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Porous organic–inorganic hybrid aerogels based on bridging acetylacetonate

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ABSTRACT

Organic–inorganic hybrid aerogels are receiving growing attention due to their high tuneability. In this contribution a novel type of organic–inorganic hybrid aerogels with high micro- and mesoporosity have been prepared successfully from a bridging bis(acetylacetonate) ligand, 3,4-diacetyl-2,5-dioxohexane, and trivalent metal ions (Al^{3+} and Cr^{3+}). The metal-acetylacetonate aerogels compose of nanoscale metal-organic particles, which aggregate to form the gel matrix. N_2 sorption shows that the aerogels have high BET surface areas up to ~1100 $m^2\ g^{-1}$ and hierarchical porosity. The porosity can be altered by introducing of second divalent metal ions into the aerogel. The aerogels show ability to adsorb various gases (H_2, CO_2 and CH_4) and vapors (MeOH and EtOH). Water sorption measurements reveal that the aerogels have relatively hydrophobic pore surface.

1. Introduction

Aerogels are a class of porous solid materials with high internal surface area, low density and large open pores [1,2]. A range of interesting properties and applications are known for aerogels in absorbents [3], catalysis [4,5], porous nanostructure templates [6], cosmic dust collectors, etc [7]. Extensive work has been done on aerogels made from silica [7], metal oxides [8–10], chalcogenides [11], carbon [3,4,12,13], organic polymer [13,14], and organic–inorganic hybrid aerogels (mainly organosilane-derived) [15–17]. Recently a new group of organic–inorganic hybrid aerogels are receiving growing attention [18,19], which are composed of metal ions linked together by polycarboxylates. They are highly tuneable in terms of metal ions and organic ligands, and readily prepared from their corresponding gels using air-stable precursors with relatively low cost and in large scale. Their corresponding gels are characteristic of unique sponge-like porous structure, which morphology is remarkably different from other supramolecular gels [20–23] (including metallogels based on pyridine and other heterocycle derivatives [24–31]), and show potential applications in sorption [32,33], (chromatographic) separation [34], catalysis [35,36], templates for porous materials [18], and so on. Such a group of porous organic–inorganic hybrid gel materials have been developed for metal carboxylates. However, for long-term use of the aerogels, hydrophobic aerogels are superior to hydrophilic ones because the former can avoid deterioration in the presence of atmospheric moisture [1]. We herein wish to report incorporation of metal acetylacetonates into this important group of organic–inorganic hybrid aerogels in order to improve their hydrophobicity (Fig. 1).

2. Experimental section

2.1. Materials and methods

All starting materials and solvents were obtained from commercial sources and used without further purification unless otherwise stated. 3,4-diacetyl-2,5-dioxohexane (H_2L) was prepared according to published procedures [37]. The morphology of the gels was characterized by scanning electron microscopy recorded on a FEI Quanta 400F thermal field emission environmental scanning electron microscope and energy-dispersive X-ray spectroscopy recorded on a Oxford Inca energy-dispersive X-ray spectrometer. The samples were prepared by dispersing in ethanol upon sonication and placing on top of aluminum foil. Transmission electron micrographs were conducted on a JEOL JEM-2010HR microscope. The samples for TEM observations were prepared by dispersing the gels in EtOH by sonication and then immersing a carbon-coated copper grid. The gas sorption isotherms were measured with a Quantachrome Autosorb-iQ analyzer. Vapor

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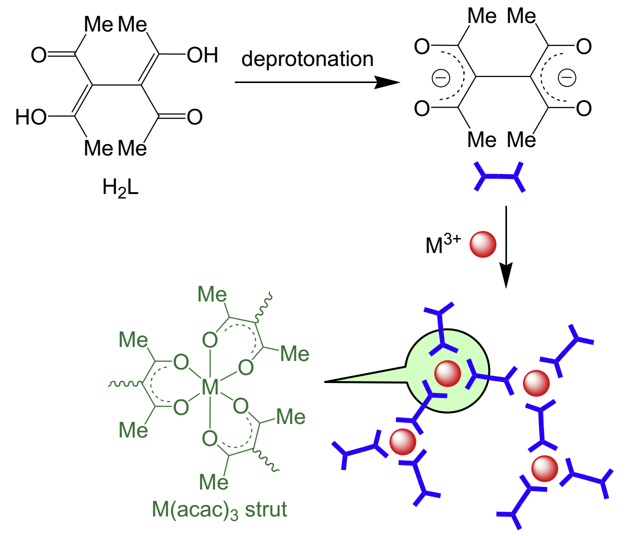

Fig. 1. Deprotonation of 3,4-diacetyl-2,5-dioxohexane (H_2L) and schematic representation of the organic–inorganic hybrid gel (M = Al, Cr).

isotherms (water, methanol and ethanol) were determined at 298 K on a Quantachrome Autosorb-iQ^2 analyzer. Before sorption measurement, the as-synthesized samples were dried at 80 °C under high vacuum for 16 h to remove the solvated molecules.

2.2. Preparation of aerogels

Typical procedure: 3,4-diacetyl-2,5-dioxohexane (H_2L) (60.6 mg, 0.3 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (75.0 mg, 0.2 mmol) were separately dissolved in DMF (1 mL) and EtOH (1 mL), respectively. The solutions were mixed together to form a clear solution via sonication. The resultant homogeneous solution was heated at 85 °C in a closed vial to obtain a gel after 24 h. The gel was further aged for 24 h, and then subjected to solvent exchange with EtOH for 24 h in a Soxhlet extractor to remove the excess ions or ligand. The solvent in the as-synthesized gel was subsequently extracted with liquid CO_2 (ca. 265 g) at 35 °C for 24 h in a 0.75 L high pressure stainless-steel Soxhlet extractor. After the autoclave was depressurized slowly at RT for about 2–3 h, an aerogel was obtained (122 mg, ca. 90%). Al-aerogel formed in DMF–EtOH (v/v 1:1) and Cr-aerogel formed in DMF were chosen for further characterization.

3. Results and discussion

3.1. Gelation Study

Acetylacetone (acacH) and related ligands are well-known for a long time, which commonly coordinate to metal ions as a bidentate ligand in their deprotonated form [37–40]. The chelating character of the acetylacetonate anion lead to ready formation of neutral $M(acac)_3$ struts with trivalent metal ions. The methyl groups provide a lipophilic sheath to the $M(acac)_3$ motifs, resulting in their high hydrophobicity [38]. As a result, the $M(acac)_3$ complexes are highly soluble in apolar solvents in sharp contrast to the metal-carboxylate complexes. In this context, 3,4-diacetyl-2,5-dioxohexane (H_2L) can serve as bridging ligand to connect $M(acac)_3$ units into 3D networks (Fig. 1) [41–43].

Various metal ions (Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Ca^{2+}) were tested for gelation (Tables 1 and A.1–3). The molar ratio of metal/ligand = 2:3 (trivalent ions) or 1:1 (divalent ions) was chosen for charge balance. Only Al^{3+} and Cr^{3+} were found to form stable gels with H_2L (0.15 mol L^{-1}) at 85 °C evaluated by turning the test tube upside down (Fig. 2). In contrast, Fe^{3+} formed unstable gels followed by precipitation with a higher molar ratio of metal/ligand ($\geqslant$3:2). The Al- and Cr-gels could be obtained in DMF, DMF–alcohol, or alcohol–water. The temperature played a key role in gelation. For example, when H_2L and $Al(NO_3)_3{\cdot}9H_2O$ were mixed in EtOH with concentration of 0.15 mol L^{-1}, the gelation time decreased from 24 to 16 to 12 h as the temperature increases from 85 to 100 to 120 °C. The precursor concentration is also crucial. When the concentration decreased from 0.15 to 0.075 mol L^{-1}, no gel could be obtained in EtOH at 85 °C and instead a precipitate was obtained. After the gelation the liquid trapped in the gel matrix was exchanged with subcritical $CO_2(l)$ to produce aerogels.

Table 1
Gelation tests of H_2L and various metal salts (c_L = 0.15 mol L^{-1}; reaction temperature, 85 °C; solvent for M: solvent for H_2L = 1:1 (v:v)).

Metal source	M:L	Solvent for M and H_2L	Result (time)
$Al(NO_3)_3{\cdot}9H_2O$	2:3	DMF–EtOH	Orange gel (1 d)
$Cr(NO_3)_3{\cdot}9H_2O$	2:3	DMF–DMF	Black gel (4 d)
$Fe(NO_3)_3{\cdot}9H_2O$	2:3	DMF–DMF	Precipitate
$Co(NO_3)_2{\cdot}6H_2O$	1:1	EtOH–DMF	Solution
$Ni(NO_3)_2{\cdot}6H_2O$	1:1	EtOH–DMF	Solution
$Cu(NO_3)_2{\cdot}3H_2O$	1:1	EtOH–DMF	Precipitate
$Zn(NO_3)_2{\cdot}6H_2O$	1:1	EtOH–DMF	Solution
$Mn(NO_3)_2{\cdot}4H_2O$	1:1	EtOH–DMF	Solution
$Ca(NO_3)_2{\cdot}4H_2O$	1:1	EtOH–DMF	Solution

Scanning electron microscope (SEM) and transmission electron microscope (TEM) were applied to observe the morphology of the Al- and Cr-aerogels. The gels have sponge-like porous networked structures consisting of small spherical interconnected particles with the presence of meso- and macropores (Fig. 3). Al-aerogel consists of relatively uniform nanoparticles with diameters of ca. 50–100 nm, while the particle sizes of Cr-aerogel are smaller with diameters of ca. 10–20 nm. TEM showed that the structures are amorphous with absence of long-range order. The amorphous nature of the gels was also evidenced by X-ray powder diffraction, which exhibited only weak and broad signals (Fig. A.1).

Fourier transform infrared (FT-IR) spectra of the aerogels showed the presence of acetylacetonate groups in the metal coordination sphere (Fig. A.2), as evidenced by the characteristic vibration ν_{asym} $(C{=}C{-}C{=}O)$ at around 1574 and 1559 cm^{-1} for Al- and Cr-aerogels, respectively, which are shifted to lower frequencies with respect to the free ligand at 1593 cm^{-1} [44]. Elemental composition analysis by energy dispersive X-ray spectroscopy (EDX) revealed the presence of Al or Cr metal atoms (Fig. A.3). The presence of trivalent Al/Cr metal ions was confirmed by X-ray photoelectron spectroscopy (XPS) (Fig. A.4). One signal at 74.9 eV

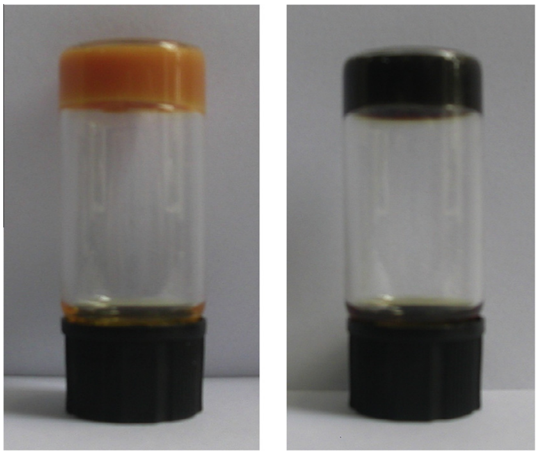

Fig. 2. Photographic images of Al-gel in DMF (left) and Cr-gel in DMF (right).