Adsorption of Carbon Dioxide on Amine Modified SBA-15 in the Presence of Water Vapor

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Novel CO_2 adsorbents were prepared by grafting of various aminosilanes on mesoporous silica SBA-15. CO_2 adsorption capacities of aminosilane modified SBA-15 in the presence of water vapor were comparable to those in the absence of water vapor. It was found that efficiency of amine increased with increasing surface density of amine.

Organically functionalized mesoporous silicas have been considered as potential catalysts and adsorbents.[1–7] Among various modified mesoporous silicas, amine modified mesoporous silicas are particularly interesting materials because of their wide spread applications. It have been reported that they exhibited high performance for adsorption of heavy metals,[3] gasses,[4,5] and proteins[6] as well as base catalyzed reactions.[7]

Recently, CO_2 separation technology has attracted considerable attention, because CO_2 capture and sequestration is one of the options to reduce CO_2 emission. However, the costs of CO_2 separation from flue gasses are accounted for approximately 70–80% of total energy cost for CO_2 sequestration. Therefore, it is important to develop a new efficient and energy-saving technique for CO_2 separation. As for the conventional PSA or PTSA process using zeolite, a dehumidification process which consumes approximately 30% of total energy is necessary, because water vapor is adsorbed more strongly than CO_2 on zeolite surface. Therefore, development of a new adsorbent which is able to adsorb CO_2 in the presence of water vapor is required.[8,9] In this letter, it was demonstrated that amine modified SBA-15 is effective for separation of CO_2 from gasses containing water vapor. Furthermore, it was found that surface density of amine is important factor for the reaction of CO_2 with amine immobilized on mesoporous support.

SBA-15 was prepared according to previous report.[10] Modification of SBA-15 was performed by grafting method using aminosilanes. Aminosilane (50 cm^3) and SBA-15 (5.0 g) which was previously dried at 398 K for 6 h in air were refluxed in dehydrated toluene (250 cm^3) at 383 K for 24 h under Ar flow. Products were washed with toluene (200 cm^3) and dried at 333 K over night. 3-aminopropyltriethoxysilane (denoted as APS) (Aldrich), *N*-(2-aminoethyl)-3-aminopropyltriethoxysilane (AEAPS) (Chisso Chem. Co.) and (3-trimethoxysilylpropyl)-diethylenetriamine (TA) (Gelest Inc.) were used as grafting agents. The obtained samples were denoted as APS/SBA, AEAPS/SBA and TA/SBA, respectively. APS/SBA(i) was prepared by the impregnation of 3-aminopropyltriethoxysilane into SBA-15.

Physical and chemical properties of adsorbents are summarized in Table 1. Although grafting of SBA-15 with aminosilanes resulted in decreasing surface areas, surface areas of amine grafted SBA-15 were much higher than that of impregnated sample (APS/SBA(i)). Pore volumes of amine grafted SBA-15 were close to those expected from aminosilane loadings. Furthermore, narrow pore size distributions were retained for amine grafted SBA-15. These results suggest that, for the amine grafted SBA-15, aminosilans were uniformly anchored on SBA-15 surface without pore plugging. On the other hand, the mesopore of impregnated sample (APS/SBA(i)) was plugged with amine compound.

CO_2 adsorption capacities of various adsorbents at 333 K in the absence and presence of water vapor are also summarized in Table 1. Adsorption performance of Na–Y and USY were very low in the presence of water vapor. On the other hand, although SBA-15 support alone did not adsorb CO_2, amine grafted SBA-15 adsorbed considerable amounts of CO_2 in the absence and presence of water vapor. It should be noted that these amine grafted SBA-15 gave similar adsorption capacity in the presence and absence of water vapor. Adsorption property of amine grafted SBA-15 was very different from that of APS/SBA(i). In the case of APS/SBA(i), sorption of CO_2 was observed only in the presence of water vapor. In spite of the low surface area, CO_2 sorption capacity of APS/SBA(i) was much higher than those of amine grafted SBA-15 in the presence of water vapor. However, it is evident from the breakthrough curves (Figure 1) that the rate of CO_2 sorption on APS/SBA(i) is much lower than

Table 1. Physicochemical properties and CO_2 adsorption performances of various adsorbents

Adsorbent	SA[a] /m^2·g^{-1}	V$_p$[b] (calc.[c]) /cm^3·g^{-1}	Amine content[d] /N-mmol·g^{-1}	CO_2 adsorption capacity/mmol·g^{-1} (Amine efficiency[e]/-) 0%-H_2O[f]	12%-H_2O[g]
SBA-15	910	1.06 (-)	-	0.05	0.04
APS/SBA	360	0.53 (0.51)	2.7	0.52 (0.19)	0.50 (0.19)
AEAPS/SBA	310	0.47 (0.45)	4.2	0.87 (0.21)	0.90 (0.21)
TA/SBA	240	0.37 (0.36)	5.1	1.10 (0.22)	1.21 (0.24)
APS/SBA(i)	2	0	6.0	0.14 (0.01)	2.32 (0.39)
Na–Y (Si/Al=2.7)[h]	830	0.34	-	1.23	0.03
USY (Si/Al=380)[i]	760	0.23	-	0.07	0.07

[a] Surface area calculated by BET method. [b] Pore volume measured by N_2 adsorption at 77 K. [c] Pore volume expected from aminosilane loadings. [d] The number of nitrogen atom per 1 gram of adsorbent. [e] Efficiency = (adsorbed CO_2 / amine content). [f] 15%-CO_2, N_2 balance. [g] 15%-CO_2, 12%-H_2O, N_2 balance. [h] Tosoh Co., HSZ-320NAA. [i] Tosoh Co., HSZ-390HUA.

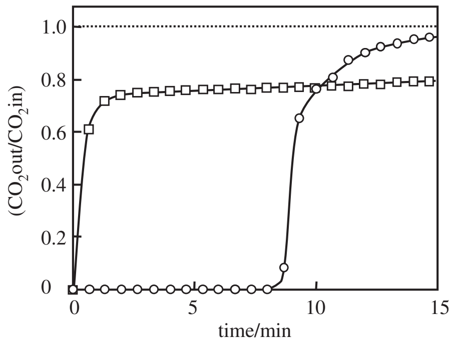

Figure 1. Breakthrough curves of CO_2 at 333 K over TA/SBA (○) and APS/SBA(i) (□). The mixture of 15% CO_2, 12% H_2O with N_2 balance (total flow rate: $30\,cm^3{\cdot}min^{-1}$) was fed to the adsorbent (1.5 g).

those on amine grafted SBA-15. This result indicate that amine–CO_2 reaction on amine grafted SBA-15 proceeds immediately, since these amine compounds were anchored and distributed on the surface of mesoporous support.

Regeneration of amine grafted SBA-15 was performed by heating the adsorbents up to 423 K in He flow after adsorption at 333 K. The typical desorption curves for TA/SBA and APS/SBA(i) are shown in Figure 2. Amounts of CO_2 desorbed from the adsorbents were consistent with the amounts of adsorbed CO_2. Furthermore, adsorption performance of these adsorbents was recovered by heating up to 423 K. Amine grafted SBA-15 was more rapidly regenerated than APS/SBA(i). These adsorption–desorption properties of amine grafted SBA-15 demonstrate that these adsorbents are effective for CO_2 separation from gases containing water vapor.

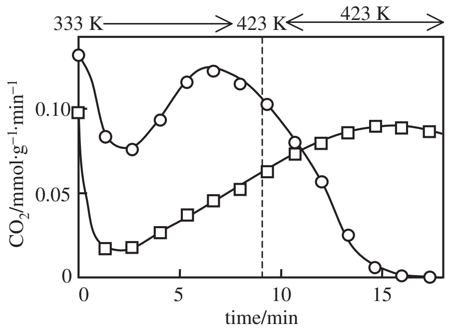

Figure 2. Desorption curves of CO_2 in He flow ($30\,cm^3\,min^{-1}$) from TA/SBA (○) and APS/SBA(i) (□) after adsorption (333 K, CO_2(15%)–H_2O(12%)–N_2(balance)).

As shown in Table 1, CO_2 adsorption capacities of amine grafted SBA-15 were increased with increasing in amine content. However, the CO_2 adsorption capacities were not simply proportional to amine content. Figure 3 shows relationship between surface density of amine and amine efficiency. It should be noted that amine efficiency increased with increasing surface density of amine. This result indicates that distance of amine is important factor for CO_2 adsorption. Adsorption of CO_2 on amine grafted SBA-15 would proceed through formation of ammonium carbamate (Eq 1).[11] In the IR spectra of APS/SBA after CO_2 adsorption, absorption bands at $3439\,cm^{-1}$ and $1630\,cm^{-1}$ were observed, and they would be attributed to N–H stretch and C=O stretch of ammonium carbamate, respectively.

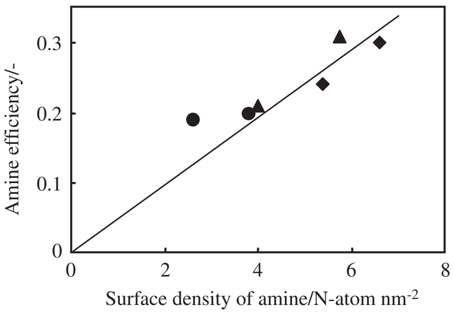

Figure 3. Relationship between amine efficiency and surface density of amine. Amine efficiency was defined as adsorbed CO_2 (mmol·g^{-1}) per amine content (mmol·g^{-1}) and calculated from amount of adsorbed CO_2 at 333 K with CO_2(15%)–H_2O(12%)–N_2(74%). Surface density of amine was defined as the number of nitrogen atom per 1 nm^2 of SBA-15 surface. (●) APS, (▲) AEAPS, (◆) TA.

$$2\text{R-NH}_2 + CO_2 \rightarrow \text{R-NHCOO}^- + \text{R-NH}_3^+ \qquad (1)$$

According to Eq 1, a pair of amino groups is required to form ammonium carbamate. Therefore, it was suggested that isolated amine on SBA-15 surface would not effective for CO_2 adsorption and densely anchored aminosilane would be effective adsorption site.

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