

## High Catalytic Activity of As-Synthesized, Ordered Porous Silicate–Quaternary Ammonium Composite for Knoevenagel Condensation

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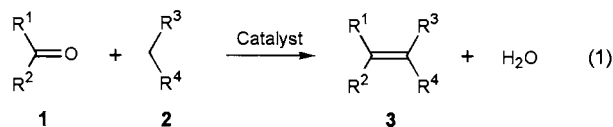
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(Received June 6, 2000; CL-000547)

The Knoevenagel condensation of carbonyl compounds with active methylene compounds catalyzed by as-synthesized, ordered porous silicate–quaternary ammonium composite materials gave corresponding  $\alpha,\beta$ -unsaturated esters in high yields under very mild liquid phase conditions.

High-silica, ordered porous materials including micro- and mesoporous materials have found great utility as catalysts and sorption materials.<sup>1</sup> 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.

In terms of solid catalysis, base catalysis is less developed than acid catalysis.<sup>2</sup> Knoevenagel condensation, which is catalyzed by a weak base catalyst, is one of carbon–carbon bond formation reactions. Amines are known to be effective homogeneous catalysts for this reaction.<sup>3</sup> As for heterogeneous catalysis, there are examples of amino group-immobilized silicas (amorphous<sup>4</sup> or ordered<sup>5</sup>). Modified ion-exchange resin can catalyze this reaction,<sup>6</sup> and in this case catalytic active sites are also immobilized amino groups.<sup>7</sup> Besides these types of catalysts, various solids such as mesoporous silicates in alkali ion form or alkali-impregnated mesoporous silicates,<sup>8</sup> zeolites in alkali ion form,<sup>9</sup> sepiolite,<sup>10</sup> and hydrotalcites,<sup>11</sup> are used as catalysts, although less mild reaction conditions are necessary in these cases.<sup>12</sup> With respect to the use of porous silicates, structure-directing agent (SDA)-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. We report here the high catalytic activity of as-synthesized mesoporous silicate (MCM-41) and large-pore microporous silicate (beta; BEA) for the Knoevenagel condensation (eq 1).



All composite materials and porous silicates were synthesized by known hydrothermal methods<sup>13–16</sup> and confirmed by powder X-ray diffraction. (HDTMA<sup>+</sup>)–[Si]–MCM-41 and (TEA<sup>+</sup>)–[Al]–BEA denote as-synthesized pure-silica MCM-41 synthesized using hexadecyltrimethylammonium (HDTMA<sup>+</sup>) cation as SDA<sup>13,17</sup> and as-synthesized aluminosilicate beta synthesized using tetraethylammonium (TEA<sup>+</sup>) cation as SDA,<sup>14</sup> respectively. These composite materials were calcined at 550 °C in air to give [Si]–MCM-41 and [Al]–BEA, respectively. (TBMP<sup>2+</sup>)–[Si]–BEA denotes as-synthesized pure-silica beta synthesized using 4,4'-trimethylenebis(1-benzyl-1-methylpiperi-

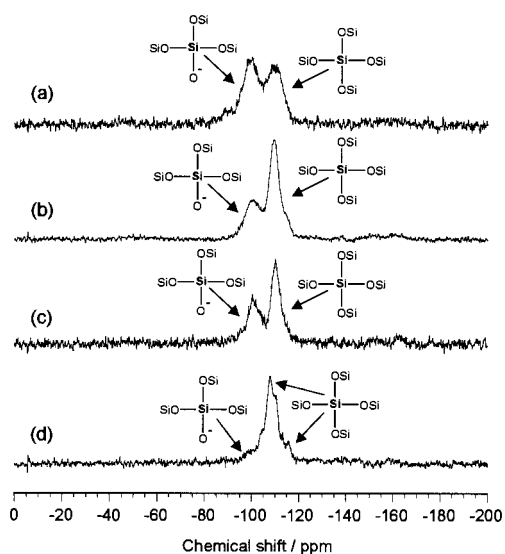
dinium) (TBMP<sup>2+</sup>) cation as SDA.<sup>15</sup> (TEA<sup>+</sup>F<sup>-</sup>)–[Si]–BEA is an as-synthesized, defect-free pure-silica beta synthesized by the method of Cambor et al., in which the actual SDA is believed to be TEA<sup>+</sup>F<sup>-</sup>.<sup>16</sup> The Knoevenagel condensation 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)<sup>18</sup> was added and stirred for 1–6 h. After filtration, the catalyst was washed thoroughly with benzene and recovered. The product was isolated from the filtrate by column chromatography (hexane/ethyl acetate = 10/1).

**Table 1.** Condensation of benzaldehyde with ethyl cyanoacetate using various catalysts<sup>a</sup>

Entry	Catalyst	Temp./°C	Time/h	Yield <sup>b</sup> of <b>3</b> /%
1	(HDTMA <sup>+</sup> )–[Si]–MCM-41	20	1	82
2	(HDTMA <sup>+</sup> )–[Si]–MCM-41	20	6	97
3	(TEA <sup>+</sup> )–[Al]–BEA <sup>c</sup>	20	6	51
4	(TBMP <sup>2+</sup> )–[Si]–BEA	20	6	49
5	[Si]–MCM-41	80	6	0
6	[Al]–BEA <sup>c</sup>	80	6	0
7	HDTMA <sup>+</sup> Br <sup>-d</sup>	20	6	6
8	TEA <sup>+</sup> Br <sup>-d</sup>	20	6	6
9	TEA <sup>+</sup> OH <sup>-e</sup>	20	6	24
10	(TEA <sup>+</sup> F <sup>-</sup> )–[Si]–BEA	20	6	0

<sup>a</sup>The reaction was carried out as described in the text. <sup>b</sup>Isolated yields. <sup>c</sup>SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=105 (determined by ICP analysis). <sup>d</sup>0.3 mmol of each catalyst was used. <sup>e</sup>0.96 mmol of catalyst was used.

Results of the reaction of benzaldehyde (**1**, R<sup>1</sup>=Ph, R<sup>2</sup>=H) with ethyl cyanoacetate (**2**, R<sup>3</sup>=CN, R<sup>4</sup>=CO<sub>2</sub>Et) using various catalysts are listed in Table 1. (HDTMA<sup>+</sup>)–[Si]–MCM-41 showed high catalytic activity and the reaction proceeded smoothly under very mild conditions to give desired product **3** in high yields (Entries 1, 2). The reactions catalyzed by (TEA<sup>+</sup>)–[Al]–BEA and (TBMP<sup>2+</sup>)–[Si]–BEA gave **3** in moderate yields, respectively (Entries 3, 4). On the other hand, calcined, SDA-free materials such as [Si]–MCM-41 and [Al]–BEA showed no catalytic activity even at elevated temperature (Entries 5, 6). HDTMA<sup>+</sup>Br<sup>-</sup> and TEA<sup>+</sup>Br<sup>-</sup>, which are raw materials for the hydrothermal synthesis, did not exhibit high activity (Entries 7, 8). When TEA<sup>+</sup>OH<sup>-</sup>, which should be stronger base than halides, was used as catalyst, the yield of **3** was still relatively low (Entry 9). These results suggest that the high activity emerges only when the silicate and quaternary ammonium parts form a composite. However, (TEA<sup>+</sup>F<sup>-</sup>)–[Si]–BEA had no activity despite the fact that this is a composite material (Entry 10). Solid-state <sup>29</sup>Si MAS NMR spectra of the representative as-synthesized materials are shown in Figure 1. The resonances corresponding to Si(3-OSi, 1-OH), i.e., Q<sup>3</sup>, are obvious in the spectra of (HDTMA<sup>+</sup>)–[Si]–MCM-41, (TEA<sup>+</sup>)–[Al]–BEA and



**Figure 1.** Solid-state  $^{29}\text{Si}$  MAS NMR spectra of as-synthesized (a) (HDTMS<sup>+</sup>)-[Si]-MCM-41, (b) (TEA<sup>+</sup>)-[Al]-BEA (c) (TBMP<sup>2+</sup>)-[Si]-BEA, and (d) (TEA<sup>F-</sup>)-[Si]-BEA.

(TBMP<sup>2+</sup>)-[Si]-BEA, whereas only little Si(3-OSi, 1-OH) resonance can be seen in the spectrum of (TEA<sup>F-</sup>)-[Si]-BEA, which is consistent with the reported results.<sup>13,16,19,20</sup> Therefore, it is suggested that the actual catalytic sites are basic (SiO)<sub>3</sub>SiO<sup>-</sup> moieties in the composite materials. Metal oxides, hydroxide ions and organic amines are absent in this reaction system. It seems that the SiO<sup>-</sup> 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.

Nitrogen adsorption measurement of active (HDTMA<sup>+</sup>)-[Si]-MCM-41 did not give Type-IV isotherm and BET surface area was 14 m<sup>2</sup> g<sup>-1</sup>, whereas the typical Type IV isotherm and a large BET surface area (1013 m<sup>2</sup> g<sup>-1</sup>) were obtained from catalytically inactive [Si]-MCM-41. This indicates that the large surface area and complete porosity are not essential 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 compared to zeolite-based materials.

It should be noted that (HDTMA<sup>+</sup>)-[Si]-MCM-41 was reusable. Almost no loss of activity was observed even at the third use. It was confirmed by means of XRD, elemental analysis, and TGA that the framework structure and organic content in the recovered catalysts were unchanged. In contrast to 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.

Lower reactivity was observed for bulkier esters of cyanoacetic acid, and higher temperature was needed to obtain high yield (Table 2, Entries 2, 3). Diethyl malonate hardly reacted with benzaldehyde (Entry 4), suggesting that either R<sup>3</sup> or R<sup>4</sup>

**Table 2.** Knoevenagel condensation of **1** with **2** using (HDTMA<sup>+</sup>)-[Si]-MCM-41<sup>a</sup>

Entry	<b>1</b>		<b>2</b>		Temp. /°C	Yield <sup>b</sup> of <b>3</b> /%
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>		
1	Ph	H	CN	CN	20	94
2	Ph	H	CN	CO <sub>2</sub> Bu <sup>t</sup>	20	60
3	Ph	H	CN	CO <sub>2</sub> Bu <sup>t</sup>	80	95
4	Ph	H	CO <sub>2</sub> Et	CO <sub>2</sub> Et	80	0 <sup>c</sup>
5	Ph	Me	CN	CN	20	37
6	Ph	Me	CN	CN	80	45 <sup>d</sup>
7	Ph	Me	CN	CO <sub>2</sub> Et	80	0
8	-(CH <sub>2</sub> ) <sub>5</sub> -		CN	CN	20	85
9	-(CH <sub>2</sub> ) <sub>5</sub> -		CN	CO <sub>2</sub> Et	20	31
10	-(CH <sub>2</sub> ) <sub>5</sub> -		CN	CO <sub>2</sub> Et	80	68

<sup>a</sup>Reaction was carried out with 2.5 mmol of **1**, 2.6 mmol of **2**, 200 mg of catalyst in 2 ml of benzene for 6 h, unless otherwise noted. <sup>b</sup>Isolated yields. <sup>c</sup>A 8% yield of **3** was obtained when the reaction was carried out in toluene at 110 °C. <sup>d</sup>Undesired polymeric by-product was formed.

should be cyano group to realize enough reactivity in this system. Malononitrile reacted with less reactive acetophenone while ethyl cyanoacetate did not (Entries 5–7). However, both malononitrile and ethyl cyanoacetate reacted with aliphatic ketone such as cyclohexanone (Entries 8–10).

In summary, unexpectedly high catalytic activity of quaternary ammonium-ordered porous silicate composite materials for Knoevenagel condensation has been found and investigated. Although these materials are not to be utilized for “shape-selective” purposes, they still should be useful for general heterogeneous catalysis, particularly for the synthesis of fine-chemicals under mild conditions in non-polar media.

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