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Catalytic activity of mesoporous silica for synthesis of methyl *N*-phenyl carbamate from dimethyl carbonate and aniline

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Mesoporous silica MCM-41, especially an Al-containing one, showed high catalytic activity for synthesis of methyl *N*-phenyl carbamate from dimethyl carbonate and aniline at 363–383 K. It was easily separated from the product solution, and the catalyst was able to be used repeatedly.

KEY WORDS: dimethyl carbonate; methyl *N*-phenyl carbamate; aniline; mesoporous silica.

1. Introduction

Removal of halogen compounds from chemical processes to avoid environmental pollution is an important subject for modern chemists. Phosgene, $COCl_2$, has been utilized as a convenient carbonylization reagent, but it is itself toxic and causes problems of corrosion, waste salt and organic halogen compound as by-product. Isocyanate compound, which is an important raw material in organic chemistry, has been produced by a non-catalytic reaction between the corresponding amine and phosgene. Replacement of this process by the production of isocyanate via carbamate compound from the amine and dimethyl carbonate is thus considered to be important for environmental protection [1].

For the reaction between aniline and dimethyl carbonate into methyl *N*-phenyl carbamate, several papers and patents appeared. Acidic and basic compounds, *e.g.* $AlCl_3$ [2], K_2CO_3 [3] and alkaline alkoxide [4], were proposed as catalysts. However, any catalysts soluble in the product solution should be unsuitable for environmental protection. As a solid catalyst, alkali-treated basic ion-exchange resin [5] and lead oxide [6] have been proposed, but these materials may soluble in the liquid and cause environmental pollution. Therefore we searched for a more efficient solid catalyst, and here report a catalyst consisting of SiO_2 and Al_2O_3, which are substantially insoluble in the liquid.

Hexagonal mesoporous silicate was first synthesized by the researchers of Mobil R&D [7] (MCM-41) and Inagaki *et al.* [8] (FSM-16). Aluminum-containing mesoporous silica was expected to show high catalytic performance for the reaction of relatively large molecules. However, only a few applications of mesoporous aluminosilicate to acid-catalyzed reaction have been realized [9]. In the present paper, we will show the effective use of mesoporous silica.

2. Experimental

2.1. Preparation of catalyst

Mesoporous silica MCM-41 was prepared according to the previous literature [10,11], from colloidal silica LUDOX HS-40, sodium hydroxide and ammonia tetradecyltrimethylammonium bromide (shown as C_{14} template in the following sections), with adjustment of pH by addition of acetic acid. In the case of Al-introduced MCM-41, sodium aluminate was added. The obtained MCM-41 was filtered, washed with hot water, dried and calcined in nitrogen flow for 1 h and then in oxygen flow for 11 h at 843 K. The aluminum-containing sample was treated with ammonium nitrate solution and calcined at 723 K for 24 h in air to convert it into the proton form.

Impregnation of aluminum on the purely siliceous MCM-41 was made in a methanol solvent in order to avoid destruction of the hexagonal structure [12]. The obtained solid was dried at 373 K for 12 h and calcined at 773 K for 5 h in air. The inductively-coupled plasma (ICP) emission spectroscopy confirmed that almost all the added aluminum remained on the solid.

As a comparison, many kinds of catalysts were tested, as shown in table 1. The MCM-41 with different pore sizes was prepared using C_{12} (dodecyltrimethylammonium bromide) and C_{16} (hexadecyltrimethylammonium bromide) templates.

2.2. Characterization of MCM-41

The powder X-ray diffraction (XRD) pattern of the calcined MCM-41 was measured by a Rigaku Miniflex

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Table 1
Activities of various catalysts for reaction of aniline (0.45 mol) and dimethyl carbonate (0.065 mol) at 373 K for 2 h

Catalyst	Source	Conversion of dimethyl carbonate	Yield of methyl *N*-phenyl carbamate (%)	Yield of *N*-methyl aniline (%)	Material balance
No catalyst (blank test)		0.0	0.0	0.4	100
Lead compounds					
$Pb(OCOCH_3)_4$*	Wako Pure Chemical Industries Ltd.	20.1	0.4	0.2	81
PbO (yellow)*	Nacalai Tesque Inc., Extra Pure	0.0	0.0	0.0	101
Zeolites					
H-Y ($Si/Al_2 = 5.5$)	Catalysts & Chemicals Ind. Co. Ltd.	3.1	0.7	1.2	99
Na-Y ($Si/Al_2 = 5.5$)	Catalysts & Chemicals Ind. Co. Ltd.	not measured	0.0	37.4	not measured
Na-X ($Si/Al_2 = 2.6$)	Tosoh Corp.	50.1	0.0	29.4	86
Ultra stable Y ($Si/Al_2 = 7.5$)	Catalysts & Chemicals Ind. Co. Ltd.	0.7	0.0	0.1	99
H-β ($Si/Al_2 = 25$)	The PQ Corp.	4.2	1.9	1.2	99
H-β zeolite ($Si/Al_2 = 25$)	Tosoh Corp.	9.6	0.2	1.2	91
H-mordenite JRC-Z-HM15 ($Si/Al_2 = 15$)	Catalysis Society of Japan	1.6	0.0	0.0	98
H-ZSM5 ($Si/Al_2 = 23.3$)	Tosoh Corp.	1.4	0.0	0.3	99
H-ZSM5 ($Si/Al_2 = 75$)	Mobil Catalyst Corp. Japan	0.8	0.0	2.0	101
Mesoporous silica and aluminosilicates					
MCM-41 (C_{14} template, pure SiO_2)	Hydrothermal synthesis	2.9	0.8	0.0	98
Al/MCM-41 (C_{14} template, 0.33 mol Al kg^{-1})	Hydrothermal synthesis	5.9	2.0	0.3	96
Al/MCM-41 (C_{14} template, 0.43 mol Al kg^{-1})	Hydrothermal synthesis	5.6	1.4	0.2	96
Al/MCM-41 (C_{14} template, 0.83 mol Al kg^{-1})	Impregnation in methanol	2.9	2.3	0.2	96
Al/MCM-41 (C_{14} template, 2.74 mol Al kg^{-1})	Impregnation in methanol	10.4	4.0	0.2	94
Al/MCM-41 (C_{14} template, 4.58 mol Al kg^{-1})	Impregnation in methanol	8.0	1.2	1.0	94
Ga/MCM-41 (C_{14} template, $Si/Ga_2 = 200$)	Hydrothermal synthesis	3.7	0.0	2.7	98
Fe-MCM-41 (C_{14} template, $Si/Fe_2 = 200$)	Hydrothermal synthesis	4.7	0.0	0.7	96
Al/MCM-41 (C_{12} template, 2.50 mol Al kg^{-1})	Impregnation in methanol	1.2	1.1	0.1	100
Al/MCM-41 (C_{16} template, 2.50 mol Al kg^{-1})	Impregnation in methanol	2.3	2.2	0.2	100
Metal oxides					
SiO_2-Al_2O_3 N631L	Nikki Kagaku Co. Ltd.	0.0	0.0	0.5	103
γ-Al_2O_3 JRC-ALO7	Catalysis Society of Japan	11.5	0.0	0.3	88
SO_4^{2-}/ZrO_2 (2.5 S-atom nm^{-2})	[15]	8.4	0.0	2.0	94
SO_4^{2-}/ZrO_2 (15 S-atom nm^{-2})	[15]	0.0	0.0	0.1	104
WO_3/ZrO_2 (5 W-atom nm^{-2})	[16]	0.4	0.0	0.3	100
$H_4SiMo_{12}O_{40}$*	Wako Pure Chemical Industries Ltd.	2.0	0.0	0.3	98
$Cs_{2.5}H_{0.5}(PMo_{12}O_{40})$*	prepared from $H_3(PMo_{12}O_{40})$	3.9	0.0	0.4	96
Miscellaneous					
K_2CO_3*	Nacalai Tesque Inc.	4.1	0.0	0.3	96
Basic resin Diaion PA306 * treated with 2 mol dm^{-3} NaOH	Mitsubishi Chemical Corp.	6.6	0.0	0.8	94
Acidic resin Amberlyst 15 E *	Organo Co. Ltd.	0.1	0.0	0.4	101

* Reaction carried out without the pretreatment of the catalyst, because these materials decompose at a high temperature.

Plus diffractometer with a Cu K_α X-ray source (30 kV, 15 mA). Nitrogen adsorption isotherm was measured at 77 K after evacuation of the sample at 773 K. Temperature-programmed desorption (TPD) of ammonia was carried out according to our paper [13]. The heat of ammonia adsorption was calculated based on the one-point method proposed in our paper [14].

2.3. Reaction

Catalyst (0.5 g) was pretreated at 773 K for 1 h in a nitrogen flow (60 cm^3 min^{-1}) and put into a mixture of 5.93 g (0.065 mol) of dimethyl carbonate (Nacalai Tesque, guaranteed reagent) and 41.9 g (0.45 mol) of aniline (Nacalai Tesque, guaranteed reagent) in a dry box; the catalyst which decomposes at a high temperature (shown by * in table 1) was not pretreated and was put into the reaction mixture directly in air. The solution was stirred at 373 K for 2 h, and the products were analyzed by a Shimadzu GC-8A gas chromatograph with a flame ionization detector and a column of silicone OV-17 (2 m length and 3 mm inner diameter, operated at 313–543 K) using tetraethylene glycol dimethyl ether (bis[2-(2-methoxyethoxy)ethyl] ether in IUPAC rules) as an inner standard material. The solution was injected into the GC from the inlet heated at 373 K, since the decomposition of methyl *N*-phenyl carbamate into *N*-methyl aniline was observed at higher temperatures. In some experiments, reaction temperature or time was varied. In order to identify and quantify the product, methyl *N*-phenyl carbamate was synthesized by a reaction between aniline and methyl chloroformate at room temperature; the product was analyzed by ^{1}H NMR (nuclear magnetic resonance, JEOL JNM-GX 270 FT NMR Spectrometer). Recycle use of the catalyst was examined after 48 h of the reaction; the catalyst was filtered using filter paper No. 101 (Toyo Roshi Kaisha, Ltd.) and put into another new reactant mixture without any pretreatment.

3. Results and discussion

3.1. Properties of Al/MCM-41

The hydrothermally-synthesized Al/MCM-41 possessed highly ordered hexagonal structure with high surface area and pore volume as described elsewhere [10]. The Al-impregnated MCM-41 also showed these properties at $<5\,\mathrm{mol\,kg^{-1}}$ of the Al loading as follows: as shown in figure 1, the characteristic XRD pattern of the hexagonal structure was principally maintained by the impregnation of aluminum less than $5\,\mathrm{mol\,kg^{-1}}$; as shown in figure 2 and table 2, high adsorption capacity and its sharp increase in the mesoporous region ($P/P^0 \simeq 0.3$) were observed at $<5\,\mathrm{mol\,kg^{-1}}$.

The acidic property of hydrothermally-synthesized Al/MCM-41 has been reported elsewhere [11]. The nature of the acid site was principally Lewis type [10]. The acidic property of the Al/MCM-41, which was prepared by the impregnation method, was also analyzed by the TPD method as shown in figure 3. The averaged adsorption heat of ammonia was $\sim 130\,\mathrm{kJ\,mol^{-1}}$, and this was similar on the hydrothermally-synthesized Al/MCM-41 [11].

3.2. Reaction of aniline and dimethyl carbonate

We first checked the reaction behavior of aniline and dimethyl carbonate mixture in the absence of catalyst. As shown in figure 4 (○ and △), no target product (methyl *N*-phenyl carbamate) was obtained at 373 to 423 K, while a side reaction to *N*-methyl aniline proceeded at >373 K. The activities of various catalysts were therefore compared at 373 K. As shown in figure 4 and table 1, no methyl *N*-phenyl carbamate was detected under these conditions without catalyst. Lead acetate, whose high activity was reported by Fu *et al.* [6], showed a small activity but was accompanied by the production of *N*-methyl aniline. Lead oxide, also reported by the same authors [6], did not show activity but caused only a side reaction. Basic ion-exchange resin PA-306 which had been treated in $2\,\mathrm{mol\,dm^{-3}}$ NaOH solution [5] was also inactive.

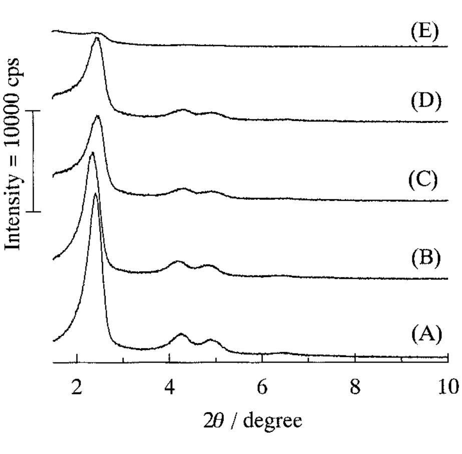

Figure 1. X-ray diffraction of MCM-41 (A: pure SiO$_2$) and Al-impregnated MCM-41 (B: 0.83; C: 2.74; D: 4.58; E: 6.41 mol Al kg^{-1}) prepared using C$_{14}$ template.

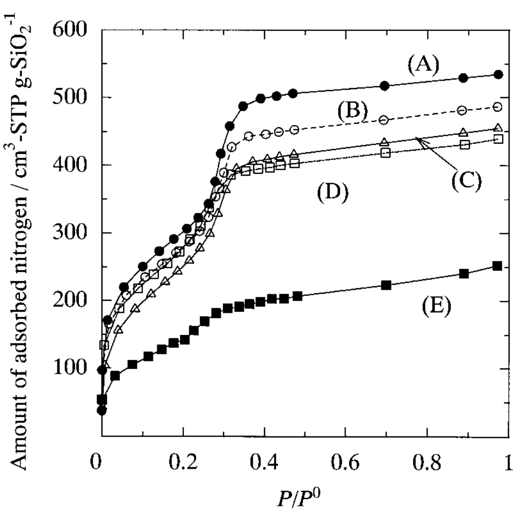

Figure 2. Nitrogen adsorption isotherm observed at 77 K on MCM-41 (A: pure SiO$_2$) and Al-impregnated MCM-41 (B: 0.83; C: 2.74; D: 4.58; E: 6.41 mol Al kg^{-1}) prepared using C$_{14}$ template.

Many kinds of acid–base catalysts were examined, but only some H-type zeolites (Y and β) and MCM-41 materials showed activity. Among the zeolites, those possessing large pore size, namely Y and β types, were active for this reaction. By contrast, small pore zeolites such as ZSM-5 and mordenite were inactive. Therefore, it is speculated that the large pore size, more exactly high accessibility of the reactant and/or intermediate to the surface, is important for the catalytic activity. This speculation is consistent with the finding that the mesoporous silica MCM-41 had high activity for the target reaction, because it had large pore size and high surface area.

We have measured the number and strength of acid sites on these solid acid catalysts exactly by the TPD of ammonia [13]. The sulfated zirconia (SO_4^{2-}/ZrO_2) with $2.5\,\mathrm{nm^{-2}}$ of the sulfur atom (Lewis superacid with $200\,\mathrm{kJ\,mol^{-1}}$ of the adsorption heat of ammonia [15]) was inactive for the desired reaction, but showed activity for the side reaction. The sulfated zirconia with the higher loading ($15\,\mathrm{nm^{-2}}$) and WO_3/ZrO_2 (Brønsted acid with 160 and $130\,\mathrm{kJ\,mol^{-1}}$ of the ammonia adsorption heat, respectively [15,16]) were also active only for the undesired reaction. Mordenite and ZSM-5 zeolites

Table 2
Structural and acidic properties of Al-impregnated MCM-41

Al loading (mol kg^{-1})	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)	Acid amount (mol kg^{-1})	Averaged adsorption heat of ammonia (kJ mol^{-1})
0	910	0.72	2.67	n.m.	n.m.
0.83	1024	0.66	2.41	0.18	140
2.74	969	0.60	2.46	0.28	132
4.58	1068	0.60	2.40	0.32	130
6.41	522	0.28	2.23	0.51	126

Note: n.m., not measured.

(relatively strong Brønsted acid, 145 and 130 kJ mol^{-1} of the adsorption heat, respectively [17]) showed no activity for the formation of methyl *N*-phenyl carbamate, while the weakly Brønsted acidic zeolites, *i.e.* the H-Y and H-β (110 and 120 kJ mol^{-1} of the adsorption heats, respectively [18,19]), possessed high activity. Probably the Brønsted acid sites with ammonia adsorption heat lower than 120 kJ mol^{-1} are responsible for the desired reaction. Also, strongly Brønsted acidic materials (acidic resin, heteropoly acid and its cesium salt) caused only the side reaction. In summary, only a weak Brønsted acid site with the heat of ammonia adsorption lower than 120 kJ mol^{-1} is suitable for the desired reaction.

On the other hand, basic catalysts, *i.e.* K_2CO_3, alumina and basic ion-exchange resin PA306 treated in NaOH, were also active only for the side reaction. Sodium-type zeolites also accelerated only the side reaction as reported [20]. It should be noted that the presence of a basic site should be detrimental to the desired reaction because of the high activity for the side reaction.

The MCM-41 material, especially the Al-containing sample, selectively showed high activity for the formation of methyl *N*-phenyl carbamate. Both the addition of aluminum by hydrothermal synthesis and impregnation were effective, and the Lewis acid site is probably active for this reaction. It should be noted that, in the case of a Lewis-type acid site, the acid strength of the Al/MCM-41 corresponding to 130 kJ mol^{-1} of the ammonia adsorption heat was effective. The highest activity was obtained by impregnating 2.7 mol kg^{-1} of aluminum. The further increase of the aluminum again decreased activity for the desired reaction but increased the activity for the side reaction. This is explained by the formation of large alumina particles with basic property by loading of the excess aluminum, since the pure alumina showed activity for the side reaction, as above.

The low selectivity observed on the Ga/MCM-41 points out that the strong Lewis acid site [12] enhanced only the side reaction. This is consistent with the low selectivity on the sulfated zirconia with Lewis-type superacidity as shown above. Addition of iron also generated no activity for the desired reaction. It is concluded that an acid site weaker than the threshold value of acid strength, <120 kJ mol^{-1} of the heat of ammonia adsorption for Brønsted and <130 kJ mol^{-1} for Lewis type, catalyzes the synthesis of methyl *N*-phenyl carbamate from aniline and dimethyl carbonate. Also lack of basic property is important to realize the desired reaction. It is noteworthy that the purely siliceous

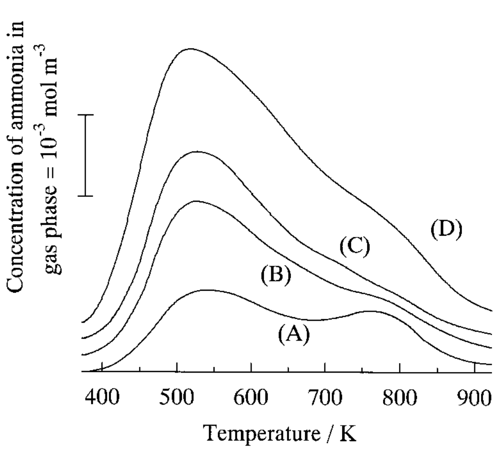

Figure 3. Ammonia TPD spectra on Al-impregnated MCM-41 (A: 0.83; B: 2.74; C: 4.58; D: 6.41 mol Al kg^{-1}) prepared using C_{14} template.

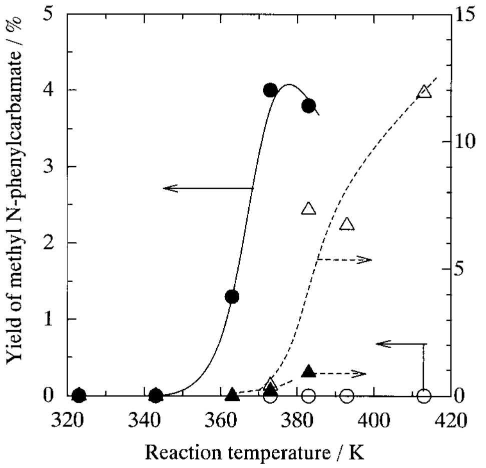

Figure 4. Yield of methyl *N*-phenyl carbamate (● and ○) and *N*-methyl aniline (▲ and △) on Al/MCM-41 (● and ▲, 2.74 mol Al kg^{-1}, impregnated in methanol) and that observed without catalyst (○ and △) at various temperatures for 2 h of reaction time.

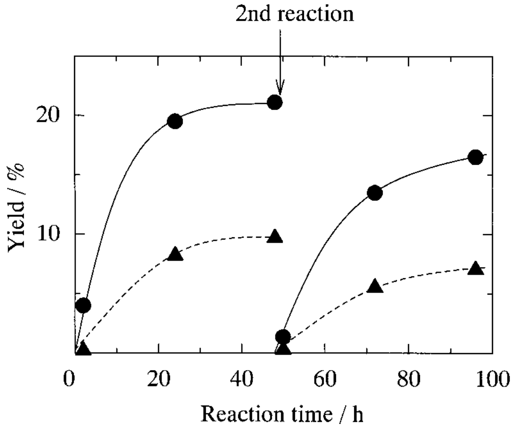

Figure 5. Yield of methyl *N*-phenyl carbamate (●) and *N*-methyl aniline (▲) on Al/MCM-41 (2.74 mol Al kg^{-1}, impregnated in methanol) against reaction time at 373 K. At 48 h, the catalyst was separated from the liquid and put into new reactant mixture.

MCM-41 showed a small activity for this reaction. It is possible that even the siliceous surface plays the role of acid, as some authors claimed that a quite weak acid site on pure SiO_2 mesoporous silica was responsible for such a facile reaction as isomerization of pinene [21].

It is emphasized that the amorphous silica–alumina N631L showed no activity for the desired reaction. This suggests that the efficiency of the porous structure and/or the specific microstructure of the silicate wall of MCM-41, which should be formed by varying the chain length of the template alkylammonium cation, were compared. The highest activity was observed on the Al/MCM-41 which had been synthesized with the C_{14} template.

The influence of the reaction temperature is shown in figure 4 (● and ▲). The methyl *N*-phenyl carbamate was produced at >360 K, but at too high a temperature (383 K), the yield was low probably because of the side reaction. The temperature 373 K gave the best yield of methyl *N*-phenyl carbamate.

Figure 5 shows that the yield of methyl *N*-phenyl carbamate on the Al/MCM-41 (2.74 mol Al kg^{-1}, impregnated in methanol) at 373 K gradually increased with the reaction time up to ~20% at 48 h. The catalyst was then separated from the reaction mixture by filtration and put into another new solution. It showed the activity again. The yield was lower than that observed in the first experiment, but it should be noted that the catalyst was re-used without any pretreatment. It is promising to regenerate the catalyst activity completely by oxidation of the adsorbed organic material.

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