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Stepwise Direct Synthesis of Aluminosilicate Mesoporous Materials for Catalyst Supports

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Abstract

Aluminosilicate mesoporous materials (AIMS) were synthesized by two different methods. In “stepwise direct synthesis” of AIMS, sodium aluminate was added at the second ageing after the first ageing of sodium silicate and surfactant mixtures with the purpose of Al incorporation on or near the surface region of the pore wall in order to provide easily accessible ion-exchange sites. Most of the Al atoms in the AIMS prepared by the “stepwise direct synthesis” were present as tetrahedral-coordinated framework in the resulting mesostructured aluminosilicate of hexagonal symmetry. FT-IR spectra of pyridine adsorbed on the AIMS revealed that the AIMS prepared by the “stepwise direct synthesis” had a higher ratio of Brønsted acid sites to Lewis acid sites than the AIMS prepared by the conventional direct synthesis. Copper ion-exchanged AIMS (Cu/AIMS) catalysts were evaluated for NO reduction by CO. The Cu/AIMS catalyst prepared by the “stepwise direct synthesis” demonstrated catalytic activity for NO reduction without an aggregation of Cu species.

Key-words : Mesoporous material, Mesoporous aluminosilicate (AIMS), Catalyst support, Stepwise direct synthesis, NO reduction.

1. Introduction

Periodic mesoporous silicas have attracted much attention because of their high surface areas and uniform pore dimensions since their synthesis methods were first published¹⁻³⁾. Mesoporous silicas are promising materials for catalyst supports of reactions involving relatively large molecules because the pore diameter of mesoporous materials (2-50 nm diameter) is larger than that of zeolites. A lot of studies have been devoted to synthesis of hybrid-atom-containing mesoporous silicas in order to provide active sites for catalytic reactions, where the hybrid-atoms exist in the forms of, for example, substitution of silicon atoms⁴⁻⁶⁾, oxide particles⁷⁻⁹⁾, and metal particles¹⁰⁻¹²⁾. The hybrid-atoms, such as metal atoms, are dispersed at atomic level when zeolites are used as catalyst supports by ion-exchange method. However, aluminium

containing mesoporous silicas (mesoporous aluminosilicates, denoted as AIMS) have a lower ion-exchange capacity than zeolites due to two possible reasons. (i) AIMS materials show relatively low acidity¹³⁻¹⁵⁾ as compared to zeolites due to the amorphous nature of the pore wall and (ii) a part of the Al atoms in AIMS cannot provide accessible ion-exchange sites because they are buried inside the wall of silica framework¹⁶⁾. Recently, Mokaya^{17,18)} has proposed that AIMS can be prepared by stepwise post-synthesis alumination of mesoporous silicas, where the Al source is added to the synthesis gel containing calcined mesoporous silicas as a silica source in the secondary crystallization step^{19,20)} to insert Al atoms on or near the surface region of the pore wall, thus providing easily accessible ion-exchange sites. In these remarkable experiments, the AIMS prepared by the stepwise post-synthesis alumination method showed high ion-exchange capacity, however, 20 % of Al atoms were extra-framework Al in octahedral coordination. In this study, we develop a novel synthesis method for AIMS material -the “stepwise direct synthesis” method- where most of the Al atoms are tetrahedral-coordinated framework Al. In this synthesis technique employing sodium sili-

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cate and sodium aluminate, the sodium aluminate was added at the second ageing after the first ageing of the sodium silicate and surfactant mixtures. Furthermore, we have prepared copper ion-exchanged AlMS (Cu/AlMS) catalysts and investigated their catalytic activities for NO reduction by CO (NO + CO reaction) in order to reveal the nature of ion-exchange sites for AlMS samples prepared by both the “stepwise direct synthesis” and by the conventional direct synthesis.

2. Experimental

2.1 Sample preparation

We synthesized AlMS by two different methods. In one method, we prepared the AlMS by the “stepwise direct synthesis” method. First, 23.2 cm³ of distilled water, 5.4 cm³ of aqueous sodium silicate solution (Aldrich, Si : 0.034 mol), and 6.4 g of cetyltrimethylammonium chloride (CTAC, Wako, 0.020 mol) were mixed for 10 min at ambient temperature. The mixture, the pH of which was adjusted to 11 by addition of sulfuric acid, was heated at 373 K for 24 h in an autoclave (the first ageing). Then, 0.40–0.65 g of sodium aluminate (Kanto Kagaku, Al : $0.69\text{--}1.1 \times 10^{-3}$ mol), which was dissolved in 2.5 cm³ of distilled water, was added to the above suspension. The amount of sodium aluminate in the suspension was adjusted based on the desired molar ratio of Si to Al. The suspension, the pH of which was adjusted to 11 by addition of sulfuric acid, was again heated at 373 K for 24 h in the autoclave (the second ageing). The solid product was filtered, washed with distilled water, and then dried at 373 K for 12 h. The product (denoted as AlMS-A) was finally calcined at 823 K for 2 h in air.

In the other method, we prepared the AlMS using the conventional direct synthesis known in the literature²¹⁾. The four components, 23.2 cm³ of distilled water, 5.4 cm³ of aqueous sodium silicate solution, 6.4 g of CTAC, and 0.40–0.65 g of sodium aluminate were simultaneously mixed for 10 min at ambient temperature. The mixture, the pH of which was adjusted to 11 by addition of sulfuric acid, was heated at 373 K for 24 h in an autoclave. After another pH-adjustment and heat-treatment in the autoclave, the solid product (denoted as AlMS-B) was filtered, washed, dried, and calcined in the same procedure as AlMS-A.

Purely siliceous mesoporous silica (denoted as MS) was synthesized as a reference sample. Aqueous sodium silicate solution and CTAC were mixed and heated in the same procedure as AlMS-A without the addition of sodium aluminate at the second ageing.

The Cu/AlMS samples were prepared by ion-

exchange method using copper nitrate solution. Appropriate amount of aqueous Cu(NO₃)₂ (Wako) solution (0.01 mol dm⁻³) was used for the ion exchange. The pH during the ion exchange was 7.5. After continuous stirring for 24 h at room temperature, the samples were filtered, washed by distilled water several times, dried at 373 K for 3 h, and then calcined at 673 K for 2 h in air. The degree (%) of the ion exchange was defined as $2 \times (\text{Cu/Al}) \times 100$.

2.2 X-ray fluorescence analysis (XRF)

The molar ratios of Si to Al (Si/Al) for AlMS were determined by XRF using a JEOL JSX-3202. The Cu amount of Cu/AlMS was also estimated by XRF.

2.3 X-ray diffraction (XRD)

XRD patterns were recorded using a Philips X'Pert Pro with Cu K α radiation. Finely ground powder samples were mounted on glass holders for the XRD measurements.

2.4 Solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR)

²⁷Al MAS NMR spectra were recorded at 7.0 T using a JEOL JNM ECP-300. Chemical shifts were given in ppm from external Al [OCH(CH₃)₂]₃.

2.5 N₂ adsorption measurement

N₂ adsorption isotherms were measured at 77 K using a Quanta Chrome Autosorb-1. The surface area and pore size distribution were calculated using BET (Brunauer-Emmett-Teller) plots and BJH (Barrett-Joyner-Halenda) method, respectively.

2.6 Fourier transform infrared (FT-IR)

FT-IR spectra were measured in an IR cell with two NaCl windows on a JASCO FT/IR-410 spectrometer. The spectra were recorded with a 4 cm⁻¹ resolution in a range of 400–4000 cm⁻¹. The sample wafer (10 mg of proton ion-exchanged AlMS²²⁾, 2.0 cm diameter) was mounted in the cell, subjected to a pre-treatment under evacuation at 573 K for 1 h, cooled to 423 K, and then exposed to pyridine vapor (2.0×10^3 Pa) at 423 K for 30 min. FT-IR spectra for pyridine adsorbed on the AlMS were measured at ambient temperature after a removal of the physisorption of pyridine by evacuation at 573 K for 30 min. Difference FT-IR spectra of adsorbed pyridine were plotted after a subtraction of IR spectrum for the AlMS before the exposure of pyridine vapor.

2.7 Transmission electron microscopy (TEM)

TEM images were measured using a Hitachi H-7650 electron microscope with a cold field-emission gun operated at 120 kV. The Cu/AlMS samples were dispersed in ethanol, then suspended on holey carbon film for TEM measurement.

2.8 Catalytic reaction

Catalytic activities of the Cu/AlMS were evaluated using a fixed-bed continuous flow reactor. A reaction gas mixture containing NO (3%), CO (3%) and He (94%) was fed at a rate of $50 \text{ cm}^3 \text{ min}^{-1}$ ($\text{SV} = \text{ca. } 4300 \text{ h}^{-1}$). The effluent gas was analyzed by two on-line gas chromatographs (Shimadzu GC-8AIT) equipped with a Molecular Sieve 5A column (for the analysis of N_2 and CO) and a Unibeads C column (for analysis of CO_2 and N_2O). The reaction temperature was changed from 473 to 773 K in 50 K steps and the steady-state catalytic activity was measured at each temperature.

2.9 X-ray photoelectron spectroscopy (XPS)

XPS was recorded on a Shimadzu AXIS-HI spectrometer using an Mg $\text{K}\alpha$ source at an X-ray power of 120 W (accelerating voltage 12 kV, current 10 mA). The sample powder, which was mounted on a conductive tape, was introduced into the spectrometer chamber at about 10^{-7} Pa. The binding energies were referred to 284.2 eV for the C 1s level.

3. Results and discussion

3.1 Characterization of AlMS

XRD patterns in the 2θ range from 1.8 to 7° for the AlMS-A and AlMS-B with different Si/Al are shown in Figure 1. XRD patterns of the AlMS-A samples with Si/Al ratios of 11.7 and 19.4 (denoted as AlMS-A10 and AlMS-A20, respectively) exhibited three distinguishable peaks due to the hexagonal phase (MCM-41 type). The peaks due to the 100 reflection for the two different Si/Al ratios were observed at 3.86 and 3.67 nm of d-spacing (d_{100}), respectively. The d_{100} of the AlMS-B samples with Si/Al of 10.9 and 22.5 (denoted as AlMS-B10 and AlMS-B20, respectively) was 3.81 nm . The d_{100} and unit cell parameter (a_0) for the different AlMS samples are summarized in Table 1. The results revealed that aluminosilicate mesoporous materials of the hexagonal phase with almost similar d_{100} were synthesized by means of the two methods, the stepwise direct synthesis method and the conventional direct synthesis method.

Fig. 1 XRD patterns of (a) AlMS-A10, (b) AlMS-A20, (c) AlMS-B10, and (d) AlMS-B20.

Fig. 2 ^{27}Al MAS NMR spectra of (a) AlMS-A10, (b) AlMS-A20, (c) AlMS-B10, and (d) AlMS-B20.

Table 1 The properties of AlMSs and MS.

Sample	Si/Al ratio	d_{100}/nm	a_0^a/nm	Pore diameter/nm	PWT ^b /nm	BET surface area/ m^2g^{-1}
AlMS-A10	11.7	3.86	4.46	2.18	2.28	713
AlMS-A20	19.4	3.67	4.24	2.74	1.50	888
AlMS-B10	10.9	3.81	4.40	2.20	2.20	721
AlMS-B20	22.5	3.81	4.40	2.73	1.67	927
MS	∞	3.39	3.92	2.46	1.46	1273

^a Calculated $a_0 = 2d_{100}/\sqrt{3}$. ^b PWT (pore wall thickness) = a_0 - pore diameter.

In order to investigate the local structure of Al atoms in the AIMS, ^{27}Al MAS NMR spectra were measured, as shown in Figure 2. All AIMS exhibited a peak at about 50 ppm due to tetrahedral-coordinated framework Al^{23} , while a very weak peak at about 0 ppm due to extra-framework Al in octahedral coordination was observed. The peak areas at 0 ppm of all AIMS after a subtraction of the satellite peaks, which were estimated by the peak deconvolution, were less than 2% of the peak areas at 50 ppm. This result revealed that most of the Al atoms were tetrahedral-coordinated framework Al in the mesostructured aluminosilicate for all the AIMS prepared in this study. In the case of

AIMS-A, Al atoms could be successfully inserted in the silica framework during the second ageing.

The N_2 adsorption-desorption isotherms and pore size distributions of the AIMS-A10, AIMS-A20, AIMS-B10, and AIMS-B20 are shown in Figure 3. The isotherms are of type IV, as defined by IUPAC, and are typical of mesoporous materials. The BET surface areas of the AIMS-A10 and AIMS-A20 were 713 and 888 $\text{m}^2 \text{g}^{-1}$ and the average pore sizes were 2.18 and 2.74 nm, respectively. Pore wall thickness (PWT) was also estimated by the difference between the unit cell parameter a_0 and the pore diameter, as summarized in Table 1. PWTs for the AIMS-A increased with Al content, compared with MS, showing that additional Al added not only onto the outer surfaces of MS but also inside the MS channels during the second ageing. The pore diameter for AIMS-A20 would be smaller than MS if the aluminosilicate had formed inside the MS channels during the second ageing. In fact the contrary was observed, which may be explained by taking into account that the bond length of Al-O is longer than that of the Si-O bond. PWTs for the AIMS-B also increased with Al content because the source of Al formed the walls of AIMS faster than the source of Si during simultaneous ageing.

Proton ion-exchanged AIMS, used for pyridine molecule adsorption FT-IR measurements, were prepared from as-synthesized AIMS by following the procedure outlined in the literature²²⁾. Initially, the as-synthesized AIMS and an ethanolic NH_4NO_3 solution were stirred at 333 K. The AIMS was then filtered, washed

Fig. 3 (a) N_2 adsorption (open mark) -desorption (closed mark) isotherms and (b) the pore size distributions for AIMS-A10 (circle) and AIMS-A20 (triangle). (c) N_2 adsorption (open mark) -desorption (closed mark) isotherms and (d) the pore size distributions for AIMS-B10 (circle) and AIMS-B20 (triangle).

Fig. 4 Difference FT-IR spectra of pyridine adsorbed on (a) AIMS-A10, (b) AIMS-A20, (c) AIMS-B10, and (d) AIMS-B20.

with ethanol, dried at 373 K, and calcined at 673 K for 2 h in air. The mesostructure of the proton ion-exchanged AIMS retained the mesostructure of the corresponding as-synthesized AIMS. Figure 4 shows the difference FT-IR spectra of pyridine adsorbed on the AIMS-A10, AIMS-A20, AIMS-B10, and AIMS-B20 at ambient temperature. The two peaks at 1550 and 1455 cm^{-1} are assigned to protonated pyridine on Brønsted acid sites and pyridine coordinatively bound to Lewis acid sites, respectively¹⁵⁾. The ratios of Brønsted acid sites to Lewis acid sites (C_B/C_L) for the AIMS-A10, AIMS-A20, AIMS-B10, and AIMS-B20 were calculated to be 0.39, 0.22, 0.23, and 0.19, respectively, from the peak intensities at 1550 and 1455 cm^{-1} using the appropriate extinction coefficients²⁴⁾. In the case of both AIMS-A and AIMS-B, C_B/C_L reasonably increased with Al content. The C_B/C_L of AIMS-A was larger than that of AIMS-B with same Al content, although most of Al atoms for both AIMS-A and AIMS-B were inserted into the silica framework in tetrahedral coordination. This result indicated that Al atoms in the AIMS-A were mainly distributed on or near the surface of the silica wall so that they made accessible Brønsted acid sites. On the other hand, Al atoms in the AIMS-B were evenly distributed inside the wall of silica framework so that a part of Al atoms could not provide accessible acid sites for pyridine molecules.

3.2 Characterization of Cu/AIMS and its catalytic activity

The XRD patterns in the 2θ range from 1.8 to 7° of the Cu/AIMS samples reveal that the prepared catalysts retained their hexagonal mesostructures. The degree of ion-exchange (IE) for Cu/AIMS was defined as the percentage of Cu atoms irrespective of relevance to ion-exchange using the following formula: $\text{IE} = 2 \times (\text{Cu}/\text{Al}) \times 100$, as summarized in Table 2. The IE increased with C_B/C_L independent of the preparation method and the Si/Al. This result suggests that Brønsted acid sites of the AIMS form the effective ion-exchange sites. XRD patterns of the Cu/AIMS-A10 and Cu/AIMS-B10 before the NO + CO reaction measured in the 2θ range from 10 to 50° are shown in Figures 5 (a) and (b), respectively. No peaks due to Cu species, such as CuO, Cu₂O and Cu metal, were observed in the XRD patterns, indicating that copper species in the Cu/AIMS-A10 and Cu/AIMS-B10 were highly dispersed in the AIMS channels.

The NO conversions for the NO + CO reaction by the Cu/AIMS-A10 and Cu/AIMS-B10 samples, which were previously subjected to a pre-treatment at 673 K

Table 2 The properties of Cu/AIMS catalysts.

Sample	Si/Al	C_B/C_L^a	Cu ion-exchange degree/%
Cu/AIMS-A10	11.7	0.39	94
Cu/AIMS-A20	19.4	0.22	82
Cu/AIMS-B10	10.9	0.23	86
Cu/AIMS-B20	22.5	0.19	75

^a The ratio of Brønsted acid sites to Lewis acid sites for AIMS before Cu ion-exchange.

Fig. 5 XRD patterns of (a) Cu/AIMS-A10 before the NO + CO reaction, (b) Cu/AIMS-B10 before the reaction, (c) the Cu/AIMS-A10 after the reaction, and (d) the Cu/AIMS-B20 after the reaction.

Fig. 6 Conversion of NO by (open circle) Cu/AIMS-A10 and (open square) Cu/AIMS-B10.

for 1 h in a flow of He, are depicted against the reaction temperature in Figure 6. The conversions in the figure represent the percentage decrease of gas phase NO. NO conversions for both Cu/AIMS-A10 and Cu/AIMS-B10 catalysts increased at ca. 523 K. This result indicates that the Cu/AIMS-A10 and Cu/AIMS-B10 catalysts had catalytic activity for NO reduction by CO.

The peaks at 43.4 and 50.4° of Fig. 5 (d) for the Cu/AIMS-B10 after the NO + CO reaction showed that cubic Cu metal (JCPDS Card Files, 4-836) par-

Fig. 7 TEM images of (a) Cu/AlMS-A10 and (b) Cu/AlMS-B10 after the NO + CO reaction.

ticles were formed. On the other hand, copper species in the Cu/AlMS-A10 after the reaction were highly dispersed in the AlMS channels as evidenced by no XRD peaks in Fig. 5 (c). Figure 7 shows TEM images of the Cu/AlMS-A10 and Cu/AlMS-B10 catalysts after the NO + CO reaction. Copper species in the Cu/AlMS-A10 after the reaction were not observed as shown in Fig. 7 (a). This leads us to believe that the copper species of the Cu/AlMS-A10 were highly dispersed in the AlMS channels. On the other hand, Cu metal particles with a mean diameter of 15-20 nm were observed in the Cu/AlMS-B10 after the NO + CO reaction, as shown in Fig. 7 (b), in agreement with the result of XRD measurement. XPS for Cu/AlMS before and after the reaction were also measured to confirm the valence states of Cu atoms. These spectra are shown in Figure 8. Before the NO + CO reaction intense Cu 2p_{1/2} and 2p_{3/2} peaks were observed at 953.8 and 933.9 eV, as shown in Figs. 8 (a) and (b). Thus, most of Cu atoms in Cu/AlMS before the reaction are postulated to be dispersed as isolated Cu²⁺ ions in AlMS^{25,26}. In case of the Cu/AlMS-A10 sample, after the reaction the XPS peaks did not shift

Fig. 8 XPS of (a) Cu/AlMS-A10 before the NO + CO reaction, (b) Cu/AlMS-B10 before the reaction, (c) the Cu/AlMS-A10 after the reaction, and (d) the Cu/AlMS-B20 after the reaction.

in binding energy, indicating that the Cu atoms in Cu/AlMS remained dispersed as isolated Cu²⁺ ions in the AlMS channels. On the other hand, in case of the Cu/AlMS-B10 sample, after the reaction Cu 2p_{1/2} and 2p_{3/2} peaks due to Cu metal were observed at 952.8 and 932.6 eV. The results of XRD, TEM, and XPS reveal that Cu metal particles were formed in the Cu/AlMS-B10 after the NO + CO reaction.

In the case of Cu/AlMS-A because the accessible Brønsted acid sites exist on or near the surface of the wall according to the FT-IR measurement, therefore the copper species in the Cu/AlMS-A were highly dispersed after the reaction. Similar to Cu ion-exchanged zeolites (typically Cu/ZSM-5), which have a unique catalytic property for NO decomposition²⁷⁻²⁹), we suggest that isolated Cu species are located near Al atoms in the silica framework of the Cu/AlMS-A resulting in a high catalytic activity for NO reduction without an aggregation of Cu species³⁰⁻³²). On the other hand, the copper atoms in the Cu/AlMS-B after the reaction were aggregated to form Cu metal particles because the AlMS-B had fewer accessible Brønsted acid sites than the AlMS-A. Hence, the AlMS prepared by the stepwise direct synthesis method had a higher number of Brønsted acid sites in comparison to the AlMS prepared by the conventional direct synthesis method and is a promising material as a catalyst support.

Detailed knowledge of the acidity of the AlMS materials is important for understanding their properties as catalyst supports. The number of acid sites as well

as their strength can be determined by measuring temperature-programmed desorption of ammonia. We are planning to investigate the acidity of the AlMS materials in detail and prepare AlMS supported catalysts based on other metals.

4. Conclusions

Aluminosilicate mesoporous materials (AlMS) with the hexagonal phase, of which most Al atoms are tetrahedral-coordinated framework Al, were synthesized by two different methods. The AlMS prepared by the stepwise direct synthesis (AlMS-A) had a higher ratio of Brønsted acid sites to Lewis acid sites than the AlMS prepared by the conventional direct synthesis. Al atoms in the AlMS-A were mainly distributed on or near the surface of the silica framework so that they made accessible Brønsted acid sites. Copper ion-exchanged AlMS-A showed catalytic activity for NO reduction without an aggregation of Cu species, similar to Cu ion-exchanged zeolites. It has been demonstrated that the AlMS prepared by the stepwise direct synthesis is a promising material as a catalyst support.

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触媒担体のためのメソポーラスアルミノシリケートの段階的直接合成法

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要 旨

メソポーラスアルミノシリケート (AIMS) を2種類の方法で調製した。AIMSの“段階的直接合成法”においては、アルミニウムを細孔壁表面あるいは近傍に導入しイオン交換サイトを発現させることを目的として、ケイ酸ナトリウムと界面活性剤混合物の第一段階熟成を行った後、アルミン酸ナトリウムを加えて第二段階熟成を行った。“段階的直接合成法”で調製したAIMSのほとんどのアルミニウム原子は骨格内に取り込まれた4配位サイトに位置しており、AIMSのメソ細孔はヘキサゴナルな配列を有している。AIMS上の吸着ピリジンのFT-IRスペクトルから、従来の直接合成法で調製したAIMSよりも“段階的直接合成法”で調製したAIMSのほうが、ルイス酸に対するブレンステッド酸の比が高いことが明らかになった。それぞれのAIMSを担体とした銅イオン交換AIMS (Cu/AIMS) を調製し、COによるNOの還元反応に対する活性を評価した。“段階的直接合成法”で調製したCu/AIMSは銅種が凝集することなくNO還元反応に対して高い活性を示すことが明らかになった。