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Organic–inorganic hybrid catalysts based on ordered porous structures for Michael reaction

Yoshihiro Kubota [a],[*], Hisanori Ikeya [b], Yoshihiro Sugi [b], Takashi Yamada [a], Takashi Tatsumi [a],[1]

[a] *Division of Materials Science and Chemical Engineering, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*
[b] *Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan*

Abstract

Two types of organic–inorganic hybrid base catalysts are prepared for the Michael reaction. Organic-functionalized molecular sieves (OFMSs), particularly "amine-immobilized porous silicates", are designed based on a common idea of immobilizing active catalytic sites on silicate surface. Silicate-organic composite materials (SOCMs), such as "ordered porous silicate-quaternary ammonium composite materials", are the precursors of ordered porous silicates obtained during the synthesis. The OFMSs are effective when the supports have large pore volume and/or surface area and the reaction is carried out in polar solvents ethanol and DMF. However, the activity of the OFMSs is considerably low in a non-polar solvent such as benzene. In contrast, the SOCMs are remarkably active in benzene. The organic cation-MCM-41 composite is more active than the composite of an organic cation and a microporous silicate such as zeolite beta and ZSM-12. In the SOCM catalysts, $(SiO)_3SiO^- (^+NR_4)$ moieties located at the accessible sites are considered to play some important roles. The active species are absent in the liquid phase after the reaction. The recycle of the catalyst was possible without significant loss of activity when the substrates are enough reactive.
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1. Introduction

The past decade has seen great advances in the synthesis of new periodical mesoporous [1] and crystalline microporous materials [2]. Recently, design and preparation of organic–inorganic hybrid catalysts based on these materials are gaining great interest [3]. They are becoming important as the heterogeneous catalysts particularly for the synthesis of fine-chemicals in the liquid phase at lower temperatures. Additionally, the heterogeneous catalysis is obviously advantageous in light of the catalyst recovery and eco-benignity. There are classical examples of base-catalyzed C–C bond forming reactions such as Knoevenagel condensation [4], aldol condensation [5], and Michael addition [6], which are still useful for the production of the fine-chemicals [7]. However, solid base catalysis [8], particularly on microporous and mesoporous materials [9], is still insufficiently investigated compared to the corresponding acid catalysis. In this work, we focused on the effect of these materials on the Michael reaction (Scheme 1). Regarding the homogeneously catalyzed Michael reaction, there are quite a few examples [10,11], and even some asymmetric reactions have been successful [12–16]. However, only limited types of heterogeneous catalysts (including acid and base catalysts) have been applied to this reaction [17–21], partly because this is considered to be more "energy-demanding" reaction [22]. For the synthesis of high-silica porous silicates, quaternary ammonium cations are very often used as structure-directing agent (SDA). The silicate-organic composite materials (SOCMs for short) are obtained as precursors followed by the removal of SDA by means of calcination or extraction to give porosity. It is logical to use SDA-free materials in order to utilize their large surface area inside pores. Therefore, immobilization of organic functional groups on internal surface of porous silicates to obtain organic-functionalized molecular sieves (OFMSs as used by Jones et al. [23,24]) is a conventional and common idea for developing heterogeneous catalytic systems.

* Corresponding author. Tel.: +81 45 339 3926/3941; fax: +81 45 339 3941.
  E-mail address: kubota@ynu.ac.jp (Y. Kubota).
[1] Present address: Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 226-8503, Japan.

Scheme 1.

(CTMA⁺)-MCM-41   MCM-41   AP-MCM-41
"**SOCM**-type" catalyst   "**OFMS**-type" catalyst
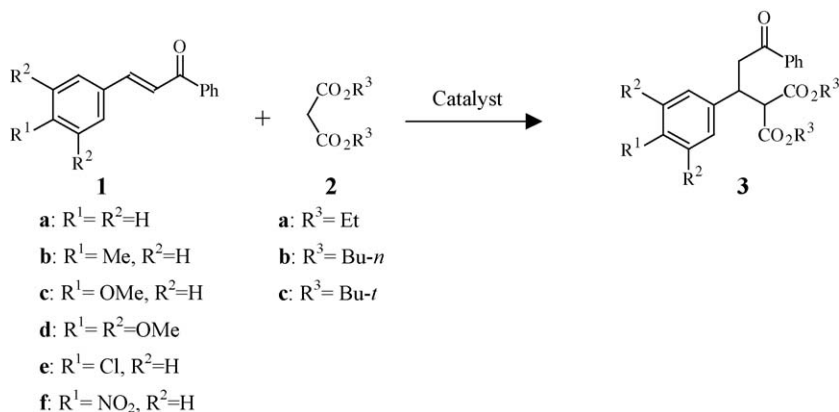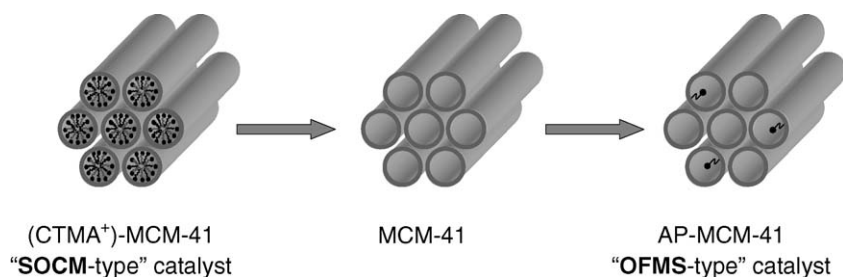
Scheme 2.

On the other hand, no attention had been paid to the catalytic activity of as-synthesized SOCM, which is the precursor obtained during the synthesis, until we found the high catalytic activity of this non-conventional type of catalyst [25]. We have already reported the preliminary results on some C–C bond forming reactions catalyzed by the SOCM catalyst [25,26]. In this paper, we describe the detailed catalytic behavior of the non-conventional SOCM type catalysts as well as the conventional OFMS type catalysts for the Michael reaction. The SOCM and OFMS catalysts are schematically illustrated in Scheme 2.

2. Experimental

2.1. Materials

Highly dealuminated Y zeolite ($SiO_2/Al_2O_3 = 380$; HY380; Tosoh HSZ-390HUA) and dealuminated H-mordenite ($SiO_2/Al_2O_3 = 230$; HM230; Tosoh HSZ-690 HOA) were supplied from Tosoh Corporation. Organic reagents were used as received without further purification.

2.2. Measurements

X-ray diffraction (XRD) data were recorded on a Shimadzu XRD-6000 or a Rigaku RINT-2200 diffractometer using Cu Kα radiation and $\lambda = 1.5404$ Å. Elemental analyses of inorganic materials were performed using ICP (JICP-PS-1000 UV, Leeman Labs Inc.). Solution NMR spectra were obtained on a JEOL α-400 spectrometer or a JEOL JNM-AL-400 FT-NMR spectrometer. Solid NMR spectra were recorded on a Varian Inova

400 FT-NMR spectrometer. A Shimadzu DTG-50 thermogravimetric analyzer was used to carry out the thermogravimetric analysis (TGA). KBr pellet technique was used to take IR spectra of the samples on a Shimadzu FTIR 8200 PC spectrometer. Nitrogen adsorption measurements were carried out on a BEL-SORP 28SA gas adsorption instrument (Bel Japan). The specific surface areas (S_{BET}) and pore volumes were estimated from the N_2 adsorption isotherms at 77 K using Brunauer–Emmett–Teller (BET) equation [27] and the t-plot method [28], respectively. Average pore-size of mesoporous material was obtained with the N_2 adsorption branch at 77 K, using the Barrett–Joyner–Halenda (BJH) method [29]. Pore diameters of microporous materials are based on crystallographic data in the literature [30].

2.3. Synthesis of catalysts

Various high-silica molecular sieves were synthesized using organic SDA. Some of the as-synthesized samples (silicate-organic composite materials) were selected and used as SOCM catalysts. To remove the SDA inside the pore, the samples were calcined in a muffle furnace in a flow of air. Silanol-containing molecular sieves, which are suitable for the supports to prepare OFMS catalysts, were obtained by calcination of appropriate silicate-organic composite materials. Highly dealuminated zeolites such as HY380 and HM230 are also suitable supports.

2.3.1. SOCM catalyst

(CTMA⁺)-[Si]-MCM-41, (TEA⁺)-[Al]-BEA, (MTEA⁺)-[Si]-MTW denote as-synthesized pure-silica MCM-41 synthesized by using hexadecyltrimethylammonium (= cetyltrimethyl-

ammonium; CTMA$^+$) [31,32], as-synthesized aluminosilicate beta synthesized by using tetraethylammonium (TEA$^+$) [33], and pure-silica ZSM-12 synthesized by using triethylmethylammonium (MTEA$^+$) [34], respectively. These composite materials were used as SOCM catalysts and also calcined in air to give [Si]-MCM-41, [Al]-BEA, and [Si]-ZSM-12, respectively, which were used as the supports of the OFMS catalysts. (TBMP^{2+})-[Si]-BEA denotes as-synthesized pure-silica beta synthesized by using 4,4′-trimethylenebis(1-benzyl-1-methylpiperidinium) (TBMP^{2+}) cation as SDA [35]. (TEA$^+$F$^-$)-[Si]-BEA is an as-synthesized, defect-free pure-silica beta synthesized by the method developed by Camblor et al., in which the actual SDA is believed to be TEA$^+$F$^-$ [36,37]. The detailed synthetic procedures have been described elsewhere [38].

2.3.2. OFMS catalyst

Various amine-functionalized silicates were prepared according to the literatures [39,40]. 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 2.44 g of 3-aminopropylsilylated [Si]-MCM-41 (denoted AP-MCM-41) as white powder. The content of amino group was estimated 1.31 mequiv./g based on elemental analysis. 3-Piperazinopropyl (PZP)-, 3-methylaminopropyl (MAP)-, and 3-dimethylaminopropyl (DMAP)-functionalized materials were also prepared.

2.4. Synthesis of chalcone derivatives

In a typical procedure, a solution of NaOH (9.86 g, 246.5 mmol) in H$_2$O (184 ml) was added to an ethanol (92 ml) solution of anisaldehyde (25.86 g, 189.9 mmol) and acetophenone (22.07 g, 183.6 mmol). The whole mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with benzene (1000 ml), washed with H$_2$O (700 ml × 3), brine (500 ml × 1), and then dried over Na$_2$SO$_4$ (50 g). The inorganic salts were filtered off and the filtrate was evaporated in vacuo to give 4-methoxylphenylmethylideneacetophenone (**1c**) as pale yellow crystals (40.43 g, 88%). m.p. 71.0–73.0 °C; IR 1658 cm^{-1} (νC=O); ^{1}H NMR (400 MHz, CDCl$_3$) δ: 3.86 (3H, s), 7.45–7.61 (5H, m), 7.42 and 7.78 (each 1H, d, J = 15.6 Hz), 6.94 and 8.01 (each 2H, d-like, J = 7.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 55.4 (CH$_3$O–), 114.4 (C–C–OCH$_3$), 119.8 (Ar–C=C–), 127.6, 127.6, 128.4, 128.9, 130.2, 132.5, 144.7 (Ar–C=C–), 161.7 (C–OCH$_3$), 190.6 (C=O).

Other chalcone derivatives were synthesized following similar procedures. Pertinent data are shown below.

4-Methylphenylmethylideneacetophenone (**1b**): Yield: 91% m.p. 96.0–97.5 °C; IR (KBr) 1656 cm^{-1} (νC=O); ^{1}H NMR (400 MHz, CDCl$_3$) δ: 2.39 (3H, s), 7.47–7.60 (6H, m), 7.80 (1H, d, J = 15.6 Hz), 7.22 and 8.01 (each 2H, d-like, J = 7.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 21.5 (CH$_3$–), 121.1 (Ar–C=C–), 128.5, 128.6, 128.6 (C–C–CH$_3$), 129.7, 132.14, 132.6, 138.3, 141.1 (C–CH$_3$), 144.9 (Ar–C=C–), 190.6 (C=O).

4-Chlorophenylmethylideneacetophenone (**1d**): Yield: 92% m.p. 113.5–115.5 °C; IR 1660 cm^{-1} (νC=O); ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.49–7.59 (6H, m), 7.76 (1H, d, J = 15.6 Hz), 7.23 and 7.99 (each 2H, d-like, J = 7.3 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 122.5 (Ar–C=C–), 128.5 (C–C–Cl), 128.7, 129.2, 129.6, 133.0, 133.0 (C–Cl), 133.4, 136.4, 143.3 (Ar–C=C–), 190.2 (C=O).

4-Nitrophenylmethylideneacetophenone (**1e**): Yield: 62% m.p. 166.0–167.0 °C; IR 1659 cm^{-1} (νC=O); ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.54 (2H, t, J = 7.8 Hz), 7.61–7.84 (5H, m), 8.03 and 8.27 (each 2H, d-like, J = 8.7 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 124.2 (Ar–C=C–), 125.7 (C–C–NO$_2$), 128.6, 128.8, 128.9, 133.4, 137.5, 141.0, 141.5 (C–NO$_2$), 148.5 (Ar–C=C–), 189.6 (C=O).

3,4,5-Trimethoxyphenylmethylideneacetophenone (**1f**): Yield: 87% m.p. 139.0–140.5 °C; IR 1661 cm^{-1} (νC=O) ^{1}H NMR (400 MHz, CDCl$_3$) δ: 3.90 (3H, s), 3.92 (6H, s), 6.87 (2H, s), 7.41 and 7.72 (each 1H, d, J = 15.6 Hz), 7.51 (2H, t, J = 7.3 Hz), 7.59 (1H, t, J = 7.3 Hz), 8.01 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 56.2 (2xCH$_3$O–), 61.0 (CH$_3$O–), 105.6 (CH–C–OCH$_3$), 121.4 (Ar–C=C–), 128.4, 128.6, 130.3, 132.7 (C–OCH$_3$), 138.2, 140.4, 145.0 (Ar–C=C–), 149.8 (2xC–OCH$_3$), 190.5 (C=O).

2.5. Reaction procedures

The Michael reaction was typically carried out as follows: under nitrogen atmosphere, vacuum-dried catalyst (100 mg) was suspended in a solution of **1c** (298.8 mg, 1.25 mmol) and diethyl malonate (**2a**, 221.7 mg, 1.38 mmol) in ethanol (0.5 ml), and the whole mixture was immediately immersed in a temperature-controlled oil bath (80 °C) followed by stirring for 2 h. After the reaction, the mixture was immediately diluted with benzene and filtered. The catalyst was washed thoroughly with benzene (60 ml) and recovered. Diethyl 2-[1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl)-1,3-propanedioate (**3ca**; 459.1 mg, 91.8%) as the Michael addition product was isolated from the filtrate by column chromatography (hexane/ethyl acetate = 8/1). The unreacted **1c** (19.9 mg, 6.6%) was also recovered.

The recovered catalyst was reused without any special treatment after drying in air at 40 °C for 24 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.03 and 1.24 (each 3H, t, J = 7.3 Hz), 3.40 (2H, dd, J = 9.3 Hz, 16.6 Hz), 3.51 (2H, dd, J = 4.9 Hz, 16.6 Hz), 3.73 (3H, s), 3.78 (1H, d, J = 9.8 Hz), 3.96 (2H, q, J = 7.3 Hz), 4.12–4.21 (3H, m), 6.77 and 7.17 (each 2H, d-like, J = 8.3 Hz), 7.42 (2H, t-like, J = 7.3 Hz), 7.53 (1H, t-like, J = 7.3 Hz), 7.90 (2H, d, J = 7.3 Hz).

^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.8 and 14.0 (CH$_3$–), 40.1 (–CH$_2$–CH–), 42.8 (–CH$_2$–CH–), 55.1 (–CH–CH–CH$_2$–), 57.8 (CH$_3$O–), 61.3 and 61.6 (CH$_3$–CH$_2$–), 113.7, 128.1, 128.5, 129.2, 132.3, 133.0, 136.8, 158.5 (C–OCH$_3$), 167.8 (–O–C=O), 168.4 (–O–C=O), 197.7 (Ph–C=O).

The representative spectroscopic data for other products are shown below.

Diethyl-2-(3-oxo-1,3-diphenylpropyl)-1,3-propanedioate (**3aa**) ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.00 and 1.23 (each 3H, t, J = 7.3 Hz), 3.45 (1H, dd, J = 9.3 Hz, 16.6 Hz), 3.54 (1H, dd, J = 4.88 Hz, 16.6 Hz), 3.82 (1H, d, J = 9.3 Hz), 3.95 (2H, q, J = 7.3 Hz), 4.15–4.23 (3H, m), 7.13–7.27 (5H, m), 7.41 (2H, t-like, J = 7.3 Hz), 7.52 (1H, t-like, J = 7.3 Hz), 7.89 (2H, d, J = 7.3 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.7 and 14.0 (CH$_3$–), 40.8 (–CH$_2$–CH–), 42.6 (–CH$_2$–CH–), 57.6 (–CH–CH–CH$_2$–), 61.3 and 61.6 (CH$_3$–CH$_2$–), 127.1, 128.1, 128.2, 128.4, 128.5, 133.0, 136.8, 140.4, 167.7 (–O–C=O), 168.3 (–O–C=O), 197.5 (Ph–C=O).

Dibutyl-2-(3-oxo-1,3-diphenylpropyl)-1,3-propanedioate (**3ab**) ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.82 and 0.90 (each 3H, t, J = 7.3 Hz), 1.15–1.23 (2H, m), 1.29–1.42 (4H, m), 1.55–1.62 (2H, m), 3.43 (1H, dd, J = 9.3 Hz, 16.6 Hz), 3.54 (2H, dd, J = 4.8 Hz, 16.6 Hz), 3.84 (1H, d, J = 9.3 Hz), 3.89 (2H, t-like, J = 6.8 Hz), 4.08–4.21 (3H, m), 7.16 (2H, t-like, J = 6.8 Hz), 7.21–7.28 (3H, m), 7.42 (2H, t-like, J = 7.3 Hz), 7.52 (1H, t, J = 7.3 Hz), 7.89 (2H, d-like, J = 7.3 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.5 and 13.6 (CH$_3$–), 18.9 and 19.0 (CH$_3$–CH$_2$–), 30.3 and 30.4 (–CH$_2$–CH$_2$–CH$_2$–), 40.7 (–CH$_2$–CH–), 42.6 (–CH$_2$–CH–), 57.6 (–CH–CH–CH$_2$–), 61.2 and 61.6 (–CH$_2$–CH$_2$–O–), 127.1, 128.1, 128.2, 128.4, 128.5, 133.0, 136.8, 140.5, 167.8 (–O–C=O), 168.4 (–O–C=O), 197.5 (Ph–C=O).

Di-t-butyl 2-(3-oxo-1,3-diphenylpropyl)-1,3-propanedioate (**3ac**) ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.19 and 1.46 (each 9H, s), 3.39 (1H, dd, J = 9.8 Hz, 16.6 Hz), 3.51 (1H, dd, J = 3.9 Hz, 16.6 Hz), 3.64 (1H, d, J = 10.3 Hz), 4.07 (1H, ddd, J = 3.9 Hz, 9.8 Hz, 10.3 Hz), 7.12–7.27 (5H, m), 7.40 (2H, t-like, J = 7.3 Hz), 7.50 (1H, t, J = 7.3 Hz), 7.88 (2H, d-like, J = 7.3 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 27.5 and 27.9 ((CH$_3$)$_3$C–), 40.9 (–CH$_2$–CH–), 43.3 (–CH$_2$–CH–), 59.3 (–CH–CH–CH$_2$–), 81.4 and 82.0 ((CH$_3$)$_3$C–), 126.9, 128.1, 128.2, 128.5, 128.5, 132.9, 136.9, 140.7, 167.0 (–O–C=O), 167.8 (–O–C=O), 197.8 (Ar–C=O).

Dibutyl-2-[1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl]-1,3-propanedioate (**3cb**) ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.83 and 0.90 (each 3H, t, J = 7.3 Hz), 1.19 (2H, ddd-like, J = 7.3 Hz, 14.6 Hz, 15.1 Hz), 1.29–1.42 (4H, m), 1.60 (2H, ddd, J = 7.3 Hz, 14.2 Hz, 15.1 Hz), 3.41 (1H, dd, J = 9.3 Hz, 16.6 Hz), 3.52 (1H, dd, J = 4.4 Hz, 16.6 Hz), 3.72 (3H, s), 3.80 (1H, d, J = 9.3 Hz), 3.91 (2H, ddd, J = 2.9 Hz, 6.3 Hz, 6.8 Hz), 4.09–4.19 (3H, m), 6.76 (2H, d-like, J = 8.8 Hz), 7.17 (2H, d-like, J = 8.8 Hz), 7.41 (2H, t-like, J = 7.3 Hz), 7.52 (1H, t, J = 7.3 Hz), 7.89 (2H, d-like, J = 7.3 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.5 and 13.6 (CH$_3$–), 18.9 and 19.0 (CH$_3$–CH$_2$–), 30.3 and 30.4 (–CH$_2$–CH$_2$–CH$_2$–), 40.1 (–CH$_2$–CH–), 42.8 (–CH$_2$–CH–), 55.1 (CH$_3$O–), 57.8 (–CH–CH–CH$_2$–), 65.1 and 65.4 (–CH$_2$–CH$_2$–O–), 113.7 (Ph–), 128.1 (Ph–), 128.5 (Ph–), 129.2 (Ph–), 132.3 (Ph–), 132.9 (Ph–), 136.8 (Ph–), 158.5 (Ph–), 167.9 (–O–C=O), 168.5 (–O–C=O), 197.7 (Ph–C=O).

Di-t-butyl 2-[1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl]-1,3- propanedioate (**3cc**) ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.21 and 1.47 (each 9H, s), 3.35 (1H, dd, J = 9.8 Hz, 16.6 Hz), 3.50 (1H, dd, J = 3.9 Hz, 16.6 Hz), 3.6 (1H, d, J = 10.3 Hz), 3.72 (3H, s), 4.02 (1H, ddd, J = 3.4 Hz, 3.9 Hz, 10.3 Hz), 6.75 (2H, d-

like, J = 8.8 Hz), 7.16 (2H, d-like, J = 8.8 Hz), 7.40 (2H, t-like, J = 7.3 Hz), 7.50 (1H, t, J = 7.3 Hz), 7.89 (2H, d-like, J = 7.3 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 27.6 and 27.9 ((CH$_3$)$_3$C–), 40.2 (–CH$_2$–CH–), 43.5 (–CH$_2$–CH–), 55.2 (–OCH$_3$), 59.5 (–CH–CH–CH$_2$–), 81.4 and 81.9 ((CH$_3$)$_3$C–), 113.6 (Ph–), 128.1 (Ph–), 128.5 (Ph–), 129.5 (Ph–), 132.7 (Ph–), 132.9 (Ph–), 137.0 (Ph–), 158.4 (Ph–), 167.1 (–O–C=O), 167.8 (–O–C=O), 197.0 (Ph–C=O).

Diethyl-2-[1-(4-methylphenyl)-3-oxo-3-phenylpropyl]-1,3-propanedioate (**3ba**) ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.02 and 1.24 (each 3H, t, J = 7.3 Hz), 2.25 (3H, s), 3.42 (1H, dd, J = 9.2 Hz, 16.5 Hz), 3.52 (1H, dd, J = 4.3 Hz, 16.5 Hz), 3.79 (1H, d, J = 9.7 Hz), 3.96 (2H, q, J = 7.3 Hz), 4.11–4.25 (3H, m), 7.03 and 7.14 (each 2H, d-like, J = 8.2 Hz), 7.41 (2H, t-like, J = 7.3 Hz), 7.52 (1H, t-like, J = 7.3 Hz), 7.89 (2H, d-like, 7.3 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.7 and 13.9 (CH$_3$–), 20.9 (CH$_3$–Ar), 40.4 (–CH$_2$–CH–), 42.6 (–CH$_2$–CH–), 57.6 (–CH–CH–CH$_2$–), 61.2 (CH$_3$–CH$_2$–), 61.5 (CH$_3$–CH$_2$–), 128.0 (Ph–), 128.1 (Ph–), 128.4 (Ph–), 129.0 (Ph–), 132.9 (Ph–), 136.5 (Ph–), 136.8 (Ph–), 137.3 (Ph–), 167.7 (–O–C=O), 168.4 (–O–C=O), 197.6 (Ph–C=O).

Diethyl-2-[1-(3,4,5-trimethoxyphenyl)-3-oxo-3-phenylpropyl]-1,3-propanedioate (**3da**) ^{1}H NMR (400 MHz, CDCl$_3$ TMS) δ: 1.05 and 1.24 (each 3H, t-like, J = 7.3 Hz), 3.43 (1H, dd, J = 8.7 Hz, 16.5 Hz), 3.50 (1H, dd, J = 4.8 Hz, 16.5 Hz), 3.76 (3H, s), 3.78 (6H, s), 3.83 (1H, d, J = 9.2 Hz), 4.00 (2H, q, J = 7.3 Hz), 4.09–4.24 (3H, m), 6.46 (2H, s), 7.43 (2H, t-like, J = 7.3 Hz, 6.8 Hz), 7.52 (1H, t-like, J = 9.2 Hz, 6.8 Hz), 7.89 (2H, d-like, 6.8 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.7 and 13.9 (CH$_3$–CH$_2$–), 20.9 (CH$_3$O–), 40.4 (–CH$_2$–CH–), 42.6 (–CH$_2$–CH–), 57.6 (–CH–CH–CH$_2$–), 61.2 and 61.5 (CH$_3$–CH$_2$–), 127.9 (Ph–), 128.0 (Ph–), 128.4 (Ph–), 129.0 (Ph–), 132.9 (Ph–), 136.5 (Ph–), 136.8 (Ph–), 137.3 (Ph–), 167.7 (–O–C=O), 168.3 (–O–C=O), 197.5 (Ph–C=O).

Diethyl-2-[1-(4-chlorophenyl)-3-oxo-3-phenylpropyl]-1,3-propanedioate (**3ea**) ^{1}H NMR (400 MHz, CDCl$_3$ TMS) δ: 1.04 and 1.24 (each 3H, t, J = 7.3 Hz), 3.43 (1H, dd, J = 9.2 Hz, 16.5 Hz), 3.53 (1H, dd, J = 4.3 Hz, 16.5 Hz), 3.78 (1H, d, J = 9.7 Hz), 3.98 (2H, q, J = 7.3 Hz), 4.13–4.26 (3H, m), 7.21 (4H, s), 7.42 (2H, t-like, J = 7.3 Hz), 7.53 (1H, t-like, J = 7.3 Hz), 7.88 (2H, d-like, 7.3 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.8 and 14.0 (CH$_3$–), 40.1 (–CH$_2$–CH–), 42.4 (–CH$_2$–CH–), 57.2 (–CH–CH–CH$_2$–), 61.4 and 61.7 (CH$_3$–CH$_2$–), 128.0 (Ph–), 128.5 (Ph–), 128.6 (Ph–), 129.6 (Ph–), 132.8 (Ph–), 133.2 (Ph–), 136.6 (Ph–), 139.0 (Ph–), 167.5 (–O–C=O), 168.1 (–O–C=O), 197.2 (Ph–C=O).

Diethyl-2-[1-(4-nitrophenyl)-3-oxo-3-phenylpropyl]-1,3-propanedioate (**3fa**) ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.07 and 1.26 (each 3H, t, J = 7.3 Hz), 3.53 (1H, dd, J = 9.3 Hz, 17.1 Hz), 3.60 (1H, dd, J = 4.4 Hz, 17.1 Hz), 3.85 (1H, d, J = 9.8 Hz), 3.98 (2H, q, J = 7.3 Hz), 4.18–4.33 (3H, m), 7.44 (2H, t-like, J = 7.3 Hz), 7.56 (1H, t-like, J = 7.3 Hz), 7.89 (2H, d-like, J = 7.3 Hz), 7.49 and 8.12 (each 2H, d-like, 8.8 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.8 and 14.0 (CH$_3$–), 40.3 (–CH$_2$–CH–), 42.0 (–CH$_2$–CH–), 56.8 (–CH–CH–CH$_2$–), 61.7 and 62.0 (CH$_3$–CH$_2$–), 123.6 (Ph–), 128.0 (Ph–), 128.7 (Ph–), 129.4 (Ph–), 133.4 (Ph–), 136.3 (Ph–), 147.0 (C–NO$_2$),

Table 1
Properties of molecular sieves used in this work

Molecular sieve[a]	Pore diameter[b] (nm)	S_{BET}[c] ($m^2\,g^{-1}$)	Pore volume[c] ($cm^3\,g^{-1}$)
MCM-41	2.9	1013 (766)	0.88 (0.48)
SBA-1	2.0	999 (769)	0.63 (0.38)
FAU	0.74[d]	810 (577)	0.30 (0.18)
BEA	0.76 × 0.64[d]	626 (260)	0.28 (0.13)
MOR	0.70 × 0.65[d]	562 (392)	0.22 (0.16)
MTW	0.60 × 0.56[d]	214 (15)	0.09 (<0.01)

[a] Abbreviations are used as described in the text.

[b] Values for molecular sieve supports before functionalization calculated by BJH method on N_2 adsorption isotherms unless otherwise noted. The value inside brackets is that for corresponding aminopropylsilylated material.

[c] The values are based on N_2 adsorption isotherms. The value inside brackets is that for corresponding aminopropylsilylated material.

[d] Diameter of the largest pore based on crystallographic data.

148.4 (Ph–), 167.3 (–O–C=O), 167.8 (–O–C=O), 196.7 (Ph–C=O).

3. Results and discussion

3.1. Organic-functionalized molecular sieves (OFMSs)

3.1.1. Properties of molecular sieve supports and aminopropylsilyl (AP)-functionalized catalysts

Every sample showed the reasonable powder XRD pattern [38]. Some other properties of corresponding samples are listed in Table 1.

In all cases including micro- and mesoporous materials, AP-functionalized samples showed lower N_2 adsorption amount than the unmodified supports, leading to smaller values for surface area and pore volume. This general tendency suggests that the organic moieties cover the inner surface of the pore, which is consistent with the slight decrease in pore diameters estimated by the BJH method. More detailed results and discussion were reported elsewhere [38].

The immobilization lowered the intensity of low-angle XRD lines as often observed in the silicate-organic composites. Connection of the aminopropylsilyl moiety to the silicate surface through covalent bonds was confirmed by ^{29}Si MAS NMR and ^{13}C CP MAS NMR spectroscopies for selected samples.

3.1.2. The Michael reaction catalyzed by the OFMS catalyst

Table 2 shows the results of the Michael reaction of chalcone (**1a**) with diethyl malonate (**2a**) catalyzed by various aminopropylsilylated molecular sieves. The molecular sieves with larger pores show the higher activity. We believe that this is one of the molecular (size) recognition phenomena. AP-MCM-41 showed high activity and gave the product in high yield. The yield decreased roughly depending on the surface area and pore volume values for the silicate supports. The use of AP-SBA-1 having much smaller pores than those of the AP-MCM-41 resulted in slower reaction.

Among the microporous materials, AP-FAU showed the highest activity, which is comparable to that of AP-MCM-41.

Other microporous catalysts showed much lower activities. The activities of the OFMS catalysts based on MOR and MTW, which have cylindrical straight channels, were particularly low.

These observations are roughly consistent with our results of the Knoevenagel reaction [35]. However, this is the case only in a polar solvent such as ethanol (EtOH) and *N,N*-dimethylformamide (DMF). Ethoxide (EtO$^-$) slightly formed under the basic conditions could catalyze this reaction in light of the classical examples [6,41]. However, the polarity itself is a rather more important factor in our case because DMF as an aprotic solvent mediated the reaction as effectively as EtOH. In fact, activity of the OFMS drastically decreased in the non-polar solvent such as benzene. The fact that enough activity for the Knoevenagel reaction retained in benzene means that the effective catalysis for the Michael reaction in a non-polar medium is a challenge.

Table 3 shows the effect of primary, secondary, and tertiary amine moieties on the reaction of 4-methoxylphenylmethylideneacetophenone (**1c**) with **2a**. AP-, PZP-, MAP-, and DMAP-functionalized materials were used as the base catalyst. It should be noted that the activity was much lower for 4-substituted chalcone derivatives than for non-substituted chalcone regardless of the solvent. In other words, 4-substituted chalcone derivatives are less reactive than non-substituted chalcone. All amine-immobilized silicates showed low activity for the Michael reaction even in ethanol as a polar solvent. This trend is totally different from that observed in the case of the Knoevenagel and aldol reactions in which primary and secondary amines are particularly active, respectively [38,42]. This suggests that neither imine- nor enamine-type intermediate is involved in the mechanism of the present reaction [39,43].

3.2. Quaternary ammonium-silicate composite materials (SOCMs)

3.2.1. The Michael addition reaction catalyzed by SOCMs

The use of the SOCM catalyst for the Michael reaction is the highlight of this paper. Results of the reaction of 4-methoxylphenylmethylideneacetophenone (**1c**) with diethyl malonate (**2a**) using various catalysts are listed in Table 4. As mentioned above, **1c** is poorly reactive when the OFMS catalyst is used (entry 1). In contrast, the reaction of **1c** with **2a** readily occurred when catalyzed by the SOCM catalyst. (CTMA$^+$)-[Si]-MCM-41 showed high catalytic activity and the reaction proceeded smoothly under mild conditions to give the desired product **3ca** in high to moderate yields (entries 2–5). On the other hand, calcined, SDA-free materials such as [Si]-MCM-41 showed no catalytic activity (entry 6). CTMA$^+$Br$^-$ did not show any activity, either (entry 7). The reaction catalyzed by (TEA$^+$)-[Al]-BEA gave **3ca** although the yield was not high (entry 8). These results suggest that the complexation between silicate and quaternary ammonium is necessary for the high activity. However, it is not always true because the composite (TEA$^+$F$^-$)-[Si]-BEA was not active at all (entry 9).

3.2.2. Solid-state NMR of the SOCM catalyst

Solid-state ^{29}Si MAS NMR spectra of the as-synthesized MCM-41 and BEA-type materials are shown in Fig. 1. The

Table 2
The Michael reaction of chalcone (**1a**) with diethyl malonate (**2a**) catalyzed by various aminopropyl-functionalized molecular sieves in different solvents[a]

Catalyst	AP-content[b] (mmol g cat.$^{-1}$)	Solvent	Time (h)	Conversion[c] (%)	Yield[d] (%)	TOF[e] (h^{-1})
AP-MCM-41	1.31	Ethanol	2	46	43	2.1
AP-MCM-41	1.31	Ethanol	24	87	87	
AP-MCM-41	1.31	DMF	2	46	46	2.2
AP-MCM-41	1.31	Benzene	2	3	3	0.1
AP-MCM-41	1.31	Benzene	24	4	4	
AP-SBA-1	1.40	Ethanol	2	20	18	0.8
AP-SBA-1	1.40	Ethanol	24	88	84	
AP-SBA-1	1.40	DMF	2	23	22	1.0
AP-SBA-1	1.40	Benzene	2	1	1	0.1
AP-SBA-1	1.40	Benzene	24	3	3	
AP-FAU	0.61	Ethanol	2	43	41	4.2
AP-FAU	0.61	Ethanol	24	88	87	
AP-FAU	0.61	DMF	2	50	50	5.1
AP-FAU	0.61	Benzene	2	1	1	0.1
AP-FAU	0.61	Benzene	24	2	2	
AP-BEA	0.95	Ethanol	2	8	6	0.4
AP-BEA	0.95	Ethanol	24	62	60	
AP-BEA	0.95	DMF	2	9	7	0.5
AP-BEA	0.95	Benzene	2	1	1	0.1
AP-BEA	0.95	Benzene	24	1	1	
AP-MOR	0.53	Ethanol	2	0	0	0.0
AP-MOR	0.53	Ethanol	24	5	4	
AP-MOR	0.53	DMF	2	1	1	0.1
AP-MOR	0.53	Benzene	2	0	0	0.0
AP-MOR	0.53	Benzene	24	0	0	
AP-MTW	0.48	Ethanol	2	0	0	0.0
AP-MTW	0.48	Ethanol	24	0	0	
AP-MTW	0.48	DMF	2	0	0	0.0
AP-MTW	0.48	Benzene	2	0	0	0.0
AP-MTW	0.48	Benzene	24	0	0	

[a] Reaction was carried out with 1.25 mmol of **1a**, 1.375 mmol of **2a**, 100 mg of catalyst in 0.5 ml of solvent at 80 °C under nitrogen atmosphere.
[b] Determined by elemental and thermogravimetric analyses.
[c] Based on the recovery of unreacted **1a**.
[d] Isolated yields.
[e] Moles of product per mol of catalyst per hour.

resonances corresponding to Si(3-OSi, 1-OH), i.e. Q^3, are obvious in the spectra of catalytically active (CTMA$^+$)-[Si]-MCM-41 and (TEA$^+$)-[Al]-BEA, whereas, only a weak Si(3-OSi, 1-OH) resonance peak can be seen in the spectrum of catalytically inactive (TEA$^+$F$^-$)-[Si]-BEA, which is consistent with the reported results [24,31,36,44]. Therefore, it is suggested that the basic (SiO)$_3$SiO$^-$($^+$NR$_4$) moieties in the composite materials play some roles for catalysis. However, there is no quantitative relationship between the activity and the intensity of Q^3 peak.

Table 3
Effect of the type of amine immobilized on MCM-41[a]

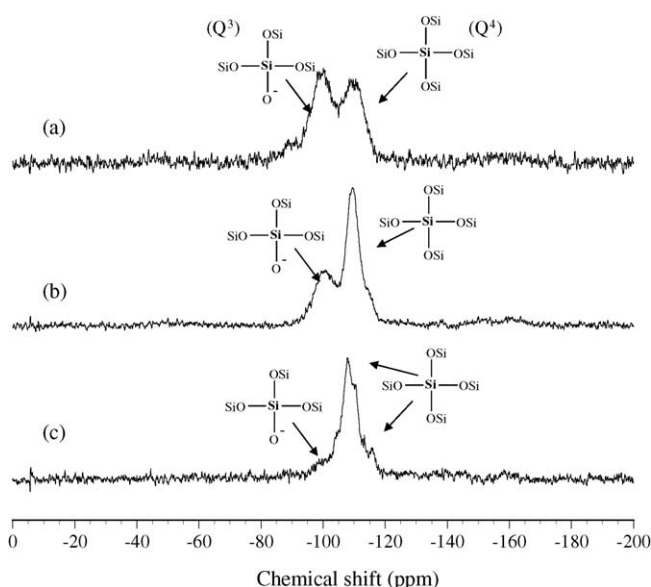| Entry	Catalyst	Conversion (%)	Yield[b] (%)
1	AP-MCM-41	5	4
2	MAP-MCM-41	3	2
3	PZP-MCM-41	7	7
4	DMAP-MCM-41	6	4

[a] Reaction was carried out with 1.25 mmol of **1c**, 1.375 mmol of **2a**, 100 mg of catalyst in 0.5 ml of ethanol at 80 °C for 2 h under nitrogen atmosphere.
[b] Isolated yields.

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

Table 4
The Michael reaction of **1c** with **2a** catalyzed by various SOCM type and related materials[a]

Entry	Catalyst	Solvent	Temperature (°C)	Conversion (%)	Yield[b] (%)
1	AP-MCM-41	Ethanol	80	4	2
2	$(CTMA^+)$-[Si]-MCM-41	Ethanol	80	93	92
3	$(CTMA^+)$-[Si]-MCM-41	Ethanol	30	69	68
4	$(CTMA^+)$-[Si]-MCM-41	Benzene	80	90	90
5	$(CTMA^+)$-[Si]-MCM-41	Benzene	30	28	26
6	[Si]-MCM-41	Ethanol	80	0	0
7	$CTMA^+Br^{-}$ [c]	Ethanol	80	0	0
8	(TEA^+)-[Al]-BEA	Ethanol	80	15	11
9	(TEA^+F^-)-[Si]-BEA	Ethanol	80	0	0
10	$(MTEA^+)$-[Si]-MTW	Ethanol	80	0	0

[a] Reaction was carried out with 1.25 mmol of **1c**, 1.375 mmol of **2a**, 100 mg of catalyst in 0.5 ml of solvent for 2 h.

[b] Isolated yields.

[c] 0.30 mmol of each catalyst was used.

Among the bulk species, only the $(SiO)_3SiO^-$ species which are accessible by the substrates could take part in the reaction. A mechanistic consideration will be presented in Section 3.2.5.

It is interesting to note that the presence of ion pair SiO^- $^+NR_4$ is taken for granted as far as 'quaternary ammonium' cations ($^+NR_4$) are occluded in the 'all-silica' frameworks. On the other hand, a rapid equilibrium $(SiOH + H_2NR \rightleftharpoons SiO^- + H_3N^+R)$ is expected in the OFMS (AP-functionalized) situation. The presence of H_3N^+R (and SiO^- as a possible active site) has been suggested using XPS by Brunel et al. [45].

3.2.3. Factors related to the effective activation of substrate

We already reported that nitrogen adsorption measurement of active $(CTMA^+)$-[Si]-MCM-41 did not give the Type-IV isotherm and the BET surface area was less than $20\,m^2\,g^{-1}$, whereas, the typical Type-IV isotherm and a large BET surface area ($1013\,m^2\,g^{-1}$) were obtained from catalytically inactive [Si]-MCM-41 [38]. This indicates that the large surface area and complete porosity are not indispensable in this reaction system. The reaction should take place at around the 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 the pore-mouth as compared to zeolite-based materials such as (TEA^+)-[Al]-BEA and $(MTEA^+)$-[Si]-MTW. As shown in Table 5, however, a large effect of the bulkiness

Table 5
The Michael reaction of **1c** with **2a** catalyzed by the SOCM type beta zeolites with different counter cations[a]

Entry	Catalyst	Conversion (%)	Yield[b] (%)
1	(NH_4^+)-[Al]-BEA[c]	90	90
2	(TEA^+)-[Al]-BEA[d]	15	11
3	$(TMBP^{2+})$-[Si]-BEA	0	0

[a] Reaction was carried out with 1.25 mmol of **1c**, 1.375 mmol of **2a**, 100 mg of catalyst in 0.5 ml of ethanol at 80 °C for 2 h.

[b] Isolated yields.

[c] $SiO_2/Al_2O_3 = 25$.

[d] $SiO_2/Al_2O_3 = 105$.

of the counter cation was observed. This means that the good accessibility to the cation–silicate interface is necessary for the activation of substrates. Particle size of each catalyst is smaller than 2 μm except for the (TEA^+F^-)-[Si]-BEA which is larger than 10 μm [46]. In terms of the exposure of catalytic sites on the surface, large particle size as well as the lack of defect site of (TEA^+F^-)-[Si]-BEA is a drawback to the catalytic activity, which can be another reason for the inertness of this material.

3.2.4. Reusability of the SOCM catalyst

Reusability of the $(CTMA^+)$-[Si]-MCM-41 was tested for the reactions (**1a** with **2a**, and **1c** with **2a**) in benzene. It was confirmed by means of XRD that the framework structures of the recovered catalysts were unchanged after the reactions. Figs. 2 and 3 show the TG profiles of the catalysts before and after the reactions. The decrease in the organic content after the 3rd run in benzene was less than 5 and 2 wt.% of the initial weight, respectively. Only slight loss of activity was observed for the reaction of **1a** with **2a** (Fig. 4a), whereas, there was significant loss of activity in the reaction of **1c** with **2a** (Fig. 4b).
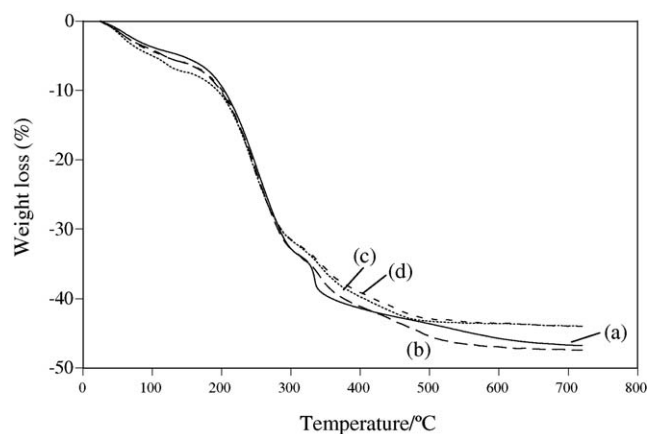

Fig. 2. Thermogravimetric analysis of $(CTMA^+)$-[Si]-MCM-41 catalyst (a) before use, (b) after the 1st use, (c) after the 2nd use, and (d) after the 3rd use. The reaction was carried out with 1.25 mmol of **1a**, 1.375 mmol of **2a**, 100 mg of catalyst in 0.5 ml of benzene at 30 °C for 2 h.
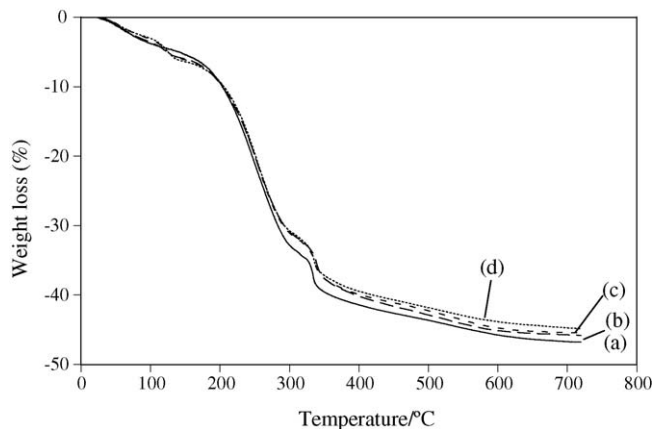
Fig. 3. Thermogravimetric analysis of (CTMA$^+$)-[Si]-MCM-41 catalyst (a) before use, (b) after the 1st use, (c) after the 2nd use, and (d) after the 3rd use. The reaction was carried out with 1.25 mmol of **1c**, 1.375 mmol of **2a**, 100 mg of catalyst in 0.5 ml of benzene at 80 °C for 2 h.
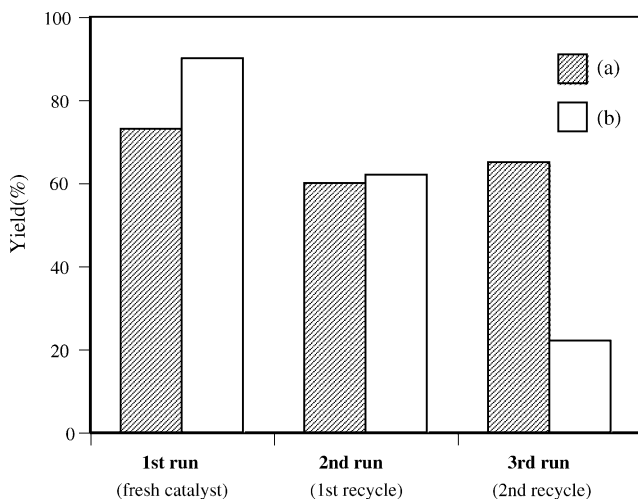

Fig. 4. Activity of the fresh and used (CTMA$^+$)-[Si]-MCM-41. Reaction conditions: (a) **1a**, 1.25 mmol; **2a**, 1.375 mmol; catalyst, 100 mg; benzene, 0.5 ml; temperature, 30 °C; time, 2 h, (b) **1c**, 1.25 mmol; **2a**, 1.375 mmol; catalyst, 100 mg; benzene, 0.5 ml; temperature, 80 °C; time, 2 h.

The cause of the loss of activity is still not clear; however, it is clear that the less reactive substrate **1c** is more sensitive to the slight change in the surface conditions of the catalyst.

After the reaction of **1c** with **2a**, the filtrate demonstrated no activity when fresh substrates were added and the reaction was carried out at 80 °C for 2 h; the ^{1}H NMR spectra of the reaction mixture taken every 30 min showed that no further reaction was taking place. This result indicates that, even if there are leached species, they do not act as the effective homogeneous catalyst.

3.2.5. Mechanistic consideration

A plausible mechanism is shown in Scheme 3. In general, this reaction starts from the abstraction of a proton by a base (B$^-$) from the active methylene compound such as diethyl malonate (step 1). The carbanion thus formed (the concentration would not always be high) attacks the β-carbon of α, β-unsaturated ketone such as chalcone derivative to form a carbon-carbon bond (step 2). The last step (step 3) consists of the formation of final product and the regeneration of base. If these steps operate completely, the catalytic cycle continues. B$^-$M$^+$ in the scheme corresponds to the $(SiO)_3SiO^-$ ($^+$NR$_4$) ion pair in the case of SOCM catalyst. It is possible that the steps 1–3 proceed on the solid surface or in its close proximity. In such case, this catalytic system is regarded as heterogeneous. It would also be possible that the M$^+$(=$^+$NR$_4$) is in the bulk liquid phase during the step 2. If this is the case, then this catalytic system cannot be considered as perfectly heterogeneous. In both cases, however, this system would act as if it were totally heterogeneous when the step 3 operates properly. Incomplete returning of the $^+$NR$_4$ cation to the solid would cause the loss of organic content of the catalyst. In the polar solvent, the step 3 would not operate properly, and the $^+$NR$_4$ could be pulled out into the solution, leading to the loss of activity upon the repeated use. Therefore, the use of non-polar solvent is rather recommended.

A possibility that very low concentration of OH$^-$ helps the catalysis in this reaction still remains. As discussed in the Section 3.2.4, however, the active species are absent in the liquid phase after the reaction. Therefore, OH$^-$ species such as CTMA$^+$OH$^-$
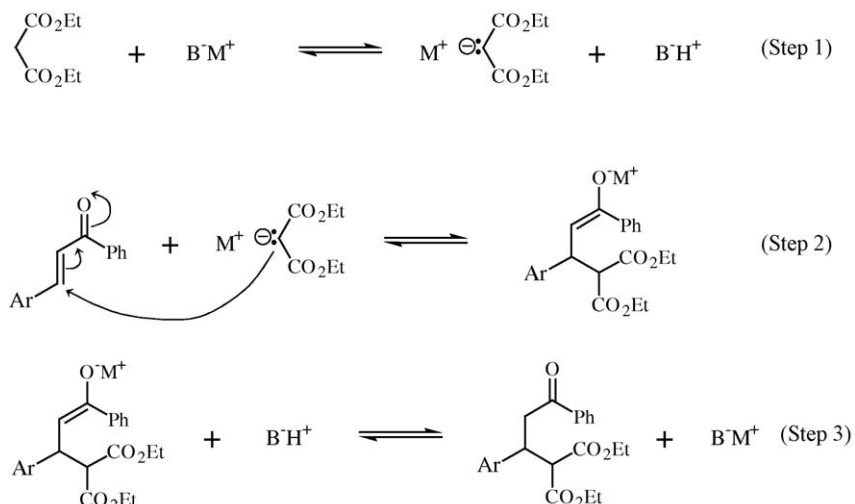
Scheme 3.

Table 6
Effect of substrates on the reaction catalyzed by (CTMA$^+$)-[Si]-MCM-41[a]

Entry	Substrate		Solvent	Conversion (%)	Yield[b] (%)
	1	**2**			
1	**1a**	**2a**	EtOH	99	98
2	**1b**	**2a**	EtOH	98	96
3	**1c**	**2a**	EtOH	93	92
4	**1c**	**2a**	Benzene	90	90
5	**1d**	**2a**	EtOH	99	99
6	**1e**	**2a**	EtOH	99	98
7	**1f**	**2a**	EtOH	99	97
8	**1c**	**2b**	EtOH	80	68 (11)[c]
9	**1c**	**2b**	Benzene	81	80
10	**1c**	**2c**	EtOH	59	58
11	**1c**	**2c**	Benzene	61	61

[a] Reaction was carried out with 1.25 mmol of **1a–f**, 1.375 mmol of **2a–c**, 100 mg of (CTMA$^+$)-[Si]-MCM-41 in 0.5 ml of solvent at 80 °C for 2 h under nitrogen atmosphere.

[b] Isolated yields.

[c] The value in parentheses is a combined yield of ester-exchanged products.

cannot be responsible for the major activity. From a different point of view, the use of high concentration OH$^-$ (including a Brönsted base-immobilized catalyst [47]) is not recommended in this reaction because it would cause the hydrolysis of ester moiety, reducing the yield. In the case of SOCM catalyst, such kind of hydrolyzed products have never been observed.

3.2.6. The reactivity of various substrates

As shown in Table 6, (CTMA$^+$)-[Si]-MCM-41 proved to be active in a variety of Michael reactions; no significant effect of the substituent attached to the aromatic ring of the substrate was observed. The reaction of **1a–f** with **2a** in ethanol gave the products **3aa–3fa** in very high yields. Reactivity of the bulkier ester as the Michael donor (**2b** or **2c**) was lower and the product yield decreased with the increase in the bulkiness of the alkoxy group. When *n*-butyl ester was used instead of ethyl ester, the ester-exchange reaction partially took place in ethanol, which lowered the yield of the desired product. This side-reaction was able to be avoided by using benzene as a solvent, indicating the usefulness of non-polar solvent in this catalytic system. When the Michael acceptors other than chalcone derivatives, such as diethylbenzalmalonate and *trans*-β-nitrostylene, were used, the SOCM catalyst was not effective mainly due to the formation of polymeric by-products although the conditions were not optimized.

4. Conclusions

Various OFMS and SOCM type materials were synthesized and used as the catalysts for the Michael reaction of chalcone derivatives with malonic esters. In the case of OFMSs, the supports with larger pore volume and/or surface area were preferable. While the OFMSs were highly active when the reaction was carried out in a polar solvent, the activity was considerably low in a non-polar solvent. In contrast, the SOCMs were remarkably active for the same reaction in both solvents. The organic cation-MCM-41 composite was more active than the composite of an organic cation and a microporous silicate such as zeolite beta and ZSM-12. In the SOCM catalysts, (SiO)$_3$SiO$^-$($^+$NR$_4$) moieties located at the accessible sites were considered to be responsible for the major activity. The active species were absent in the liquid phase after the reaction. The (CTMA$^+$)-[Si]-MCM-41 was recyclable without significant loss of activity in the case of the reaction of chalcone with diethyl malonate in benzene. This catalyst was effective for some other substrates preferably in non-polar solvent.

We believe that investigation of the function of these materials is useful for developing the catalyst design based on the utilization of the defined structures.

References

[1] G. Kickelbick, Angew. Chem. Int. Ed. 43 (2004) 3102.
[2] M.E. Davis, Nature 417 (2002) 813.
[3] A.P. Wight, M.E. Davis, Chem. Rev. 102 (2002) 3589.
[4] G. Jones, in: A.C. Cope (Ed.), Organic Reactions, vol. 15, John Wiley and Sons, New York, 1967, pp. 204–599.
[5] J. March, Advanced Organic Chemistry, 4th ed., John Wiley and Sons, New York, 1992 (Chapter 16).
[6] E.D. Bergmann, D. Ginsburg, R. Pappo, in: R. Adams (Ed.), Organic Reactions, vol. 10, John Wiley and Sons, New York, 1959, pp. 179–555.
[7] K. Tanabe, W.F. Hölderich, Appl. Catal. A: Gen. 181 (1999) 399.
[8] H. Hattori, Chem. Rev. 95 (1995) 537.
[9] J. Weitkamp, M. Hunger, U. Rymsa, Micropor. Mesopor. Mater. 48 (2001) 255.
[10] J. Christoffer, Eur. J. Org. Chem. (1998) 1259.
[11] H. Hagiwara, N. Komatsubara, H. Ono, T. Okabe, T. Hoshi, T. Suzuki, M. Ando, M. Kato, J. Chem. Soc., Perkin Trans. 1 (2001) 316.
[12] G.A. Boyle, T. Govender, H.G. Hendrik, E.M.G. Maguire, Tetrahedron Asymmetry 15 (2004) 3775.
[13] S. Matsunaga, T. Ohshima, M. Shibasaki, Adv. Synth. Catal. 344 (2002) 3.
[14] B. List, Synlett (2001) 1675.
[15] J.M. Betancort, K. Sakthivel, R. Thayumanavan, C.F. Barbas III, Tetrahedron Lett. 42 (2001) 4441.
[16] M. Yamaguchi, T. Shiraishi, M. Hirama, J. Org. Chem. 61 (1996) 3520.
[17] A. Corma, S. Iborra, Fine Chem. Heterogen. Catal. (2001) 309–326.
[18] M.J. Climent, A. Corma, S. Iborra, A. Velty, J. Mol. Catal. A: Chem. 182/183 (2002) 327.
[19] K. Shimizu, M. Miyagi, T. Kan-no, T. Kodama, Y. Kitayama, Tetrahedron Lett. 44 (2003) 7421.
[20] J.-M. Clacens, D. Gennit, L. Delmotte, A. Garcia-Ruiz, G. Bergeret, R. Montiel, J. Lopez, F. Figueras, J. Catal. 221 (2004) 483.
[21] P.D. Shinde, V.A. Mahajan, H.B. Borate, V.H. Tillu, R. Bal, A. Chandwadkar, R.D. Walharkar, J. Mol. Catal. A: Chem. 216 (2004) 115.
[22] M. Yasuda, K. Chiba, N. Ohigashi, Y. Katoh, A. Baba, J. Am. Chem. Soc. 125 (2003) 7299.
[23] C.W. Jones, K. Tsuji, M.E. Davis, Nature 393 (1998) 52.

[24] C.W. Jones, K. Tsuji, M. Davis, Micropor. Mesopor. Mater. 33 (1999) 223.
[25] Y. Kubota, Y. Nishizaki, Y. Sugi, Chem. Lett. 29 (2000) 998.
[26] Y. Kubota, Y. Nishizaki, H. Ikeya, J. Nagaya, Y. Sugi, Stud. Surf. Sci. Catal. 141 (2002) 553.
[27] S. Brunauer, P.H. Emmet, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.
[28] B.C. Lippens, J.H. De Boer, J. Catal. 4 (1965) 319.
[29] E.P. Barrett, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373.
[30] Ch. Baerlocher, W.M. Meier, D.H. Olson, Atlas of Zeolite Framework Types, 5th ed., Elsevier, Amsterdam, 2001, http://www.iza-structure.org/databases/.
[31] C.-Y. Chen, H.-X. Li, M.E. Davis, Micropor. Mater. 2 (1993) 17.
[32] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[33] M.K. Rubin, U.S. Patent 5164169, 1992.
[34] S. Ernst, P.A. Jacobs, J.A. Martens, J. Weitkamp, Zeolites 7 (1987) 458.
[35] K. Tsuji, M.E. Davis, Micropor. Mater. 11 (1997) 53.
[36] M.A. Camblor, A.C. Corma, S. Valencia, Chem. Commun. (1996) 2365.
[37] M.A. Camblor, L.A. Villaenscusa, M.J. Dìaz-Cabañas, Top. Catal. 9 (1999).
[38] Y. Kubota, Y. Nishizaki, H. Ikeya, M. Saeki, T. Hida, S. Kawazu, M. Yoshida, H. Fujii, Y. Sugi, Micropor. Mesopor. Mater. 70 (2004) 135.
[39] E. Angeletti, C. Canepa, G. Martinetti, P. Venturello, J. Chem. Soc., Perkin Trans. 1 (1989) 105.
[40] A. Cauvel, G. Renard, D. Brunel, J. Org. Chem. 62 (1997) 749.
[41] R. Connor, D.B. Andrews, J. Am. Chem. Soc. 56 (1934) 2713.
[42] Y. Kubota, K. Goto, S. Miyata, Y. Goto, Y. Fukushima, Y. Sugi, Chem. Lett. 32 (2003) 234.
[43] F. Fajula, D. Brunel, Micropor. Mesopor. Mater. 48 (2001) 119.
[44] E.J.R. Sudhölter, R. Huis, G.R. Hays, N.C.M. Alma, J. Coll. I. Sci. 103 (1985) 554.
[45] D. Brunel, A.C. Blanc, E. Garrone, B. Onida, M. Rocchina, J.B. Nagy, D.J. Macquarrie, Stud. Surf. Sci. Catal. 142 (2002) 1395.
[46] K. Tsuji, C.W. Jones, M. Davis, Micropor. Mesopor. Mater. 29 (1999) 339.
[47] I. Rodriguez, S. Iborra, A. Corma, F. Rey, J.L. Jordá, Chem. Commun. (1999) 593.