Selective acetylation of toluene to 4-methylacetophenone over zeolite catalysts

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Abstract

The vapour phase acetylation of toluene has been catalysed by acidic H-ZSM-5, H-mordenite and REY zeolite catalysts at 453 K in a tubular reactor at atmospheric pressure. H-ZSM-5 exhibited the best results during the reaction with respect to rate of acetylchloride conversion (TOF $= 7.5 \, \text{mol s}^{-1} \, \text{mol}^{-1} \, \text{Al} \times 10^{-4}$), conversion of acetyl chloride (60.2 wt.%) and selectivity for 4-methylacetophenone (88.3%) compared to both H-mordenite and REY zeolites. It is revealed that the activity and selectivity of the catalyst strongly depend on the acidic properties and pore openings of the zeolites, respectively. It is observed that isomer ratio (4-methylacetophenone/2-methylacetophenone) is influenced by the reaction conditions and type of zeolite used in the reaction. With increasing reaction temperature and toluene to CH_3COCl molar ratio, the conversion of CH_3COCl (ACT) increases, while it decreases with the increase in reaction time, weight hourly space velocity (WHSV), Na-content and silica to alumina molar ratio of H-ZSM-5 in the acetylation of toluene. H-ZSM-5 is deactivated under the reaction conditions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Acetylation of toluene; Preparation of 4-methylacetophenone; Acetylation over H-ZSM-5

1. Introduction

4-Methylacetophenone (4-MACP) is used for blossom notes in mimosa and for the production of hawthorn type perfumes, especially in soap perfumes [1,2]. The Friedel–Crafts acylation reactions which are one of the most important processes in organic synthesis are generally carried out by using $AlCl_3$ or $FeCl_3$ as a Lewis acid catalysts [3–5]. Conventionally, 4-MACP is prepared from toluene and acetic anhydride or acetyl chloride by a Fridel–Crafts catalyst $AlCl_3$ [2,3]. The acetylation of toluene is also known to proceed over hafnium trifluoromethane sulphonate catalyst using acetic anhydride as the acetylating agent [6]. In addition, solid super acid catalysts (ZrO_2–SO_4^{2-}) [7,8], cation exchanged clays [9,10] and soluble metal acetates of Cu(II) and Pd(II) [11] have also been employed for the acetylation of toluene. These non-shape-selective catalysts tend to give either lower conversion of acetyl chloride or lower yield of the *para*-isomer (4-MACP). Furthermore, the homogeneous catalysts are difficult to separate from the reaction mixture and require additional processing stages and stoichiometric amount of the catalyst with respect to the acetylating agent. In order to overcome the difficulties of the homogeneous systems, the development and utilisation of a solid catalyst is important to replace homogeneous acid catalysts. Zeolites or molecular sieves due to their thermostability and shape selectivity have been used

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in the organic synthesis [12,13]. However, relatively little attention has been paid to the use of zeolite catalysts in the acylation reactions [14–26]. Such catalysts are interesting and efficient for organic synthesis because the catalyst is easily separated from the product and the organic reactions occur inside the uniform and narrow cavities of zeolites and hence the reactivity and selectivity may be different from those in homogeneous solutions. The aim of the present work is to develop a new catalytic method for the *para*-selective acetylation of toluene to 4-MACP using acidic zeolite (H-ZSM-5) as the catalyst and acetyl chloride as the acetylating agent. We also report the results of the effect of various zeolite catalysts, acidity of the zeolite catalysts, time on stream, degree of Na-exchange of H-ZSM-5, silica to alumina ratio of zeolite H-ZSM-5, reaction temperature, toluene to acetyl chloride molar ratios and weight hourly space velocity (WHSV) on the conversion of acetyl chloride and selectivity for 4-MACP. Acetylation of toluene over H-ZSM-5 zeolite has not been reported so far in the open literature.

2. Experimental

Zeolites were synthesised, characterised and ion-exchanged (H^+, Na^+ or RE^{3+}) according to the procedures described in the literature [22–27]. Total acid site density and acid strength distribution of the catalysts were measured by temperature programmed desorption of ammonia [23,28,29]. The main properties of zeolites are listed in Table 1. All the catalysts were activated in air at 773 K for 4 h before activity measurements.

The vapour phase reaction of acetyl chloride with toluene was carried out at atmospheric pressure in a quartz microflow reactor with an inner diameter of 14 mm. The reactor was loaded with 2 g catalyst (compressed and crushed sieve fraction of 15–30 mesh size). The catalyst was pre-treated in situ for 4 h at 813 K. Then, the catalyst temperature was brought down to 453 K and the mixture of toluene and acetyl chloride, consisting of 2 mol of toluene and 1 mol of acetyl chloride, was fed into the reactor by a syringe pump. The products were analysed by a gas chromatograph (Blue Star Model 421) equipped with flame ionisation detector and a capillary column (50 m × 0.2 mm) with methyl silicone gum. The products were

identified on a Shimadzu GC-MS, QP 2000 A gas chromatograph-mass spectrometer.

The conversion of acetyl chloride (wt.%), turnover frequency (TOF) and selectivity are calculated using following equations:

$$\text{Conversion of acetyl chloride (wt.\%)}$$
$$= \frac{\text{amount of acetyl chloride reacted}}{\text{amount of acetyl chloride fed}} \times 100$$

$$\text{TOF} = \text{moles of acetyl chloride converted per second per mole of aluminium}$$

$$\text{Selectivity} = \text{percentage of converted acetyl chloride transformed into given product}$$

3. Results and discussion

High intensity of the peaks and absence of any baseline drift in the XRD patterns indicated that the sample were highly crystalline. Zeolites H-ZSM-5, H-mordenite and H-REY used in this study were having SiO_2/Al_2O_3 molar ratio of 41.0, 22.0 and 4.1, respectively. The corresponding acidity as measured by temperature programmed desorption was 1.21, 0.71 and 0.74 mmol equivalent NH_3 per gram zeolite. The surface area and scanning electron micrographs revealed well defined materials without any occluded samples in the zeolites. The physico-chemical properties of the zeolites are presented in Table 1.

3.1. Various catalysts

The catalytic measurement of the acetylation of toluene over various zeolites have been performed under comparable experimental conditions and the catalytic results obtained with different zeolite catalysts are listed in Fig. 1. The data for comparison are taken after 2 h of run. The main product of the reaction are 2-methylacetophenone (2-MACP) and 4-MACP. Small amounts of consecutive diacetylated products (others) are also formed. The products obtained in the acetylation of toluene are found to be similar to those reported earlier in the Friedel–Crafts acylation of toluene using $AlCl_3$ as a catalyst and acetyl chloride as the acetylating agent [2,3]. Fig. 1 shows that a

Table 1
Properties and acid strength distribution of zeolite catalysts

Catalysts	SiO$_2$/Al$_2$O$_3$ (molar ratio)	Degree of H$^+$ or RE^{3+} exchange[a] (%)	Crystal size (μm)	Surface area[b] (m^2 g^{-1})	NH$_3$ desorbed (mmol g^{-1}) in various steps					NH$_3$ chemisorbed at 303 K[c] (mmol g^{-1})
					303–353 K	353–433 K	433–513 K	513–653 K	653–773 K	
H-ZSM-5	41.0	>98	0.4	413	0.55	0.16	0.05	0.26	0.21	1.21
H-mordenite	22.0	>98	1.0	552	0.20	0.17	0.15	0.12	0.07	0.71
H-REY[d] (70.6)	4.1	>70.6	1.0	659	0.17	0.10	0.26	0.11	0.10	0.74

[a] Cation-exchange (H$^+$ or RE^{3+}) values reported as percent of the total cation sites taken as the aluminium content 100%.

[b] Measured by N$_2$ adsorption.

[c] NH$_3$ chemisorbed at 303 K (mmol g^{-1}).

[d] Value given in parenthesis represents the percentage of RE^{3+}-exchange in NaY zeolite.
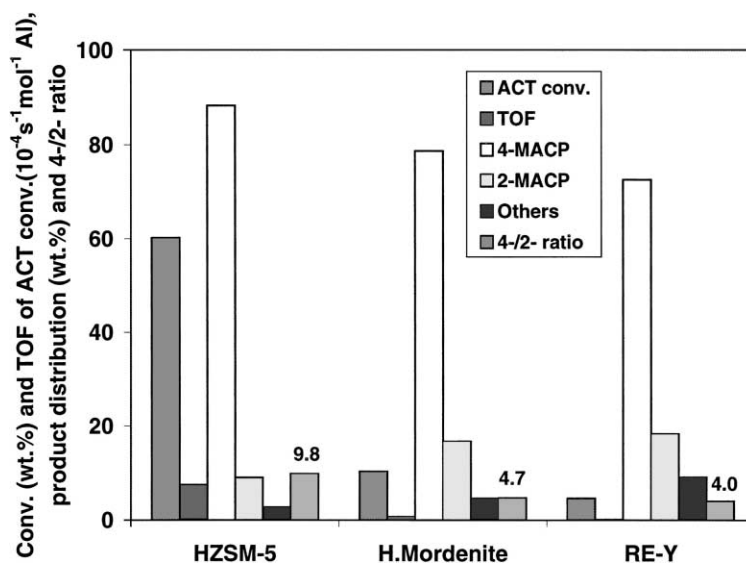
Fig. 1. Acetylation of toluene over various catalysts. Reaction conditions: catalyst weight = 2 g; toluene/CH₃COCl (molar ratio) = 2; feed rate = 2 ml h⁻¹; reaction temperature = 453K. Rates of acetyl chloride conversion are indicated as turnover frequency (TOF, moles of CH₃COCl converted per second per mol of aluminium); 4-MACP: 4-methylacetophenone; 2-MACP: 2-methylacetophenone; Others: di- and tri-acetylated products.

good yield of 4-MACP is obtained from the acetylation of toluene by acetyl chloride over acidic H-ZSM-5 zeolite catalysts, demonstrating the feasibility of using solid acidic zeolite catalysts for the synthesis of 4-MACP. Based on the reaction conditions and acetyl chloride (ACT) conversion (Fig. 1), the activity and selectivity of zeolite catalyst in the conversion of acetyl chloride and formation of 4-MACP decreased in the order: H-ZSM-5 > H-mordenite > REY.

H-ZSM-5 converted the highest amount of acetyl chloride (60.2 wt.%) compared to both H-mordenite (10.3 wt.%) and REY (4.6 wt.%). The TOF which is equal to the number of moles of acetyl chloride converted per second per mol of aluminium (mol s⁻¹ mol⁻¹ Al × 10⁻⁴) are found to be 7.5, 0.7 and 0.08 for H-ZSM-5, H-mordenite and REY zeolites, respectively. The corresponding isomer ratios (4-MACP/2-MACP) are 9.8, 4.7 and 4.0, respectively, showing that H-ZSM-5 exhibited the highest activity and selectivity in the acetylation of toluene. The acidic strength of H-ZSM-5 is found to be stronger than the H-mordenite and REY zeolite catalysts (Table 1) and it is likely that the stronger acid sites of the H-ZSM-5 result in higher rate of acetyl chlo-

ride conversion in the acetylation of toluene [25,26]. The difference in the selectivity for the products over various zeolites may be interpreted in terms of geometrical constrants produced by different zeolite geometries which have a strong impact on the reaction selectivity. The results from Fig. 1 show that geometrical constrants produced by H-ZSM-5 did not allow the formation of bulkier 2-MACP and consecutive products in the small channels of H-ZSM-5 and hence a higher selectivity for 4-MACP is achieved over H-ZSM-5 than those of H-mordenite and REY zeolites.

3.2. Time on stream

Fig. 2 shows changes in catalytic activities over H-ZSM-5, H-mordenite and REY zeolites with time on stream at a reaction temperature of 453 K. The catalytic activity of all zeolites decreases gradually with time on stream. The rapid decrease of activity may be attributed to the deactivation of zeolite catalysts probably due to the formation of coke.

In addition, Fig. 3 shows the conversion of acetyl chloride and product distribution with time on stream
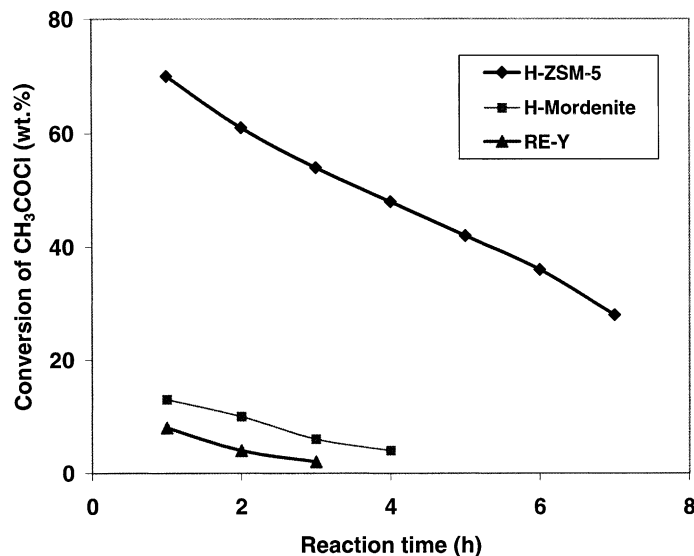
Fig. 2. Conversion of CH3COCl versus reaction time over various zeolites. Reaction conditions same as in Fig. 1.

over H-ZSM-5 catalyst in the acetylation of toluene. During seventh hour of the run, the conversion of acetyl chloride dropped from 70.0 to 29.8 wt.%. However, the product distribution roughly remained unchanged.

3.3. Influence of degree of Na-exchange in H-ZSM-5

In order to investigate the influence of acidic sites of the zeolites, the acetylation of toluene is also performed over different degree of Na-exchange samples
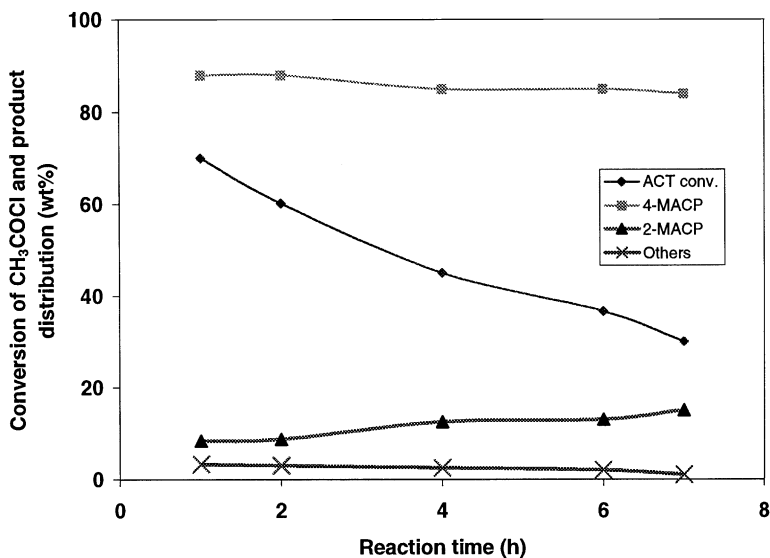

Fig. 3. Effect of reaction time on the conversion of CH3COCl and product distribution over H-ZSM-5. Reaction conditions same as in Fig. 1.

Table 2
Influence of Na-exchange in H-ZSM-5[a]

| Catalysts	Conversion of CH$_3$COCl (wt.%)	TOF[b] (mol s^{-1} mol^{-1} Al × 10^{-4})	Product distribution[c] (wt.%)			4-MACP/ 2-MACP
			2-MACP	4-MACP	Others	
H-ZSM-5	60.2	7.5	9.0	88.3	2.7	9.8
H-Na(28.9)-ZSM-5[d]	42.3	5.3	6.0	92.0	2.0	15.3
H-Na(34.1)-ZSM-5[d]	26.5	3.3	5.8	93.4	0.8	16.1
H-Na(37.3)-ZSM-5[d]	18.4	2.3	6.0	91.9	2.1	15.3

[a] Cation-exchange (H$^+$ or RE^{3+}) values reported as percent of the total cation sites taken as the aluminium content 100%.

[b] Measured by N$_2$ adsorption.

[c] NH$_3$ chemisorbed at 303 K (mmol g^{-1}).

[d] Values in parenthesis represent the Na-exchange (%) in H-ZSM-5.

of H-ZSM-5. The data presented in Table 2 shows that the activity of the catalyst in facilitating the reaction of toluene with acetyl chloride decreases in order:

H-ZSM-5 > H-Na(28.9)ZSM-5

> H-Na(34.1)ZSM-5 > H-Na(37.3)ZSM-5
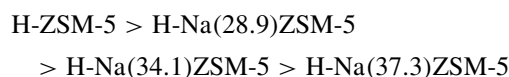
H-ZSM-5 zeolite is much more active than all Na-ZSM-5 catalysts, but is found to be less selective for 4-MACP and more amount of 2-MACP is produced over H-ZSM-5 than Na-ZSM-5 catalysts. In addition, the amount of others are found to be nearly similar over all catalysts. These data suggest that all the acid sites (weak, medium and strong) are active in catalysing the reaction [15]. However, strong Brönsted acid sites enhance the conversion (wt.%) and rate (mol s^{-1} mol^{-1} Al) of acetyl chloride conversion significantly in the reaction [22,23].

3.4. Influence of silica to alumina ratio

Results of the activity tests in a fixed bed reactor for H-ZSM-5 catalyst of different SiO$_2$/Al$_2$O$_3$ molar ratios are presented in Fig. 4. It is shown that the conversion of acetyl chloride in the acetylation of toluene is markedly affected by the SiO$_2$/Al$_2$O$_3$ molar ratio of H-ZSM-5. The higher the SiO$_2$/Al$_2$O$_3$ molar ratio of H-ZSM-5, the lower the acetyl chloride conversion. However, Fig. 4 indicates that there is an increase in TOF from 7.5 to 20.9 mol s^{-1} mol^{-1} Al × 10^{-4} when framework SiO$_2$/Al$_2$O$_3$ is changed from 41 to 200, respectively. These results are in agreement with the earlier reports of Friedel–Crafts acylation reaction

[15]. Furthermore, it is observed that the isomer ratio (4-MACP/2-MACP) is also affected significantly by the SiO$_2$/Al$_2$O$_3$ ratio of H-ZSM-5. The catalyst with SiO$_2$/Al$_2$O$_3$ molar ratio of 200 showed the highest selectivity for 4-MACP (95.8 wt.%).

3.5. Influence of reaction temperature

Fig. 5 shows the variation of conversion of acetyl chloride (wt.%), rates of acetyl chloride conversion (mol s^{-1} mol^{-1} Al × 10^{-4}), product distribution and isomer ratio of 4-MACP/2-MACP as a function of reaction temperature. A significant increase in the rate of acetyl chloride conversion is achieved with the increase in reaction temperature. Although the TOF for acetyl chloride conversion increased from 6.6 to 8.7, the desired product (4-MACP) selectivity declined from 92.9 to 76.7 wt.% when the reaction temperature is raised from 433 to 473 K. Presumably, the higher temperature favours the formation of 2-MACP and little amounts of consecutive products (others) and hence it changes the isomer ratio of 4-MACP/2-MACP significantly.

3.6. Influence of WHSV

The effect of space velocity is tested by varying the amount of feed and keeping the catalyst content same under identical reaction conditions. Fig. 6 shows the changes in the conversion of acetyl chloride, product distribution and isomer ratio (4-MACP/2-MACP) versus WHSV. At higher space velocity the conversion
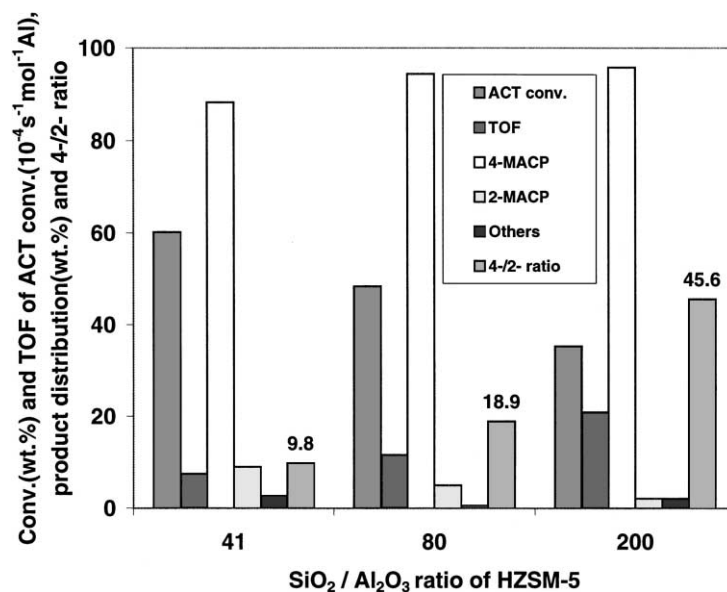
Fig. 4. Effect of SiO_2/Al_2O_3 ratio of H-ZSM-5 on the conversion of CH_3COCl, TOF, 4-MACP/2-MACP ratio and product distribution. Reaction conditions same as in Fig. 1.

of acetyl chloride decreases at faster rate and the formation of others is also suppressed to some extent. The 4-MACP selectivity as high as 91.1 wt.% is obtained at acetyl chloride conversion of 27.4 wt.% when a WHSV of 0.84 is employed.

3.7. Influence of toluene to acetyl chloride molar ratio

The influence of toluene to acetyl chloride molar ratio on the vapour phase acetylation of toluene at
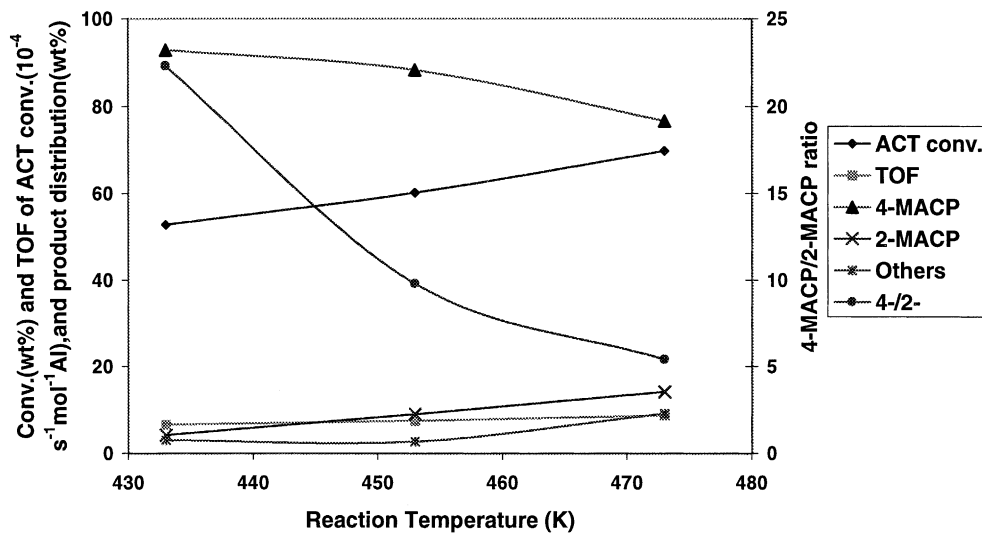

Fig. 5. Effect of reaction temperature on the conversion of CH_3COCl, TOF, 4-MACP/2-MACP ratio and product distribution. Reaction conditions same as in Fig. 1.
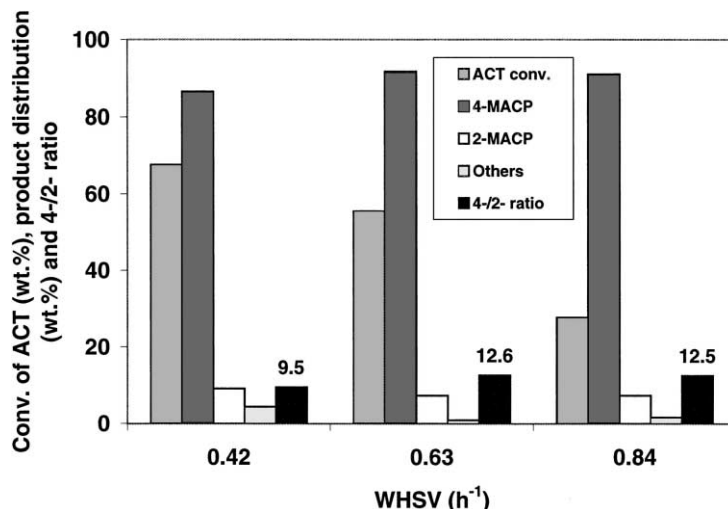
Fig. 6. Effect of WHSV (h^{-1}) on the conversion of CH_3COCl, 4-MACP/2-MACP ratio and product distribution. Reaction conditions: catalyst (H-ZSM-5) = 2 g; toluene/CH_3COCl (molar ratio) = 2; reaction temperature = 453K.

453 K is investigated over H-ZSM-5 catalyst (Fig. 7). The variation of the toluene to acetyl chloride molar ratio is achieved by keeping the amount of toluene constant. Both the conversion of acetyl chloride and the isomer ratio (4-MACP/2-MACP) are increased by higher molar ratios of toluene to acetyl chloride. Additionally, a sharp increase in the isomer ratio of 4-MACP/2-MACP is observed when reactants mo-

lar ratio (toluene/acetyl chloride) is increased from 2 to 4. The sharp increase may be attributed to the decrease in 2-MACP formation.

3.8. Influence of various acetylating agents

Acetylation can also be obtained by the reaction of toluene with other acetylating agents such
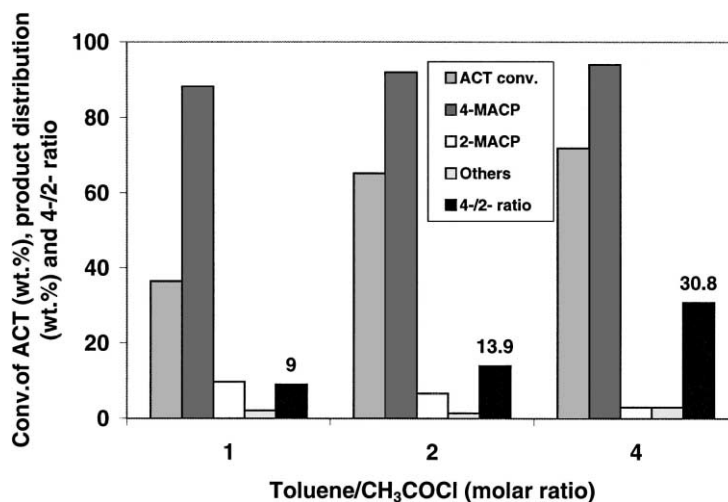

Fig. 7. Effect of toluene/CH_3COCl molar ratio on the conversion of CH_3COCl, 4-MACP/2-MACP ratio and product distribution. Reaction conditions: catalyst (H-ZSM-5) = 2 g; feed rate = 2 ml h^{-1}; reaction temperature = 453 K.

Table 3
Influence of acetylating agents[a]

Acetylating agents	Conversion of acetylating agent (wt.%)	Product distribution[b] (wt.%)			4-MACP/ 2-MACP
		2-MACP	4-MACP	Others	
CH_3COCl	69.9	9.0	88.3	2.7	9.8
$(CH_3CO)_2O$	18.7	10.3	86.5	3.2	8.4
CH_3COOH	11.4	13.2	78.3	8.5	5.9

[a] Cation-exchange (H^+ or RE^{3+}) values reported as percent of the total cation sites taken as the aluminium content 100%.
[b] NH_3 chemisorbed at 303 K ($mmol\,g^{-1}$).

as $(CH_3CO)_2O$ and CH_3COOH (Table 3). Generally, the product mixture contains 4-MACP as the principal component of the reaction with all acetylating agents. However, the conversion of acetylating agents decreases in the order: CH_3COCl > $(CH_3CO)_2O$ > CH_3COOH. The conversion of CH_3COCl, $(CH_3CO)_2O$ and CH_3COOH under our reaction condition is found to be 69.9, 18.7 and 11.4 wt.%, respectively. The corresponding isomer ratios (4-MACP/2-MACP) are 9.8, 8.4 and 5.9, respectively.

4. Conclusions

In summary, H-ZSM-5 catalyses the acetylation of toluene to 4-methylacetophenone selectively and efficiently using CH_3COCl as acetylating agent. H-mordenite and REY zeolite catalysts are less effective in the reaction. The rate of acetylchloride conversion and yield of the products largely depend on the pore size, acidity of the zeolite catalysts and experimental conditions. The conversion of CH_3COCl increases with increasing reaction temperature and toluene to CH_3COCl molar ratio, while it decreases with the increase in reaction time, WHSV, Na-content and silica to alumina molar ratio of H-ZSM-5. A selectivity of the order of 88.3% to 4-MACP could be achieved at 60.2% wt.% conversion of CH_3COCl under certain reaction conditions. H-ZSM-5 is deactivated under the reaction conditions. Acetic anhydride and acetic acid are also found to produce lower yield of products.

Acknowledgements

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