

PRIORITY COMMUNICATION

Highly Active Si-MCM-41-Supported Ga₂O₃ and In₂O₃ Catalysts for Friedel–Crafts-Type Benzoylation and Acylation Reactions in the Presence or Absence of MoistureVasant R. Choudhary,¹ Suman K. Jana, and B. P. Kiran

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Ga₂O₃ and In₂O₃ (which are amphoteric and basic in nature, respectively) supported on mesoporous Si-MCM-41, or even on micro- or macroporous inert catalyst carriers, are highly active and reusable catalysts for the benzoylation of benzene and acylation of aromatic compounds, even in the presence of moisture. Moisture has a beneficial effect, more particularly for the acylation reaction. It causes an increase in the reaction rates for both the reactions and also a large increase in the induction period for the benzoylation reaction but not for the acylation. The induction period is due to the presence of moisture adsorbed on the catalyst, which is to be replaced by the reactant(s) to start the catalytic reaction. © 2000

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Key Words: benzoylation of benzene; benzoylation of aromatic compounds; benzoylation of aromatic compounds; Ga₂O₃/Si-MCM-41; In₂O₃/Si-MCM-41.

INTRODUCTION

Liquid-phase benzoylation and acylation of aromatic compounds, using homogeneous acid catalysts, are commonly practiced Friedel–Crafts-type reactions in organic synthesis (1). However, the commonly used homogeneous acid catalysts (*viz.*, AlCl₃, BF₃, and H₂SO₄) pose several problems, such as difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity, etc. Moreover, these catalysts are highly moisture sensitive and hence demand moisture-free solvent and reactants, anhydrous catalyst, and dry atmosphere for their handling. Development of reusable solid acid catalysts having high activity and little or no moisture sensitivity for liquid-phase Friedel–Crafts reactions is, therefore, of great practical importance. Hence, worldwide efforts have been made to achieve this goal, using a number of highly acidic solid acid catalysts, such as: heteropolyacids (2–4), sulfated ZrO₂ or Fe₂O₃ (5),

Nafion-H (3), and Fe- or Ga-substituted H-ZSM-5 (6) for benzoylation of benzene; HY, H-beta, and H-ZSM-5 zeolites (7) for benzoylation of toluene; and heteropolyacids (3), H-beta (8, 9), H-ZSM-5 (10), and sulfated ZrO₂ (11) for benzoylation of aromatic compounds. The benzoylation or benzoylation of aromatic compounds containing an electron donating group (e.g., alkyl, alkoxy, OH) can be accomplished with ease, but in the absence of such an aromatic ring-activating group (e.g., benzene) this is difficult (1). It is interesting to note that, in spite of their high acidity, the H-ZSM-5, HY, and H-beta zeolites and sulfated ZrO₂ show very low activity, even for the benzoylation (7) or benzoylation (9, 11) of toluene. We have here shown that Ga₂O₃ and In₂O₃ catalysts supported on mesoporous Si-MCM-41, which are amphoteric and basic, respectively, in nature, are very active in the benzoylation (by benzyl chloride) and acylation (by benzoyl chloride or acetyl chloride) of benzene and other aromatic compounds, even in the presence of moisture, and they also are reusable for the reactions. When supported on other nonacidic micro- or macroporous supports, these catalysts also show high benzoylation activity.

EXPERIMENTAL

Supported Ga₂O₃ and In₂O₃ catalysts (loading of metal oxide, 5–20 wt%) were prepared by impregnating fine particles of support (low surface area macroporous inert silica-alumina (LS) (SA-5205, surface area (sa) = <0.05 m² g⁻¹, pore volume (pv) = 0.35 cm³ g⁻¹), silica (LS) (SS-5231, sa ≈ 0.2 m² g⁻¹, pv = 0.25 cm³ g⁻¹), and ZrO₂ (LS) (SZ-5564, sa ≈ 0.1 m² g⁻¹, pv = 0.15 cm³ g⁻¹), all obtained from M/s NORTON Co., USA, silica gel (sa = 280 m² g⁻¹), γ -alumina (sa = 151 m² g⁻¹); H-ZSM-5 (Si/Al = 30), silicalite-I (high-silica ZSM-5 with Si/Al > 1000), Si-MCM-41 (Si/Al > 1000, sa = 1180 m² g⁻¹), silica-alumina (HS) (sa = 255 m² g⁻¹), and H-Al · Si-MCM-41 (Si/Al = 30, sa = 810 m² g⁻¹)) with corresponding metal nitrate from the aqueous solution by

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TABLE 1

Results for Benzylation of Benzene over Supported Micro-, Meso-, and Macroporous Ga₂O₃ and In₂O₃ Catalysts at 80°C (Reaction Conditions: Reaction Mixture, 13 ml Benzene and 1 ml Benzyl Chloride; Amount of Catalyst, 0.1 g)

Catalysts	Surface area (m ² g ⁻¹)	Pore type (micro, meso, or macro)	Pyridine chemisorbed at 400°C (mmol g ⁻¹)	Reaction induction period ^a (min)	Time for 50 and 90% conversion of benzyl chloride	
					50%	90%
Ga ₂ O ₃ (10%)/silica-alumina (LS)	3	macro	0.0	0.4	4.7	15.2
Ga ₂ O ₃ (10%)/silica-alumina (LS) ^b	3	macro	0.0	10.7	14.6	22.0
Ga ₂ O ₃ (10%)/silica-alumina (HS)	255	meso	0.10	8.0	81.0	230.0
Ga ₂ O ₃ (10%)/silica (LS)	3.7	macro	0.0	0.5	16.0	48.0
Ga ₂ O ₃ (10%)/silica gel	330	micro/meso	0.0	0.8	11.0	33.8
Ga ₂ O ₃ (5%)/Si-MCM-41	1125	meso	0.0	1.4	12.0	34.0
Ga ₂ O ₃ (10%)/Si-MCM-41	1012	meso	0.0	0.9	5.3	16.0
Ga ₂ O ₃ (20%)/Si-MCM-41	994	meso	0.0	0.2	2.5	7.8
Ga ₂ O ₃ (20%)/Si-MCM-41 ^b	994	meso	0.0	5.1	7.4	12.5
Ga ₂ O ₃ (5%)/silicalite-I	291	micro	0.0	0.5	6.0	18.5
Ga ₂ O ₃ (5%)/H-ZSM-5	286	micro	0.18	0.6	6.2	18.8
Ga ₂ O ₃ (10%)/γ-alumina	188	meso	0.03	75.0	306	—
Ga ₂ O ₃ (10%)/ZrO ₂ (LS)	5.3	macro	0.0	0.5	5.4	18.0
In ₂ O ₃ (10%)/silica-alumina (LS)	3.1	macro	0.0	0.3	4.1	12.1
In ₂ O ₃ (10%)/silica-alumina (LS) ^b	3.1	macro	0.0	5.4	8.6	15.5
In ₂ O ₃ (10%)/ZrO ₂ (LS)	3.9	macro	0.0	0.9	7.3	22.8
In ₂ O ₃ (10%)/Si-MCM-41	861	meso	0.0	0.8	4.9	13.1
In ₂ O ₃ (20%)/Si-MCM-41	846	meso	0.0	0.2	2.4	7.5
In ₂ O ₃ (20%)/Si-MCM-41 ^b	846	meso	0.0	4.3	6.4	11.3
In ₂ O ₃ (20%)/Al-Si-MCM-41	723	meso	0.05	0.6	3.3	8.9
In ₂ O ₃ (without support)	6.1	—	0.0	3.5	12.8	29.0

^a Obtained from the intercept on the time axis of the benzyl chloride conversion vs time plot extrapolated to zero conversion.

^b Moist catalyst and benzene saturated with water (at room temperature) used for the reaction.

the incipient wetness technique, drying at 110°C for 6 h, and then calcining in static air at 500°C for 4 h. For example, Ga₂O₃ (or In₂O₃) (20%)/Si-MCM-41 was prepared by impregnating 10 g Si-MCM-41 with 5.46 g Ga(NO₃)₃ · xH₂O (or 5.63 g In(NO₃)₃ · 5H₂O) contained in 35 ml aqueous solution by the incipient wetness technique followed by drying and calcining of the impregnated mass as described above. The surface area of the Si-MCM-41 was 1180 m² g⁻¹. The deposition of Ga₂O₃ or In₂O₃ on the Si-MCM-41 resulted in a significant decrease in its surface area (Table 1). Before use, the catalysts were pretreated in a flow of moisture-free helium (20 cm³ min⁻¹) at 300°C for 2 h to remove the adsorbed moisture from them. The benzylation or acylation reactions over the supported metal oxide catalysts were carried out in a magnetically stirred glass reactor (capacity 25 cm³) fitted with a reflux condenser and a mercury thermometer and arranged for continuously bubbling moisture-free N₂ (30 cm³ min⁻¹) through the liquid reaction mixture. The detailed experimental procedures for carrying out the reactions and product analysis have been given earlier (6). In all cases, the product formed was mainly mono-benzylated or acylated, and there was no formation of polybenzyl or polyacyl chloride. The amount of benzylated or acylated product formed was equivalent (within 2–4% error) to the amount of benzylating or acylating agent consumed in the

reaction. In order to study the effect of moisture present in the catalyst and in the reaction mixture, the catalyst stored over water at room temperature for 14 h and the benzene or toluene saturated with water at room temperature, respectively, were used for the reaction. In the presence of moisture, no hydrolysis of benzylating or acylating agent was observed.

RESULTS AND DISCUSSION

The results of the benzylation of benzene over the different Ga₂O₃ and In₂O₃ catalysts are presented in Table 1. From the results, the following important observations can be made:

—Both the Ga₂O₃ and In₂O₃ catalysts supported on mesoporous Si-MCM-41 have very high benzene benzylation activity; the supported In₂O₃ is, however, more active.

—The activity of In₂O₃ is increased markedly by supporting it on the different supports, most probably due to its dispersion on the supports, causing an increase in its surface area.

—The benzylation activity of the Ga₂O₃ (which is amphoteric in nature) and In₂O₃ (which is basic in nature) (12) supported on nonacidic supports, such as Si-MCM-41,

TABLE 2

Results for Benzylation of Different Aromatic Compounds over Supported Ga₂O₃ and In₂O₃ Catalysts at 80°C (Reaction Conditions: Reaction Mixture, 13 ml Aromatic Compound and 1 ml Benzyl Chloride; Amount of Catalyst, 0.1 g)

Aromatic compound	Catalyst	Reaction induction period (min)	Time (min) required for benzyl chloride conversion	
			50%	90%
Toluene	Ga ₂ O ₃ (10%)/silica–alumina (LS)	0.5	4.3	12.7
<i>p</i> -Xylene	Ga ₂ O ₃ (10%)/silica–alumina (LS)	1.8	5.9	15.0
Mesitylene	Ga ₂ O ₃ (10%)/silica–alumina (LS)	1.0	6.4	18.0
Toluene	Ga ₂ O ₃ (20%)/Si-MCM-41	0.2	3.2	8.9
<i>p</i> -Xylene	Ga ₂ O ₃ (20%)/Si-MCM-41	1.0	3.7	10.0
Mesitylene	In ₂ O ₃ (20%)/Si-MCM-41	0.9	3.8	9.8
Durene ^a	In ₂ O ₃ (20%)/Si-MCM-41	0.7	4.6	13.0
2-Methyl naphthalene ^a	In ₂ O ₃ (20%)/Si-MCM-41	1.0	5.0	14.2

^a Reaction mixture: 1.5 g durene or 2-methyl naphthalene + 13 cm³ dichloroethane + 1 cm³ benzyl chloride.

silica–alumina (LS), silicalite-I, and silica gel is comparable or even much higher in some cases than that of the In₂O₃ and Ga₂O₃ supported on acidic supports, such as H-AlSi-MCM-41, silica–alumina (HS), H-ZSM-5, and γ -

alumina, respectively. This indicates that acidity does not play a significant role in the reaction over these catalysts. However, supported Al₂O₃ (which is amphoteric) and B₂O₃ (which is acidic) catalysts showed little activity (<5%

TABLE 3

Results for Acylation by Benzoyl Chloride or Acetyl Chloride of Different Aromatic Compounds over Ga₂O₃(20%) and In₂O₃(20%) Catalysts Supported on Si-MCM-41

Substrate	Acyating agent	Reaction mixture	Temperature (°C)	Induction period (min)	Time (min) required for 50 and 80% conversion of acylating agent	
					50%	80%
(A) Catalyst: In ₂ O ₃ (20%)/Si-MCM-41						
Benzene	benzoyl chloride	13 ml substrate + 1 ml acylating agent + 0.4 g catalyst	80	0.1	286.0	—
Toluene	benzoyl chloride	13 ml substrate + 1 ml acylating agent + 0.4 g catalyst	110	0.1	26.8	130.0
Toluene ^a	benzoyl chloride	13 ml substrate + 1 ml acylating agent + 0.4 g catalyst	110	0.0	15.0	90.0
<i>p</i> -Xylene	benzoyl chloride	20 ml substrate + 1.2 ml acylating agent + 0.28 g catalyst	140	0.2	6.4	32.0
Phenol	benzoyl chloride	1 g substrate + 1.2 ml acylating agent + 13 ml dichloroethane + 0.1 g catalyst	80	0.1	1.6	6.4
2-Naphthol	acetyl chloride	2.5 g substrate + 1 ml acylating agent + 15 ml dichloroethane + 0.2 g catalyst	30	0.1	12.0	34.4
(B) Catalyst: Ga ₂ O ₃ (20%)/Si-MCM-41						
Toluene	benzoyl chloride	13 ml substrate + 1 ml acylating agent + 0.4 g catalyst	110	0.2	45.0	182.0
2-Naphthol	benzoyl chloride	1.5 g substrate + 1.2 ml acylating agent + 15 ml dichloroethane + 0.1 g catalyst	80	0.1	2.0	8.4
Phenol	acetyl chloride	2 g substrate + 1 ml acylating agent + 15 ml dichloroethane + 0.2 g catalyst	30	0.2	7.0	22.0

^a The catalyst was saturated with water vapors at room temperature and the toluene was also saturated with water at room temperature.

conversion of benzyl chloride in 2 h) in the benzylation reaction.

—The Ga₂O₃ (or In₂O₃) (20%)/Si-MCM-41 and Ga₂O₃ (or In₂O₃) (10%)/silica–alumina (LS) catalysts show high benzylation activity even in the presence of moisture in the reaction mixture (i.e., when the catalyst is saturated with water vapors at room temperature and the substrate, benzene, is also saturated with water). However, because of the presence of moisture, the reaction induction period is increased very markedly.

Among the supported Ga₂O₃ and In₂O₃ catalysts, the In₂O₃/Si-MCM-41 shows the best performance in the benzylation reaction. This catalyst can also be reused repeatedly for the reaction. When the In₂O₃(20%)/Si-MCM-41 is reused five times for the benzylation of benzene, in the fifth reuse of the catalyst, the time required for the 50% conversion of benzyl chloride was 2.8 min, which is very close to that observed for the fresh catalyst (2.5 min). The procedure for the preparation of these catalysts is simple; the catalyst prepared in different batches showed reproducible results. The Ga₂O₃ catalyst supported on silica–alumina (HS) and γ -alumina shows poor activity, indicating strong metal oxide–support interactions causing catalyst deactivation.

The Ga₂O₃ and In₂O₃ catalysts supported on macroporous low surface area silica–alumina and mesoporous Si-MCM-41 also show high activity in the benzylation of other aromatic compounds (Table 2). However, unlike with the acidic catalysts (13), the benzene benzylation activity of these catalysts is comparable to or even higher than that observed for the benzylation of substituted benzenes having electron-donating methyl groups (Tables 1 and 2).

Results showing high activity of the Ga₂O₃ and In₂O₃ catalysts supported on Si-MCM-41 in the acylation of benzene and other aromatic compounds are presented in Table 3. It is interesting to note that, because of the presence of moisture, both in the catalyst and in the substrate, the time required for the 50% (or 80%) conversion of benzoyl chloride in the benzoylation of toluene is decreased appreciably, and consequently, the benzoylation reaction rate is increased.

The benzylation and acylation activities of the present Si-MCM-41 supported Ga₂O₃ and In₂O₃ catalysts are compared with those of the highly acidic catalysts, reported earlier (3, 5–11), in Table 4. The In₂O₃/Si-MCM-41 is basic in nature. The Ga₂O₃/Si-MCM-41 is poorly acidic in nature; unlike zeolites, it does not contain strong acid sites that can chemisorb pyridine at 400°C or even at 300°C. The comparison shows that the present catalysts are much

TABLE 4
Comparison of the Earlier Highly Acidic Solid Catalysts with the Present Ones for Their Benzylation and Acylation Activity

Aromatic substrate	Catalyst	Catalysts/ (C ₆ H ₅ CH ₂ Cl or C ₆ H ₅ COCl) wt. ratio	Temperature (°C)	Conversion of benzyl or benzoyl chloride and reaction time		Ref.
				Conversion (%)	Time (min)	
Benzylation with benzyl chloride						
Benzene	sulfated ZrO ₂	0.1	80	50	135	(5)
Benzene	sulfated ZrO ₂ -Fe ₂ O ₃	0.1	80	50	33	(5)
Benzene	heteropolyacids	0.05	80	100	120	(3)
Benzene	Nafion-H	0.1	80	24	120	(3)
Benzene	H-AlMFI	0.1	80	no reaction for 2 h		
Benzene	H-FeMFI	0.1	80	90	25	(6)
Benzene	H-GaMFI	0.1	80	90	82.5	(6)
Benzene	H-GaAlMFI	0.1	80	90	56.2	(6)
Benzene	Ga ₂ O ₃ (20%)/Si-MCM-41	0.1	80	90	7.8	present work
Benzene	In ₂ O ₃ (20%)/Si-MCM-41	0.1	80	90	7.5	present work
Toluene	HY (ultrastable)	0.1	110	50	42	(7)
Toluene	H-Beta	0.1	110	50	370	(7)
Toluene	H-ZSM-5	0.1	110	50	1200	(7)
Toluene	Ga ₂ O ₃ (20%)/Si-MCM-41	0.1	80	50	3.2	present work
Benzoylation with benzoyl chloride						
Benzene	H-Beta	0.33	80	54	1080	(8)
Benzene	In ₂ O ₃ (20%)/Si-MCM-41	0.33	80	54	330	present work
Toluene	H-Beta	0.33	110	83	1080	(9)
Toluene	sulfated ZrO ₂	0.5	110	50	192	(11)
Toluene	Ga ₂ O ₃ (20%)/Si-MCM-41	0.33	110	83	205	present work
Toluene	In ₂ O ₃ (20%)/Si-MCM-41	0.33	110	83	148	present work
<i>p</i> -Xylene	heteropolyacids	0.2	140	77	120	(3)
<i>p</i> -Xylene	In ₂ O ₃ (20%)/Si-MCM-41	0.2	140	77	26	present work

more active than the highly acidic catalysts reported earlier. Moreover, since the Ga₂O₃ and In₂O₃ catalysts are supported on meso- and macroporous supports, these can be used for reaction with large aromatic compounds. Also, because of their poorly acidic or basic nature, these catalysts can be used for reactions with acid-sensitive organic compounds.

In the case of the benzylation reaction over the supported Ga₂O₃ and In₂O₃ catalysts, the presence of moisture causes only an increase in the reaction induction period, but after the induction period, the reaction proceeds at almost the same rate (or even at a faster rate) (Table 1). In case of the benzylation reaction over the In₂O₃/Si-MCM-41 catalyst, the catalytic activity (or reaction rate) is increased markedly due to the presence of moisture (Table 3). The observed high activity of the supported Ga₂O₃ and In₂O₃ catalysts, even in the presence of moisture in the reaction mixture, and moreover the beneficial rate enhancement effect of moisture on the benzylation and acylation reactions are of great practical importance.

When the (Ga₂O₃ (or In₂O₃) (20%)/Si-MCM-41 or Ga₂O₃ (or In₂O₃) (10%)/silica-alumina (LS)) was refluxed with benzene for 4 h in the absence of any benzylating or acylating agent, the reaction induction period for the benzylation of benzene (at 80°C) was found to be negligibly small (<0.1 min). This and the results in Tables 1 and 3 show that the induction period for the benzylation reaction is due to the presence of adsorbed moisture on the catalyst, and it is the period required for replacing the adsorbed moisture by the reactant(s) to start the catalytic reaction. The observed induction period for the acylation reaction (Table 3) is negligibly small as compared to that for the benzylation

reaction (Table 1). This is mostly because of the fact that the benzoyl chloride is adsorbed on the catalyst more strongly than benzyl chloride, and hence the former can replace the moisture adsorbed on the catalyst faster, thus requiring a much smaller induction period for the reaction to start.

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