ARTICLE IN PRESS

Advanced Powder Technology xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Preferential adsorption of volatile hydrocarbons on high surface area chalcogels $KMBiTe_3$ (M = Cr, Zn, Fe)

Fatimah Edhaim *, Alexander Rothenberger

Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

ARTICLE INFO

Article history:
Received 20 August 2017
Received in revised form 3 December 2017
Accepted 12 December 2017
Available online xxxx

Keywords:
Adsorption
Chalcogel
Gas separation
Hydrocarbon
Mesoporous

ABSTRACT

Three chalcogels $KCrBiTe_3$, $KZnBiTe_3$, and $KFeBiTe_3$ were synthesized by the sol–gel metathesis route. K^+ and the transition metal cations Cr^{2+}, Zn^{2+} or Fe^{2+} connect $[BiTe_3]^{3-}$ anions to form amorphous black compounds. Supercritical drying of the black gels produced porous materials with BET surface areas of 230 m^2/g ($KCrBiTe_3$), 450 m^2/g ($KZnBiTe_3$) and 514 m^2/g ($KFeBiTe_3$). The adsorption properties of the resulting chalcogenide aerogels or chalcogels have been studied using volatile organic hydrocarbons (VOCs) and gases as adsorptives. The results show preferential adsorption of toluene vapor over cyclohexane vapor. The adsorption capacity toward toluene is 5.02 mmol/g for $KCrBiTe_3$, 5.58 mmol/g for $KZnBiTe_3$ and 7.89 mmol/g for $KFeBiTe_3$. Preferential adsorption of CO_2 over CH_4 or H_2 was observed for the chalcogels: $KCrBiTe_3$ (CO_2/H_2: 175, CO_2/CH_4: 50), $KZnBiTe_3$ (CO_2/H_2: 180 and CO_2/CH_4: 60) and $KFeBiTe_3$ (CO_2/H_2: 225 and CO_2/CH_4: 65).

1. Introduction

Separation and purification of mixtures of volatile organic compounds (VOCs) is a major problem in chemical and petrochemical industries. Recently, removing toxic aromatic compounds such as benzene derivatives from fuel has attracted attention because aromatic hydrocarbons often exceed the maximum permissible concentrations in fuels [1]. Volatile organic compounds cause photochemical pollution as they have high photochemical ozone creativity potential (POCP) [2]. They have also been proven to be a public health hazard [2]. However, separation of hydrocarbons from alkanes with similar boiling points is difficult to achieve using conventional methods such as fractional distillation [2,3]. The main drawback of the fractional distillation is the low separation factor for aromatic compounds. Furthermore, thermal separation processes are energy inefficient, potentially dangerous and require large amounts of cooling water [2,4]. Currently, alternative separation technologies are being developed, *e.g.*, adsorptive separation using a rotating disc contactor (RDC) based ionic liquid [5] or separation by supported liquid membranes (SLMs) with an ionic liquid [6]. Although this method enhances the separation process, the concentration of ionic liquid in the raffinate phase is low [3]. The cost of ionic liquids such as 4-methyl-*N*-butylpyridinium tetrafluoroborate ([mebupy][BF_4]) [5], 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]) [7] or 1-butyl-3-methylimidazolium trifluoromethylsulfonyl ([C_4mim][NTf_2]) [7], however, has so far limited commercial applications [5,3]. Also, ionic liquids containing halides, such as $[Cl]^-$, $[I_3]^-$ or $[F]^-$, are corrosive [3].

Polymeric membranes such as 4,4′-(hexafluoroisopropylidene) diphthalic anhydride, 4,4′-diaminodiphenylsulfide, and 3,5-diaminobenzoic acid (DABA) have also been employed for volatile hydrocarbon separations, but they require high temperatures from 70 °C to 110 °C [1].

Physical adsorption or physisorption-based separation methods, in which porous materials are used as adsorbents, could become a promising alternative to thermal hydrocarbon separations. In such a setup, gases are adsorbed into the pores of the material and desorbed as a function of temperature or pressure [8]. An appropriate adsorbent should be capable of being regenerated after the adsorption process, have an optimized surface area, reasonable storage capacity and high selectivity to optimize separation processes [8]. Several types of porous adsorbents, such as zeolites [8–10], molecular sieves [8], silica gel [11], granulated activated carbon (GAC) [12], and metal organic frameworks (MOF) [13] have been investigated in the context of purification and separation of hydrocarbon molecules.

Recently, our group considered metal chalcogenide aerogels or chalcogels as adsorbents for the separation of volatile organic hydrocarbons [14,15]. The sol–gel metathesis route is the most

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* Corresponding author.
E-mail address: fatimah.edhaim@kaust.edu.sa (F. Edhaim).

https://doi.org/10.1016/j.apt.2017.12.010

Please cite this article in press as: F. Edhaim, A. Rothenberger, Preferential adsorption of volatile hydrocarbons on high surface area chalcogels $KMBiTe_3$ (M = Cr, Zn, Fe), Advanced Powder Technology (2018), https://doi.org/10.1016/j.apt.2017.12.010

approach uses to synthesize chalcogels. In this method, chalcogenide building blocks are connected to transition metal ions forming polymeric frameworks [16]. These materials are amorphous porous materials with high surface area, low density, broad pore size distribution, large pore volume and high surface polarizability. Such properties make chalcogels promising candidates for different applications such as ion exchange [17], heavy metal removal [18] and selective adsorption of volatile hydrocarbon and gas separations [14a,19,20,2].

Most quaternary metal chalcogels are synthesized using building blocks containing Ge, Sn, or Sb with lighter chalcogenide atoms like sulfides and selenides [21]. However, some binary metal telluride aerogels, *e.g.*, CdTe [22], and PbTe [21], and one quaternary antimony telluride aerogel (KFeSbTe$_3$) [14a] have been described.

In this work, a systematic study has been carried out with the aims to construct chalcogels containing $[BiTe_3]^{3-}$ anions and the first-row transition metal cations, and to study the adsorption properties of the resulting materials. The quaternary metal chalcogels KMBiTe$_3$ (M = Cr, Zn, Fe) were synthesized using the sol–gel metathesis route while other 1st-row transition metal ions reacted too rapidly with $[BiTe_3]^{3-}$ forming precipitates or remained in solution without further polymerization and gelation. It is recognized that bismuth telluride materials have narrow band gap layered semiconductor with a trigonal unit cell. Thus, their binary and ternary compounds have been widely used as thermoelectric materials for cooling and power generation applications at ambient temperature [23,24]. However, to the best of our knowledge quaternary aerogels containing bismuth and tellurium have not yet been reported.

The trigonal pyramidal anions $[BiTe_3]^{3-}$ were chosen because they can be prepared as soluble well-characterized salt K_3BiTe_3 [25]. By metathesis reactions with transition metal salts, the anions $[BiTe_3]^{3-}$ remain intact and bind to the transition metal ions (Cr^{2+}, Zn^{2+}, Fe^{2+}) forming anionic porous networks. Alkali metal (K) is present in the framework to neutralize the anionic framework $[MBiTe_3]^-$ (M = Cr, Zn, Fe). The polarity of the $[BiTe_3]^{3-}$ building blocks along with the presence of the softer and more polarizable Te atoms on the chalcogels' surfaces offer the opportunity to explore the interaction of these materials with various volatile hydrocarbon and gases. The results showed high adsorption capacity and selectivity of the resulting chalcogels toward toluene and CO_2.

2. Experimental

2.1. Synthesis

Chromium (II) chloride (Alfa, 97% anhydrous), zinc nitrate hexahydrate(Alfa, 99.9), iron(II) acetate (Strem Chemicals, 97% anhydrous), dimethylformamide (Sigma, 99.8% anhydrous), absolute ethanol (Aldrich, 99.8%), toluene (Fisher Scientific, 99.9%) and cyclohexane (Roth Chemicals, 99.5%) were used as received. K_3BiTe_3 was prepared by reacting the elements in a stoichiometric ratio at 750 °C for 48 h (the heating rate was 100 °C/h), followed by cooling to 396 °C. The material was kept at this temperature (396 °C) for four days, then gradually cooled to RT (Fig. S1, Supporting Information) [26]. The solvents were degassed by bubbling N_2 gas through them for about 12 h, then transferred to a nitrogen-filled glovebox ($c(O_2) < 0.1$ ppm, $c(H_2O) < 0.1$ ppm). Synthesis and solvent exchange of the chalcogels were carried out in the glovebox.

2.1.1. Synthesis of KCrBiTe$_3$ chalcogel

A light green solution of 30.7 mg (0.25 mmol) $CrCl_2$ in 3.00 mL of dimethylformamide (DMF) was slowly added to 3.00 mL of DMF containing 177 mg (0.25) mmol of K_3BiTe_3 with stirring. Upon mixing the two solutions, a clear dark black solution was obtained. The viscosity of this solution significantly increased, and the solution solidified into a black monolithic wet gel within one week. The remaining dimethylformamide was decanted, and the wet gel was subsequently washed with absolute ethanol 8 to 10 times to remove all unreacted precursors and counter ions. Afterward, the wet gel was dried using supercritical CO_2 drying at 35 °C to obtain fluffy, brittle black aerogel with inelastic modulus (Fig. 1).

2.1.2. Synthesis of KZnBiTe$_3$ chalcogel

The same method was applied as illustrated for KCrBiTe$_3$. Instead of $CrCl_2$, 74,4 mg (0.25 mmol) of $Zn(NO_2)_3\ 6H_2O$ was used. After one week, a rigid black gel of KZnBiTe$_3$ was formed, and after the solvent exchange and the supercritical drying, very fluffy black chunks of the chalcogel with low tensile strength were obtained (Fig. 1).

2.1.3. Synthesis of KFeBiTe$_3$ chalcogel

This material was synthesized using the same procedure described for KCrBiTe$_3$, but instead of using $CrCl_2$, 43.5 mg (0.25 mmol) of $Fe(CH_3CO_2)_2$ was used. A rigid black chalcogel of KFeBiTe$_3$ was obtained after one week. The resulting chalcogel obtained after the solvent exchange and the supercritical drying is brittle and consists of very fluffy black particles (Fig. 1).

2.2. Supercritical drying

Supercritical fluid dryer, A Tousimis Autosamdri-815B, was used to convert the wet gels to aerogels. The samples were transferred into the instrument chamber and soaked in liquid CO_2 for seven hours. Fresh liquid CO_2 was introduced every hour. The drying process was achieved by elevating the chamber temperature and pressure up to a critical point of CO_2 (35 °C, 1350 psi) for 2 min.

2.3. Characterization

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

SEM and EDS of the chalcogels were performed using an FEI Nova nanoSEM 630. The samples were deposited on a carbon tape.

2.3.2. Transmission electron microscopy (TEM)

The powder chalcogels were suspending in absolute ethanol and casting onto a carbon-coated Cu grid. High-resolution TEM images were taken with an FEI Titan 80–300 Super Twin operated at 300 kV.

2.3.3. Thermogravimetric analysis (TGA)

A Netzsch STA 449 F3 thermogravimetric analyzer was used for TGA measurements with a heating rate of 20 K min^{-1} under N_2 flow (20 mL min^{-1}). The sample preparation was carried out inside a glovebox using Al sample pans with punched lids.

2.3.4. Powder diffraction

A Stoe STADI MP powder diffractometer was used to record the powder diffraction patterns. The diffractometer is equipped with Cu-Kα_1 radiation and a Mythen 1 K silicon strip detector, which covers 90° in 2θ. The silicon standard was used for calibration. The diffraction patterns (raw data) were compared to the crystalline phase of Bi_2Te_3 deposited in the ICSD database [27].

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

In order to determine the elemental compositions of the chalcogel samples, the powder chalcogels were first suspended in water,

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