Supplementary Information

Remarkable Acceleration of Cyanosilylation by Mesoporous Al-MCM-41 Catalyst

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Instruments

GC analysis was performed on a Shimadzu GC-14B gas chromatograph with an FID detector equipped with a DB-1 capillary column (J&W Scientific, 0.25 mm i.d. × 30 m). ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-Lambda 400 spectrometer at 400 and 100 MHz, respectively, in $CDCl_3$ with tetramethylsilane as an internal standard. Mesoporous materials were characterized by Bruker AXS D8-Advance X-ray diffractometer. The surface area and the pore volume were measured by nitrogen adsorption at 77 K using Bel Japan BELSORP-mini II. The pore size distribution was calculated from the adsorption branch of nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) method.

Materials

Al-MCM-41 was prepared by a direct hydrothermal synthesis method in an alkaline medium according to the literature[1] using cetyltrimethylammonium bromide (CTMABr, Tokyo Chemical Industry Co., Ltd.) as a template. The Si and Al sources were colloidal silica (Cataloid SI-30, 30 wt% SiO_2, Catalysis & Chemicals Ind. Co., Ltd.) and sodium aluminate (Wako Pure Chemical Ind., Ltd.), respectively. The molar ratio of CTMABr:SiO_2:$NaAlO_4$:NaOH:NH_3:H_2O was 1.1:20:1.0:5.5:1.1:940. The gel mixture was initially stirred for 1 h at room temperature, and then heated to 97 °C. After 1 day, the mixture was cooled to room temperature and the pH of the reaction mixture was adjusted to 10.2 by adding 30 wt% acetic acid. The heating and pH adjustment procedures were repeated twice. The resulting solid was filtered, washed with deionized water, dried at 97 °C, and then calcined in air at 550 °C for 18 h. The catalyst was subjected to the XRD (Fig. 1) and nitrogen adsorption measurements (Fig. 2). BET surface area: 969 $m^2\ g^{-1}$, pore volume: 1.14 $cm^3\ g^{-1}$; average pore diameter: 2.76 nm. Elemental analysis: Si 42.5%, Al 1.82%, Na 0.22%.

MCM-41 was prepared in the same manner, but sodium aluminate was not added to the synthesis mixture. BET surface area: 1056 $m^2\ g^{-1}$, pore volume: 1.06 $cm^3\ g^{-1}$, average pore diameter: 2.92 nm. Amorphous SiO_2-Al_2O_3 (Si/Al = 20) was prepared in the same manner, but CTMABr was not added to the synthesis mixture. BET surface area: 157 $m^2\ g^{-1}$, pore volume: 1.21 $cm^3\ g^{-1}$.

Amorphous SiO_2-Al_2O_3 (Si/Al = 2, JRC-SAH-1, BET surface area: 528 $m^2\ g^{-1}$, pore volume: 0.97 $cm^3\ g^{-1}$), amorphous SiO_2-Al_2O_3 (Si/Al = 5, JRC-SAL-2, BET surface area: 617 $m^2\ g^{-1}$, pore volume:

0.83 cm^3 g^{-1}), and γ-Al_2O_3 (JRC-ALO-8, BET surface area: 161 m^2 g^{-1}, pore volume: 1.46 cm^3 g^{-1}) were obtained from Catalysis Society of Japan as reference catalysts (JRC).

H-Y zeolite was prepared from Na-Y (Si/Al = 2.3, HSZ-320NAA, Tosoh Corp.) by an ion-exchanging method. Na-Y was treated in a 1 M NH_4Cl solution at 100 °C for 6 h. After cooling, the NH_4Cl solution was decanted. The exchange procedures were repeated three times. The solid was filtered, washed with deionized water, and dried at 97 °C. The zeolite sample was then calcined in air at 550 °C for 12 h. H-ZSM-5 was prepared in the same manner from Na-ZSM-5 (Si/Al = 11.9, HSZ-820NAA, Tosoh Corp.).

Dichrolomethane was distilled from CaH_2. Trimethylsilyl cyanide was purchased from Tokyo Chemical Industry Co., Ltd. and distilled prior to use. Benzaldehyde and cyclohexanone were used after distillation and the other carbonyl compounds were used as received.

Typical experimental procedure (Table 2, Entry 1)

Benzaldehyde (106 mg, 1.0 mmol) in dichloromethane (1.5 mL) was added to a suspension of Al-MCM-41 (5.0 mg), which was pretreated *in vacuo* at 120 °C for 1 h, and trimethylsilyl cyanide (TMSCN; 160 μL, 1.2 mmol) in dichloromethane (0.5 mL), and stirred at room temperature under an argon atmosphere. After 1 min, the catalyst was removed via filtration and the solvent was evaporated *in vacuo*. ^1H NMR analysis (400 MHz) of the product using 1,1,2,2-tetrachloroethane as an internal standard showed that α-(trimethylsiloxy)-phenylacetonitile was obtained in a quantitative yield. The product also gave a satisfactory ^{13}C NMR spectrum.

Flow reactor experiment (Figure 2)

The continuous cyanosilylation of benzaldehyde with TMSCN was carried out at room temperature in a fixed-bed flow reactor. The reactor was a Pyrex glass tube (4 mm inner diameter and 30 mm long), which was loaded with Al-MCM-41 (100 mg) pretreated *in vacuo* at 120 °C for 1 h. The liquid feed, which contained benzaldehyde (6.7 wt%), TMSCN (6.6 wt%) (molar ratio of benzaldehyde:TMSCN = 1:1.05), phenanthrene as an internal standard (1.8 wt%), and dichloromethane (for balance), was continuously introduced into the reactor with a syringe pump (Harvard type 55-1111, Harvard Apparatus Inc.) at a flow rate of 3.8 g h^{-1}. The weight hourly space velocity (WHSV) was 38 h^{-1}. The liquid products were collected for 1 min every hour and analyzed by GC. During the reaction, the color of the Al-MCM-41 catalyst changed from white to yellow. But the yellow color faded after washing the used Al-MCM-41 catalyst with dichloromethane and drying. The used catalyst thus recovered was subjected to the XRD (Fig. 3) and nitrogen adsorption measurements (Fig. 4, BET surface area: 764 m^2 g^{-1}, pore volume: 0.78 cm^3 g^{-1}, average pore diameter: 2.38 nm).

Reference

1. (*a*) J. M. Kim, J. H. Kwak, S. Jun and R. Ryoo, *J. Phys. Chem.*, 1995, **99**, 16742; (*b*) H. Nur, H. Hamid, S. Endud, H. Hamdan and Z. Ramli, *Mater. Chem. Phys.*, 2006, **96**, 337.

Characterization of Al-MCM-41

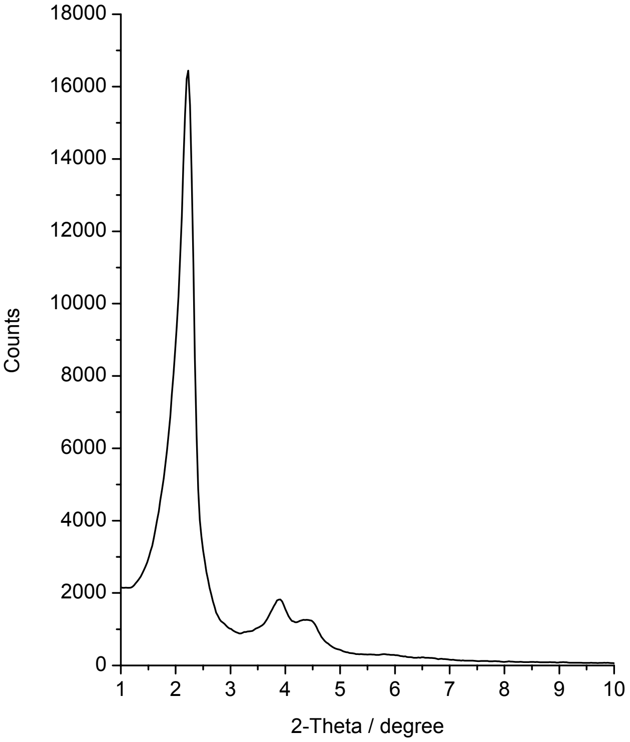


Fig. 1. XRD pattern of Al-MCM-41.

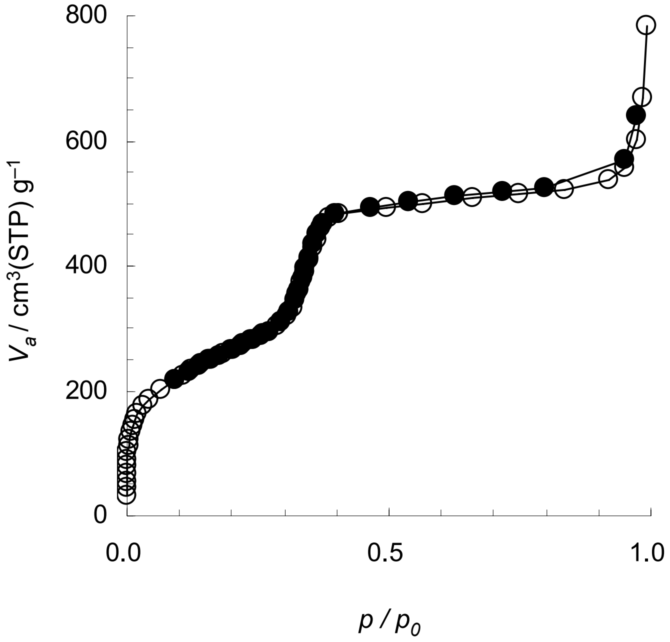


Fig. 2. N_2 adsorption–desorption isotherms of Al-MCM-41 at 77 K.

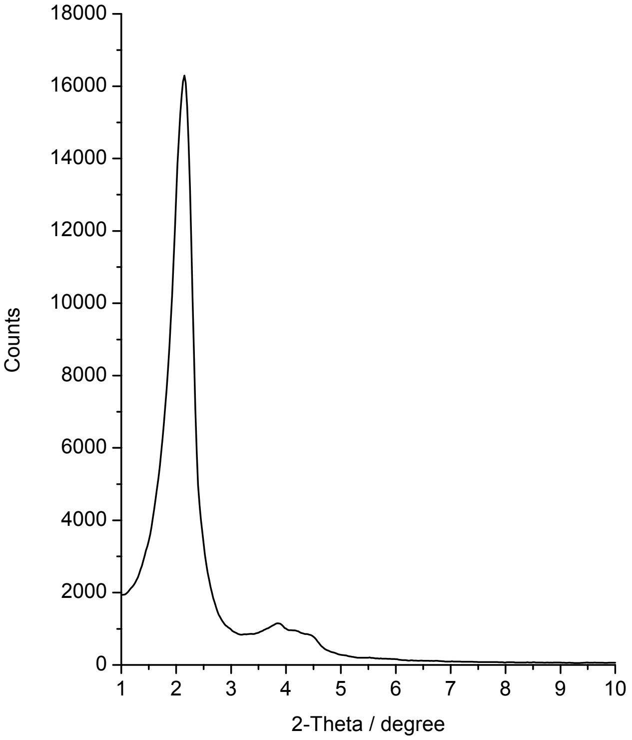


Fig. 3. XRD pattern of Al-MCM-41 used for the continuous flow reaction.

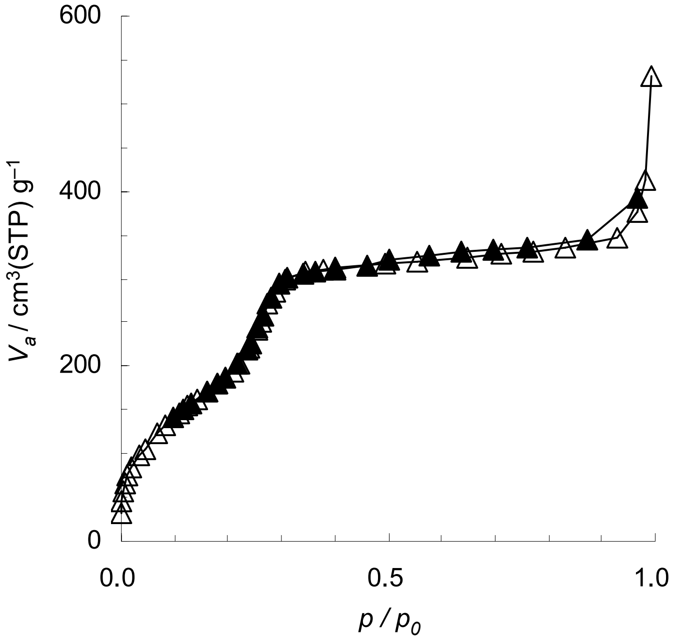
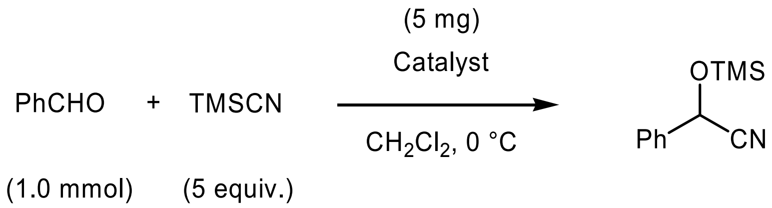


Fig. 4. N_2 adsorption–desorption isotherms of Al-MCM-41 used for the continuous flow reaction at 77 K.

Kinetic plots for cyanosilylation of benzaldehyde



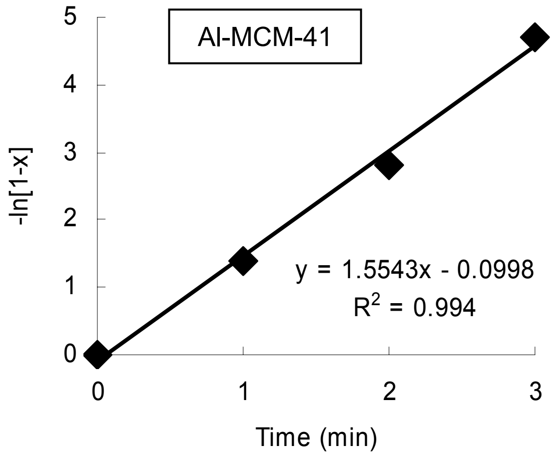


Fig. 5. Cyanosilylation of benzaldehyde catalyzed by Al-MCM-41 (x = [cyanohydrin]/[PhCHO]$_0$).

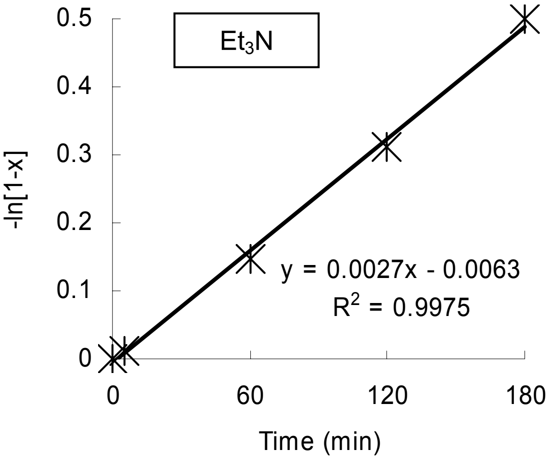
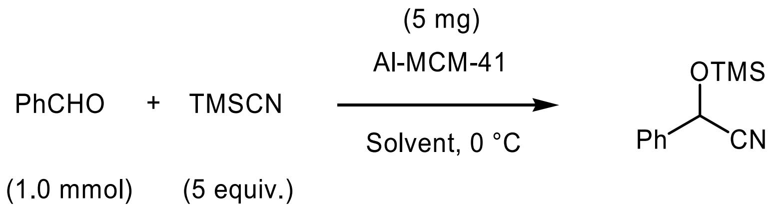


Fig. 6. Cyanosilylation of benzaldehyde catalyzed by Et$_3$N (x = [cyanohydrin]/[PhCHO]$_0$).

Effect of solvents



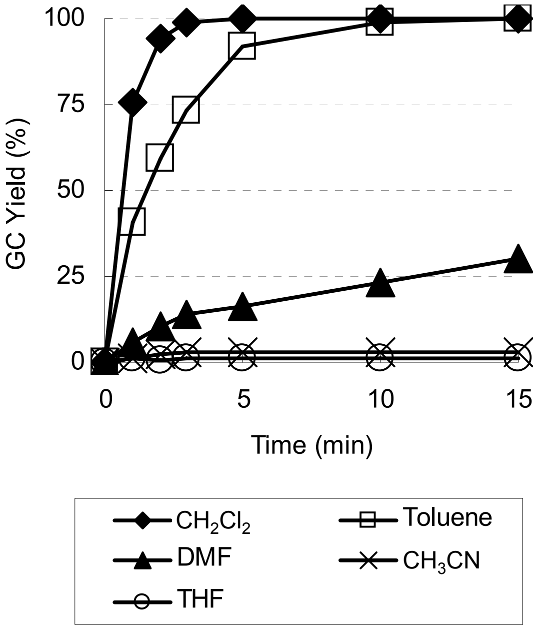


Fig. 7. Cyanosilylation of benzaldehyde in various solvents.