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A novel catalytic method for the acylation of aromatics to the corresponding ketones over zeolite catalysts

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A novel and convenient procedure for the catalytic acylation of a series of aromatic compounds such as benzene, toluene, xylenes (*o*-, *m*-, *p*-), mesitylene, isopropylbenzene and N,N-dimethylaniline to the corresponding ketones using medium- and large-pore zeolites as catalyst and acetic acid or acetyl chloride as acylating agent at different reaction temperatures in a tubular reactor is demonstrated for the first time. The H-ZSM5 and H-beta zeolite catalysts exhibited the higher turnover rates ($\mathrm{TOF} \times 10^{-3}\ \mathrm{s}^{-1}\ \mathrm{mol}^{-1}\ \mathrm{Al}$) for the acetic acid or acetyl chloride conversion to the products. In some cases, nearly total conversion of acylating agent with very high selectivity to the para product is achieved. It is found that the reactivity of the aromatic compounds increases with the increase of $-CH_3$ groups in the benzene ring. Mechanistically, it is assumed that an active species (CH_3CO^+) is generated catalytically from the acylating agent by an acidic zeolite which attacks the aromatic ring and produces corresponding aromatic ketones.

Keywords: acylation of aromatics, aromatic ketones, acylation over zeolite

1. Introduction

The acylation of aromatic substrates is of considerable interest for making aromatic intermediates which are used for the production of pharmaceuticals, insecticides, plasticizers, dyes, perfumes and other commercial products [1]. Conventionally, in the Friedel–Crafts ketone synthesis, an acyl group is introduced in the aromatic nucleus using homogeneous Lewis acid catalysts such as $AlCl_3$ and BF_3 [2]. Other highly active metallic halides recommended for use with acyl halides include $FeCl_3$, $FeBr_3$, $SbCl_5$, $TiCl_4$ and $ZrCl_4$ [3]. Some of these may give yields comparable to those obtained with $AlCl_3$. However, a common problem, particularly in an industrial process, is that the acylation reaction requires a stoichiometric amount of $AlCl_3$ which cannot be used because of its instability in the usual aqueous workup [4]. In addition, the use of $AlCl_3$ may give rise to side reactions such as intra- or intermolecular migration of alkyl groups, removal of alkyl groups and preceding or accompanying acylation [3]. In order to overcome all these difficulties of Lewis acid catalysts, several other catalysts such as iron sulfate [5], iron oxide [6], heteropolyacid [7] and trifluoromethanesulphonic acid [8] have been used as alternative catalysts. Recently, a solid acid catalyst, lanthanide trifluoromethane sulphonate has been developed for the Friedel–Crafts acylation of substituted benzenes [4]. The problems created by Lewis acid catalysts could be easily overcome using a zeolite catalyst. The use of zeolite as acid catalyst has been studied over the past decade in the field of petrochemistry [9,10]. However, their use in fine organic synthesis and particularly in the acylation reactions is limited [11–16]. Here we disclose our preliminary results of the acylation of benzene and substituted benzenes using zeolites H-ZSM5 and H-beta as catalysts and acetic acid or acetyl chloride as acylating agents.

2. Experimental

The catalysts ZSM-5 and beta were synthesized according to the literature procedures [17,18]. Organic templates were eliminated from the zeolite channels by calcination in dry air at 823 K for 16 h. To convert them into their protonic forms, the solids were exchanged thrice with 1 M ammonium nitrate solution for 8 h and then calcined at 823 K for 12 h. Both the samples were characterized by AAS (Hitachi 800) for their chemical compositions, X-ray powder diffraction (Rigaku, D-Max/III-VC model, Cu Kα radiation) for crystallinity and phase purity and scanning electron microscopy (Cambridge Stereoscan 400) for morphology and crystal size. The surface area of the zeolites was measured by nitrogen BET method using an Omnisorb 100 CX apparatus. The main characteristics of the zeolites used are summarized in table 1.

The acylation of aromatics was carried out in a flow reactor (1.4 cm i.d.) between 453 and 548 K under atmospheric pressure. The catalyst sample (1.75 g) was utilized in particles with dimensions in the 15–30 mesh range. A mixture of substrate and acylating agent (2 : 1 molar ratio) was fed into the reactor by a syringe pump. The products were collected in an ice trap and analyzed by a gas-chromatograph (Blue Star model 421) equipped

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Table 1
Physico-chemical properties of the catalysts

Catalyst	SiO_2/Al_2O_3 (molar ratio)	Degree of H^+-exchange	Surface area [a] (m^2/g)	Crystal size (μm)
H-ZSM5	41.0	> 98	413	0.4
H-beta	26.0	> 98	745	0.5

[a] Surface area obtained by N_2 adsorption.

with a flame ionization detector and a capillary column (5 μm thick crosslinked methyl silicone gum, 0.2 mm×50 m long). The products were identified by GC-MS (Shimadzu, QP 2000A) and compared with authentic samples.

3. Results and discussion

Results of the acylation reactions of some aromatic compounds with acetic acid or acetyl chloride catalysed by zeolites, H-ZSM5 and H-beta, are listed in table 2. It is observed that large amounts of monoacetylated aromatics such as **1** and **2** (scheme 1) are present in the products. In some cases, a significant amount of secondary diacylated products, **3** (consecutive products, scheme 1) are also formed. The products obtained in the acylation of various aromatics in the present study are found similar to those reported earlier in the Friedel–Crafts acylation of aromatics using hafnium triflate as a catalyst and acetic anhydride as the acylating agent [19]. The results in table 2 indicate that the zeolite H-ZSM5 is very active and selective for the acylation of benzene, toluene, and isopropylbenzene, however, it failed to give any product with the other substrates (table 2). The inactivity of H-ZSM5 for xylenes, mesitylene and N,N-dimethylaniline in the acylation reactions may be attributed to its small pore size as compared to the size of the substrates as well as products. On the other hand, zeolite H-beta proved to be very effective in the acylation of large molecules. The higher activity of H-beta in the acylation of xylenes, mesitylene and N,N-dimethylaniline might be explained on the basis of its larger pore openings (7.5 × 5.5 Å) than the H-ZSM5 (5.4 × 5.6 and 5.1 × 5.5 Å).

3.1. Benzene

The conversion of acylating agent (CH_3COOH), turnover rates and product distribution of the acylation of benzene with acetic acid over H-ZSM5 catalyst are presented in table 2 (run 1). The primary product of the reaction is acetophenone with small amounts of consecutive products (others). The conversion of acetic acid, TOF (10^{-3} s^{-1} mol^{-1} Al) and selectivity to acetophenone are found to be 76 wt%, 91.2 and 88.1% respectively, at 548 K reaction temperature. The selectivity towards consecutive products is about 11.9%.

3.2. Toluene

Likewise, it is also found that H-ZSM5 is catalytically active in the acylation of toluene with acetic acid. The reaction conditions and the results are summarized in table 2 (run 2). The main products of the reaction are 2-methylacetophenone (2-MACP) and 4-methylacetophenone (4-MACP). Some amounts of consecutive products are formed by the subsequent acylation of 2-MACP and 4-MACP. Under the reaction conditions 55.5 wt% of acetic acid was converted to 2-MACP, 4-MACP and others (**3**, scheme 1) at 523 K in selectivity of 41.4, 43.7

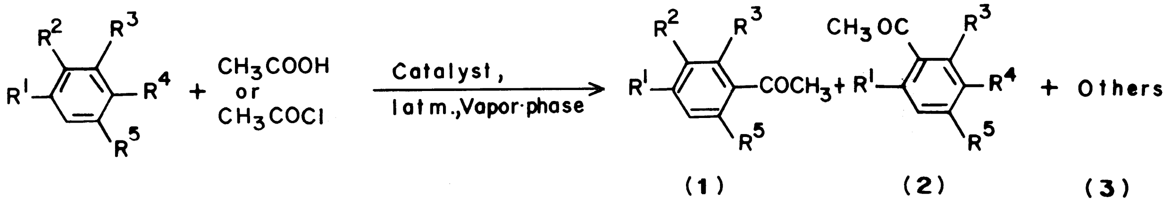
Table 2
Acylation of aromatics [a]. See scheme 1 for substrate and product codes used

Run	Catalyst	Substrate					Acylating agent	Reaction temp. (K)	Conv. of acylating agent (wt%)	TOF [b] (10^{-3} s^{-1} mol^{-1} Al)	Product distribution (wt%)		
		R^1	R^2	R^3	R^4	R^5					**1**	**2**	**3** [c]
1	H-ZSM5	H	H	H	H	H	CH_3COOH	548	76.0	91.2	88.1	–	11.9
2	H-ZSM5	CH_3	H	H	H	H	CH_3COOH	523	55.5	48.9	43.7	41.4	14.9
3	H-beta	CH_3	CH_3	H	H	H	CH_3COCl	453	83.0	41.7	83.7	–	16.3
4	H-beta	CH_3	H	CH_3	H	H	CH_3COCl	453	86.0	43.3	87.0	3.5	9.5
5	H-beta	CH_3	H	H	CH_3	H	CH_3COCl	453	85.7	43.1	79.1	–	20.9
6	H-beta	CH_3	H	CH_3	H	CH_3	CH_3COCl	453	97.3	44.1	86.8	–	13.2
7	H-ZSM5	$CH(CH_3)_2$	H	H	H	H	CH_3COCl	473	98.5	67.2	43.2	52.1	4.7
8	H-beta	$N(CH_3)_2$	H	H	H	H	CH_3COCl	453	97.0	47.3	97.4	–	2.6

[a] Reaction conditions: catalyst weight: 1.75 g; substrate/acylating agent (molar ratio 2 : 1); feed rate: 2 ml/h.

[b] Turnover rates are expressed as turnover frequencies (TOF, mole of CH_3COOH or CH_3COCl converted s^{-1} mol^{-1} Al).

[c] Others: diacetyl products (consecutive products).



Scheme 1.

and 14.9% respectively. The turnover rates of acetic acid conversion on H-ZSM5 are found to be 48.9.

3.3. Xylenes (o-, m-, p-)

Ortho-, meta-, and para-xylenes were separately acylated by acetyl chloride over the H-beta catalyst at 453 K under identical reaction conditions. The results are shown in table 2 (runs 3–5). The results indicate that H-beta is para-selective for the gas-phase acylation of xylenes. The position of methyl groups on the benzene ring plays a key role in defining the type of products. The acylation of *o*-xylene leads to the formation of 3,4-dimethylacetophenone in higher selectivity (83.7%, table 2, run 3). With *m*-xylene, the reaction gives mainly 2,4-dimethylacetophenone (87.0%). In addition, a trace amount of 2,6-dimethylacetophenone (3.5%) is also observed in the products (table 2, run 4). Similarly, acylation of *p*-xylene gives almost merely monoacylated product viz. 2,5-dimethylacetophenone in 79.1% selectivity (table 2, run 5). Similar products have been reported earlier in the acylation of xylenes [19,20]. Further, small amounts of diacetyl xylenes (others) are obtained from all xylenes probably by the subsequent acylation of monoacylated products. The conversion of acetyl chloride in the reaction of *o*-, *m*-, *p*-xylenes for the gas-phase acylation are arbitrarily ranked based on the level of acylating agent conversion under comparable reaction conditions. It appears from the results that reactivities of xylenes towards acetyl chloride in the reaction are nearly similar.

3.4. Mesitylene

The gas-phase acylation of 1,3,5-trimethylbenzene (table 2, run 6) was studied over H-beta under conditions similar to that used for the reactions of the xylenes. The conversion of acetyl chloride to the products is determined to be 97.3 wt% at 453 K. The selectivities towards monoacylated products (2,4,6-trimethylacetophenone) and diacetylated products are about 86.8 and 13.2%, respectively. The turnover rates for acetyl chloride conversion is found to be 44.1.

3.5. Isopropylbenzene

The acylation of isopropylbenzene with acetyl chloride was carried out at 473 K over H-ZSM5 catalyst (table 2, run 7). 98.5 wt% conversion of acetyl chloride was achieved. The only products of the reaction were 2-isopropylacetophenone (52.1 wt%), 4-isopropylacetophenone (43.2 wt%) and small peaks were identified as heavier products (others). As can be seen from table 2, run 7, the selectivity for the monoacylated product is as high as 95.3%. The turnover rates for the acetyl chloride conversion in the reaction are also found to be 67.2.

3.6. N,N-dimethylaniline

It is found that N,N-dimethylaniline could be acylated with CH_3COCl using zeolite H-beta at 453 K. Zeolite H-beta showed high activity and selectivity for the formation of a single product 4-N,N-dimethylacetophenone. In addition, consecutive products (others) are also formed (2.6%) to a trace level. The turnover rates for acetyl chloride conversion are as high as 47.3.

4. Influence of $-CH_3$ groups

The influence of $-CH_3$ groups on the reactivity of aromatics is illustrated in table 2. One can see that non-activated substrate shows lower conversion to the acylated products than the activated substrates. Compared with toluene, the acylation of benzene takes place at higher temperature (table 2). The higher temperature increases the reactivity of benzene towards acetic acid. For comparison of the reactivities of the substrates, the acylations of *o*-, *m*-, *p*-xylene, mesitylene and N,N-dimethylaniline were carried out under similar reaction conditions using H-beta as catalyst and CH_3COCl as acylating agent. The reactivities of these substrates with acetyl chloride appear to be in the order of *p*-xylene ≈ *m*-xylene ≈ *o*-xylene < mesitylene ≈ N,N-dimethylaniline. The results presented here reveal that the reactivity of the substrate is related to the number of $-CH_3$ groups attached to the benzene ring.

5. Mechanism

Fig. 1 shows the catalytic cycle of a plausible mechanism which involves the reaction of acylating agent (CH_3COOH/or CH_3COCl) with the acidic zeolite cat-

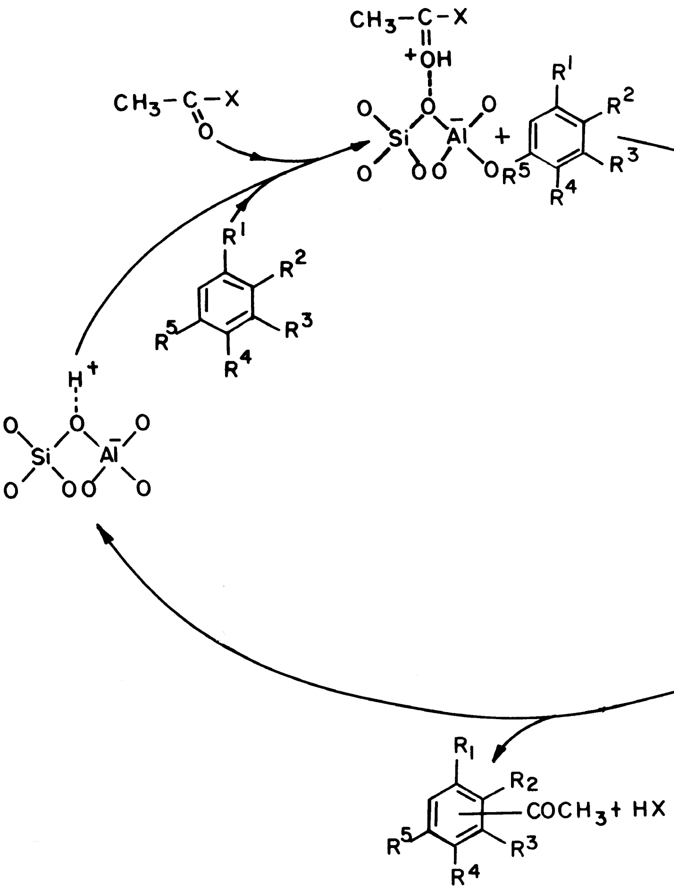


Fig. 1. Plausible mechanism for the acylation of aromatics. ($X = O\bar{H}, C\bar{l}$; R^1, R^2, R^3, R^4, R^5 = H or CH_3 or $–CH_3(CH_3)_2$ or $–N(CH_3)_2$.)

alyst which polarises the acylating agent and in turn produces an electrophile (CH_3CO^+) [12]. Thus the generated electrophilic species attacks the aromatic ring resulting in the formation of the corresponding ketones [12,15,21,22].

6. Conclusions

In summary, benzene and substituted benzenes can be acylated in the gas phase using zeolites as catalyst and acetic acid or acetyl chloride as acylating agent. H-ZSM5 exhibits higher activity in the acylation of benzene, toluene and isopropylbenzene whereas H-beta catalyses efficiently the acylation of larger molecules such as xylenes, mesitylene and N,N-dimethylaniline. The inactivity of H-ZSM5 towards larger molecules is attributed to its small pore openings. In most of the cases, the acylation of these substrates gives para products as main product in higher selectivities. The reactivities of the aromatic compounds towards acylating agent increase with increase in the number of $–CH_3$ groups on the benzene ring. The reactivities of the substrates with acetyl chloride over H-beta at 453 K is found to be in the order of p-xylene $\approx$ m-xylene $\approx$ o-xylene $<$ mesitylene $\approx$ N,N-dimethylaniline. Most probably, the acylation reaction takes place by an electrophile (CH_3CO^+) which is produced by an acidic catalyst from the CH_3COOH/or CH_3COCl.Thus the generated electrophile attacks the aromatic ring and produces the respective ketones.

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