Efficient liquid phase acylation of alcohols over basic ETS-10 molecular sieves

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Abstract—Acylation of alcohols with acetic acid can be carried out efficiently in the liquid phase over microporous titanosilicate ETS-10-type catalysts. The reaction was studied over ETS-10 exchanged with, Li, Na, K, Rb, Cs, Ba and H ions. Activity for acylation of primary alcohols depends on the exchanged alkali ion and increases in the order Li<Na<K<Ba ~ H ~ Rb ~ Cs–ETS-10. These molecular sieves are also suitable for the acylation of secondary alcohols and esterification with long chain carboxylic acids. © 2001 Elsevier Science Ltd. All rights reserved.

ETS-10 molecular sieves exchanged with alkali metal cations have been used as basic catalysts for aldol-type condensations[1] and alcohol dehydrogenation reactions.[2] It has been shown that the basicity of ETS-10 depends on the exchanged cation and increases in the order Li<Na<K<Rb and Cs.[3] Acylation of the hydroxyl group is an important transformation in organic synthesis. Both acetic anhydride and acetyl chloride are routinely used as acylating agents in the presence of amine bases such as triethylamine, pyridine or 4-(*N*,*N*-dimethylamino)pyridine (DMAP).[4]

Recently, various acid catalysts such as ZnCl$_2$,[5] Co(II)Cl$_2$,[6] La(Opr^i)$_3$,[7] Sc(OTf)$_3$,[8] TMSOTf,[9] TaCl$_5$–SiO$_2$,[10] In(OTf)$_3$,[11] Cu(OTf)$_3$,[12] Bi(OTf)$_3$,[13] montmorillonite[14] and zeolite LaY[15] have been reported to be useful as catalysts for acylation with acetic acid or acetic anhydride. Acylation with acetic anhydride without a catalyst has also been reported.[16] Though acylation of alcohols can also be brought about by the action of Lewis acid reagents in conjunction with carboxylic acids, the Lewis acid is destroyed in the work-up procedure resulting in substantial waste production. From an industrial point of view, anhydrides and acid chlorides are more expensive than the corresponding carboxylic acids. We now report the convenient acylation of alcohols with acetic acid and other long chain carboxylic acids using basic microporous alkali exchanged ETS-10 as catalyst.

The alkali contents of the ETS-10 samples and their BET surface areas are presented in Table 1. Activity for acylation of 2-phenylethanol increases as the cation M in M–ETS-10 is varied in the order: Li<Na<K<Rb ~

Table 1. Alkali metal compositions and surface areas of M–ETS-10 (where M = H, Li, Na, K, Rb, Cs and Ba)

Nos	Sample (M–ETS-10)	Metal content (wt%)			BET surface area (m^2/g)
		Na	K	Cation (M)	
1	As synthesized (**A**)	63.7	36.3	–	460
2	H	12.3	15.0	72.7	470
3	Li	8.2	6.7	85.1	455
4	Na	–	14.8	85.2	443
5	K	13.8	–	86.2	428
6	Rb	22.2	12.3	65.5	396
7	Cs	18.3	12.8	68.9	381
8	Ba	16.1	10.7	73.2	372

H $\sim$ Ba $\sim$ Cs as shown in Fig. 1. Alcohol conversions of 91–96% are reached in 4 h over Rb, Cs, Ba and H exchanged samples. The original sample containing both Na and K [ETS-10 (**A**)] ions is also highly active. The activity of the Na–K form [ETS-10 (**A**)] ion the acylation of a number of secondary alcohols with acetic acid at 120°C is presented in Table 2. The reaction is nearly complete within 8 h with good selectivity for the acylated product. The catalyst shows good activity even after three cycles (Table 2). The ETS-10 molecular sieve was highly crystalline before and after reaction as confirmed by X-ray diffraction patterns. Primary alcohols are more active than secondary alcohols (>90% yield for primary alcohols and<90% for secondary alcohols). In the case of the optically active alcohol (1*R*,2*S*,5*R*)-(−)-menthol (Table 2), optical activity is retained in the product. When the product ester was hydrolyzed to menthol, the alcohol was found to be identical to the starting menthol.

Normally 10 equivalents of acetic acid ensures near quantitative conversion of the alcohol. When the molar ratio is reduced to a stoichiometric amount, the conversion decreases to $\sim$ 50% (not presented in Table 2). The catalyst was also found to be active for the acylation of long chain alcohols. The acylation of 2-phenylethanol with acetic anhydride over ETS-10 (**A**) is rapid even at room temperature (42 and 85% conversion in 8 and 24 h, respectively). However, this catalyst is not active in the acylation of phenol and β-naphthol.

ETS-10 (**A**) molecular sieves also catalyze the acylation of 2-phenylethanol with long chain (octanoic, nonanoic and decanoic) acids (Table 3). Acylation with propanoic acid gives $\sim$ 99% conversion. As the carbon number of the carboxylic acid increases, the conversion decreases and by-products also increase. In the case of decanoic acid, the conversion is $\sim$ 76%.
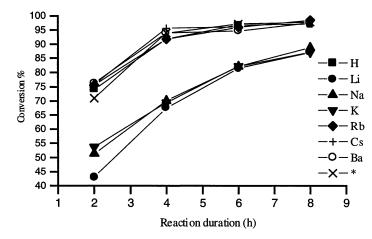

Figure 1. Influence of reaction time on conversion of 2-phenylethanol over different M exchanged ETS-10 molecular sieves. *As prepared sample (Na–K form); reaction conditions: temperature = 120°C; substrate = 5 mmol; acetic acid = 4 mL; and duration of run = 8 h.

Table 2. Acylation of various alcohols with acetic acid over Na–K–ETS-10

Nos.	Substrate	Conversion	Others[a]	Acylation selectivity[b]
1	Benzyl alcohol	97.2	1.2	98.7
2	2-Phenylethanol	97.8	0.8	99.2
3	1st recycle[c]	96.2	0.9	99.0
4	2nd recycle[c]	94.2	0.7	99.2
5	3rd recycle[c]	91.3	0.8	99.1
6	2-Phenylethyl alcohol[d]	31.1	1.2	97.3
7	Tetrahydrofurfuryl alcohol	98.0	0.9	99.1
8	1-Nonanol	91.5	0.1	99.8
9	1-Dodecanol	99.4	–	100
10	1-Dodecanol[d]	29.3	0.1	99.8
11	β-Citronellol	99.5	9.0	90.9
12	Hexane-3-ol	87.2	4.3	95.1
13	Cyclohexanol	83.7	–	100
14	Cyclohexanol[d]	23.7	0.2	99.1
15	Menthol	70.3	–	100

Reaction conditions: temperature = 120°C; substrate = 5 mmol; acetic acid = 4 mL; duration of run = 8 h.
[a] Mainly *C*-alkylated products.
[b] Selectivity = (mol% expected product/mol% conversion)×100.
[c] Catalyst recycled for acylation of 2-phenylethanol.
[d] Without catalyst.

Table 3. Acylation of 2-phenylethanol with various carboxylic acids over Na–K–ETS-10

Nos	Acylating agent	Conversion	Others[a]	Acylation selectivity[b]
1	Acetic acid	97.8	0.8	99.2
2	Propanoic acid	99.4	1.4	98.5
3	Octanoic acid	96.8	6.0	93.8
4	Nonanoic acid	90.7	10.2	89.8
5	Decanoic acid	76.3	12.7	87.3

Reaction conditions: temperature = 120°C; substrate = 5 mmol; acetic acid = 4 mL; other acids = 5 mmol; and duration of run = 8 h.
[a] Mainly *C*-alkylated products.
[b] Selectivity = (mol% expected product/mol% conversion) × 100.

In conclusion, ETS-10 molecular sieves are useful in the acylation of primary and secondary alcohols with acetic acid and long chain carboxylic acids (C_8–C_{10}). Alcohol conversion increases with the basicity of the catalyst.

General procedure for catalyst preparation

ETS-10 was prepared according to the procedure reported earlier.[17] The Si/Ti ratio was 5.61. The ETS-10 sample was converted into different ion-exchanged forms by exchanging thrice with the required metal chloride solution (20 mL of 1 M solution/g of catalyst at 80°C for 3 h). After washing with demineralized water, filtering and drying, the M-ETS-10 samples (M = Li, Na, K, Rb, Cs and Ba) were calcined at 500°C for 4 h. Powder X-ray diffraction data of the calcined samples (collected on Rigaku Model D-MAX III VC) revealed the samples to be highly crystalline. Elemental analyses were done by atomic adsorption spectroscopy (AAS).

General procedure for the acylation reaction

All the reactions were carried out in the liquid phase in a round bottom flask fitted with a cold water condenser. Substrate (5 mmol), acetic acid (4 mL) (in the case of long chain C_8–C_{10} acids, a stoichiometric amount was used) and 50 mg of catalyst were refluxed at 120°C for 8 h. Conversions have been calculated on the basis of alcohol used. The progress of the reaction was monitored by a gas chromatography (HP-5880) using a capillary column (HP-5, cross-linked methyl–silicone gum, 50 m×0.5 mm). After completion, the reaction mixture was quenched with a saturated solution of $NaHCO_3$ and extracted with ethyl acetate. The organic layer was washed with water and brine and the solvent was evaporated in vacuo to give almost pure products.

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