Preparation and Characterization of Polyamine-functionalized Mesoporous Silica

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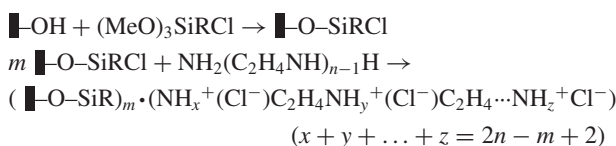*79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501*
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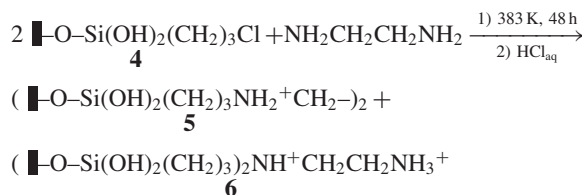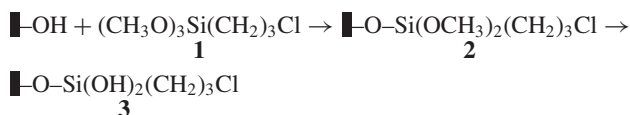
Polyamine-functionalized mesoporous MCM-41 and SBA-15 were synthesized by the substitution of surface chloroalkyl group by linear polyamines. The structure of the functional group was determined by elemental analysis, ^{29}Si and ^{13}C MAS NMR, and IR spectroscopy to explore the effects of chain length and pore size on aqueous ion adsorption capability.

The adsorption of toxic ions is one of the most intriguing applications of functionalized mesoporous silicas. Among the commonly available synthetic adsorbents, amine-functionalized MCM-41, MCM-48, and SBA-1 show high adsorption capacities for the type of oxyanions that cause groundwater contamination, such as arsenate and chromate.[1] Furthermore, a considerable amount of Fe^{3+} and Cu^{2+} can also be trapped by these functionalized silicas, which have been proved to work as selective adsorption sites for arsenate, selenate, and chromate ions.[2–4] Although the grafting of aminosilane is a facile way of achieving amine-functionalization, the kinds of commercially available silanes are limited, which restricts the range of variation of the surface functional groups. The effect of chain length of the amine in a mesopore is another issue of interest that has so far only been compared between $NH_2(CH_2)_3-$, $NH_2(CH_2)_2NH(CH_2)_3-$, and $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_3-$ in terms of oxyanion adsorption.[1] Since a wide variety of polyamines can be easily obtained, we propose here a general and versatile method for functionalization with polyamine chains using the reaction between a polyamine molecule and a chloroalkyl group pre-grafted onto the mesopore surface. The procedure is presented by the following scheme where ▮– = silica site.

▮–OH + (MeO)$_3$SiRCl → ▮–O–SiRCl

m ▮–O–SiRCl + NH$_2$(C$_2$H$_4$NH)$_{n-1}$H →

(▮–O–SiR)$_m$·(NH$_x^+$(Cl$^-$)C$_2$H$_4$NH$_y^+$(Cl$^-$)C$_2$H$_4$···NH$_z^+$Cl$^-$)

$$(x + y + \ldots + z = 2n - m + 2)$$

This method can basically be applied to all kinds of linear polyamines.

The synthesis of MCM-41 (BET specific surface area (S_{BET}) = 1011 m^2 g^{-1} and pore diameter ($2R_p$) = 2.9 nm) and the grafting of 3-chloropropyltrimethoxysilane were carried out according to Ref. 1. The resulting 3-chloropropylsilylated MCM-41 is denoted as ClPrM41. The reaction of ethylenediamine (EDA) with ClPrM41 produced a diamino-functionalized MCM-41 (EDA-PrM41);

▮–OH + (CH$_3$O)$_3$Si(CH$_2$)$_3$Cl → ▮–O–Si(OCH$_3$)$_2$(CH$_2$)$_3$Cl →
                       1   **2**

▮–O–Si(OH)$_2$(CH$_2$)$_3$Cl
         3

2 ▮–O–Si(OH)$_2$(CH$_2$)$_3$Cl +NH$_2$CH$_2$CH$_2$NH$_2$ $\xrightarrow[\text{2) HCl}_{aq}]{\text{1) 383 K, 48 h}}$
      4

(▮–O–Si(OH)$_2$(CH$_2$)$_3$NH$_2^+$CH$_2$–)$_2$ +
      5

(▮–O–Si(OH)$_2$(CH$_2$)$_3$)$_2$NH$^+$CH$_2$CH$_2$NH$_3^+$
      6

The structure of **2** was determined by ^{29}Si MAS NMR [δ -109.1 (Q^4), -101.3 (Q^3), and -49.6 (T^1)] and ^{13}C CP-MAS NMR [δ 7.6 (α-carbon), 26.2 and 23.9 (β-carbon), 46.1 (γ-carbon), and 49.4 (–OCH$_3$)]. The peaks due to T^2 and T^3 Si were not found in the 29Si MAS NMR spectrum. Elemental analysis (C/N = 4.3), IR absorption (1648 cm^{-1} (–N$^+$H$_2$–), 1596 cm^{-1} (–N$^+$H$_3$ asymmetric), 1506 cm^{-1} (–N$^+$H$_3$ symmetric), and 1456 cm^{-1} (–CH$_2$–) in conjunction with ^{13}C CP-MAS NMR [δ 8.3 (α-carbon), 22.2 (β-carbon), 39.8 (ε-carbon), and 50 (γ and δ-carbons)] demonstrated that the stoichiometry of the fixation (ClPr:EDA) was 2:1 and also that primary and secondary amines were present. Therefore, the possible structures of EDA–PrM41 are the bridge **5** and the bicrural **6** forms. We also carried out reactions with diethylenetriamine ($n = 3$; DETA), triethylenetetramine ($n = 4$; TETA), tetraethylenepentamine ($n = 5$; TEPA), and pentaethylenehexamine ($n = 6$; PEHA) to produce DETA–, TETA–, TEPA–, and PEHA–PrM41, respectively. The result of elemental analysis of these (C/N = 3.1, 2.9, 3.1, and 2.8 for DETA–, TETA–, TEPA–, and PEHA–PrM41, respectively) implies that the mode of polyamine fixation is the same as EDA–PrM41, i.e. that the stoichiometry of PrM41: amine is 2:1. Although the IR band at 1648 cm^{-1} was stronger than that at 1596 cm^{-1} in EDA–PrM41, the former band appeared as a shoulder peak of the latter band in DETA– and TETA–PrM41. The dominant vicinal-bridge formations, i.e. the 1,4-attachment in DETA–PrM41 and the 1,4- and 1,7-attachments in TETA–PrM41, can be used to explain the alternation of the intensities of the IR bands.

When we grafted chloromethyltrimethoxysilane instead of 3-chloropropyltrimethoxysilane, the amino group that was finally obtained was a "linear" chain, ▮–O–Si(OH)$_2$CH$_2$NH$_2^+$CH$_2$-CH$_2$NH$_3^+$ (determined by the result of elemental analysis C/N = 1.6). We believe that the formation of a different structure from that in EDA–PrM41 is due to the short chain length of methylene and the small degree of freedom in the conformation of the chloromethyl group.

These polyamine-functionalized MCM-41 moieties showed large adsorption capacities for both cations and anions. For the series of polyamines based on PrM41, the adsorption capacity for Fe^{3+} increased monotonously with the number of amino groups in the chain, as shown in Table 1. The measured Fe/N ratio, 0.20–0.29, implies that the average coordination structure

is four amine ligands around one Fe^{3+}-center. In terms of arsenate adsorption, the value of As/N for EDA–PrM41 (0.23) is almost the same as for $NH_2CH_2CH_2NHPrSi(OCH_3)_3$-grafted MCM-41 (As/N = 0.22).[1] The even number effect, where the adsorption is enhanced when the number of amino groups in a polyamine molecule is even, can be clearly identified in Table 1, suggesting that the diamine and tetramine coordinations are especially stable and form the major structures of the adsorption site.

Table 1. Specific adsorption of ferric ions and arsenate ions on polyamine-functionalized MCM-41

Amine	EDA	DETA	TETA	TEPA	PEHA
adsorption of Fe^{3+} (mg g^{-1})	16	22	23	25	30
Fe/N	0.23	0.29	0.23	0.22	0.20
adsorption of $HAsO_4^{2-}$ (mg g^{-1})	42	36	69	50	73
As/N	0.23	0.19	0.27	0.18	0.19

When SBA-15 (prepared according to the literature,[5] $S_{BET} = 640\,m^2\,g^{-1}$, and $2R_p = 8.2\,nm$) was used in grafting 3-chloropropyltrimethoxysilane to produce ClPrS15 instead of ClPrM41, the reaction with polyamine differed from that with MCM-41. The ratio of C/N in the elemental analysis (2.8, 2.8, 3.0, 2.5, and 2.7 for EDA–, DETA–, TETA–, TEPA–, and PEHA–PrS15, respectively) reveals that the stoichiometry of ClPrS15:EDA is 1:1, while it changed to 2:1 when converted to TETA, TEPA, and PEHA. C/N for DETA (2.8) is somewhere between 1:1 (theoretically C/N = 2.333) and 2:1 (theoretically C/N = 3.333) stoichiometries, suggesting that both fixation modes coexist. The gradual change of the stoichiometry can be reasonably explained by the larger distance between the chloropropyl groups on the surface of ClPrS15 than on ClPrM41. The bridging of two chloropropyl groups by an EDA molecule is impossible but is possible for TETA or larger amine molecules on ClPrS15, while all polyamine molecules was settled through the stoichiometry of ClPrM41:amine = 2:1 on ClPrM41. Thus the most likely structures of EDA–, DETA–, and TETA–PrS15 are linear, linear + 1,7-bridge, and 1,10-bridge, respectively. These proposed structures are supported by their IR spectra.

Although the measured averages over the whole solid were 1.3 and 1.2 Cl/nm^2 for ClPrS15 and ClPrM41, respectively, it

has frequently been claimed that the grafted functional groups are localized and that the population in such a localized region will be a key factor for determining the microstructure of organic groups. The value of Fe/N in Fe^{3+} adsorption on the polyamine-functionalized SBA-15 was 0.50 ± 0.15, as shown in Table 2, which was larger than that for the MCM-41-derived adsorbent. This result also implies a lower surface density of amino groups in SBA-15 than in MCM-41. In terms of adsorption capacity for arsenate ions, the even number effect was not found, unlike the case of MCM-41. The As/N ratio decreased according as the number of amino groups in the polyamine chain.

Table 2. Specific adsorptions of ferric ions and arsenate ions on polyamine-functionalized SBA-15

Amine	EDA	DETA	TETA	TEPA	PEHA
adsorption of Fe^{3+} (mg g^{-1})	50	47	34	34	51
Fe/N	0.50	0.66	0.48	0.33	0.54
adsorption of $HAsO_4^{2-}$ (mg g^{-1})	84	59	39	45	36
As/N	0.36	0.33	0.22	0.18	0.16

The difference in the mode of amine fixation and the different adsorption behavior can be explained by the pore size and the density of Si–OH groups in the mesoporous silicas. The effect of confinement by mesopores on the structure of the functional groups and their coordination to the ions are under investigation by using a series of polyamine-functionalized Cab-o-sil M-7D samples ($S_{BET} = 200\,m^2\,g^{-1}$ and non-porous).

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