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Friedel-Crafts Acylation of Anisole with Carboxylic Anhydrides of Large Molecular Sizes on Mesoporous Silica Catalyst

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Abstract The titled reaction was well catalyzed on mesoporous silica MCM-41. The acylation of anisole with carboxylic anhydrides of large molecular sizes such as hexanoic anhydride and benzoic anhydride proceeded with excellent or good yields at 453 K, while the small molecules including propionic and acetic anhydrides gave moderate yields. The presence of nano-sized pores of MCM-41 was essential to generate the catalytic activity while the Al content showed little effect on the catalysis.

Keywords Acylation · Carboxylic anhydride · Mesoporous silica · Acid catalysis

1 Introduction

Friedel-Crafts acylation (FCA) is one of the most fundamental and important organic reactions to prepare substituted aromatic ketones. The reaction between aromatic compounds and carboxylic acid anhydrides or chlorides is well catalyzed by Lewis or Brønsted acids. The major disadvantages of the conventional FCA process are the use of stoichiometric or more amounts of hazardous acids such as $AlCl_3$, sulfuric acid, or HF and the production of a large amount of wastes. From the viewpoint of the environmentally benign chemical processes, the use of solid acid catalysts has been required to minimize the emission of toxic by-products [1].

Various zeolites [2–7], clays [8, 9], heteropoly acids [10–14], modified zirconia [15–18] and the others [19, 20] were already applied as solid acid catalysts for the FCA reaction. Among them beta zeolite is one of the best solid catalysts. For example, the reactions of propionic and butyric anhydrides with anisole on beta zeolite were reported to give the yields of 97 and 98% respectively [7]. The yield in the reaction of hexanoic anhydride, however, was limited to approximately 75% probably due to the narrow pores of zeolite. The shape-selective acylation was indeed recognized on beta zeolite catalysts [2]. To overcome the disadvantage, several types of metal-containing mesoporous silica materials (MCM-41 etc.) were examined as the catalysts in the past decade [21–27] since the mesoporous silica possesses nano-sized pores into which various large molecules can be diffused. For example, van Bekkum et al. reported the FCA reaction of 2-methoxynaphthalene on Al-enriched mesoporous silica [21]. Ga or In-doped mesoporous silica materials and $AlCl_x$-grafted MCM-41 were also active [22–27]. In addition, acid-functionalized mesoporous silica materials such as arenesulfonic acid containing SBA-15 or "Nafion"-functionalized MCM-41 were recently developed for this reaction [28–37]. Although the suggested catalysts gave the moderate or good yields, there remain serious disadvantages that the active species such as metal ions or acid materials were dissolved during the reaction and the thermal stability of active organic compounds were insufficient.

On the other hand, the present and the other groups have found novel acidic properties of pure silica mesoporous materials, MCM-41 and FSM-16 [38–42]. Their acidity was not strong but very unique; for example, the acetal compounds showed much higher reactivity for the Mukaiyama-Aldol condensation on the catalysts than the corresponding carbonyl compounds [41], which is unusual from the viewpoint of the reactivity of respective compounds. We considered that the anomalous property could be applied for

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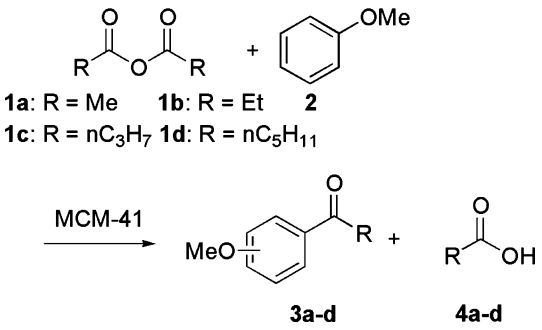


Scheme 1 Friedel-Crafts acylation reaction on MCM-41

the FCA reaction, and therefore examined here the catalytic activity of MCM-41 itself. Note that we studied the catalytic activity of silica MCM-41 itself, which is quite different from the previous reports investigating the modified mesoporous silica catalysts [21–37]. The FCA reaction of anisole with various carboxylic acid anhydrides of large molecular sizes was mainly studied (Scheme 1). The correlation between the aluminum content of the catalyst and the catalytic activity was also studied to clarify the origin of the catalysis.

2 Experimental

MCM-41 (M41) was synthesized from colloidal silica and dodecyltrimethyl-ammonium bromide by the reported method [43]. The hexagonal structure of M41 obtained was confirmed by XRD measurements. The BET surface area and the BJH pore diameter determined by N_2 adsorption–desorption measurements at 77 K were 1,060 m^2/g and 2.12 nm, respectively. The Si/Al atomic ratio of the M41 was 240. In a typical reaction procedure, the mixture of 90 mg of M41, hexanoic anhydride (**1d**: 1.0 mmol), anisole (**2**: 5.0 mmol), tetradecane (internal standard, 0.5 mmol), and nitrobenzene (2.0 mL) was admitted into a flask reactor and heated to a desired temperature. The yields were determined by purification of the mixture by TLC or with a GC/MS analysis.

3 Results and Discussion

The temperature dependence was first studied for four kinds of acid anhydrides. As shown in Fig. 1, desired ketones could be obtained and the yields were strongly dependent on the reaction temperature. The amounts of products were maximized at 453 or 483 K. The results indicated that M41 indeed catalyzed the FCA reaction of acid anhydride and anisole in nitrobenzene, and that high reaction temperature was essential to achieve the reaction.

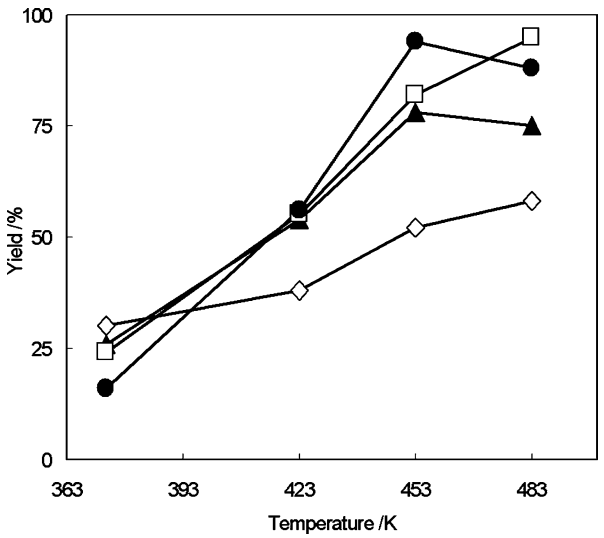


Fig. 1 Changes in the yield of ketone with the reaction temperature. *Diamond* = **3a**, *Triangle* = **3b**, *Square* = **3c**, *Circle* = **3d**. *Conditions*: M41 90 mg, Anisole 5.0 mmol, Acid anhydrides 1.0 mmol, Nitrobenzene 2.0 ml, Reaction time 4 h

The elimination of hexanoic anhydride **1d** and the yields of desired ketone **3d** and by-product hexanoic acid **4d** at 453 K are plotted in Fig. 2 as a function of reaction time. Clearly anhydride was rapidly consumed and the corresponding acid **4d** appeared with the almost same reaction rate, whereas the yield of ketone **3d** was gradually increased and reached at 94% after 4 h. The results suggest two points that first about 3% of anhydride was decomposed to give two acid molecules without formation of ketone and secondly there might be stabilization or adsorption of some intermediates active for the FCA reaction in the mesopores or the slow desorption of the product **3d** from the mesopores. The reusability of M41 was separately examined. The yield of ketone was decreased to 20% in the second use of the catalyst though there were little changes in the XRD patterns and the surface areas on the used catalysts. The reason of the decrease in the catalytic activity upon the repeated use is unknown yet.

The representative results of the various anhydrides are summarized in Table 1 where all experiments were carried out at 453 K. It should first be pointed out that very high or middle ketone yields were observed at the reaction temperature as high as 453 K. It indicates that the acid sites in the present mesoporous silica little caused side reactions leading formation of the other monoacylated isomers and diacylated compounds etc. This would result from the uniformity of the present acid sites. The most important result in the table is the order of the yields at 453 K when linear aliphatic acid anhydrides were employed as the substrates. It was hexanoic (**1d**: C5) > butyric (**1c**: C3) > propionic (**1b**: C2) > acetic (**1a**: C1). It follows that the

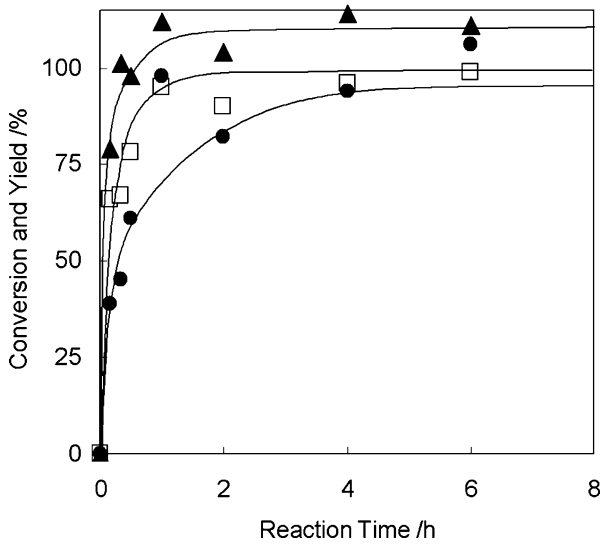
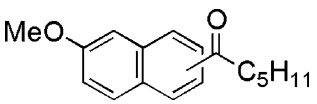


Fig. 2 Time course of the acylation reaction of anisole and hexanoic anhydride on MCM-41 at 453 K. *Open square* = Conversion of **1d**, *Closed circle* = Yield of **3d**, *Closed triangle* = Yield of **4d**. *Conditions*: MCM-41 90 mg, Hexanoic Anhydride 1.0 mmol, Anisole 5.0 mmol, Nitrobenzene 2.0 ml

Table 1 Friedel-Crafts acylation with various anhydrides on MCM-41

Run	Product	Time/h	Yield/%[a]
1	**3a**	4	52[b]
2	**3b**	4	78[b]
3	**3c**	4	82[b]
4	**3d**	4	94[b]
5	**3e:** R = ^{t}Bu	12	60[c]
6	**3f:** R = c-Hex	6	73[c,d]
7	**3g:** R = Ph	24	58[c]
8		24	59[c,e]

All reactions were performed at 453 K. Conversions of acylating reagents were >99% in the respective experiments

[a] *p-/o-* = 96/4–97/3

[b] GC yield

[c] Isolated yield

[d] Cyclohexanecarbonyl chloride was used instead of the corresponding acid anhydride

[e] 6-/1- = 14/86

present catalyst is particularly effective for the reaction of long chain acid anhydride. This is in contrast with those using the other catalysts [5, 7, 12, 14, 18, 19, 44–46]. The yields of ketones on the previous ones were almost constant or were gradually decreased with increasing carbon numbers of anhydrides. The mild acidic property and nano-sized pores of M41 might provide appropriate reaction environment for the achievement of highly selective reaction with long chain acid anhydride: The reason for this phenomenon should be clarified in the near future.

Runs 5–8 in Table 1 revealed that the M41 catalyst could be used for branched, aromatic acid anhydrides and 2-methoxynapththarene. As shown in Run 8 of Table 1, the ratio of 2,6-isomer and 1,2- was 14/86 on the present M41 catalyst. Davis et al. reported that 1,2-isomer was produced on the external surface of the beta zeolite in acylation of 2-methoxynapththarene while 2,6-isomer was selectively formed in the pores of the zeolite due to the shape-selectivity. Our results show that the catalysis in the pores of MCM-41 is almost similar to that on the external surface of the beta zeolite. It is reasonable that there was little effect for the shape-selective catalysis in the M41 pores because the pore diameters of M41 were enough wide to the substrate and product molecules. The results imply the possibility of the FCA reaction of various large molecules on the present catalyst.

The effect of the Al contents for the catalysis was finally examined. We prepared here three kinds of M41 and each catalytic activity was compared in Table 2. The first catalyst was the mother M41 used in the above experiments. The second was aluminum-planted M41 (Al-M41, Si/Al = 44) prepared by the template ion-exchange method [47]. The third was dealuminated M41 (H-M41, Si/Al = 1,012) prepared by acid treatment of the mother M41 [48, 49]. The yield of ketone in the reaction of anisole and propionic anhydride on the mother M41 was 65% (isolated yield, Run 1). The increment or decrement of Al content of the catalysts little influenced the yields of ketone (57 and 52% on Al-M41 and H-M41). In addition, silica gel was separately prepared by using the same starting materials as those employed in the preparation of M41 but it did not show any catalytic activity (Run 4). Note that the BET surface area of the silica gel obtained was 243 m^2 g^{-1} and therefore 370 mg of the sample was used as the catalyst to

Table 2 Comparison of catalytic activity of various silica materials

Run	Silica material (Si/Al)[a]	S_{BET}/ m^2 g^{-1}	Amount of used cat./mg	Yield/%[b]
1	Mother M41 (240)	1,060	90	65
2	Al-M41 (44)	1,001	90	57
3	H^+-treated M41 (1012)	990	90	52
4	Silica gel[c] (240	243	370	Trace

Conditions: M41 90 mg, **2a** 1.0 mmol, Anisole 5.0 mmol, $PhNO_2$ 2.0 ml, 453 K, 24 h. Conversions of acylating reagents were not measured

[a] Determined by ICP analysis

[b] Isolated yield

[c] Prepared from the same starting materials as those in the preparation of M41 without hydrothermal treatment

unify the surface areas applied for the reaction. All of the findings follows that first the Al impurity contained in the mother M41 is not the origin of the acidity and secondly the presence of nanopore structure is essentially significant for the appearance of the catalysis.

4 Conclusions

In the present study, we have demonstrated that the acidic property of mesoporous silica material MCM-41 was applicable to Friedel-Crafts acylation of anisole with various carboxylic anhydrides. The activity increased with increasing the carbon numbers of the anhydrides, which is in contrast with those of the other types of solid acids. The activity for the catalysis was suggested to result from the nanopore structure. The number of surface silanol groups on M41 is estimated to be ca. 3–4 mmol g^{-1} [50–54] and thus the turnover number of the present catalytic system can be calculated to be at least 2.5, assuming that all of the silanol groups act as catalytically active sites. The turnover number is two or more times larger than that of classical $AlCl_3$ [55, 56].

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