



Adsorption of volatile hydrocarbons in iron polysulfide chalcogels



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ABSTRACT

We report the synthesis, characterization and possible applications of three new metal-chalcogenide aerogels $\text{KFe}_3\text{Co}_3\text{S}_{21}$, $\text{KFe}_3\text{Y}_3\text{S}_{22}$ and $\text{KFe}_3\text{Eu}_3\text{S}_{22}$. Metal acetates react with the alkali metal polychalcogenides in formamide/water mixture to form extended polymeric frameworks that exhibit gelation phenomena. Amorphous aerogels obtained after supercritical CO_2 drying have BET surface area from 461 to 573 m^2/g . Electron microscopy images and nitrogen adsorption measurements showed that pore sizes are found in micro (below 2 nm), meso (2–50 nm), and macro (above 50 nm) porous regions. These chalcogels possess optical bandgaps in the range of 1.55–2.70 eV. These aerogels have been studied for the adsorption of volatile hydrocarbons and gases. A much higher adsorption of toluene in comparison with cyclohexane and cyclopentane vapors have been observed. The adsorption capacities of the three volatile hydrocarbons are found in the following order: toluene > cyclohexane > cyclopentane. It has been observed that high selectivity in adsorption is feasible with high-surface-area metal chalcogenides. Similarly, almost an eight to ten times increase in adsorption selectivity towards CO_2 over H_2/CH_4 was observed in the aerogels. Moreover, reversible ion-exchange properties for K^+/Cs^+ ions have also been demonstrated.

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1. Introduction

Volatile hydrocarbons are toxic substances, for example, aromatic compounds and cycloalkanes which are primarily generated by petrochemical or pharmaceutical industries as well as by mobile exhausts, power plants, solvent use, etc. [1–5]. They have usually low boiling points and high vapor pressures. Owing to their high vapor pressure, they evaporate easily under ambient conditions and enter the atmosphere. Indeed, these compounds are not only toxic to the human health and the environment, even at very low concentration, but also harmful to the microorganisms (especially those are involved in wastewater and waste gas treatment, bioremediation, and biocatalysis) [6,7]. Therefore, an efficient removal of such toxic substances from the environment has become an important subject from a biological, technological and environmental point of view.

A number of strategies have been developed for the effective abatement of such toxic materials e.g., filtration, absorption, adsorption, membrane separation, ionization, ozonation, thermal and photocatalytic oxidation [8–10]. Among them, adsorption using porous materials (adsorbents) has been recognized as an energy-efficient, highly selective, and relatively inexpensive

technique for the effective removal of volatile organic compounds [11]. Porous materials, having large surface area and pore volume are the most frequently used adsorbents, including zeolites [12], polymeric resins [13], metal organic frameworks [14], silica gel and activated carbons [15–17] have demonstrated great adsorption capacities. However, there are no studies reported about the adsorption of volatile hydrocarbons onto metal chalcogels.

Metal chalcogels are porous inorganic materials in which nano-sized building blocks are interconnected to yield a polymeric framework incorporating high surface area, very low densities, and large pore sizes [18–20]. The high-surface area and porosity of chalcogels make them ideal materials for adsorption, transport or purification studies of different gases [21–23]. Although the sol–gel synthesis of typical porous metal oxides (e.g., SiO_2 , Al_2O_3 , and TiO_2), carbon and metals is well known [24,25], successful attempts to apply this approach to metal chalcogenides have recently come into focus [18,21–23,26,27]. By replacement of O^{2-} in porous materials with electron-rich chalcogenide ions $[\text{Q}_x]^{2-}$ ($\text{Q} = \text{S}, \text{Se}, \text{Te}; x = 1-5$), the polarizability of the internal surface is increased. The interaction of polarizable adsorbates with the softer surface of chalcogenide-based aerogels is believed to be stronger than interactions with conventional aerogels like metal oxides, carbons, and organic polymers [21,22]. Therefore, we have been motivated to investigate the adsorption capacity of chalcogels for various applications in diffusion and separation of polarizable volatile hydrocarbons.

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Kanatzidis and co-workers have been successful to synthesize a variety of chalcogenide aerogels using primary building blocks such as tetrahedral clusters ($[MQ_4]^{4-}$ and $[M_2Q_6]^{4-}$, $M = Mo, Sn, Ge/Q = S, Se$) [18,21–23,26] or adamantane clusters ($[M_4Q_{10}]^{4-}$, $M = Sn, Ge/Q = S, Se$) [28], and ditopic linear polychalcogenido anions (S_x^{2-} ; $x = 3–6$) [27,29]. The choice of different inorganic building blocks produced an array of aerogels with enormous porous structures and wide-range of functionalities in metal-chalcogenides (e.g., selective adsorption of gases, ions or molecules and ion-exchange) [18,21–23,26–29] that can surpass traditional metal-oxide aerogels.

In this study, we describe the synthesis, characterization and possible applications, including adsorption of volatile hydrocarbons, gases and ion-exchange of three new mixed metal-chalcogenide aerogels $KFe_3Co_3S_{21}$, $KFe_3Y_3S_{22}$ and $KFe_3Eu_3S_{22}$. These porous metal-chalcogenides have been developed by reacting transition metal acetates with ditopic linear polysulfide ligand S_x^{2-} . It has been observed that the long polychalcogenide ligands (S_x^{2-}) could support and bridge metal centers to introduce cavities and porosity into metal polychalcogenide networks [27,29]. In comparison to known metal chalcogels [18,21–23,26–29], our synthesized materials possess an additional functionality, selective volatile hydrocarbon adsorption, to the best of our knowledge, represent first example of this kind of chalcogels. We carried out the chemical and physical characterization of the polysulfide chalcogels that demonstrated selective toluene vapors and CO_2 adsorption as well as excellent reversible ion-exchange properties for aqueous environmental waste remediation.

2. Experimental

2.1. Synthesis

The starting metal salts $Fe(CH_3CO_2)_2$, $Co(CH_3CO_2)_2 \cdot 4H_2O$, $Y(CH_3CO_2)_3 \cdot 4H_2O$, $Eu(CH_3CO_2)_3 \cdot 4H_2O$ and solvent like formamide and ethanol used in this synthesis were purchased from Alfa Aesar. K_2S_5 was freshly prepared according to the literature procedure [27,29] (Caution: In order to avoid a spontaneous start of the exothermic reaction, during sealing, the quartz tube contents must be cooled by liquid N_2 . Moreover, a slight agitation can also initiate the reaction). The syntheses of metal chalcogels were carried out in formamide solution in N_2 -filled glovebox at room temperature. Solvents (toluene, cyclohexane, and cyclopentane) were purchased from Carl Roth GmbH + Co. KG, Karlsruhe, Germany. High purity gases (N_2 , CO_2 , CH_4 and H_2) were obtained from Abdullah Hashim Industrial Gases & Equipment Co. Ltd. Jeddah, Saudi Arabia. The solvents were deoxygenated by bubbling N_2 gas through the solvents for about 2 h before taking them into the glovebox.

2.1.1. Synthesis of $KFe_3Co_3S_{21}$ chalcogel

A mixture consists of 0.087 g (0.5 mmol) of $Fe(CH_3CO_2)_2$ and 0.125 g (0.5 mmol) of $Co(CH_3CO_2)_2 \cdot 4H_2O$ were dissolved under inert atmosphere in 2.0 mL of degassed deionized H_2O , and 1.0 mL of degassed formamide was added to it. The solution of iron acetate and cobalt acetate was slowly added with stirring to an orange solution of 0.476 g (2.0 mmol) of K_2S_5 (K_2S_5 was prepared by heating a stoichiometric amount of K_2S and S for 6 h at 823 K in an evacuated sealed quartz tube [27,29]) in 2.0 mL of degassed formamide under inert atmosphere. The reaction mixture was turned immediately into an apparently black clear solution which was filtered and left at room temperature undisturbed for 1 week for gel formation. After 1 week, black $KFe_3Co_3S_{21}$ wet chalcogel was obtained (Fig. 1) and solvent exchange was carried out with a 50:50 mixture of ethanol/water 7 times. Treatment of the gel

then involved washings with absolute ethanol over a week followed by supercritical CO_2 drying. After critical drying, the obtained aerogels consist of very fluffy black particles (Figs. 2a and 6a).

2.1.2. Synthesis of $KFe_3Y_3S_{22}$ chalcogel

Same procedure was applied as described for $KFe_3Co_3S_{21}$, instead of cobalt acetate, 0.169 g (0.5 mmol) of $Y(CH_3CO_2)_3 \cdot 4H_2O$ was used. After 1 week, dark green $KFe_3Y_3S_{22}$ rigid chalcogel was obtained and after solvent exchange and critical drying, the obtained aerogels consist of very fluffy dark green particles (Figs. 3a and 6b).

2.1.3. Synthesis of $KFe_3Eu_3S_{22}$ chalcogel

Same procedure was applied as described for $KFe_3Co_3S_{21}$ and $KFe_3Y_3S_{22}$, instead of cobalt acetate or yttrium acetate, 0.201 g (0.5 mmol) of $Eu(CH_3CO_2)_3 \cdot 4H_2O$ was used. After 2 weeks, dark green $KFe_3Eu_3S_{22}$ rigid chalcogel was obtained and after solvent exchange and critical drying, the obtained aerogel consists of very fluffy dark green particles (Figs. 4a and 6c).

2.2. Supercritical drying

Critical point drying of the chalcogels was carried out with an Autosamdri-815B instrument. During supercritical drying process, the sample was soaked with liquid carbon dioxide and depending on the amount of gel, the soaking time and exchange time varies. Finally, aerogels were obtained after supercritical drying at 310 K.

2.3. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS)

SEM images and EDS of the aerogel samples were taken with Quanta 3D FEG.

2.4. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis

In order to determine the elemental compositions of chalcogel samples, powder aerogels were first suspended in water, and then the samples were digested in 6.0 mL of 69% Nitric acid in closed volumetric flasks using Ethos 1 microwave digestion system at 493 K until the whole solid was completely dissolved. Accurate determinations of K, Fe, Co, Y, Eu, and S concentrations were performed using Varian 720-ES ICP-OES instrument.

2.5. CHN analysis

The chalcogel samples were ground and packed in tin discs for measurement. Analysis of the lighter elements (C, H, N) was performed using Flash 2000 EOA Thermo analyzer to determine the presence of residual organic solvent (formamide) and acetate ligand within the chalcogel framework. Inert gas He was used as the carrier gas and CHN analysis was performed via combustion of chalcogel samples at 1173 K.

2.6. Infrared spectroscopy

Infrared spectra of solid samples were obtained on a Thermo Nicolet 6700 FT-IR system. IR spectra were recorded using Diffuse Reflectance IR Spectroscopy technique as well as using self-supported discs (transmission mode) with a resolution of 2 cm^{-1} .

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