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Amino Silica Gels Acting as a Carbon Dioxide Absorbent

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Amino silica gels, silica gels bound with amines through covalent bond, were prepared by hydrolysis-condensation polymerization using three aminoalkyltrimethoxysilanes. The 2-[4-(2-aminoethylaminomethyl)phenyl]ethyl group absorbed CO_2 with equal efficiency both in the silica gel and in the aminoalkyltrimethoxysilane. Suspension of amino silica gels in DMF and in water absorbed CO_2 effectively and reversibly.

Development of efficient methods of CO_2 recovery from industrial waste gases is important in relation to both reutilization of CO_2 as carbon resources and an atmospheric environmental issue concerned with "the greenhouse effect".

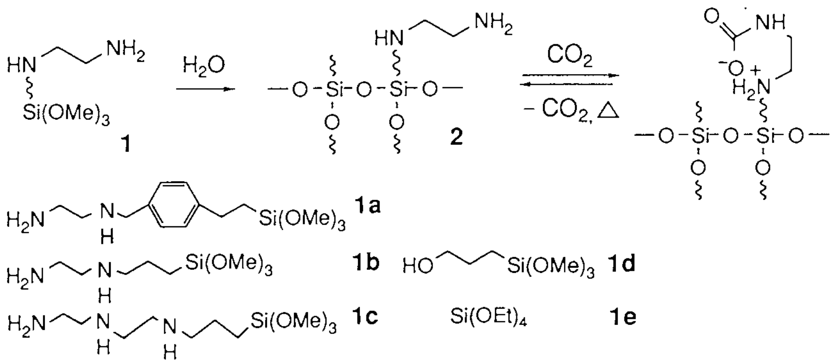
One of the most commonly used processes for CO_2 recovery nowadays is chemical CO_2 absorption using aqueous solution of amines such as mono- and diethanolamines (Eqs. 1 and 2).[1] Synthesis of efficient solid CO_2 absorbents by attaching amines to solid supports through covalent bond is interesting because of their easy handling and recovery for reusing. To our knowledge, however, there is no report on this kind of solid CO_2 absorbents.[2] Here we report amino silica gels acting as a carbon dioxide absorbent.

$$2\ RR'NH + CO_2 \rightleftharpoons RR'NCO_2^{-}\ {}^{+}NRR'H_2 \qquad (1)$$

$$RR'NCO_2^{-}\ {}^{+}NRR'H_2 + H_2O \longrightarrow HCO_3^{-}\ {}^{+}NH_2RR' + RR'NH \qquad (2)$$

Twelve amino silica gels **2a**-**2cde** listed in Table 1 were prepared according to Scheme 1 using hydrolysis-condensation polymerization of three aminoalkyltrimethoxysilanes containing an ethylenediamine moiety, that is, 2-[4-(2-aminoethylaminomethyl)phenyl]ethyltrimethoxysilane(**1a**), 3-(2-aminoethylaminopropyl)trimethoxysilane(**1b**), and 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (**1c**) with and without alkoxysilanes having no amino group, i. e., 3-hydroxypropyltrimethoxysilane(**1d**) and tetraethoxysilane(**1e**). Amino silica gels obtained were white to pale yellow powders.

A CO_2 absorption experiment was carried out under a nitrogen atmosphere using the amino silica gel of about 0.1 g in a 290 ml two-necked flask closed with a rubber



Scheme 1 .

Table 1. CO_2 uptake (CO_2 mmol / gel g) by amino silica gels **2** at 30 °C[a)]

Comonomer	Aminoalkyltrimethoxysilane		
	1a [0.21]	**1b** [0.28]	**1c** [0.17]
———	1.2 (**2a**) [0.19]	0.28 (**2b**) [0.025]	0.72 (**2c**) [0.063]
1d	0.72 (**2ad**) [0.21]	0.33 (**2bd**) [0.081]	0.57 (**2cd**) [0.10]
1e	1.1 (**2ae**) [0.25]	0.22 (**2be**) [0.030]	0.17 (**2ce**) [0.018]
1d + **1e**	0.41 (**2ade**) [0.13]	0.22 (**2bde**) [0.043]	0.57 (**2cde**) [0.11]

a) The value in [ ] is CO_2 mol / N gram atom.

septum. An excess of CO_2 gas, usually 20.0 ml, and 10.0 ml of methane gas as a GC (gas chromatography) internal standard were added through the rubber septum by a hypodermic syringe and the CO_2 absorption was monitored by GC. In the case of the CO_2 absorption by an amino silica gel suspension (vide post), a dispersion medium of 2.50 ml was used.

CO_2 absorption capacity (CO_2 mmol/gel g) of **2a**-**2cde** was determined at 30 °C under a nitrogen atmosphere, where CO_2 uptake presumably occurs according to Eq. 1. The results are summarized in Table 1. CO_2 absorption by amino silica gels gradually proceeded to reach approximately constant values after 2-7 h, which are listed in Table 1. Amino silica gels containing a phenyl group generally exhibited greater CO_2 absorption capacity than those not having the phenyl group. A silica gel having no amino group prepared from an equimolar mixture of **1d** and **1e** showed only CO_2 uptake of 0.055 (CO_2 mmol/gel g). This finding suggests that CO_2 uptake by amino silica gels **2a**-**2cde** is mainly caused by chemical interaction between the amino group and CO_2, i. e., carbamate formation (Eq. 1). There is presently no decisive explanation of the unique function of the phenyl group. Analysis of a surface structure of the gel by ESCA or electron microscope did not differentiate **2a** from **2b**. The phenyl group might alter a gel structure by its steric bulkiness to generate an environment to favor the interaction of the amino group with CO_2.

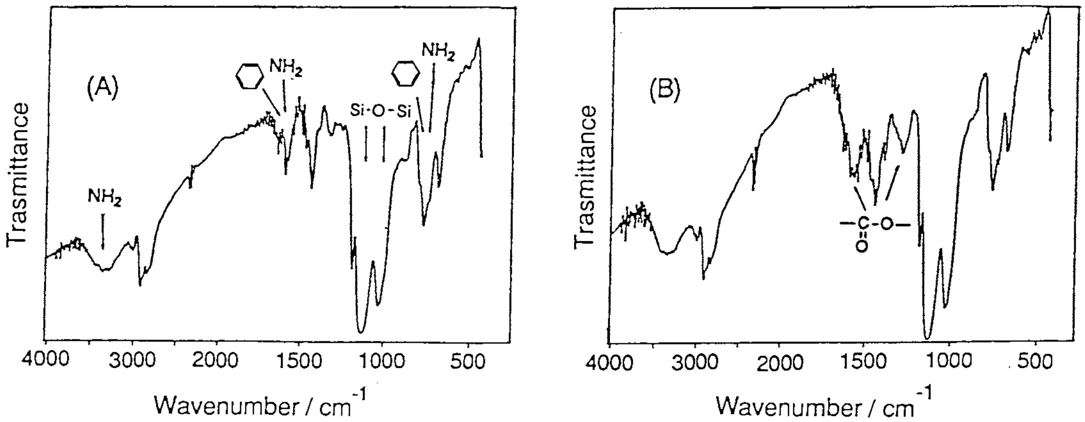


Fig. 1. IR spectrum of the amino silica gel **2a** (A) and the carboxylated amino silica gel **2a** (B).

The CO_2 moiety fixed in **2a** was demonstrated by IR spectroscopy and gasometry. Thus, the carboxylated **2a** prepared from **2a** and CO_2 of ordinary pressure showed two broad IR absorptions at 1580 and 1330 cm^{-1} (Fig. 1B), which were not observed in **2a** (Fig. 1A). The carboxylated **2a** prepared under CO_2 pressure of 50 kg/cm^2 exhibited these two absorptions with increased intensities. These carboxylated **2a** evolved CO_2 gas by heating at 120 °C to restore the original IR spectrum of **2a**. Ammonium carbamate[3)] is known to absorb at 1485 and 1265 cm^{-1} and transition metal carbamate compounds are reported to show strong IR absorptions assignable to an NCO_2 moiety in the region of 1685-1560 cm^{-1}.[4)]

The CO_2 absorption capacity per one nitrogen atom (CO_2 mol/N gram atom) of **2a**-**2cde** determined on the basis of their nitrogen elemental analyses are also summarized in Table 1. CO_2 uptake by aminoalkyltrimethoxysilanes **1a**-**c** was also measured (Table 1). It is noteworthy that the nitrogen atom of **2a**, **2ad**, and **2ae** exhibited the CO_2 absorption capacity similar to that of the nitrogen atom of **1a**, that is, the 2-[4-(2-aminoethylaminomethyl)phenyl]ethyl group absorbed CO_2 with equal efficiency both in silica gels **2a**, **2ad**, and **2ae** and in the liquid aminoalkyltrimethoxysilane **1a**. Enhancing effect of coexistence of a hydroxy group upon the CO_2 absorption by the amino silica gel is observed for **2bd**, **2bde**, **2cd**, and **2cde** (Table 1) although not marked.

Table 2. CO_2 uptake (CO_2 mol / N gram atom) by amino silica gels **2** and amines **1** at 30 °C[a)]

Gel	**2a**		**2b**
	in DMF	in H_2O	in DMF
	0.37 [2.6]	0.33 [2.3]	0.36 [4.1]
Amine	**1a** in DMF		**1b** in DMF
	0.34		0.43

a) The value in [ ] is CO_2 mmol / gel g.

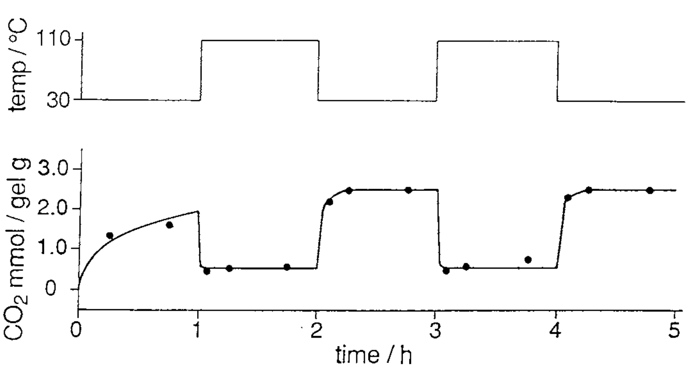


Fig. 2. Reversible CO_2 uptake by **2a** in DMF.

Interestingly coexistence of a polar organic solvent of dimethylformamide (DMF) remarkably enhanced the CO_2 absorption capacity of **2a** along with **2b** under nitrogen atmosphere as is shown in Table 2. There was no difference between the CO_2 absorption capacity (CO_2 mol/N gram atom) of **2a** and that of **2b**, that is, the unique effect of the pheny group of **2a** observed in the solid state disappeared in the DMF suspension. It is noteworthy that **2a** and **2b** had the similar CO_2 absorption capacity to that of the liquid aminoalkyltrimethoxysilanes **1a** and **1b** in DMF, respectively. This finding means that the liquid CO_2 absorbents of **1a** and **1b** could be "solidified" without reducing their CO_2 absorption capacity by their conversion into the amino silica gels **2a** and **2b**. One possible explanation for the enhancing effect of DMF upon the CO_2 absorption is stabilization of the ammonium carbamate intermediate by solvation.

Reversibility of CO_2 absorption by the amino silica gel at 30 °C and CO_2 release from the carboxylated amino silica gel by heating was examined. Such property is indispensable for a CO_2 absorbent. Amino silica gels **2a**, **2ad**, and **2ae** were able to uptake CO_2 reversibly. The reversible CO_2 uptake by the suspension of **2a** in DMF is shown in Fig. 2, which also indicates the rapid CO_2 absorption in DMF after heating.

Amino silica gel **2a** also effectively absorbed CO_2 in water (Table 2), where CO_2 uptake presumably proceeds by intermediacy of the ammonium bicarbonate species of eq 2. Heating the carboxylated **2a** in water evolves CO_2 gas: the CO_2 absorption by **2a** in water at 80 °C was 1.47 (CO_2 mmol/gel g).

Thus, the suspension of the amino silica gel in DMF or water acts as an effective CO_2 absorbent. It is formally situated between a liquid CO_2 absorbent and a solid CO_2 absorbent: it retains a feature of the liquid CO_2 absorbent, i. e., the high CO_2 absorption capacity and it also has a characteristic of the solid CO_2 absorbent, i. e., facile recovery of the absorbent by filtration. The CO_2 absorption capacity (CO_2 mmol/gel g) of **2a-b** in DMF or water is comparable to that[5] of solid CO_2 absorbents of zeolites, which are a representative solid CO_2 absorbent absorbing CO_2 physically.

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References

1) See, for example, G. Sartori and D. W. Savage, Ind. Eng. Chem. Fundam., 22, 239, (1983) and references therein.
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