

Benzoylation of benzene and substituted benzenes by benzoyl chloride over $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ catalyst

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Abstract

Liquid phase benzoylation of benzene by benzoyl chloride over In_2O_3 , Ga_2O_3 and ZnO supported on high silica mesoporous MCM-41 at 80 °C has been investigated. The supported In_2O_3 , Ga_2O_3 and ZnO catalysts showed high activity for the benzoylation of benzene. The redox function and activation of aromatic substrate by the supported basic In_2O_3 and amphoteric Ga_2O_3 or ZnO seem to play a very important role in the benzoylation process. Among the catalysts, the $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ showed the highest activity for the benzoylation of benzene. The activity of this catalyst for the benzoylation of benzene and substituted benzenes is in the following order: anisole > mesitylene > *p*-xylene > toluene > benzene. The In_2O_3 (or Ga_2O_3)/Si-MCM-41 showed high benzoylation activity of benzene even in the presence of appreciable amounts of moisture in the reaction mixture. Solvent and its nature (polar or non-polar) also play important role in the benzoylation over the supported In_2O_3 catalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Benzoylation of benzene by benzoyl chloride; Benzoylation of substituted benzenes by benzoyl chloride; $\text{In}_2\text{O}_3/\text{Si-MCM-41}$; $\text{Ga}_2\text{O}_3/\text{Si-MCM-41}$; $\text{ZnO}/\text{Si-MCM-41}$

1. Introduction

Friedel–Crafts type acylation of aromatic compounds to aromatic ketones (important intermediates for the production of fine chemicals) is one of the most important synthesis methods in organic chemistry [1,2]. Worldwide efforts have been made for replacing the commonly used homogeneous AlCl_3 catalyst, which is highly moisture sensitive and environment-unfriendly, by a number of solid acid catalysts such as heteropolyacids [3–8], sulphate or tungstate-modified ZrO_2 or Fe_2O_3 [9–11], H-ZSM-5, H-ZSM-12, H-mordenite, HY, H- β and Ga-, Fe- or In-substituted H- β [12–15], and EPZG [16] for the benzoylation of benzene [12,16] and other aromatic

compounds [3–11,13–15]. Some of these catalysts show good activity for the benzoylation reactions (Table 1). Further development of reusable heterogeneous solid catalysts, having higher activity but little or no moisture sensitivity, for the liquid phase Friedel–Crafts type acylation reactions is of great practical importance.

In our preliminary studies [17], we have found that In_2O_3 (which is basic in nature) and Ga_2O_3 (which is amphoteric in nature) supported on the mesoporous Si-MCM-41 showed high activity in the acylation of aromatic compounds even in the presence of moisture, indicating the importance of their redox properties rather than their Lewis acidity in the acylation. It is therefore interesting to carry out a detailed investigation on the benzoylation of benzene and other aromatic compounds over supported metal oxide catalysts having redox function such as In_2O_3 , Ga_2O_3 and ZnO

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Table 1

Comparison of the benzylation activity of the In₂O₃ (20%)/Si-MCM-41 catalyst with that of the earlier reported catalysts

Aromatic substrate	Catalyst	Catalyst/C ₆ H ₅ COCl weight ratio	Temperature (°C)	Conversion of benzoyl chloride and reaction time		Ref.
				Conversion (%)	Time (h)	
Benzene	H-β	0.33	80	54	18	[12]
	EPZG (Clayzic)	–	130–140	66	30	[16]
	H-AlSi-MCM-41	0.33	80	<3	30	Present work
	In ₂ O ₃ /Si-MCM-41	0.33	80	54	5.8 or 5.0 ^a	Present work
Toluene	H-mordenite	0.33	110 (reflux)	19.5	18	[14]
	HY	0.33	110 (reflux)	18.8	18	[14]
	H-ZSM-12	0.33	110 (reflux)	41	18	[14]
	HREY	0.33	110 (reflux)	61.7	18	[14]
	H-β	0.33	110 (reflux)	83.4	18	[14]
	WO ₃ /ZrO ₂ (or TiO ₂)	1.78	100	19–20	3	[10]
	MoO ₃ /ZrO ₂	1.78	100	18	3	[10]
	WO ₃ /Fe ₂ O ₃	1.78	100	74	3	[10]
	Sulphated ZrO ₂	0.5	110	50	3.2	[11]
	In ₂ O ₃ /Si-MCM-41	0.33	110	85	2.5 or 2.0 ^b	Present work
Anisole	Sulphated ZrO ₂	0.54	140	86	7.0	[9]
	In ₂ O ₃ /Si-MCM-41	0.33	80	86	4.9	Present work
<i>p</i> -Xylene	HY	0.05	140 (reflux)	9	2	[8]
	H ₃ PW ₁₂ O ₄₀	0.05	140 (reflux)	30	2	[8]
	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	0.05	140 (reflux)	57	2	[8]
	Nafion-H	0.05	140 (reflux)	48	2	[8]
	Zn-Mont. K10	0.2	140 (reflux)	35	2	[8]
	In ₂ O ₃ /Si-MCM-41	0.19	140 (reflux)	50	0.11	[17]

^a When the substrate was saturated with water at room temperature (30 °C).^b When the substrate was saturated with water and the catalyst was stored over water in a closed vessel at room temperature.

supported on Si-MCM-41. The present investigation was undertaken for this purpose.

2. Experimental

Supported metal oxide catalysts (loading of metal oxide = 5–20 wt.%) were prepared by impregnating Si-MCM-41 (high silica mesoporous MCM-41 having surface area of 1150 m² g⁻¹) with metal nitrate (Aldrich) from their 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. The synthesis and characterisation of the Si-MCM-41 and H-AlSi-MCM-41 were given elsewhere [18].

The benzylation reaction over the catalysts 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: reaction mixture = 13 ml of moisture-free benzene, toluene, *p*-xylene, mesitylene or anisole (or 2.0 ml of moisture-free benzene in 11.0 ml of moisture-free solvent for studying the solvent effect) + 1.0 ml of benzoyl chloride, amount of catalyst = 0.4 g and temperature = 80 or 110 °C. Before use, the catalyst was pretreated at 250 °C in a flow of moisture-free nitrogen for 1 h to remove the adsorbed moisture. The course of the reaction was followed by measuring quantitatively the HCl evolved in the reaction by acid–base titration. The detailed experimental procedures are given elsewhere [17]. In all the cases, no product other than mono-benzoylated aromatics were formed.

The product of the acylation was isolated as follows. After the reaction, the catalyst was separated from the reaction mixture by filtration and the product from the filtrate was recovered by washing the filtrate with 0.1 M NaOH solution and removing the solvent and unconverted aromatic substrate by vacuum distillation. The product was then purified by column chromatography using silica gel (SRL 60–120 mesh) as the stationary phase and benzene as the eluent. The structure of the product was determined by NMR spectroscopy. The purified product was weighed and its structure was confirmed by $^1\text{H-NMR}$. The isolated product yield was defined as follows: yield (%) = ((moles of isolated product)/(moles of benzoyl chloride used)) \times 100.

In order to study the effect of moisture present in the reaction mixture on the benzylation reaction, additional experiments were carried out by using the aromatic substrate saturated with water at room temperature (30 °C), or by injecting water directly in the reaction mixture and/or by using the catalyst saturated with moisture (obtained by storing the catalyst over water in a closed vessel at room temperature for 12 h).

3. Results and discussion

3.1. Comparison of the supported metal oxide catalysts for benzene benzylation

The Si-MCM-41 supported In_2O_3 , Ga_2O_3 and ZnO and H-AlSi-MCM-41 catalysts are compared for their performance in the benzene benzylation (at 80 °C) in Fig. 1.

From the comparison of results in Fig. 1, following important observations can be made:

- The catalyst support (Si-MCM-41) shows no catalytic activity in the benzylation of benzene. Even the H-AlSi-MCM-41 shows almost no benzene benzylation activity. However, the Si-MCM-41 supported In_2O_3 , Ga_2O_3 and ZnO catalysts are active in the benzene benzylation.
- Among the different metal oxide supported catalysts, the $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ showed highest activity and the $\text{ZnO}/\text{Si-MCM-41}$ showed the lowest activity in the benzene benzylation.

It is interesting to note that the benzene benzylation activity of both the $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ and

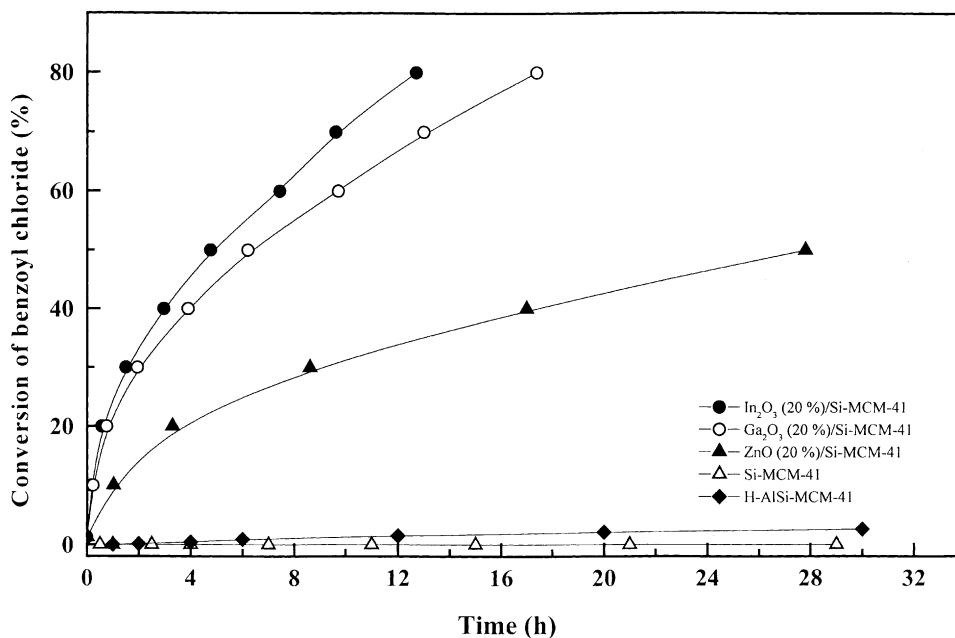


Fig. 1. Conversion vs. reaction time plots for the benzylation of benzene by benzoyl chloride (at 80 °C) over supported In_2O_3 , Ga_2O_3 and ZnO catalysts.

$\text{Ga}_2\text{O}_3/\text{Si-MCM-41}$ is much higher than that reported for the H- β zeolite [12], EPZG [16] and mesoporous H-AlSi-MCM-41 (Table 1). The $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ catalyst also shows higher activity than that reported earlier for a number of acidic catalysts in the benzylation of toluene, *p*-xylene and anisole (Table 1).

In_2O_3 is a basic oxide and Ga_2O_3 and ZnO are amphoteric in nature but the benzylation activity of the supported metal oxide catalysts is in the following order: $\text{In}_2\text{O}_3/\text{Si-MCM-41} > \text{Ga}_2\text{O}_3/\text{Si-MCM-41} > \text{ZnO}/\text{Si-MCM-41}$. This indicates that the acidic nature of these catalysts does not play important role for deciding their benzylation activity.

3.2. Effect of metal oxide loading

The influence of metal oxide loading on the conversion of benzoyl chloride in the benzylation of benzene over the $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ catalyst is shown in Fig. 2. The time required for half of the benzylation reaction ($t_{1/2}$) is decreased markedly with increasing the metal oxide loading on the Si-MCM-41 support. For the In_2O_3 loading of 5, 10 and 20%, the observed value of $t_{1/2}$ is 14.2, 7.6 and 4.8 h, respectively.

The increase in the catalytic activity with increasing the In_2O_3 loading is almost linear. This is expected because of the increased concentration of In_2O_3 for the reaction. Further studies were carried out using the catalyst with the highest In_2O_3 loading (20%).

3.3. Effect of solvent

Results showing the effect of solvent on the rate of benzylation of benzene over $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ are presented in Fig. 3. The time required for half of the benzene benzylation reaction with different solvents is in the following order: dichloroethane (2.8 h) < acetonitrile (3.2 h) < *n*-heptane (6.5 h). Results indicate that the benzylation activity of the catalyst is higher when polar solvent (e.g. acetonitrile or dichloroethane) is used but it is relatively lower when non-polar solvent (e.g. *n*-heptane) is used. Among the polar solvents, dichloroethane is a better solvent for the benzylation reaction.

It is interesting to note that the half reaction period when the polar solvents (dichloroethane and acetonitrile) are used in the benzene benzylation is appreciably lower than that ($t_{1/2} = 4.8$ h) in the absence of

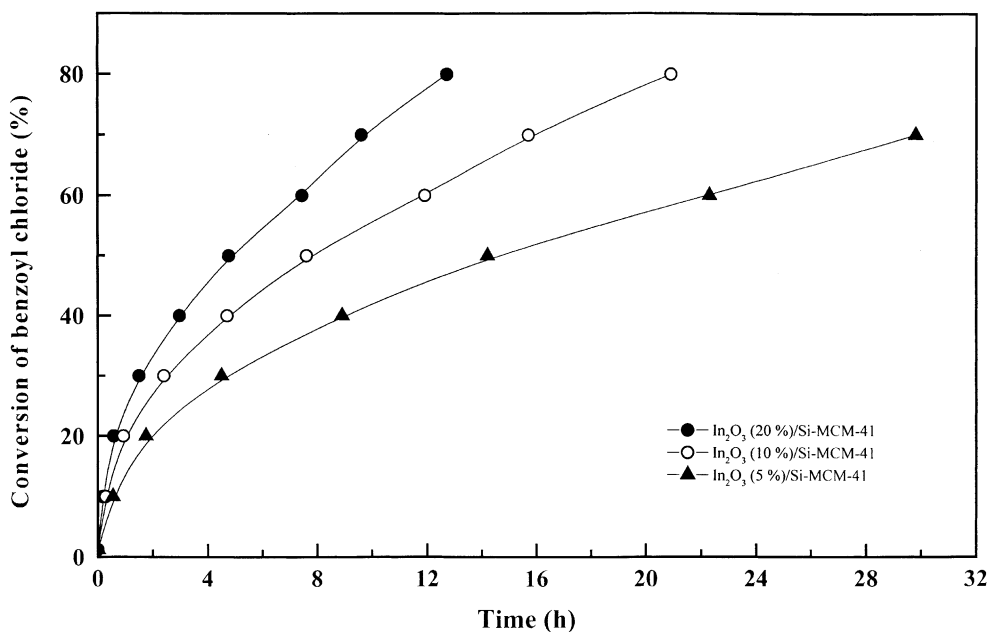


Fig. 2. Effect of metal oxide loading in the $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ catalyst on its activity in the conversion of benzoyl chloride in the benzylation of benzene (at 80 °C).

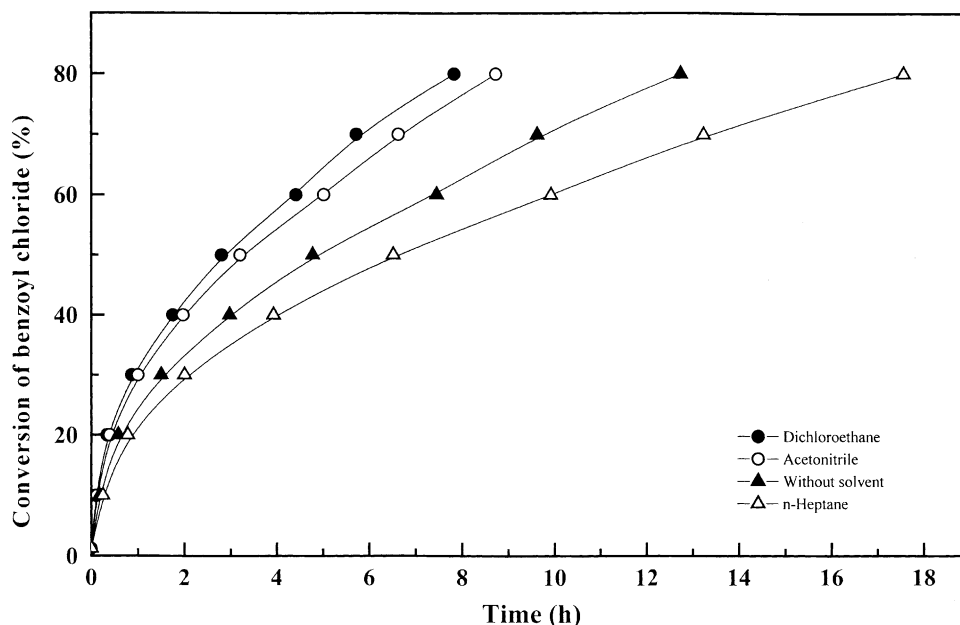


Fig. 3. Effect of solvent on the conversion of benzoyl chloride in the benzoylation of benzene over In_2O_3 (20%)/Si-MCM-41 catalyst (at 80 °C).

solvent. Thus, the catalyst is more active for the reaction in the presence of polar solvent. This is consistent with that observed earlier; it is believed that the benzoyl carbocations (formed from benzoyl chloride) are stabilised in the presence of polar solvent [1]. Because of their stabilisation, the formation of benzoyl carbocations is expected to be favoured or enhanced in the presence of polar solvent. However, the observed decrease in the activity of the catalyst in the presence of *n*-heptane (non-polar solvent) is expected mostly because of competitive adsorption between the reactants and the solvent on the catalyst.

3.4. Effect of moisture on the catalytic activity

Results showing the effect of moisture present in the reaction mixture on the benzoylation of benzene (at 80 °C) and toluene (at 110 °C) over the In_2O_3 (or Ga_2O_3)/Si-MCM-41 catalyst are presented in Figs. 4 and 5, respectively.

The benzene benzoylation activity of both the supported In_2O_3 and Ga_2O_3 catalysts is increased significantly due to the presence of moisture in the reaction mixture (Fig. 4). The increase in the

amount of moisture in the reaction mixture from 0 to 1.35 mmol g^{-1} (catalyst) (i.e. when the benzene saturated with water is used as the substrate) has caused a decrease in the time required for half of the benzene benzoylation reaction ($t_{1/2}$) from 6.2 to 5.7 h for the Ga_2O_3 /Si-MCM-41 and from 4.8 to 4.0 h for the In_2O_3 /Si-MCM-41. The increase in the amount of water from 1.35 to 13.5 mmol g^{-1} (which corresponds to water/catalyst weight ratio of 0.25) has also resulted in a further small increase in the benzoylation activity of the In_2O_3 /Si-MCM-41, the $t_{1/2}$ is decreased from 4.0 to 3.7 h (Fig. 4a). However, a further increase in the amount of water injected in the reaction mixture from 13.5 to 54 mmol g^{-1} (which corresponds to water/catalyst weight ratio of 1.0) caused a reduction in the yield of isolated benzophenone by about 50%. This is expected because of the absorption of water by the catalyst forming a separate aqueous phase, which results in a decrease in the benzoylation activity and also in the formation of benzoic acid by the hydrolysis of benzoyl chloride. Thus the high concentration of water in the reaction mixture (water/catalyst weight ratio ≈ 1.0) is detrimental to the benzoylation process.

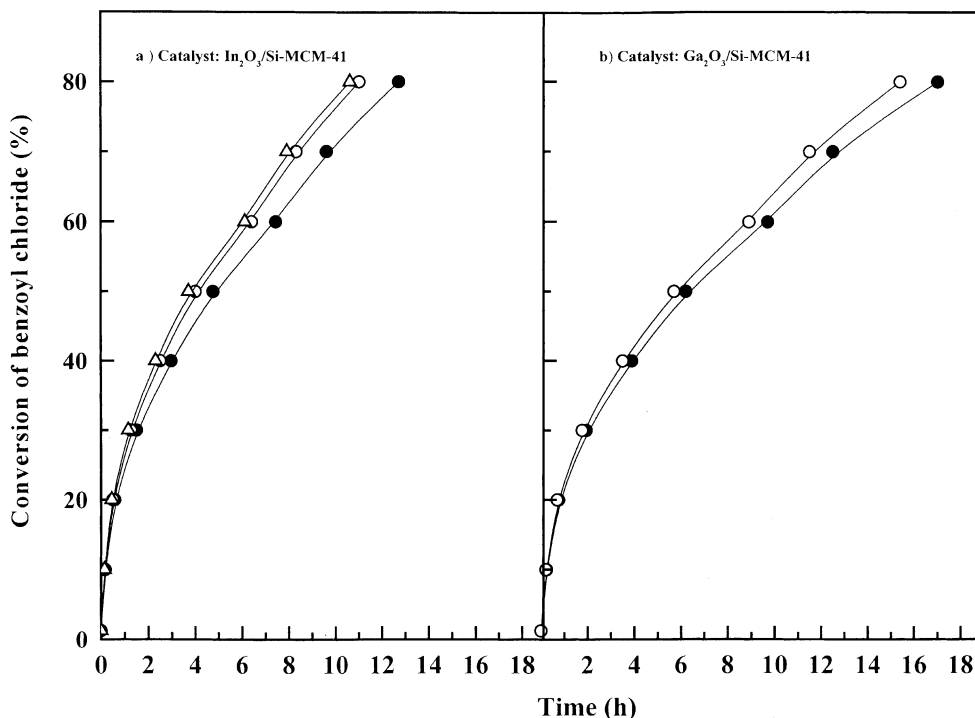


Fig. 4. Effect of moisture on the conversion of benzoyl chloride in the benzoylation of benzene over In_2O_3 or Ga_2O_3 (20 %)/Si-MCM-41 at 80°C : (●) data in the absence of moisture; (○) data when the substrate was saturated with water (1.35 mmol g^{-1} catalyst); (△) data when 0.1 ml water (13.5 mmol g^{-1} catalyst) was injected in the reaction mixture.

Like in case of the benzene benzoylation, the catalytic activity of the $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ in the toluene benzoylation (at 110°C) is also increased appreciably, when the substrate was saturated with water (at room temperature) and the catalyst used was presaturated with moisture by storing it over water in a closed vessel at the room temperature. In this case, the time required for half of the reaction is decreased from 0.45 to 0.25 h (Fig. 5).

The above observations reveal that, unlike aluminium chloride and other Lewis acid catalysts, the supported In_2O_3 (or Ga_2O_3) catalyst does not demand stringent moisture-free conditions for it to be highly active in the benzoylation process. The presence of moisture in the substrate, solvent and/or catalyst at an optimum concentration has in fact a beneficial effect; it enhances the benzoylation activity of the catalyst. This is of great practical importance as there is no need for thorough drying of substrate, solvent and catalyst and also for maintaining the moisture-free

atmosphere or conditions while carrying out the benzoylation reactions.

The observed beneficial effect of moisture may be attributed to the formation of new active sites, probably Bronsted acid sites (which catalyse the formation of benzoyl carbocations from benzoyl chloride) on the catalyst surface. This aspect needs further detailed investigation. In our earlier studies on the benzoylation (by benzyl chloride) of benzene over In_2O_3 or Ga_2O_3 supported on Si-MCM-41 or other inert supports, the presence of moisture also caused an appreciable increase in the reaction rate, after the reaction induction period [17].

3.5. Effect of electron donating substituent group(s)

Results showing high activity of the $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ catalyst in the benzoylation of benzene and substituted benzenes by benzoyl chloride at 80°C are

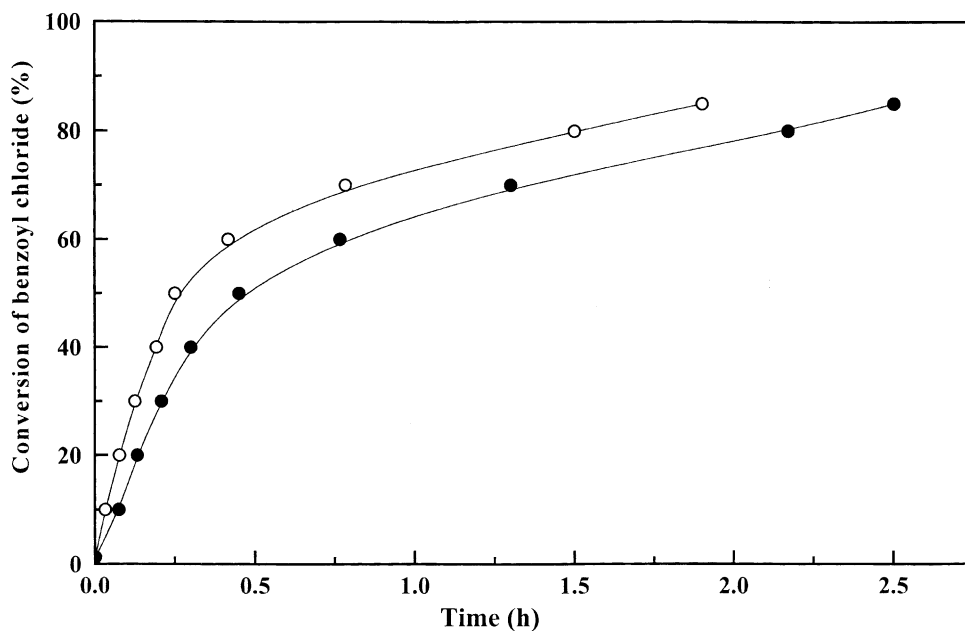


Fig. 5. Effect of moisture on the conversion of benzoyl chloride in the benzoylation of toluene over In_2O_3 (20%)/Si-MCM-41 at 110°C : (●) data in the absence of moisture (○) data when the substrate was saturated with water and the catalyst was stored over water in a closed vessel at room temperature (30°C).

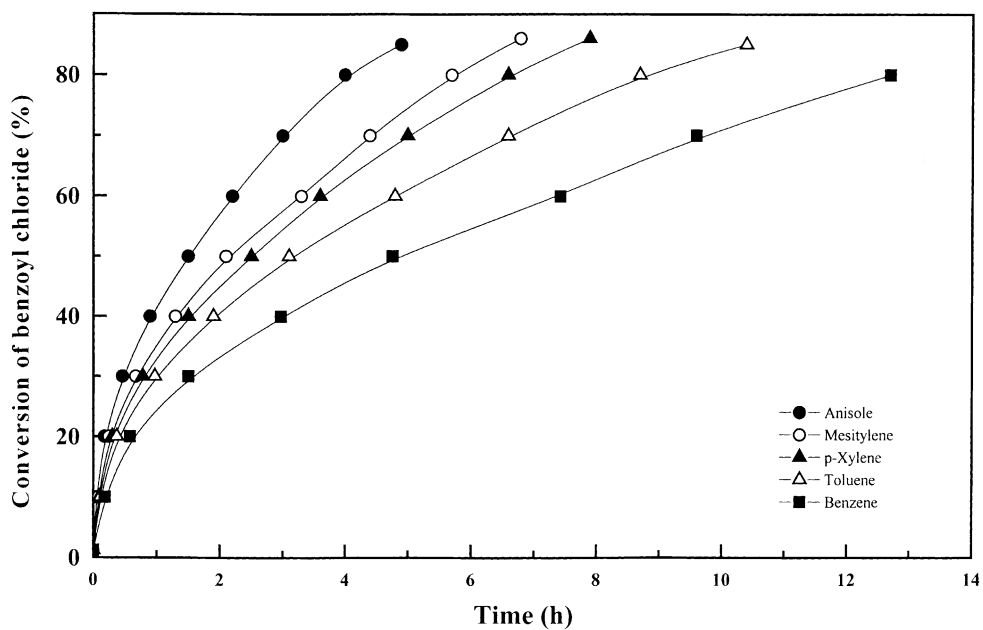


Fig. 6. Conversion vs. reaction time plots for the benzoylation of benzene and substituted benzenes by benzoyl chloride (at 80°C) over In_2O_3 (20%)/Si-MCM-41 catalyst.

presented in Fig. 6. The yields of the isolated products of the benzylation of different aromatic compounds are as follows:

- benzophenone (from benzene in 13.1 h), 74.2%;
- 4-methyl benzophenone (from toluene in 10.2 h), 79.6%;
- 2,5-di-methyl benzophenone (from *p*-xylene in 7.3 h), 74.3%;
- 2,4,6-tri-methyl benzophenone (from mesitylene in 7.1 h), 81.4%;
- 4-methoxy benzophenone (from anisole in 6.1 h), 89.7%.

The above products have been characterised by NMR. The time required for half of the benzoyl chloride conversion for the benzylation of benzene and substituted benzenes is in the following order: benzene (4.8 h) > toluene (3.1 h) > *p*-xylene (2.5 h) > mesitylene (2.1 h) > anisole (1.5 h). The results indicate that the benzylation activity of the catalyst is increased due to the presence of electron donating groups such as methyl and methoxy groups, in the aromatic substrate. This is consistent with that observed in the earlier studies [1]. Because of the presence of electron donating group, the electron density on the benzene ring is increased. Hence, the electrophilic attack of benzoyl carbocation on the benzene ring is favoured, leading to the formation of benzylated aromatic compound at higher rate than that expected in the absence of any electron donating group.

3.6. Reaction mechanism

ZnO and Ga₂O₃ are amphoteric metal oxides and hence can be acidic, having Lewis acidity, whereas In₂O₃ is basic metal oxide. However, the performance of In₂O₃/Si-MCM-41 (which is basic) in the benzylation is superior to that of the Ga₂O₃/Si-MCM-41 and much better than that of ZnO/Si-MCM-41. The presence of moisture, which generally destroys Lewis acid sites, causes not a decrease but an increase in the benzylation activity of the supported Ga₂O₃ and In₂O₃ catalysts. These observations reveal that some properties of the catalysts other than their Lewis acidity are responsible for the observed order of their benzylation activity.

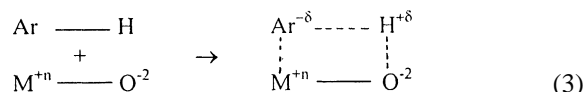
It is interesting to note that the order for the benzylation activity of the supported metal oxide catalysts is quite similar to that for the redox potential of the metal in the catalysts ($E_{\text{In}^{3+}/\text{In}^+}^0 (-0.44 \text{ V}) = E_{\text{Ga}^{3+}/\text{Ga}^+}^0 (-0.44 \text{ V}) > E_{\text{Zn}^{2+}/\text{Zn}}^0 (-0.74 \text{ V})$ and $E_{\text{In}^{3+}/\text{In}}^0 (-0.34 \text{ V}) > E_{\text{Ga}^{3+}/\text{Ga}}^0 (-0.53 \text{ V})$). This indicates a close relationship between the redox potential and the catalytic activity of the supported metal oxide catalysts. The redox properties of the catalysts are, therefore, expected to play an important role in deciding their benzylation activity.

Formation of benzoyl carbocation (which is essential for the reaction to occur) and chloride ion from benzoyl chloride over the supported metal oxide catalysts is expected by the redox mechanism similar to that described earlier [19,20]. The increased rate of benzylation due to the presence of moisture suggests that benzoyl carbocations are probably formed on the Bronsted acid sites created by the interaction of moisture with the Lewis acid sites present on the supported metal oxide catalysts. The benzoyl carbocation thus formed is expected to attack aromatic nucleus (benzene ring) of the aromatic substrate, leading to the formation of benzylated aromatic compound and HCl, as follows:



In the case of zeolites (which have a large number of strong protonic acid sites) such as HY, H-RE-Y, H-ZSM-5, H-β, H-mordenite and H-AlSi-MCM-41, the formation of benzoyl carbocation from benzoyl chloride is expected to accomplish with ease. However, the benzylation activity of these highly acidic zeolite catalysts as compared to that of the In₂O₃ (or Ga₂O₃)/Si-MCM-41 is very poor (Fig. 1 and Table 1). This indicates that just the formation of benzoyl carbocation is not enough for achieving the high rates of benzylation. This also suggests that, the observed high benzylation activity of the In₂O₃ (or Ga₂O₃)/Si-MCM-41 catalyst is attributed not only to the formation of benzoyl carbocation over this catalyst by the redox mechanism [19,20], but also to the activation of aromatic substrate by the catalyst. The activation may result from an interaction of the aromatic substrate with the

metal oxide as follows:



Such activation is not possible in the case of zeolites. Thus, apart from the activation of benzoyl chloride, leading to the formation of benzoyl carbocations, the activation of aromatic substrate as above seems to be essential for a catalyst to be highly active in the benzylation process.

4. Conclusions

Following important conclusions have been drawn from this investigation:

1. $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ is a highly active catalyst for the benzylation of aromatic compounds, even in the presence of moisture in the reaction mixture. $\text{Ga}_2\text{O}_3/\text{Si-MCM-41}$ is also a moisture insensitive catalyst, useful for the benzylation. However, $\text{ZnO}/\text{Si-MCM-41}$ shows much lower activity than the two in the benzene benzylation. The order for the benzene benzylation activity of the supported basic In_2O_3 and amphoteric Ga_2O_3 and ZnO catalysts is found to be same as that for the redox potential of the metal present in the supported metal oxide catalysts, indicating the importance of their redox properties over the acidic ones in the benzylation process.
2. The benzene benzylation over $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ is strongly influenced by the solvent used in the process. The order of its catalytic activity for the different solvents is as follows: dichloroethane > acetonitrile > without solvent > *n*-heptane.
3. The presence of moisture (upto 13.5 mmol g^{-1} (catalyst) or water/catalyst weight ratio ≤ 0.25) in the reaction mixture has no detrimental effect on the catalytic activity when In_2O_3 (or Ga_2O_3)/ Si-MCM-41 catalyst is used in the benzene benzylation. On the contrary, it has a beneficial effect; it enhances the reaction rate.
4. The activity of the $\text{In}_2\text{O}_3/\text{Si-MCM-41}$ in the benzylation of benzene and substituted benzenes is in the following order: benzene < toluene < *p*-xylene < mesitylene < anisole.

5. Not only the activation by the In_2O_3 (or Ga_2O_3)/ Si-MCM-41 catalyst of benzoyl chloride but also that of aromatic substrate seems to play an important role in deciding the high benzylation activity of the catalyst.

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