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ACYLATION OF AROMATIC COMPOUNDS USING MOISTURE INSENSITIVE MESOPOROUS Si-MCM-41 SUPPORTED Ga₂O₃ CATALYST

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ABSTRACT

Mesoporous Si-MCM-41 supported Ga₂O₃ is a highly active catalyst for the acylation of aromatic compounds with different acyl chlorides. Moreover, this catalyst is not deactivated by water and hence does not require moisture-free reaction conditions.

Key Words: Acylation of aromatic compounds; Si-MCM-41 supported gallium oxide; Moisture insensitive catalyst; Benzoylation of aromatic compounds

INTRODUCTION

Friedel–Crafts type acylation of aromatic compounds with acyl chlorides using anhydrous AlCl₃, as a catalyst is a commonly practiced synthetic

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method for the preparation of aromatic ketones.^[1] The use of anhydrous AlCl_3 as a homogeneous catalyst in the acylation, however, poses several serious problems, such as requirement of the catalyst in more than stoichiometric amounts, difficulty in the separation and recovery of the catalyst, disposal of the spent catalyst, corrosion problems, etc. Moreover, this catalyst is highly moisture sensitive and hence demands moisture-free reactants and solvent and also dry atmosphere for its handling. Because of its higher moisture sensitivity, the results obtained with this catalyst are seldom reproducible. Hence development of easily separable solid catalysts having high activity but little or no moisture sensitivity for the acylation reactions is, therefore, of great practical importance. A number of solid acid catalysts, such as H β , HY and H-ZSM-5 zeolites,^[2-4] heteropoly acids,^[5] modified ZrO_2 ^[6] have been reported earlier for the acylation reactions. However, these catalysts have poor activity for the acylation.

Our earlier studies^[7] reveal that Ga_2O_3 (or In_2O_3)/Si-MCM-41 has very high activity with little or no moisture sensitivity in the benzylation of benzene. We report here the synthesis of different aromatic ketones in high yields at a short reaction period (3 h), by the acylation of different aromatic compounds even in the presence of moisture using Ga_2O_3 /Si-MCM-41, which can be separated simply by filtration.

RESULTS AND DISCUSSION

Results showing the influence of solvent, moisture in solvent and loading of Ga_2O_3 on Si-MCM-41 on the yield of methoxy benzophenone in the benzoylation of anisole by benzoyl chloride (at 80°C) over the Ga_2O_3 /Si-MCM-41 catalyst are presented in Table 1. The product yield for the different solvents is in the following order: *n*-heptane < acetonitrile < dichloroethane. As expected, the yield is also increased with increasing the Ga_2O_3 loading. It is interesting to note that, the presence of moisture in the solvent has a beneficial effect on the product yield; it has caused a significant increase in the product yield.

The results showing the product yields in the acylation of different aromatic compounds with different acyl chlorides (at 80°C) over the Ga_2O_3 (20%)/Si-MCM-41 catalyst in the presence or absence of moisture in the reaction mixture are presented in Table 2. From the results, following important observations can be made:

- In all the cases, the product yield is quite high, indicating high acylation activity of the catalyst.

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Table 1. Effect of Solvent, Moisture in Solvent, and Ga₂O₃ Loading on the Yield in the Benzoylation of Anisole over Ga₂O₃/Si-MCM-41 Catalyst at 80±1°C (Reaction Period = 3 h)

Ga ₂ O ₃ Loading (wt%)	Solvent Used	Isolated Yield (%) Methoxy Benzophenone
0.0	Dichloroethane	0
5.0	Dichloroethane	37
10.0	Dichloroethane	63
20.0	Dichloroethane	76
20.0	Dichloroethane ^a	80
20.0	Acetonitrile	75
20.0	<i>n</i> -Heptane	25

^aSolvent saturated with water at room temperature.

- Because of the presence of moisture in the substrate or catalyst (i.e., in the reaction mixture) the product yield is not decreased; in fact it is increased significantly indicating a beneficial effect of the moisture in the reaction mixture.
- In the benzoylation of different aromatic compounds, the product yield depends on the substituent group(s) present in the aromatic substrate. The order of the product yield for the different substituents is as follows.

For substituted benzenes: without substituent < methyl < di-methyl < tri-methyl < methoxy. For substituted naphthalenes: without substituent < methyl < methoxy. The above order is consistent with that observed earlier.^[1]

The observed high acylating activity of Ga₂O₃/Si-MCM-41 catalyst in the presence of moisture suggests that Lewis acids of the Ga₂O₃ catalyst does not play significant role in the acylation. The standard reduction potential for gallium, $E_{(Ga^{3+}/Ga^{1+})}^0$ is -0.44 V and hence the redox properties of the Ga₂O₃/Si-MCM-41 catalyst are expected to play an important role in the acylation. A probable redox mechanism for the acylation reactions over the Ga₂O₃/Si-MCM-41 catalyst is given below.



**Table 2.** Results on the Acylation of Different Aromatic Compounds over Ga₂O₃ (20%)/Si-MCM-41 Catalyst at 80°C (Solvent: Dichloroethane, reaction period = 3 h)

Entry	Substrate	Acylating Agent	Product	Yield (%)
1	Anisole	C ₆ H ₅ COCl	4-Methoxy benzophenone	76
2	Anisole ^a	C ₆ H ₅ COCl	4-Methoxy benzophenone	79
3	Anisole ^b	C ₆ H ₅ COCl	4-Methoxy benzophenone	80
4	Benzene	C ₆ H ₅ COCl	Benzophenone	42
5	Benzene ^b	C ₆ H ₅ COCl	Benzophenone	43
6	Toluene	C ₆ H ₅ COCl	4-Methyl benzophenone	50
7	Toluene ^b	C ₆ H ₅ COCl	4-Methyl benzophenone	52
8	<i>p</i> -Xylene	C ₆ H ₅ COCl	2,5-Dimethyl benzophenone	64
9	<i>p</i> -Xylene ^b	C ₆ H ₅ COCl	2,5-Dimethyl benzophenone	66
10	Mesitylene	C ₆ H ₅ COCl	2,4,6-Trimethyl benzophenone	71
11	Mesitylene ^b	C ₆ H ₅ COCl	2,4,6-Trimethyl benzophenone	73
12	Naphthalene	C ₆ H ₅ COCl	2-Benzoyl naphthalene	54
13	2-Methyl naphthalene	C ₆ H ₅ COCl	1-Benzoyl 2-methyl naphthalene	62
14	2-Methoxy naphthalene	C ₆ H ₅ COCl	1-Benzoyl 2-methoxy naphthalene	79
15	Anisole	C ₂ H ₅ COCl	4-Methoxy propiophenone	79
16	Anisole ^b	C ₂ H ₅ COCl	4-Methoxy propiophenone	82
17	2-Methoxy naphthalene	C ₂ H ₅ COCl	1-Propio 2-methoxy naphthalene	81
18	Anisole	C ₃ H ₇ COCl	4-Methoxy butyrophenone	77
19	Anisole ^b	C ₃ H ₇ COCl	4-Methoxy butyrophenone	80
20	Anisole	C ₆ H ₅ CH ₂ COCl	4-Methoxy phenyl acetophenone	61
21	Anisole ^b	C ₆ H ₅ CH ₂ COCl	4-Methoxy phenyl acetophenone	63

^aMoist catalyst (the catalyst stored over water at room temperature for 12 h).^bAromatic compound saturated with water.

[Ar = C₆H₅, (CH₃)C₆H₄, (CH₃)₂C₆H₃, (CH₃)₃C₆H₂, (CH₃O)C₆H₄, C₁₀H₇, (CH₃)C₁₀H₆ or (CH₃O)C₁₀H₆]



The above mechanism is similar to that proposed earlier by Brio et al. for the acylation reactions over cation-exchanged clays.^[8]

In summary, the Si-MCM-41 supported Ga₂O₃ is a highly active catalyst for the acylation of aromatic compounds by acyl chlorides and the

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catalysts do not demand stringent moisture-free conditions for them to be active in the acylation process. Moreover, because of the presence of moisture, the yield of acylated aromatic compound is increased which is of great practical importance.

EXPERIMENTAL PROCEDURE**Catalyst Preparation**

Supported Ga₂O₃ catalysts (loading of Ga₂O₃ = 5–20 wt%) were prepared by impregnating Si-MCM-41 (high silica mesoporous MCM-41 having surface area of 1140 m² g⁻¹) with gallium nitrate (Aldrich) from its aqueous solution by incipient wetness technique, evaporating the water in vacuum oven at 120°C for 8 h and then calcining in static air at 500°C for 5 h. Before use, the catalyst was pretreated at 150°C in a flow of moisture-free nitrogen for 1 h to remove the adsorbed moisture.

General Procedure for Friedel–Crafts Type Acylation Reaction

The acylation reaction over the supported Ga₂O₃ catalyst was carried out in a magnetically stirred glass reactor (capacity: 25 cm³) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture-free N₂ (30 cm³ min⁻¹) through the liquid reaction mixture at the following reaction conditions by the procedure described earlier:^[7] 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, and temperature = 80 ± 1°C (under reflux).

The reaction work-up involved filtration and washing the filtrate twice with distilled water (15 mL) and 0.1 M NaOH solution (40 mL). The product was purified by column chromatography using silica gel (SRL 60–120 mesh) as a stationary phase and benzene as an eluent. The structure of the product was determined by NMR and MASS spectroscopy.

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