Environmentally Benign Catalysts for C-C Bond Forming Reactions

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The Knoevenagel condensation of carbonyl compounds with active methylene compounds catalyzed by amine-immobilized silicates (Type I catalysts) and as-synthesized, ordered porous silicate–quaternary ammonium composite materials (Type II catalysts) gave corresponding α,β-unsaturated esters in high yields under very mild liquid phase conditions. The activity of Type II catalyst was as high as that of Type I catalyst. In the case of other carbon-carbon bond forming reactions such as aldol and Michael reactions, the activity of the Type II catalyst was much higher than that of Type I catalyst. Type I catalysts were reusable for at least four times and Type II for two times in all reactions tested without loss of activity.

Key words: Environmentally benign catalyst, C-C bond, Silicate, Mesoporous material

1. INTRODUCTION

High-silica, ordered porous materials including micro- and mesoporous materials are known to be very useful as catalysts and sorption materials [1,2]. From the environmental points of view, silica-based solid catalysts could be utilized for recyclable, waste-minimum, non-hazardous, and energy-minimum reaction systems since they can be readily separated and recovered. Solid base catalysis is less investigated than acid catalysis [3]. Knoevenagel condensation, which is catalyzed by a weak base catalyst, is one of carbon-carbon bond formation reactions. Traditionally, amines and other homogeneous bases are known to be effective catalysts for this reaction [4]. As for heterogeneous catalysis, there are examples of amino group-immobilized silicas (amorphous [5] or ordered [6]), and we call these "Type I catalyst". Modified ion-exchange resins can catalyze this reaction [7,8], and in these cases catalytic active sites are also immobilized amino groups (In both cases, 'push-pull' type mechanisms are proposed.). Besides these types of catalysts, various solids such as mesoporous silicates in alkali ion form or alkali-impregnated mesoporous silicates [9], zeolites in alkali ion form [10], sepiolite [11], and hydrotalcites [12], are used as catalysts, although less mild reaction conditions are necessary in most cases. In the case of porous silicates, template-free materials have been considered as catalysts, which is logical to utilize their large surface area inside pores. On the other hand, no attention has been paid to the catalytic activity of as-synthesized organic-silicate composites (Type II catalysts). Recently, as the examples of Type II catalyst, we reported the high catalytic activity of as-synthesized mesoporous silicate (MCM-41) and large-pore microporous silicate (beta; BEA) for the Knoevenagel condensation (Eq. 1) [13]. Additionally, the same catalysts were used for some other carbon-carbon bond forming reactions such as aldol reaction (Eq. 2) [14] and Michael reaction (Eq. 3) [15], and proved to be active as well [16]. Main interest of this work is to compare the performance of Type II catalyst with that of Type I catalyst.

2. EXPERIMENTAL SECTION

2.1. Materials

(HDTMA$^+$)-[Si]-MCM-41 denotes as-synthesized pure-silica MCM-41 synthesized using hexadecyltrimethylammonium (HDTMA$^+$) cation as templating agent [17,18]. On the basis of elemental analysis, the amount of HDTMA$^+$ cation occluded in the (HDTMA$^+$)-[Si]-MCM-41 is 1.65 mmol/g-composite.

(TEA$^+$)-[Al]-BEA denotes as-synthesized aluminosilicate beta synthesized using tetraethylammonium (TEA$^+$) cation as template [19]. This was synthesized from a gel having composition $1.0SiO_2$–$0.3TEAOH$–$0.6TEABr$–$0.02NaOH$–$0.0084Al_2O_3$–$0.22N[(CH_2)_2OH]_3$–$15H_2O$. In a typical synthesis procedure, 11.91 g of TEABr (90 mmol) was dissolved in 14.5 g of de-ionized water. 18.93 g (45 mmol) of 35wt%TEAOH solution (Aldrich) and 0.276 g of sodium aluminate (Nacalai, $42.8\%Al_2O_3$, $33.7\%Na_2O$) were added with stirring. The stirring was continued for 10 min, and 22.53 g of colloidal silica (Ludox HS40, 150 mmol) and 5.01 g (33 mmol) of triethanolamine (Wako) were added to the homogeneous mixture. The gel was further stirred for 3 h to make it completely homogeneous. The mixture was then transferred to Teflon-lined autoclave (125 ml) and heated statically in a convection oven at 150°C for 8 d. The product was recovered by filtration and washed with deionized water, and then dried at room temperature.

(TMBP^{2+})-[Si]-BEA denotes as-synthesized pure-silica beta synthesized using 4,4'-trimethylenebis(1-methyl-1-(2-methylbutyl)piperidinium) (TMBP^{2+}) cation as template. TMBP^{2+}(OH$^-$)$_2$ was synthesized by the quaternization of 4,4'-trimethylenebis(1-methylpiperidine) with (S)-(+)-1-iodo-2-methylbutane in ethyl acetate under reflux for 18 h, followed by conversion into dihydroxide form with ion-exchange resin (DIAION$^®$ SA10A(OH), Mitsubishi Chemical Co.). The hydrothermal synthesis was carried out statically from a gel having composition SiO_2–$0.3TMBP^{2+}(OH^-)_2$–$50H_2O$ at 150 °C for 20 days. The product was recovered by filtration and washed with deionized water, and then dried at room temperature.

(TEA$^+$F$^-$)-[Si]-BEA is an as-synthesized, pure-silica

beta synthesized by the method of Camblor et al., in which the amount of defect site is very low [20,21]. This was synthesized as follows: 6.82 g (16.2 mmol) of 35%TEAOH solution (Aldrich) was gently stirred in a Teflon vessel. Then 6.25 g (30.0 mmol) of tetraethylorthosilicate (Tokyo Chemical Industry) was added and the mixture was stirred at room temperature for 18 h allowing evaporation of ethanol. To the resulting clear solution, 0.59 g (16.2 mmol) of HF (55% aqueous solution, Stella Chemifa) was added. The gel became semi-solid after the addition of HF. Manual stirring with a Teflon rod was necessary to make the gel homogeneous. The final composition of the synthesis mixture was SiO_2-0.54TEAOH-0.54HF-10.7H_2O. The gel was divided into three parts and each part was transferred to Teflon-lined stainless-steel autoclaves (23 ml each) and heated to 150°C with rotation (66 rpm) using a convection oven equipped with a rotator. After 5 d, the product was recovered by filtration and washed with deionized water, and then dried at room temperature.

Part of (HDTMA$^+$)-[Si]-MCM-41 and (TEA$^+$)-[Al]-BEA were calcined at 550°C in air to give [Si]-MCM-41 and [Al]-BEA, respectively.

Aminopropyl-functionalized [Si]-MCM-41 (denoted AP-MCM-41), which was used for comparison, was also prepared [5,22]. In a typical procedure, [Si]-MCM-41 (2.0 g) vacuum dried at 250°C for 1 h was suspended in anhydrous toluene (30 ml). To this suspension, 0.494 g (2.75 mmol) of 3-aminopropyltrimethoxysilane was added and the mixture was stirred under reflux for 2 h. Toluene containing methanol (ca. 10 ml) was distilled off and toluene (10 ml) was added again; the reflux was continued for another 0.5 h. The product was recovered by filtration and washed with deionized water, and then dried at room temperature to give 2.438 g of white powder. The content of amino group was estimated 1.31 mequiv./g based on elemental analysis.

2.2. Measurements

X-ray diffraction data were recorded on a Shimadzu XRD-6000 diffractometer. Elemental analyses were performed using ICP (JICP-PS-1000 UV, Leeman Labs Inc.). ^{1}H and ^{13}C NMR spectra were obtained on a JEOL α-400 FT-NMR spectrometer. ^{27}Si MAS NMR spectra were recorded on a Varian Inova 400 FT-NMR spectrometer. N_2 adsorption measurements were carried out on a BELSORP 28SA instrument. A Shimadzu DTG-50 analyzer was used to carry out the thermogravimetric analysis (TGA).

2.3. Reaction procedures

The Knoevenagel condensation was typically carried out as follows: to a solution of a carbonyl compound (**1**, 2.5 mmol) and an active methylene compound (**2**, 2.6 mmol) in benzene (2 ml), solid catalyst (200 mg) was added and stirred for 1-6 h. After filtration, the catalyst was washed thoroughly with benzene and recovered. Ethyl α-cyano-β-phenylacrylate (**3**: R^1=Ph, R^2=H, R^3=CN, R^4=CO$_2$Et) was isolated from the filtrate by column chromatography.

In a typical procedure of the aldol reaction, solid catalyst (120 mg) was added to a solution of aryl aldehyde (**4**, 1.0 mmol) and excess ketone (**5**, 10-68 mmol) and stirred for 6 h. After filtration, the catalyst was washed thoroughly with benzene and recovered. The products **6** and **7** were isolated from the filtrate by column chromatography.

The typical procedure of the Michael reaction was as follows: under N_2 atmosphere, solid catalyst (100 mg) was added to a solution of chalcone (**8**, 1.25 mmol) and ethyl malonate (**9**, 1.4 mmol) in benzene (2 ml), and stirred for 6 h. After filtration, the catalyst was washed with benzene and recovered. The product **10** was isolated from the filtrate by column chromatography.

All products were confirmed by means of ^{1}H, ^{13}C NMR spectroscopy and GC.
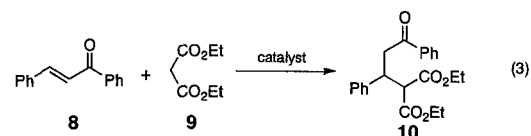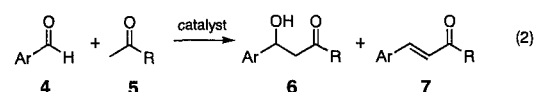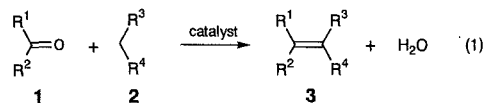
3. RESULTS AND DISCUSSION

Results of the reaction of benzaldehyde (**1**, R^1=Ph, R^2=H) with ethyl cyanoacetate (**2**, R^3=CN, R^4=CO$_2$Et) using various catalysts are listed in Table 1. (HDTMA$^+$)-[Si]-MCM-41 showed high catalytic activity and the reaction proceeded smoothly under very mild conditions to give desired product **3** in high yields (Runs 1, 2). The reactions catalyzed by (TEA$^+$)-[Al]-BEA and (TMBP^{2+})-[Si]-BEA gave **3** in moderate yields, respectively (Runs 3, 4). On the other hand, calcined, template-free materials such as [Si]-MCM-41 and [Al]-BEA showed no catalytic activity even at elevated temperature (Runs 5, 6). HDTMA$^+$Br$^-$ and TEA$^+$Br$^-$, which are raw materials for the hydrothermal synthesis, did not exhibit high activity (Runs 7, 8). When TEA$^+$OH$^-$, which should be stronger base than halides, was used as catalyst, the yield of **3** was still relatively low (Run 9). These results suggest that the high activity emerges only when the silicate and quaternary ammonium parts form a composite. However, (TEA$^+$F$^-$)-[Si]-BEA had no activity despite the fact that this is a composite material (Run 10).

Table 1   Condensation of benzaldehyde with ethyl cyanoacetate using various catalysts [a]

Run	Catalyst	Temp. (°C)	Time (h)	Yield [b] of 3 (%)
1	(HDTMA$^+$)-[Si]-MCM-41	20	1	82
2	(HDTMA$^+$)-[Si]-MCM-41	20	6	97, 94[c], 80[d], 60[e]
3	(TEA$^+$)-[Al]-BEA[f]	20	6	51
4	(TMBP^{2+})-[Si]-BEA	20	6	49
5	[Si]-MCM-41	80	6	0
6	[Al]-BEA[f]	80	6	0
7	HDTMA$^+$Br$^-$ [g]	20	6	6
8	TEA$^+$Br$^-$ [g]	20	6	6
9	TEA$^+$OH$^-$ [h]	20	6	24
10	(TEA$^+$F$^-$)-[Si]-BEA	20	6	0

[a] The reaction was carried out as described in the text.   [b] Isolated yields.
[c] The 2nd use of catalyst.   [d] The 3rd use.   [e] The 4th use.
[f] SiO_2/Al_2O_3=105.   [g] 0.30 mmol of each catalyst was used.   [h] 0.96 mmol.

Solid-state ^{29}Si MAS NMR spectra of the representative as-synthesized materials are shown in Fig. 1. The resonances corresponding to Si(3-OSi, 1-OH), i.e. Q^3, are obvious in the spectra of (HDTMA$^+$)-[Si]-MCM-41, (TEA$^+$)-[Al]-BEA and (TMBP^{2+})-[Si]-BEA, whereas only little Si(3-OSi, 1-OH) resonance can be seen in the spectrum of (TEA$^+$F$^-$)-[Si]-BEA, which is consistent with the reported results [17,20,23-25]. Therefore, it is suggested that the actual catalytic sites are basic (SiO)$_3$SiO$^-$ moieties in the composite materials. Metal oxides, hydroxide ions and organic amines are absent in this reaction system. It seems that the SiO$^-$ moiety is an effective base in a non-polar medium with the assistance of quaternary ammonium cation. This is essentially different situation from the case that hydroxide or alkoxide could be generated from metal cation in aqueous or alcoholic media and function as a base. The basic function is located on the side of parent silicate framework unlike the case in which mobile hydroxide or alkoxide could take part in the reaction mechanism as a base.
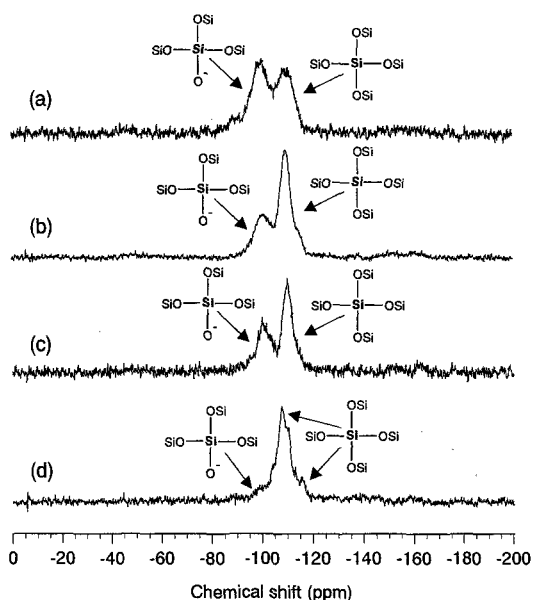

Fig. 1.   Solid-state ^{29}Si MAS NMR spectra of as-synthesized (a) (HDTMA$^+$)-[Si]-MCM-41, (b) (TEA$^+$)-[Al]-BEA, (c) (TMBP $^{2+}$)-[Al]-BEA, and (d) (TEA$^+$F$^-$)-[Si]-BEA.

Nitrogen adsorption measurement of active (HDTMA$^+$)-[Si]-MCM-41 did not give Type-IV isotherm and BET surface area was less than 50 m^2/g (Fig. 2b), whereas the typical Type IV isotherm and a large BET surface area (1010 m^2/g) were obtained from catalytically inactive [Si]-MCM-41 as shown in Fig. 2a. This indicates that the large surface area and complete porosity are not indispensable in this reaction system. The reaction should be taking place at around pore-mouth of the silicates, not deeply inside the pore. The efficient catalysis by MCM-41-based material may be due to the more exposed catalytic sites at pore-mouth as compared to zeolite-based materials.

(HDTMA$^+$)-[Si]-MCM-41 was reusable, although the activity significantly decreased after 3rd run (Table 1, Run 2). It was confirmed by means of X-ray diffraction, elemental analysis (Table 2), TGA (Fig. 3), and DTA that

the framework structure and organic content in the recovered catalysts were unchanged after 1st run. Significant loss of activity after 3rd run may correspond to the slight change in organic content as seen in Fig. 3c. The change in the profile of TGA (Fig. 3c) after 4th run is prominent at 200-250°C, suggesting the loss of active sites are mainly from near surface. Unlike the recovered catalyst, the filtered reaction mixture demonstrated no activity after adding fresh substrates. Therefore, the probability of homogeneous catalysis by any leached species (including amine) was excluded.
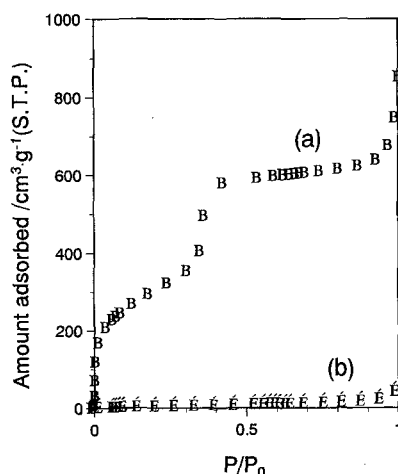

Fig. 2.   Nitrogen adsorption isotherm of (a) (HDTMA$^+$)-[Si]-MCM-41 and (b) [Si]-MCM-41.

Table 2

Content of N, C and H in the (HDTMA$^+$)-[Si]-MCM-41 catalyst before and after use

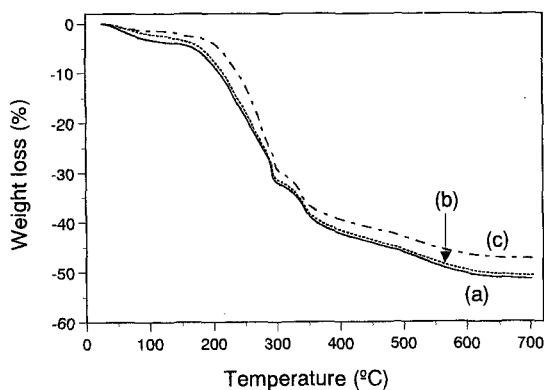|	N (%)	C (%)	H (%)
Before use	2.52	33.78	7.10
After 1st use	2.56	34.61	7.04
After 2nd use	2.46	34.91	6.56

Fig. 3.   Thermogravimetric analysis of (HDTMA$^+$)-[Si]-MCM-41 catalyst (a) before use, (b) after 1st use, and (c) after 4th use.

Regarding the Knoevenagel condensation, there were no significant difference in activity between (HDTMA$^+$)-[Si]-MCM-41 and aminopropyl-functionalized MCM-41 (AP-MCM-41) as shown in Table 3.

Table 3
Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate [a]

Run	Catalyst	Temp. (°C)	Conv. (%)	Yield [b] of 3 (%)
1	(HDTMA⁺)-[Si]-MCM-41	20	96	92
2	AP-MCM-41	20	99	94

[a] The reaction was carried out in benzene for 2 h as described in the text.
[b] Isolated yields.

Next we investigated more 'demanding' reactions, such as aldol and Michael reactions. Table 4 lists the result of the aldol reaction of 4-nitrobenzaldehyde (4: Ar = 4-nitrophenyl) with acetone (5: R=Me) or acetophenone (5: R=Ph) catalyzed by the (HDTMA⁺)-[Si]-MCM-41 or AP-MCM-41. When the ketone component was acetone, the activity of (HDTMA⁺)-[Si]-MCM-41 was significantly higher than that of AP-MCM-41 (Runs 1, 2). The product 6 predominantly formed in both cases. The difference in activity between (HDTMA⁺)-[Si]-MCM-41 and AP-MCM-41 was much larger when the ketone component was acetophenone. The (HDTMA⁺)-[Si]-MCM-41 showed high activity at 60°C and the use of it gave the condensation product 7 in 73% yield, whereas AP-MCM-41 exhibited no activity (Runs 3, 4).

Table 5 shows the result of the Michael reaction of chalcone (8) with ethyl malonate (9). In this reaction, the (HDTMA⁺)-[Si]-MCM-41 was again much more active than AP-MCM-41. The use of (HDTMA⁺)-[Si]-MCM-41 at 40°C gave 10 in 96% yield, while 10 was obtained only in 4% yield even at elevated temperature when AP-MCM-41 was used.

Table 4   Aldol reaction of 4-nitrobenzaldehyde
(4: Ar = 4-nitrophenyl) with ketone (5) [a]

Run	R	Catalyst	Temp. (°C)	Conv. (%)	Yield (%) [b] 6	Yield (%) [b] 7
1	Me	(HDTMA⁺)-[Si]-MCM-41	20	98	78	3
2	Me	AP-MCM-41	20	93	85	4
3	Ph	(HDTMA⁺)-[Si]-MCM-41	60	79	4	73
4	Ph	AP-MCM-41	60	0	0	0

[a] The reaction was carried out for 6 h as described in the text.
[b] Isolated yields.

Table 5
Michael reaction of chalcone (8) with ethyl malonate (9) [a]

Run	Catalyst	Temp. (°C)	Conv. (%)	Yield [b] of 10 (%)
1	(HDTMA⁺)-[Si]-MCM-41	40	98	96
2	AP-MCM-41	80	8	4

[a] The reaction was carried out in benzene for 2 h as described in the text.
[b] Isolated yields.

4. CONCLUSIONS

Unexpectedly high catalytic activity of quaternary ammonium–ordered porous silicate composite materials (Type II catalysts) for Knoevenagel condensation has been found and investigated. The catalysts were as active as amine-immobilized silicates (Type I catalysts). Type II catalysts were much more active than Type I catalysts in other carbon-carbon bond forming reactions

such as aldol and Michael reactions. These catalysts should be useful for the development of recyclable, environmentally benign catalytic system, particularly for the synthesis of fine-chemicals under mild conditions in non-polar media.

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