity of Acph (%)
1 : 2	2	58	45	77.5
	5	52	40	76.9
1 : 1	2	72.5	60	82.7
	5	67.0	54	80.5
2 : 1	**2**	**86.4**	**82.1**	**95.0**
	5	74.1	68.9	93.0
3 : 1	2	58.4	40.5	69.3
	5	50	33.2	66.4

[a] Molar ratio benzene : acetic anhydride = 2 : 1; WHSV = 0.5 h^{-1}.

Table 6
Variation of weight hour space velocity (WHSV) on benzene acylation over CeHZSM-5(30).[a]

WHSV	TOS (h)	Conversion of AC_2O (wt%)	Yield of Acph (wt%)	Selectivity of Acph (%)
0.25	2	64.2	51	79.4
	5	60	46.2	77
0.5	**2**	**86.4**	**82.1**	**95.0**
	5	74.1	68.9	93.0
0.75	2	64.1	56	87.3
	5	54	42	77.7
1	2	57	44.6	78.2
	5	40.1	26	64.8

[a] Molar ratio benzene : acetic anhydride = 2 : 1; T_R = 250 °C.

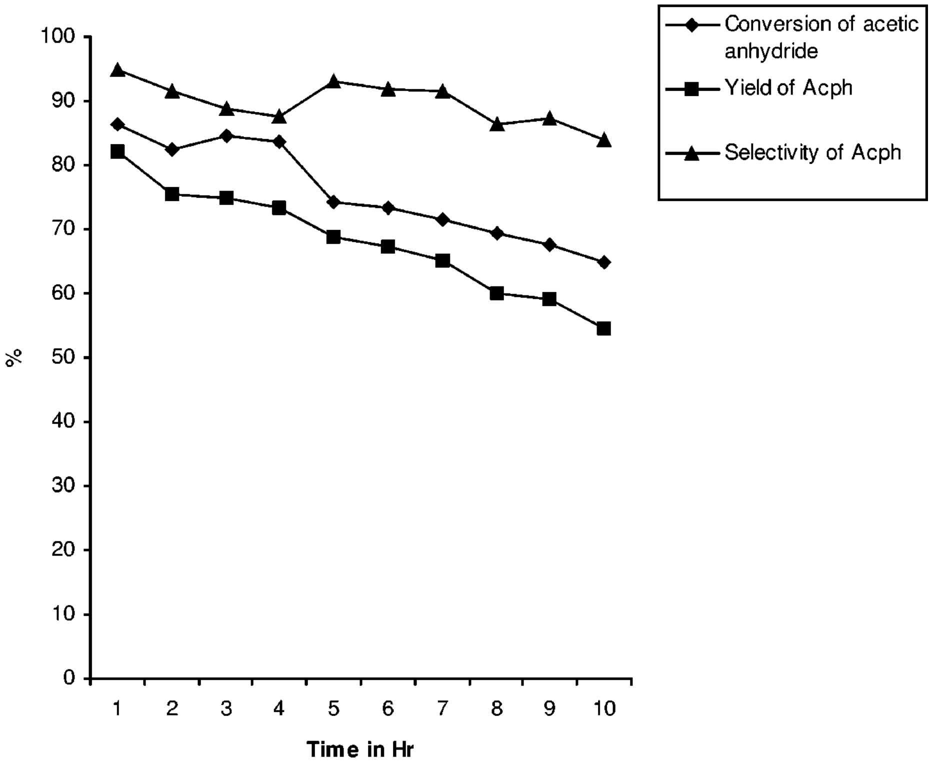
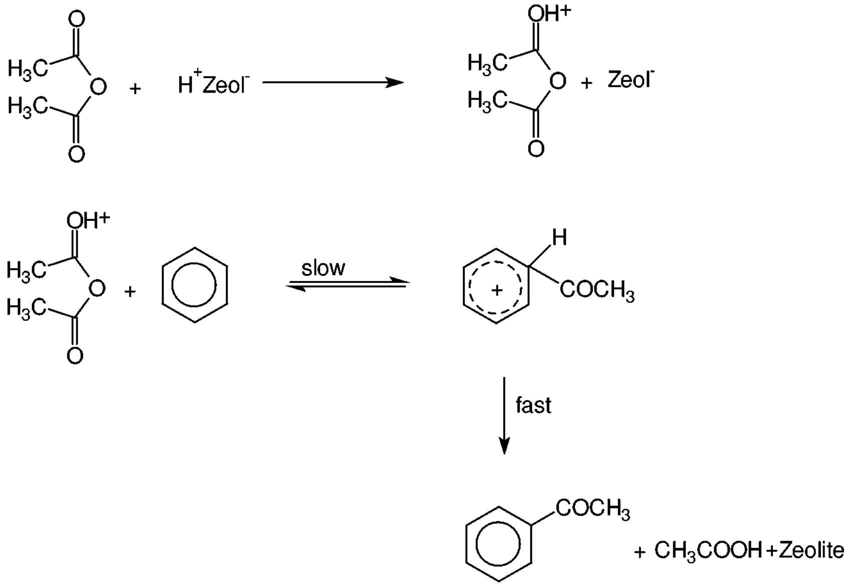


Figure 3. Effect of time-on-stream (TOS) over CeHZSM-5(30) in benzene acylation at 250 °C reaction temperature.



Scheme 2.

deficient species, the electrophile, attacks the aromatic ring (scheme 2) thereby forming a cyclohexadiadienyl cation (Wheland intermediate or σ complex) in the rate-determining step [25,28].

4. Conclusion

Acetophenone was obtained at higher yields in vapor-phase acylation of benzene. It was observed that the HZSM-5 system showed higher activity than the HY zeolite system. The best catalyst for benzene acylation is CeHZSM-5(30). The reaction favored on Brønsted acid sites. The maximum yield of acetophenone is 82.1 wt% with 95% selectivity obtained over CeHZSM-5(30) at a reaction temperature of 250 °C and at a 2 : 1 molar ratio of benzene to acetic anhydride composition with 0.5 h^{-1} WHSV. The time-on-stream yields were gradually decreasing over a period of 9 h.

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