

Friedel–Crafts alkylation of aromatics with benzyl alcohols catalyzed by rare earth metal triflates supported on MCM-41 mesoporous silica

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Received 9 October 2004; received in revised form 21 April 2005; accepted 23 April 2005

Abstract

Friedel–Crafts alkylation of aromatics with benzyl alcohol as alkylating agent has been investigated over rare earth metal triflates, $\text{Sc}(\text{OTf})_3$, $\text{Hf}(\text{OTf})_4$, $\text{La}(\text{OTf})_3$, and $\text{Yb}(\text{OTf})_3$ supported on MCM-41. The catalytic activity of triflates, particularly, $\text{Sc}(\text{OTf})_3$ and $\text{Hf}(\text{OTf})_4$ was enhanced by being loaded onto MCM-41 because of increased dispersion, and gave the benzylated product in high yield. They were reusable without the loss of the activity for their recycling. Water generated during the benzylation with benzyl alcohol (BnOH) did not affect on the catalytic activity of the $\text{Sc}(\text{OTf})_3$ supported on MCM-41 ($\text{Sc}(\text{OTf})_3/\text{MCM-41}$). The catalytic activity of $\text{Sc}(\text{OTf})_3/\text{MCM-41}$ was not affected by the further addition of water equimolar to BnOH. The benzylation of aromatics (toluene, *p*-xylene, mesitylene, and naphthalene) with benzyl alcohol, and of benzene with benzyl alcohols (4-methylbenzyl alcohol and 4-chlorobenzyl alcohol) were studied over $\text{Sc}(\text{OTf})_3/\text{MCM-41}$ at 353 K. The rate of the benzylation of benzene over $\text{Sc}(\text{OTf})_3/\text{MCM-41}$ was accelerated by electron donating groups and retarded by electron withdrawing groups. The benzylation of aromatics proceeds with direct benzylation with benzyl alcohol, and the dehydration product, i.e., dibenzyl ether (DBE), which is a by-product formed during the benzylation of aromatics; however, it participates in the benzylation with benzene via BnOH with the decrease in BnOH.

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Keywords: $\text{Sc}(\text{OTf})_3/\text{MCM-41}$; Friedel–Crafts alkylation; Diphenylmethane; Benzyl alcohol

1. Introduction

Liquid phase Friedel–Crafts alkylation is usually carried out under the homogeneous conditions using alkyl halides as alkylating agents and Lewis acids such as AlCl_3 or Brønsted acids such as H_2SO_4 as catalysts [1]. However, these homogeneous materials suffer from the inherent problem of corrosiveness, non-reusability, environmental hazards and waste control after the reaction. Moreover, these catalysts are highly moisture sensitive and hence demand moisture-free solvent, reactants and anhydrous catalysts, and also a dry atmosphere for their handling. To overcome this unfavorable

situation, great efforts have been made to replace these materials with environmentally benign and easy handling solid catalysts.

Trifluoromethanesulfuric acid (triflic acid) was discovered by Hazeldine and Kidd in 1954 [2]. In the recent decades, there has been a rapid growth in the catalytic application of triflic acid and metal triflates [3–5]. There are many reports on the rare earth metal triflates such as scandium(III) triflate [$\text{Sc}(\text{OTf})_3$] and ytterbium(III) triflate [$\text{Yb}(\text{OTf})_3$] [4,6–9] which are used as homogeneous Lewis acid catalysts for various synthetic reactions. These catalysts are active even in the presence of water. Kobayashi and his co-workers developed rare earth metal triflate catalysts for Friedel–Crafts alkylation and acylation reactions [10–13]. Olah et al. [14] reported that the boron, aluminum, and gallium triflate are efficient Friedel–Crafts catalysts for alkylation, isomerization, and acylation reactions. Tsuchimoto et al. found that $\text{Sc}(\text{OTf})_3$ was the most efficient catalyst among the rare earth

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metal triflates screened for the benzylation of benzene with benzyl alcohol [8].

There are some reports available on the metal triflate supported heterogeneous catalysts for the organic reactions to immobilize on organic and inorganic solids. Kobayashi and co-workers reported heterogeneous polymer supported scandium(III) triflate catalyst for various organic syntheses [15–19]. Gu and his co-workers have investigated a nanostructured, polymer-supported Sc(III) catalyst (NP-Sc) based on a cross-linked lyotropic liquid crystal (LLC) assembly that is capable of heterogeneous Lewis acid catalysis in water [20]. A novel microencapsulation technique for the immobilization of Bi(OTf)₃ in the pores of polystyrene was reported by Choudary and his co-workers [21]. Kaneda and his co-workers evaluated the catalytic activity of heterogeneous montmorillonite-enwrapped scandium catalyst for Michael reaction [22]. Very recently, Iimura et al. [23] reported hydrophobic polymer-supported scandium(III) catalyst for carbon-carbon bond forming reactions in water. However, rare earth metal triflates supported on high surface area ordered mesoporous silica have not yet been investigated. We are interested in the high dispersion of rare earth metal triflate on mesoporous silica with high surface area to enhance the catalytic performance. In this paper, we describe the enhancement of catalytic activity of rare earth metal triflates, Sc(OTf)₃, Hf(OTf)₄, La(OTf)₃, and Yb(OTf)₃ on MCM-41 for the benzylation of aromatics using benzyl alcohols.

2. Experimental

2.1. Materials

Sc(OTf)₃, Hf(OTf)₄, Yb(OTf)₃, and La(OTf)₃ were purchased from Aldrich, Japan. Benzene, toluene, *p*-xylene, mesitylene, naphthalene, benzyl alcohol (BnOH), dibenzyl ether (DBE), and diphenylmethane (DPM) were purchased from Nacalai Tesque, Japan. 4-Methylbenzyl alcohol (4-MeBnOH) and 4-chlorobenzyl alcohol (4-ClBnOH) were purchased from Tokyo Kasei Kogyo Ltd., Japan. All chemicals were used as received.

2.2. Catalysts preparation

Mesoporous MCM-41 silica was synthesized hydrothermally as per the procedure reported in the literature [24]. As synthesized MCM-41 silica was calcined at 813 K (heating rate = 1 K/min) for 6 h in a flow of air. Sc(OTf)₃, Hf(OTf)₄, La(OTf)₃, and Yb(OTf)₃ supported on MCM-41 (loading of metal triflate: 2–40 wt.%) were prepared by the impregnation method.¹ In an ethanol solution (10 ml) of

required amount of metal triflate, calcined MCM-41 (1 g) was dispersed, and the mixture was stirred for 6 h at room temperature. Solvent was evaporated in vacuo to dryness at 303 K, and the catalysts were also dried in vacuo at 383 K for 4 h.

2.3. Characterization

X-ray diffraction patterns were measured on a Shimadzu XRD-6000 diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm). Nitrogen adsorption–desorption isotherms were obtained at 77 K using a Belsorp 28SA instrument (Bel, Japan). Thermal stability of the catalysts was measured in a flow of air (flow rate = 30 cm³ min⁻¹) by thermogravimetric analysis (TG/DTA) using a Shimadzu DTG-50 instrument. Energy dispersive X-ray analysis (EDX) elemental analysis of fresh and used catalysts was performed using a Shimadzu Rayn EDX 700 instrument.

2.4. Catalytic testing

The liquid phase benzylation on rare earth metal triflate supported on MCM-41 was carried out in a magnetically stirred round bottom flask (capacity: 25 cm³) fitted with a reflux condenser. Kinetics of the benzylation was monitored by withdrawing aliquots of the reaction mixture and analyzing them by a Shimadzu Gas Chromatograph 14A equipped with FID (Column: 25 m capillary column Ultra-1). The products were identified by a Shimadzu Gaschromatograph–Mass Spectrometer GC-MS 5000. The calibration of the sensitivity of reactant and products for GC was done by the comparison with standard compounds separated from reaction products or purchased commercially. The yield of each product was calculated on the molar basis.

In order to study the reusability of the catalyst, Sc(OTf)₃(25)/MCM-41 was reused for the benzylation. The catalysts were recovered through the following procedure: the catalysts after the reaction were separated by the filtration from the reaction mixture, washed with benzene, and finally dried at 373 K for 2 h.

3. Results and discussion

3.1. Characterization of catalysts

XRD patterns of MCM-41 and Sc(OTf)₃/MCM-41 at different loadings are shown in Fig. 1. MCM-41 has highly ordered structure typical of mesoporous materials [25]. It is observed that the intensities of the XRD peaks were decreased gradually with the increase in the loading of Sc(OTf)₃ on MCM-41. Yang and his co-workers [26] observed that the long-range order of the mesoporous MCM-41 decreased drastically with the loading of 12-tungstophosphoric acid (HPW), which was evidenced by the decrease in XRD peak intensities. The intensity of XRD peaks indicates a

¹ Loading amount of the catalysts is showed at wt.% of the triflate by the number in parenthesis.

Table 1
Properties of MCM-41 and rare earth metal triflate supported on MCM-41

Sample	Pore diameter ^a (nm)	Pore volume ^a (cm ³ g ⁻¹)	BET surface area (m ² g ⁻¹)
MCM-41	2.72	0.83	940
Sc(OTf) ₃ (2)/MCM-41	2.72	0.82	928
Sc(OTf) ₃ (10)/MCM-41	2.68	0.81	802
Sc(OTf) ₃ (25)/MCM-41	2.52	0.63	649
Sc(OTf) ₃ (40)/MCM-41	2.32	0.48	498
Hf(OTf) ₃ (25)/MCM-41	2.42	0.61	635
La(OTf) ₃ (25)/MCM-41	2.32	0.56	632

^a By D–H method.

decrease in the long-range order of the catalyst by high loading of Sc(OTf)₃: the decrease in the intensity does not mean the loss of the ordered structure of MCM-41 by the loading.

The porosity of the MCM-41 and metal triflate supported catalysts was evaluated by N₂ adsorption isotherms. BET surface area, average pore diameter, and pore volume are shown in Table 1. The BET surface area and pore volume gradually decreased with the increase in loading of Sc(OTf)₃ on MCM-41, and the pore diameter was slightly decreased by filling the pores with the triflate. The decrease in porosity is due to the increase in coverage of the triflates, although it is not always proportional to the loading. Similar changes in the properties have also been observed for Hf(OTf)₄/MCM-41.

These results indicate that decreases in XRD peak intensities and surface area of the catalysts supported on MCM-41 are due to the increase in surface coverage of supported metal triflates, and resulting loss of long-range order of mesoporous structure.

It has been observed from the thermogravimetric analysis (Fig. 2) that Sc(OTf)₃ supported on MCM-41 is thermally more stable than the corresponding Hf(OTf)₄. The decomposition of Sc(OTf)₃ and Hf(OTf)₄ supported on MCM-41 began at 553 and 453 K, respectively. A peak around 350 K is due to liberated water from MCM-41.

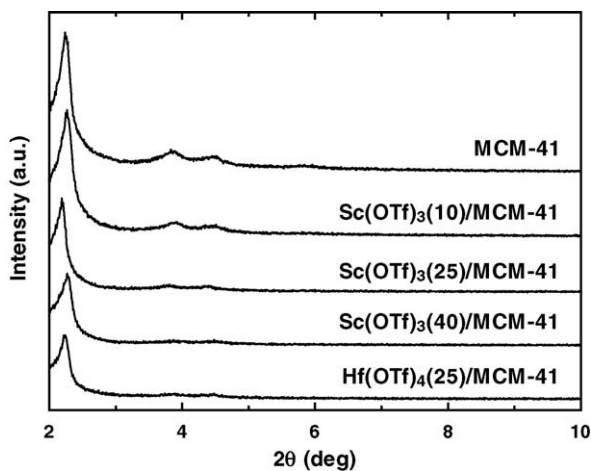


Fig. 1. Powder XRD patterns of MCM-41, Sc(OTf)₃/MCM-41, and Hf(OTf)₄/MCM-41.

3.2. The benzylation of aromatics with benzyl alcohols

3.2.1. Activity of rare earth metal triflate supported on MCM-41 in the benzylation of benzene with benzyl alcohol

Table 2 summarizes the activity of the metal triflates, Sc(OTf)₃, Hf(OTf)₄, La(OTf)₃, and Yb(OTf)₃ supported on MCM-41 for the benzylation of benzene with BnOH. They yielded diphenylmethane (DPM), dibenzylbenzenes (DBB), tribenzylbenzenes (TBB), and dibenzyl ether (DBE). Sc(OTf)₃ and Hf(OTf)₄ supported on MCM-41 showed the highest activity among four catalysts. This is due to the stronger Lewis acidity of Sc(OTf)₃ and Hf(OTf)₄ [27,28]. La(OTf)₃ and Yb(OTf)₃ supported on MCM-41 showed very low activity for the benzylation of benzene with BnOH. Sc(OTf)₃/MCM-41 exhibited significantly higher activity than unsupported Sc(OTf)₃. As shown in Table 2, Sc(OTf)₃/SiO₂ also showed higher activity than unsupported Sc(OTf)₃; however, it had lower activity than Sc(OTf)₃/MCM-41. The enhancement of catalytic activity of Sc(OTf)₃ by the loading on solid supports is ascribed to high dispersion of the triflate on the ordered mesoporous MCM-41 silica, resulting in the improvement in the contact of catalytically active species with the substrates. The higher performance of MCM-41 in comparison with amorphous silica may be due to its ordered mesoporous structure because the substrate and products can enter in every pore and make contact with catalytically active species freely.

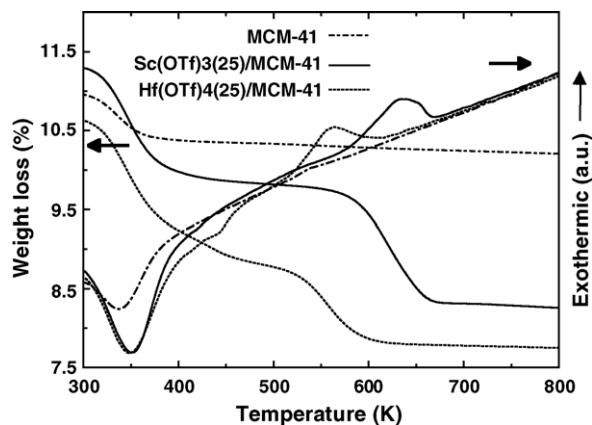


Fig. 2. TG/DTA profile of MCM-41, Sc(OTf)₃(25)/MCM-41, and Hf(OTf)₄(25)/MCM-41.

Table 2

Benzylation of benzene with benzyl alcohol catalyzed by rare earth metal triflate supported on MCM-41

Catalyst	Conversion (%)	Yield (%)			
		DPM	DBB	TBB	DBE
Sc(OTf) ₃ (25)/MCM-41	100	91	6.7	0.9	1.7
Hf(OTf) ₄ (25)/MCM-41	100	92	5.8	0.6	1.4
La(OTf) ₃ (25)/MCM-41	2.5	Not determined			
Yb(OTf) ₃ (25)/MCM-41	1.7	Not determined			
Sc(OTf) ₃ (25)/SiO ₂	79	56	2.1	0.3	21
Sc(OTf) ₃ ^a	16	8.3	0.6	–	7.1
MCM-41	No reaction for 12 h				

Reaction condition; reaction mixture: substrate = 10 ml; BnOH = 2 mmol; amount of catalyst = 40 mg; temperature: 353 K; time: 2 h.

^a Amount of catalyst used = 10 mg.

Formation of DBE, a concomitant dehydration product, was negligibly small at the end of the reactions; DBE was produced more at the early stage of reactions [26].

Fig. 3 shows the results of kinetics study of the benzylation of benzene in the presence of a small amount of water (2 mmol) over Sc(OTf)₃ and Hf(OTf)₄ supported on MCM-41. Hf(OTf)₄/MCM-41 showed the highest activity among all the catalysts, whereas the activity decreases by the addition of water to the reaction mixture. On the other hand, the activity of Sc(OTf)₃/MCM-41 was not affected by the addition of water. From these results, the Sc(OTf)₃ supported on MCM-41 were chosen for the catalysts for the detailed study of the benzylation.

The reusability of the Sc(OTf)₃(25)/MCM-41 for the benzylation of benzene with BnOH is shown in Table 3. Slight decrease in the conversion of BnOH was observed in the second reuse; however, there was almost no further decrease in the conversion for the third reuse. The amount of metal triflate on the supported catalyst was determined by the EDX analysis before and after the reaction. There was almost no

loss of metal triflate from the supported catalyst was observed after four reuses.

3.2.2. Benzylation of benzene and other aromatic hydrocarbons with benzyl alcohol

Fig. 4 shows the time on course of the benzylation of aromatic hydrocarbons, benzene, toluene, *p*-xylene, mesitylene, and naphthalene, with BnOH over Sc(OTf)₃(25)/MCM-41. Activated aromatic hydrocarbons, such as toluene, *p*-xylene, and mesitylene, reacted satisfactorily to yield corresponding benzylation products and DBE. The initial rates of the formation of benzylation products are also shown in Fig. 4. The rate of the benzylation was the slowest for benzene, and the fastest for toluene. Other hydrocarbons, *p*-xylene, mesitylene, and naphthalene showed comparable reaction rates for their benzylation with BnOH.

The yield of the corresponding benzylation products increased with the reaction time in the benzylation of benzene, toluene, *p*-xylene, mesitylene, and naphthalene. The final yield of benzylation products reached the level of 90%. However, the yield of DBE decreased through a maximum with increasing reaction time, and decreased towards zero with the progress of the reaction.

The yield of DBE in benzylation of activated aromatic hydrocarbons, such as toluene, *p*-xylene and mesitylene, was very small as compared to the benzylation of benzene. This is due to the rapid benzylation of activated aromatics with the formation of DBE judging from the difference of initial rate of DPM and DBE formation. The faster rate of the benzylation of activated aromatics as compared to the benzylation of benzene is due to the presence of the –CH₃ group

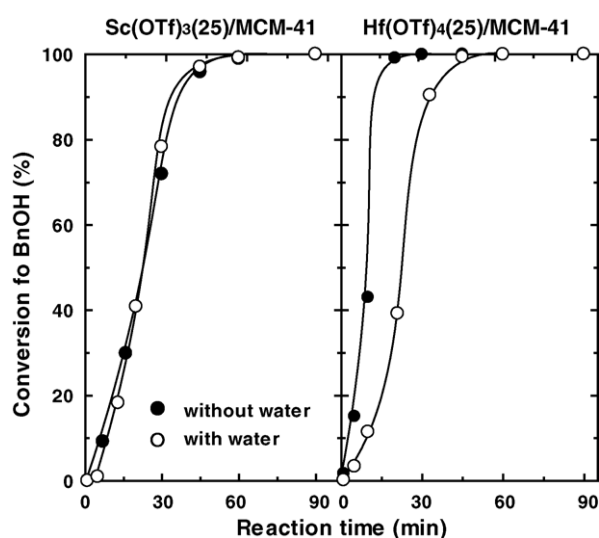


Fig. 3. Effects of the water addition on the conversion of benzyl alcohol in the benzylation of benzene. Reaction conditions: benzene, 10 ml; BnOH, 2 mmol; water, 2 mmol; catalyst: Sc(OTf)₃(25)/MCM-41 or Hf(OTf)₄(25)/MCM-41, 40 mg; temperature, 353 K.

Table 3

The reuse of recovered Sc(OTf)₃(25)/MCM-41 in the benzylation of benzene

Fresh/reused catalyst	BnOH conversion (%)	Yield (%)			
		DPM	DBB	TBB	DBE
Fresh	100	91	6.7	0.9	1.7
First reuse	98.9	89	6.7	0.8	2.6
Second reuse	98.5	89	6.5	0.8	2.6
Third reuse	98.7	90	7.1	0.5	2.2

Reaction condition; reaction mixture: benzene = 10 ml, BnOH = 2 mmol, amount of catalyst = 40 mg; temperature: 353 K; time: 2 h.

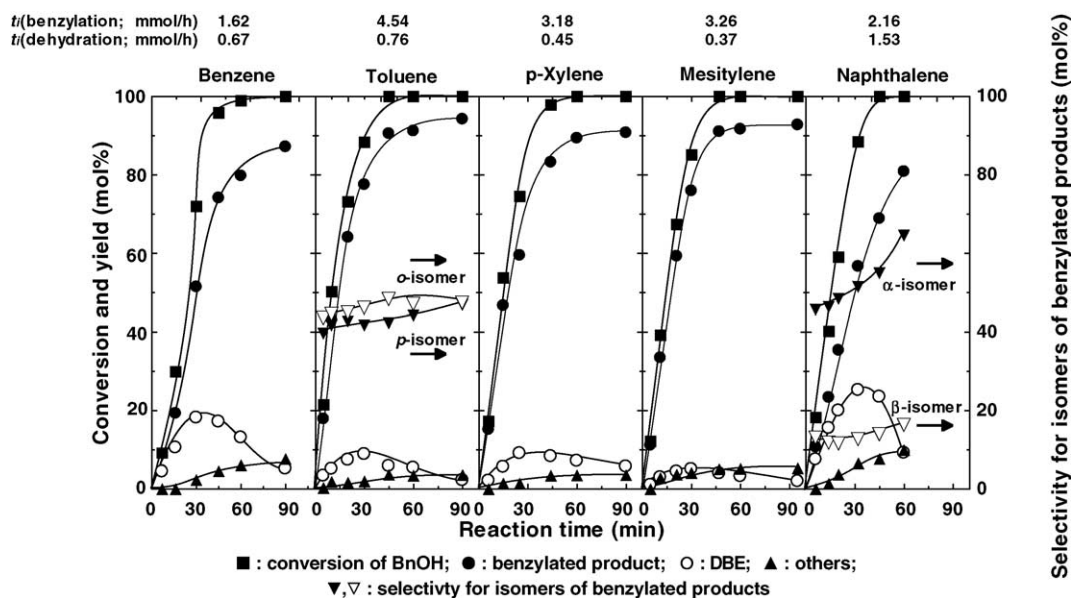


Fig. 4. Reaction profiles in the benzylation of aromatic hydrocarbons with benzyl alcohol. Reaction conditions: aromatic hydrocarbons, 10 ml; BnOH, 2 mmol; catalyst: $\text{Sc}(\text{OTf})_3(25)/\text{MCM-41}$, 40 mg; temperature, 353 K. For the benzylation of naphthalene: naphthalene, 4 mmol; solvent, 1,2-dichloroethane, 10 ml.

(electron donating group) activated aromatics compared with DBE.

The benzylation of toluene and naphthalene yielded the isomeric mixtures of benzylated products. The selectivity for phenyltolylmethane was almost unity during the reaction. The benzylation of naphthalene gives a mixture of α - and β -benzyl naphthalenes. The selectivity for the α -isomer was higher than that for the β -isomer. These results indicate that MCM-41 has no shape-selective character in the benzylation.

3.2.3. Benzylation of benzene with substituted benzyl alcohols

To understand effects of electronic influence of electron donating or withdrawing group on benzyl alcohols, the kinetic studies were conducted for benzene with BnOH, 4-methylbenzyl alcohol (4-Me-BnOH), and 4-chlorobenzyl alcohol (4-Cl-BnOH) over $\text{Sc}(\text{OTf})_3(25)/\text{MCM-41}$ at 353 K (Fig. 5). The initial rate for the benzylation of benzene was in the following order: 4-Me-BnOH (initial rate for the benzylation (4 min after starting) = 11.14 mmol/h) \gg BnOH

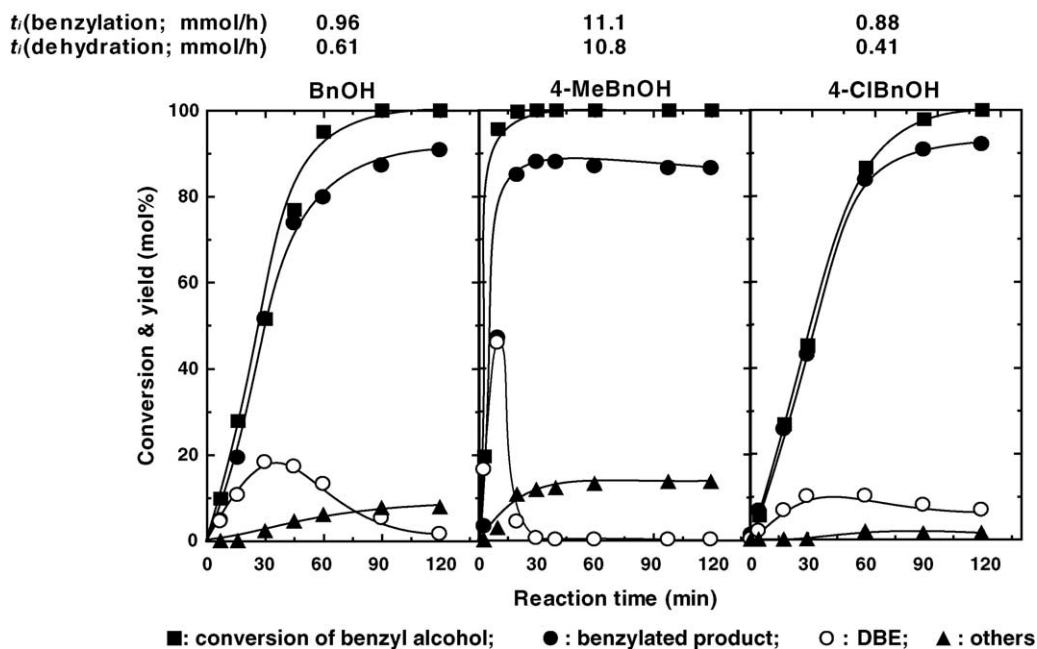


Fig. 5. The benzylation of benzene with benzyl alcohols. Reaction conditions: benzene, 10 ml; BnOH, 2 mmol; catalyst: $\text{Sc}(\text{OTf})_3(25)/\text{MCM-41}$, 40 mg; temperature, 353 K.

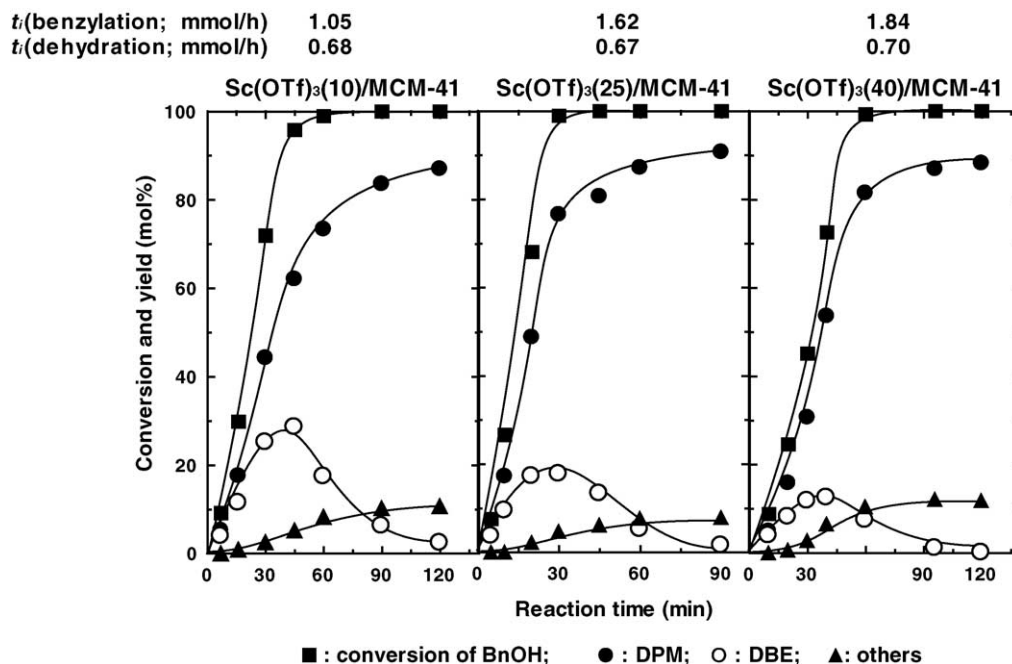


Fig. 6. Effects of loading of $\text{Sc}(\text{OTf})_3$ on MCM-41 in the benzylation of benzene. Reaction conditions: benzene, 10 ml; BnOH, 2 mmol; catalyst: $\text{Sc}(\text{OTf})_3/\text{MCM-41}$, 40 mg; temperature, 353 K.

(0.96 mmol/h). The rate of the benzylation of toluene with BnOH was also much higher than that of benzene as shown in Fig. 4. These results show that the electron donating $-\text{CH}_3$ group enhances the benzylation reaction because the transition state are stabilized by the electron donating groups both on benzene and benzyl alcohol. However, a similar level of the rate for the benzylation products was observed for the benzylation of benzene with BnOH and 4-Cl-BnOH [29]. The $-\text{Cl}$ group on aromatic ring has generally the electron withdrawing character; however, the influences of electron-withdrawal by the $-\text{Cl}$ substituent of 4-ClBnOH are not decisive for the benzylation [29].

3.2.4. Effects of loading amount of $\text{Sc}(\text{OTf})_3$ on MCM-41 on the benzylation of benzene with benzyl alcohol

Fig. 6 shows the influence of loading amount of $\text{Sc}(\text{OTf})_3$ on MCM-41 on the reaction rate, and yield of DPM, DBE, and others in the benzylation of benzene. As shown in Table 2, unsupported $\text{Sc}(\text{OTf})_3$ had only low activity; however, the rate of conversion of BnOH increased with increasing loading of $\text{Sc}(\text{OTf})_3$. There was no significant influence of loading of $\text{Sc}(\text{OTf})_3$ on the yield of DPM. The yield of DBE at the initial stage of the reaction was the highest for 10 wt.% loading and the lowest for 40 wt.% loading of $\text{Sc}(\text{OTf})_3$; it decreased through a maximum with the progress of the reaction.

The initial rate of DPM formation was increased with the loading of $\text{Sc}(\text{OTf})_3$. This increase is due to the increase in active species at higher loading. However, the rate of DBE formation was not increased with the increase in the loading. These results suggest the formation of DPM and DBE has slightly different characters as discussed below.

3.3. Mechanistic aspects of the catalysis

As discussed in the previous sections, the characteristic features of the benzylation of aromatic hydrocarbons are the formation of DBE or its substitutes. It is important to understand the role of DBE in the catalysis. The formation of DBE suggests two possible mechanisms.

- (A) DBE is an intermediate to form DPM by a consecutive mechanism.
- (B) The formation of DPM occurs predominantly from BnOH. DBE is formed by a side reaction. DBE participates in the benzylation after its hydrolysis to BnOH.

To elucidate the detail of the mechanism, the benzylation of benzene with BnOH was examined in the presence of excess DBE. The reaction profile is shown in Fig. 7. The benzylation with BnOH occurred in the early stages with no significant decrease in DBE, and the decrease in DBE started after 30 min when a half of BnOH disappeared. The benzylation became slow after the disappearance of BnOH. These results show that the benzylation with BnOH is a principal path for the formation of DPM, and probably the benzylation of benzene with DBE to DPM is a slower reaction compared with the principal reaction from BnOH. These results show that DBE is not the precursor of DPM as shown in the case A, and that DBE participates in the benzylation by its hydrolysis to BnOH with the decrease in the amount of BnOH. However, the rate of the hydrolysis of DBE is considered to be slower than the formation of DBE and DPM, because there is no participation of excess DBE in the benzylation as shown in Fig. 7.

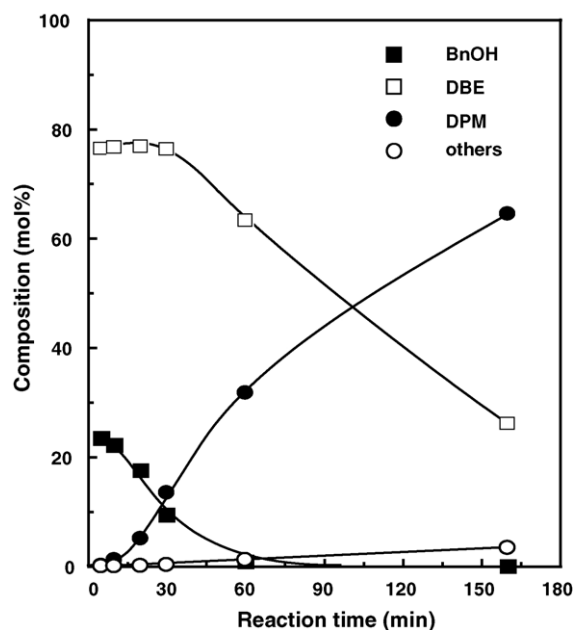


Fig. 7. The benzylation of benzene with benzyl alcohol in the presence of excess dibenzyl ether. Reaction conditions: benzene, 10 ml; BnOH, 2 mmol; DBE, 4 mmol; catalyst, $\text{Sc}(\text{OTf})_3(25)/\text{MCM-41}$, 100 mg; temperature, 353 K.

From these results, DBE formation is only a side reaction in the benzylation of benzene with BnOH, and the plausible mechanism is the case B. The conclusion is supported by the decrease in DBE formed during the reaction with the increase in $\text{Sc}(\text{OTf})_3$ loading as shown in Fig. 6, and also by the fact that the rate became slower after the disappearance of BnOH as shown in Fig. 7.

The initial rate of DPM formation was increased with the loading as shown in Fig. 6. However, the rate of DBE formation was not increased with the increase in the loading. The formation of DPM and DBE has a different character although both of them are formed by acid catalysis. These results support the above conclusion: the benzylation occurs through BnOH, and the formation of DBE is the side reaction because of the relatively low rate of the benzylation. However, DBE participated in the benzylation with benzene via BnOH with the decrease in BnOH.

Olah and his co-workers also reported that DBE was produced more in the beginning of the reaction and took part in the reaction as a benzylating agent [30]. Jadav and his co-workers demonstrated that DBE is a major product of the benzylation of toluene with BnOH over various catalysts (sulfated zirconia, Filtrol-24, and Amberlist-15) [31]. Despande and his co-workers also reported that DBE was a by-product formed by the dehydration of BnOH over K10 supported Sb catalyst in the benzylation [32]. These results support our conclusion that the DBE once formed acts as alkylating agent via BnOH.

4. Conclusions

Rare earth metal triflates, $\text{Sc}(\text{OTf})_3$, $\text{Hf}(\text{OTf})_4$, $\text{Yb}(\text{OTf})_3$, and $\text{La}(\text{OTf})_3$, were supported on ordered mesoporous MCM-41 silica in order to improve their catalytic properties in the benzylation of aromatics with benzyl alcohols. The activity of rare earth metal triflates on MCM-41 decreased in the following order: $\text{Sc}(\text{OTf})_3 \approx \text{Hf}(\text{OTf})_4 > \text{Yb}(\text{OTf})_3 > \text{La}(\text{OTf})_3$. $\text{Sc}(\text{OTf})_3/\text{MCM-41}$ was the best catalyst for the benzylation of benzene among four types of metal triflates on MCM-41, and gave diphenylmethane (DPM) in high yields. The catalytic activity of $\text{Sc}(\text{OTf})_3$ was enhanced by being loaded on MCM-41 because of increased dispersion, and gave the benzylated product in high selectivity. They were reusable without the loss of the activity for their recycling. Water generated during the benzylation reaction with BnOH did not affect on the catalytic activity of $\text{Sc}(\text{OTf})_3/\text{MCM-41}$. Furthermore, the catalytic activity of $\text{Sc}(\text{OTf})_3/\text{MCM-41}$ was not affected by the addition of water equimolar to BnOH. The rate of the benzylation of benzene over $\text{Sc}(\text{OTf})_3/\text{MCM-41}$ was accelerated by electron donating groups and retarded by electron withdrawing groups. The benzylation of aromatics proceeds through the direct benzylation with BnOH, and the dehydration product, i.e., DBE is a by-product formed during the benzylation of aromatics. However, DBE participated in the benzylation with benzene after its hydrolysis with the decrease in BnOH.

Acknowledgement

A part of this work was financially supported by a Grant-in-Aid for Scientific Research (B) 16310056, The Ministry of Education, Culture, Sports, Science and Technology. K.M. is grateful to the Japan Society for the Promotion of Science (JSPS) for the postdoctoral fellowship.

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