

Polyethyleneimine and Macrocylic Polyamine Silica Gels Acting as Carbon Dioxide Absorbents

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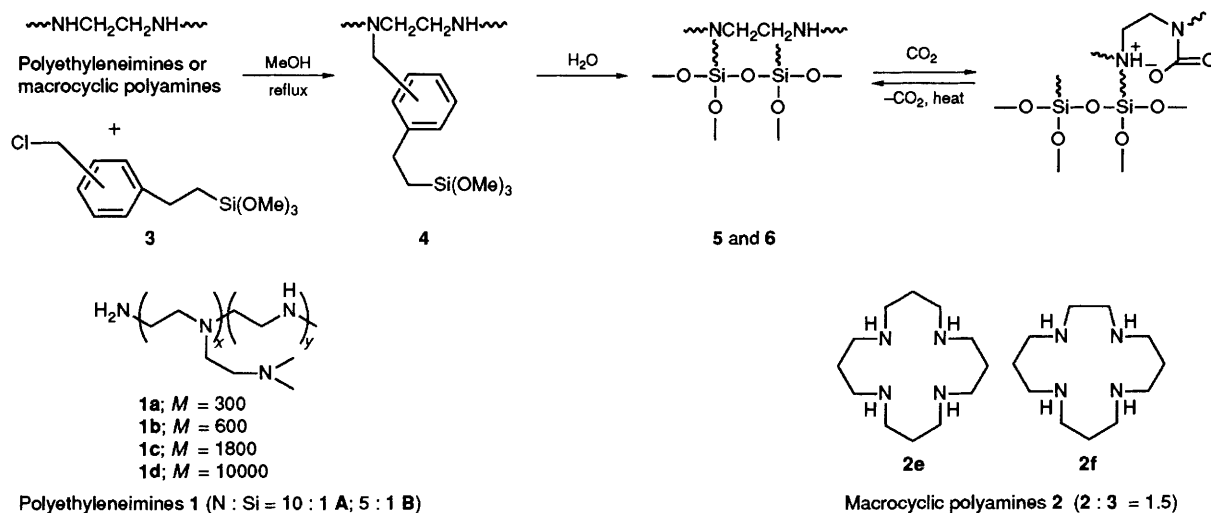
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A dimethylformamide or water suspension of amino-silica gels, which are silica gels bound with polyethyleneimines or macrocylic polyamines through a covalent bond, absorbed CO₂ effectively and reversibly.

Development of efficient methods of CO₂ recovery from industrial waste gases *etc.* is important in relation to both reutilization of CO₂ as carbon resources and an atmospheric environmental issue concerned with the 'greenhouse effect'.

One of the most commonly used processes for CO₂ recovery is chemical absorption using an aqueous solution of amines

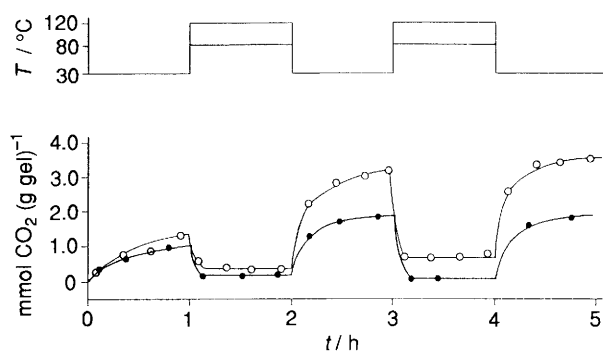
[eqns. (1) and (2)].¹ Synthesis of a solid CO₂ absorbent of amino-silica gels by attaching amines to silica gels through a covalent bond is interesting because of their high CO₂ absorption capacity along with their easy handling and recovery. To our knowledge, however, there is no report on this kind of solid CO₂ absorbents.² Here we report CO₂



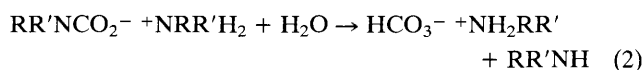
Scheme 1

Table 1 CO₂ uptake/mol CO₂ (g N atom)⁻¹ by polyethyleneimine silica gels **5** and polyethyleneimines **1** in DMF at 30 °C^a

N:Si ^b	M = 300 1a	M = 600 1b	M = 1800 1c	M = 10000 1d
10:1(A)	0.27 [3.7] (5aA)	0.30 [5.1] (5bA)	0.31 [4.8] (5cA)	0.20 [3.1] (5dA)
5:1(B)	0.27 [3.5] (5aB)	0.30 [3.5] (5bB)	0.29 [3.3] (5cB)	0.19 [2.4] (5dB)
Polyethyl- eneimine	0.38	0.33	0.31	0.27

^a Values in square brackets are measured in mmol CO₂ (g gel)⁻¹.^b Feed ratio.**Fig. 1** Reversible CO₂ uptake by **5bB** (○, 120 °C) and **6e** (●, 80 °C) in DMF

uptake by amino-silica gels derived from polyamines such as polyethyleneimines and macrocyclic polyamines from the standpoint of developing an efficient CO₂ absorbent.

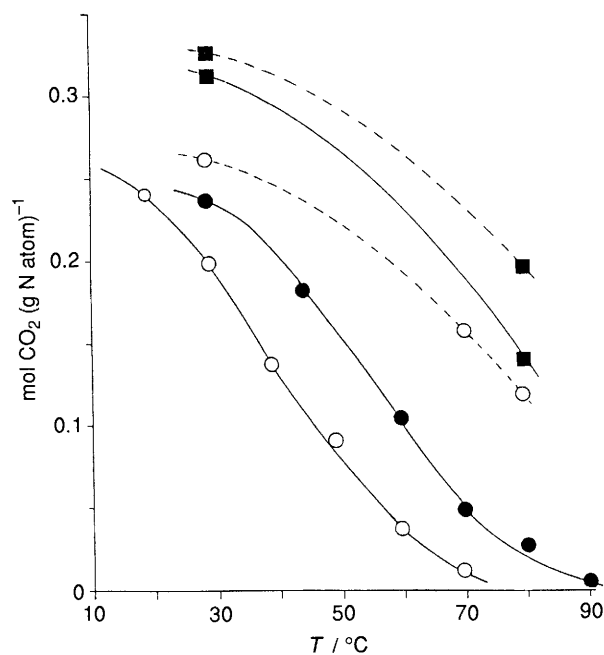


Eight polyethyleneimine silica gels **5aA–dB** derived from four polyethyleneimines **1a–d** having different molecular masses and two macrocyclic polyamine silica gels **6e** and **f** derived from **2e** and **f** were prepared according to Scheme 1 using hydrolysis–condensation polymerization of **4** prepared *in situ* by alkylation of **1** and **2** with **3**. The amino-silica gels obtained were white to pale-yellow powders.

A CO₂ absorption experiment was carried out under a nitrogen atmosphere using the amino-silica gel (*ca.* 0.1 g) in a 290 ml two-necked flask closed with a rubber septum. An excess of CO₂ 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 CO₂ absorption was monitored by GC. In the case of the CO₂ absorption by an amino-silica gel suspension, a dispersion medium of 2.50 ml was used.

CO₂ absorption by **5aA–dB** and **6e** and **f** at 30 °C under a nitrogen atmosphere, where the CO₂ absorption presumably takes place according to eqn. (1), proceeded slowly to show low CO₂ absorption capacity of 0.3–0.7 mmol CO₂ (g gel)⁻¹ after *ca.* 3 h.

The CO₂ moiety fixed in the amino-silica gel **6e** was demonstrated by IR spectroscopy and gasometry. Thus, the carboxylated **6e** showed two broad IR absorptions assignable to the CO₂ moiety^{2,3} at 1580 and 1330 cm⁻¹, which were not

**Fig. 2** Temperature dependence of CO₂ uptake by amino-silica gels in DMF (—) and in H₂O (---) for **6e** (●), **6f** (○) and **5cA** (■)

observed in **6e**. The carboxylated **6e** prepared under a CO₂ pressure of 50 kg cm⁻² exhibited these two absorptions with increased intensities. The carboxylated **6e** evolved CO₂ gas by heating at 120 °C to restore the original IR spectrum of **6e**.

Interestingly, the addition of a polar solvent such as dimethylformamide (DMF) or water was found to promote remarkably the CO₂ absorption of **5aA–dB**. Thus, their suspensions in DMF exhibited a much greater CO₂ absorption capacity than that of **5aA–dB** themselves, the activities were determined after *ca.* 1 h and are shown in Table 1.

CO₂ absorption capacity per nitrogen atom [mol CO₂ (g N atom)⁻¹] of **5aA–dB** in DMF was calculated using their nitrogen elemental analyses, which are also included in Table 1 together with that of **1a–d** in DMF. It is noteworthy that, in DMF, the nitrogen atom of **5aA–dB** exhibited similar CO₂ absorption capacity to that of the nitrogen atom of **1a–d**. In other words, liquid polyethyleneimines could be 'solidified' without reducing their CO₂ absorption capacity by their conversion into polyethyleneimine silica gels. The DMF suspension of macrocyclic polyamine silica gels behaved similarly; CO₂ absorption capacities of **6e** and **6f** were 1.9 and 1.8 mmol CO₂ (g gel)⁻¹ [0.23 and 0.20 mol CO₂ (g N atom)⁻¹], respectively.

A suspension of **5bA** or **6f** in water also absorbed CO₂ effectively; 5.0 and 2.3 mmol CO₂ (g gel)⁻¹ [0.32 and 0.26 mol CO₂ (g N atom)⁻¹], respectively, where CO₂ uptake presumably proceeds by intermediacy of the ammonium hydrogencarbonate as shown in eqn. (2). By comparison, the CO₂ absorption capacity of **1b** and **2f** in water were 0.34 and 0.48 mol CO₂ (g N atom)⁻¹, respectively.

Reversibility of CO₂ absorption by the amino-silica gel at 30 °C and CO₂ release from the carboxylated amino-silica gel by heating was demonstrated in DMF using **5bB** and **6e** (Fig. 1).

Fig. 2 shows temperature dependence of CO₂ absorption of the amino-silica gels. Macrocyclic polyamine silica gels are featured with facile CO₂ release in DMF at lower temperature.

Thus, the suspension of the amino-silica gel in DMF or water acts as an effective CO₂ absorbent. It is formally situated between a liquid CO₂ absorbent and a solid CO₂ absorbent: it retains a feature of the liquid CO₂ absorbent, *i.e.* the high CO₂ absorption capacity and it also has a character-

istic of the solid CO₂ absorbent, *i.e.* facile recovery of the absorbent by filtration. The CO₂ absorption capacity [mmol CO₂ (g gel)⁻¹] of **5aA–dB** and **6e–f** in DMF or water is comparable to that⁴ of solid CO₂ absorbents of zeolites, which are a representative solid CO₂ absorbent absorbing CO₂ physically.

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References

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