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Acylation of aromatic compounds using moisture insensitive $InCl_3$ impregnated mesoporous Si-MCM-41 catalyst

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Abstract—Acylation of aromatic compounds (benzene, toluene, *p*-xylene, mesitylene, anisole, naphthalene, methylnaphthalene and methoxynaphthalene) by an acyl chloride (benzoyl chloride, phenylacetyl chloride, propionyl chloride or butyryl chloride) in high yield, in a short reaction period (3 h), even in the presence of moisture in the aromatic substrate or solvent (dichloroethane), can be accomplished at low temperature (80±1°C) using an $InCl_3$ impregnated Si-MCM-41 catalyst in low catalyst concentration.

Aromatic ketones are important fine chemicals and/or intermediates for the preparation of fine chemicals in the dyestuffs, pharmaceutical and other chemical industries. The conventional method for the preparation of aromatic ketones is based on the homogeneous Friedel–Crafts acylation of aromatic hydrocarbons with acid chlorides using more than stoichiometric amounts of anhydrous $AlCl_3$ as catalyst.[1] However, the use of anhydrous $AlCl_3$ as a catalyst poses several problems, such as difficulty in its separation and recovery, disposal of spent catalyst, corrosion problems, etc. Moreover, this catalyst is highly moisture sensitive and hence demands moisture-free reactants and solvents and also must be handled under a dry atmosphere. Because of its very high moisture sensitivity, the results obtained with this catalyst are seldom reproducible. Hence the development of easily separable solid catalysts having high activity but little or low moisture sensitivity in the acylation reactions is, therefore, of great practical importance. In earlier studies, a number of solid acid catalysts, such as Hβ, HY, H-ZSM-5 zeolites,[2–4] heteropoly acids[5] and modified ZrO_2[6] have been reported for acylation reactions. However, these solid acid catalysts show poor activity for the acylation. In contrast, In_2O_3/Si-MCM-41, which is basic in nature, shows very good acylation activity.[7] Our earlier studies indicated that, in comparison to In_2O_3/Si-MCM-41, the $InCl_3$/Si-MCM-41 catalyst shows much higher benzene benzylation activity.[7,8] Hence, it is interesting to study the acylation of aromatic compounds using the $InCl_3$/Si-MCM-41 catalyst. We report here that, the $InCl_3$ impregnated mesoporous Si-MCM-41 catalyst shows high activity in the acylation of different aromatic compounds by acyl chlorides and, also, that this catalyst does not demand moisture-free reaction conditions for the acylation reaction.

Results showing the product yields in the acylation of different aromatic compounds with acyl chlorides (viz. benzoyl chloride, phenylacetyl chloride, propionyl chloride and butyryl chloride) (at 80±1°C)[9] using the $InCl_3$/Si-MCM-41 catalyst (loading of $InCl_3 = 20$ wt%),[10] using dichloroethane (DCE), acetonitrile (ACN) or *n*-heptane as a solvent, in the presence or absence of moisture in the reaction mixture, are presented in Table 1.

The product yield in all the cases is quite high, indicating the high acylation activity of the catalyst, even in the presence of moisture in the aromatic substrate and/or solvent. In the cases of the substituted benzenes and naphthalenes, acylation at the *ortho* position relative to that of the *para* position was found to be very small, indicating a high regioselectivity in the acylation. The presence of moisture has a beneficial effect leading to an increase in the product yield. A similar beneficial effect of moisture was observed in the acylation of toluene using the In_2O_3/Si-MCM-41 catalyst.[7]

Among the three solvents used for the acylation of anisole, *n*-heptane is the least preferred and ACN and DCE showed comparable performance. For the

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Keywords: acylation of aromatic compounds; $InCl_3$ impregnated mesoporous Si-MCM-41 catalyst.

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Table 1. Results on the acylation reactions of different aromatic compounds using the $InCl_3$/Si-MCM-41 catalyst (reaction mixture: 20.0 mmol of moisture-free aromatic compound + 11.0 ml of moisture-free solvent + 8.6 mmol of acyl chloride, amount of catalyst = 0.4 g, temperature = 80 ± 1°C, reaction period = 3 h

Entry	Substrate	Acylating agent	Solvent	Main product[c]	Yield (%)
1	Anisole	C_6H_5COCl	DCE	4-Methoxybenzophenone	83
2	Anisole[a]	C_6H_5COCl	DCE	4-Methoxybenzophenone	84
3	Anisole	C_6H_5COCl	DCE[b]	4-Methoxybenzophenone	84
4	Anisole[a]	C_6H_5COCl	DCE[b]	4-Methoxybenzophenone	84
5	Anisole	C_6H_5COCl	ACN	4-Methoxybenzophenone	82
6	Anisole	C_6H_5COCl	*n*-Heptane	4-Methoxybenzophenone	25
7	Benzene	C_6H_5COCl	DCE	Benzophenone	57
8	Benzene[a]	C_6H_5COCl	DCE	Benzophenone	57
9	Toluene	C_6H_5COCl	DCE	4-Methylbenzophenone	69
10	Toluene[a]	C_6H_5COCl	DCE	4-Methylbenzophenone	70
11	*p*-Xylene	C_6H_5COCl	DCE	2,5-Dimethylbenzophenone	74
12	Mesitylene	C_6H_5COCl	DCE	2,4,6-Trimethylbenzophenone	79
13	Naphthalene	C_6H_5COCl	DCE	1-Benzoylnaphthalene	67
14	2-Methylnaphthalene	C_6H_5COCl	DCE	1-Benzoyl-2-methylnaphthalene	74
15	2-Methoxynaphthalene	C_6H_5COCl	DCE	1-Benzoyl-2-methoxynaphthalene	88
16	Anisole	C_2H_5COCl	DCE	4-Methoxypropiophenone	89
17	2-Methoxynaphthalene	C_2H_5COCl	DCE	1-Propio-2-methoxynaphthalene	92
18	Anisole	C_3H_7COCl	DCE	4-Methoxybutyrophenone	87
19	Anisole	$C_6H_5CH_2COCl$	DCE	α-(4-Methoxyphenyl) acetophenone	74

[a] Aromatic compound saturated with water.

[b] Solvent saturated with water.

[c] In the cases of the substituted benzenes and naphthalenes, the yield of *ortho* acylated product was very small (<8%).

acylation of other aromatic compounds, DCE was used as the solvent.

The presence of moisture in the reaction mixture has no detrimental effect on the acylation activity of the catalyst. This is of great practical importance, as the catalyst does not demand a thoroughly dried aromatic substrate or solvent nor handling of the catalyst under moisture-free conditions. The results obtained are quite reproducible.

The benzene benzoylation activity of the $InCl_3$/Si-MCM-41 catalyst is much higher than that of the earlier reported In_2O_3/Si-MCM-41,[7] Hβ zeolite[2] and clayzic[11] catalysts. For these catalysts, the product yield obtained in the benzene benzoylation and the temperature and reaction period required were as follows: In_2O_3/Si-MCM-41 catalyst 50%, after 5 h at 80°C; Hβ zeolite catalyst 54%, after 18 h at 80°C; and the clayzic catalyst 66%, after 30 h at 130–140°C.

The moisture insensitivity of the $InCl_3$/Si-MCM-41 catalyst indicates that acylation reactions over this catalyst are not catalyzed by the Lewis acid sites of the catalyst. The high acylation activity may be attributed to the redox property of the catalyst [$E^{\circ}_{\mathrm{In}^{3+}/\mathrm{In}^{1+}} = -0.44$ V]. A probable redox mechanism for acylation reactions over this catalyst is given below.

$$2RCOCl + In^{3+} \rightarrow 2RCOCl^{+\bullet} + In^{1+} \tag{1}$$

[$R = C_6H_5$, $C_6H_5CH_2$, C_2H_5 or C_3H_7].

$$2RCOCl^{+\bullet} \rightarrow 2\ RCO^{+} + 2Cl^{\bullet} \tag{2}$$

$$2Cl^{\bullet} + In^{1+} \rightarrow In^{3+} + 2Cl^{-} \tag{3}$$

$$RCO^{+} + ArH \rightarrow RCOAr + H^{+} \tag{4}$$

[$Ar = C_6H_5$, $(CH_3)C_6H_4$, $(CH_3)_2C_6H_3$, $(CH_3)_3C_6H_2$, $(CH_3O)C_6H_4$, $C_{10}H_7$, $(CH_3)C_{10}H_6$ or $(CH_3O)C_{10}H_6$].

The above mechanism is similar to that proposed earlier by Brio et al. for acylation reactions over cation-exchanged clays.[12] This mechanism may, however, be considered as a speculative one.

In summary, $InCl_3$ impregnated Si-MCM-41 is a highly active catalyst for the acylation of aromatic compounds by acyl chlorides even in the presence of moisture in the reaction mixture.

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9. *General procedure for acylation reactions*: The acylation reactions over the $InCl_3$/Si-MCM-41 were carried out in a magnetically stirred glass reactor (capacity: 25 cm^3) under reflux (at 80±1°C) for 3 h, while continuously bubbling moisture-free N_2 (30 cm^3 min^{-1}) through the liquid reaction mixture. After the reaction, the catalyst was separated from the reaction mixture by filtration and the product was recovered from the filtrate by washing with 0.1 M NaOH solution and removing the solvent and unconverted aromatic substrate by vacuum distillation. The product was purified by column chromatography using silica gel (SRL 60–120 mesh) as the stationary phase and benzene as the eluent. The structures of the products were determined by NMR spectroscopy.
10. *Catalyst preparation*: $InCl_3$/Si-MCM-41 catalyst (loading of $InCl_3 = 20$ wt%) was prepared by impregnating Si-MCM-41 (high silica mesoporous MCM-41 with a surface area of 1140 m^2 g^{-1}) with indium chloride (Aldrich) from its acetonitrile solution by the incipient wetness technique (i.e. using the solution of indium chloride just sufficient to wet the Si-MCM-41) and evaporating the solvent in a vacuum oven at 100°C for 8 h. The Si-MCM-41 was prepared by its crystallization from a gel of composition: tetraethyl orthosilicate (0.17 mol)+sodium hydroxide (0.04 mol)+tetramethylammonium hydroxide (0.02 mol)+cetyltrimethylammonium bromide (0.04 mol)+distilled water (18.9 mol), at room temperature (27°C) for 24 h by a procedure reported elsewhere.[13] The solid product was obtained by filtration, washed with distilled water, dried in air at room temperature and finally calcined at 550°C for 16 h.
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