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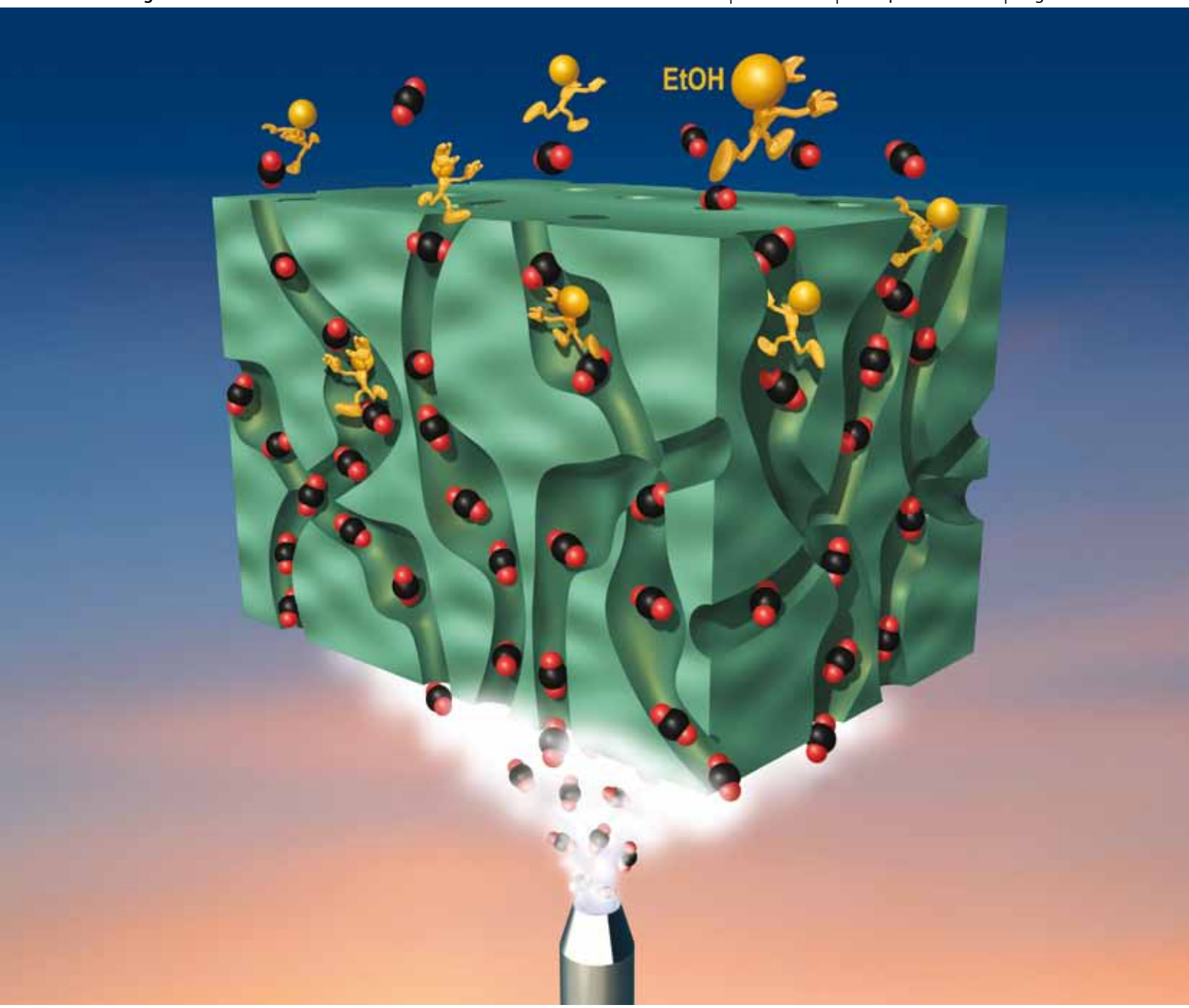

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Metal organic gels (MOGs): a new class of sorbents for CO_2 separation applications†

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MOGs with excellent thermal stability and porosity have been synthesized at room temperature. The strength of the MOGs obtained depend on the raw materials used, reaction time, temperature, concentration of reactants and the processing conditions. MOGs with higher internal surface areas were obtained using near supercritical processing conditions. Measurement of CO_2 sorption isotherm of MOG-1a at high pressure (30 bar) suggests 33 wt% (7.5 mmol g^{-1}) of CO_2 with a reversible uptake and release. To our knowledge this is the first study on the utilization of the MOGs for CO_2 capture applications. Significant uptake of CO_2 at high pressure (~30 bar) clearly reveals the significant potential of these materials for their applications as solid sorbents.

Fossil fuels constitute about 85% of the total world energy needs and still remain as the major source of anthropogenic carbon dioxide (CO_2). In recent year's significant attention have been devoted to identifying various classes of materials to capture and separate the carbon dioxide from various point sources. Working in this line of direction, researchers across the world including us have developed various classes of materials including zeolites, metal–organic frameworks (MOFs),[1] zeolite imidazolate frameworks (ZIFs),[2] porous membranes[3] and aqueous alkyl amine solutions[4] to capture and separate CO_2 economically.[5] Among all these materials, MOFs have been shown to be very attractive due to their high mass flux, thermal stability, tunable porosity and ease in synthesis, however a key challenge is to produce these materials in a desired shape.[6] In contrast, very little attention has been devoted to the development of metal–organic gels (MOGs), which provide a desired shape with relatively lower cost and have large interior surface areas with irregular open pores. Also it is very important to note that the formation of MOGs have been observed in many instances when multipodal ligands (with Fe and Cr) are used in regular MOF synthesis and are completely neglected until today. In continuation of our research efforts[7] to develop various classes of compounds for effective CO_2 capture, we herein present the synthesis of MOG-**1** and MOG-**2** and their CO_2 sorption properties. To our knowledge this is the first study on the utilization of MOGs for CO_2 capture applications.

MOG-**1** was synthesized by slightly modifying the procedure reported by Kaskel and co-workers.[8] Typically 0.2 M ethanolic solutions of $Fe(NO_3)_3 \cdot 9H_2O$ or $FeCl_3$ and 1,3,5 benzene tricarboxylic acid were mixed (3 : 2; total volume 20 mL) at room temperature or at higher temperature (in case of $FeCl_3$). Formation of MOG-**1** occurred instantaneously in case of $Fe(NO_3)_3$ whereas with $FeCl_3$ the weak gel is obtained after ~6–10 h at 65 °C and in both cases the gel is allowed to age for about 24 h. Thus obtained **MOG-1** was further purified to remove the excess unreacted starting materials using Soxhlet extractor. After purification, the gel is placed in a pressure cell and charged with 50 bar CO_2 at room temperature for 24 h to replace the solvent ethanol in the pores by gas CO_2 (Fig. 1). Subsequent drying at 80 °C; or at room temperature in vacuum desiccator led to the formation of MOG-**1a–b**.

Several experiments were performed to understand the effect of reaction conditions on the gelation time. In one experiment the concentration of the 1,3,5-benzene tricarboxylic acid was varied keeping the concentration of iron salt constant, in another experiment the concentration of the iron salt kept constant and varied the concentration of 1,3,5-benzene tricarboxylic acid. We realized that pragmatic gelation time curtails with the increase in the concentration of starting materials. The weak gels obtained with lower concentration (~0.05 M or Low) of $Fe(NO_3)_3$ or $FeCl_3$ and 1,3,5-benzene tricarboxylic acid experienced difficulties in purification using a Soxhlet extractor. The strength of the gels obtained depends on the raw materials, time, temperature and their concentrations.

We also investigated the effect of processing conditions on the overall efficacy of the gels obtained. We performed the BET surface

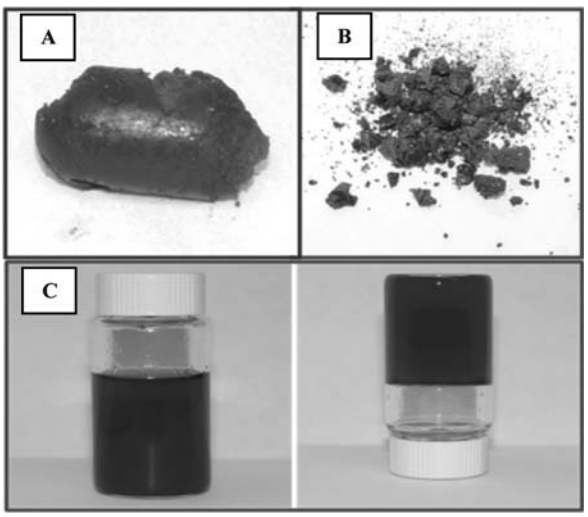

Fig. 1 (A) MOG-**1** obtained using $Fe(NO_3)_3$ and 1,3,5-benzene tricarboxylic acid after purification using soxhlet extractor. (B) Illustration of MOG-**1a** drying at 80 °C in vacuum desiccators. (C) MOG-**2** obtained using $FeCl_3$ and 1,3,5-benzene tricarboxylic acid before purification using soxhlet extractor.

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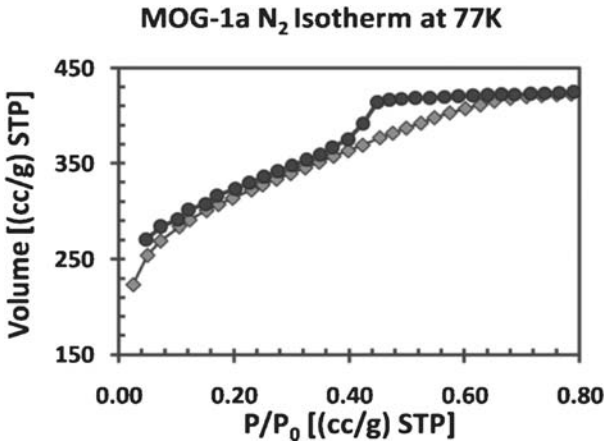

Fig. 2 BET surface area measurements on MOG-**1a** at 77 K using liquid nitrogen. Diamonds and circles represent adsorption and desoprtion respectively.

area analysis on three samples obtained from the MOG-**1** processed under different conditions MOG-**1a–c** with and without CO_2 at RT and 80 °C in vacuum desiccators. In order to investigate the porosity of the MOGs obtained under various conditions, BET experiments were conducted using nitrogen adsorption at 77 K. Aerogel samples were calcined at 170 °C for 12 h under a vacuum, and the nitrogen sorption experiments were performed. MOG-**1a** exhibited typical type I behavior (Fig. 2) with a surface area of 1016 m^2 $g^{-1}$and micropore volume of 0.67 cm^3 g^{-1} (Table 1).

It is very interesting to realize that after MOG-**1** charging with CO_2 at RT for 24 h and drying at 80 °C in vacuum desiccators the gels gave the finest compounds with large surface area (1016 m^2 g^{-1}). The higher internal surface areas of MOG-**1a** obtained using near supercritical processing conditions is corroborated by the observations of Hupp and co-workers[9] It is expected that under these conditions surface tension is nearly eliminated thereby preventing the pore collapse resulting in overall higher surface area.[9] Solvent removing using supercritical processing conditions is an attractive strategy considering the stand point of the overall improved performance of the material compared to that obtained using normal solvent removal conditions; and of course using inexpensive CO_2. In order to confirm the porosity and understand the thermal stability of MOG-**1a**; we performed thermal analysis, powder X-ray and CO_2 gas sorption measurements. Thermogravimetric (TG) analysis of MOG-**1a** shows the gels after careful drying are stable up to 250 °C and demonstrate 15% weight loss between room temperature and 200 °C, which corresponds to the loss of solvent ethanol and water molecules (ESI; Fig. S2†). TG analysis of MOG-**1–2**, which were obtained using different processing conditions, exhibited different weight loss (10–20%) between room temperature and 250 °C signifying the effect of processing conditions on the overall thermal stability and the porosity. We also performed powder XRD, due to lack of strong peaks, comparison of structural topology was nearly impossible.

Triggered by the provoking BET results and also considering the fact that significant attention has been devoted to the development of hydrogels, Si-aerogels, MOF aerogels is relatively untouched area, we invoked the CO_2 sorption isotherm measurements on MOG-**1a** to elucidate the uptake behavior in this new class of materials. To our knowledge this is the first ever investigation on the use of such materials for the CO_2 sorption isotherm measurements. MOG-**1a** was activated overnight at 170 °C under vacuum, and sorption experiments were performed using an HPVA-100 volumetric gas analyzer. Fig. 3 illustrates the uptake and release of CO_2 at room temperature. The CO_2 isotherm in Fig. 3 is typically a representative

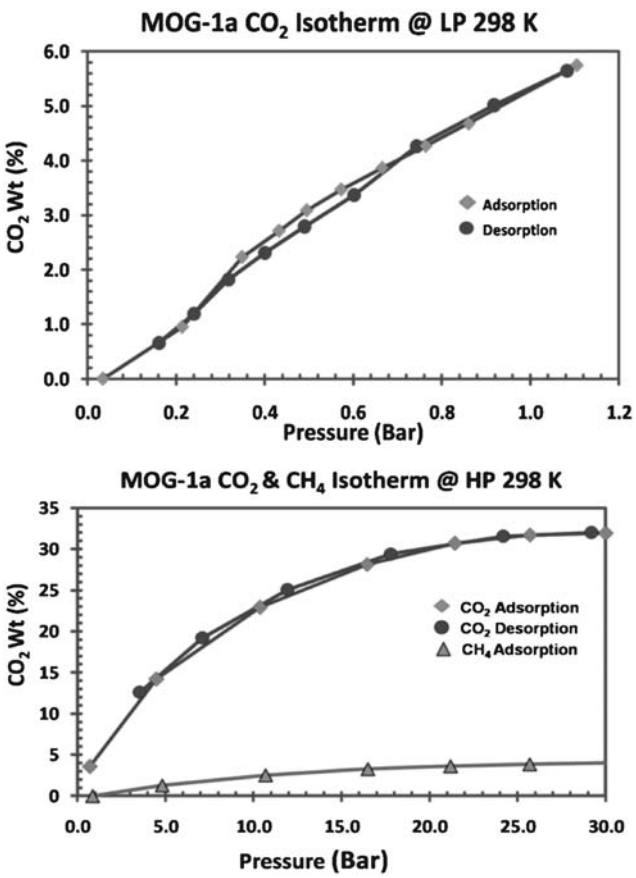

Fig. 3 Carbon dioxide and methane adsorption and desorption in MOG-**1a** at room temperature at low pressure CO_2 (top) and high pressure CO_2 and CH_4 (bottom). Notice the selectivity between CO_2 and CH_4.

Table 1 Formation of MOGs under different processing conditions

MOG	CO_2- 50 bar 80 °C Dry	CO_2-50 bar RT Dry	No CO_2 80 °C Dry	No CO_2 RT Dry
MOG-1[a]/BET (m^2 g^{-1})	MOG-**1a**/1016	MOG-**1b**/368	MOG-**1c**/873	MOG-**1d**/nd[c]
MOG-2[b]/BET (m^2 g^{-1})	MOG-**2a**/906	MOG-**2b**/1	MOG-**2c**/nd[c]	MOG-**2d**/nd[c]

[a] MOG-**1** = $Fe(NO_3)_2$ + 1,3,5-BTC. [b] MOG-**2** = $FeCl_3$ + 1,3,5-BTC. [c] nd: not determined.

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of Type I isotherm with no hysteresis, indicating the presence of permanent porosity in MOG-**1a**. At low CO_2 pressure, the calculated CO_2 wt% of MOG-**1a** is 5.9 wt% (1.3 mmol g^{-1}) with a reversible uptake and release of CO_2 at low pressure. The CO_2 measurements at low (1 bar) and high pressures (30 bar) suggest that MOG-1a uptakes 6 and 33 wt%, which is in line with MOFs reported in the literature[6a,10] Significant uptake of CO_2 at high pressure (~30 bar) clearly reveals that there is a significant potential in these materials for their applications as solid sorbents. We performed TG analysis of the MOG-**1a** after gas sorption measurements and exposing the same sample for 72 h to air that exhibit ~14% weight loss unambiguously demonstrating the thermal stability.

In conclusion, we report for the first time synthesis and characterization of metal organic gels for CO_2 capture applications. Investigations on the effect of processing conditions to produce gels with higher CO_2 uptake are underway in our research laboratories.

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