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Gas phase adsorption of alkanes, alkenes and aromatics on the sulfone-DUT-5 Metal Organic Framework

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ABSTRACT

A sulfone functionalized DUT-5 Metal Organic Framework 'SO_2-DUT-5' was synthesized using 4,4′-bibenzoic acid-2,2′-sulfone linkers. Its adsorption properties were studied and compared to those of the pristine DUT-5 material. The inverse gas chromatographic method was used to study the adsorption of C_5–C_7 linear, branched and cyclic alkanes, alkenes and aromatic molecules. SO_2-DUT-5 shows shape-selective behaviour in the adsorption of linear, branched and iso-alkanes, whereas DUT-5 is non-selective. The presence of sulfone groups results in both a reduced pore size and more specific interaction sites, leading to the shape-selective behaviour towards linear alkanes and the slightly elevated preference for aromatic compounds in the low coverage area.

The separation of *n*-hexane/benzene and 1-hexene/benzene mixtures at higher coverage was studied by performing breakthrough experiments at different temperatures and pressures. A remarkable change in selectivity is observed when the loading of the adsorbing molecules increases. At low degree of pore filling, no significant separation between *n*-hexane/benzene or 1-hexene/benzene occurs, while at higher loading separation becomes apparent with a preferential adsorption of benzene. This separation at high loading is a result of the more favourable packing of benzene in this unidimensional pore system.

1. Introduction

The incorporation of functional groups in Metal-Organic Frameworks (MOFs) allows modifying their adsorption and separation properties. This approach has been applied to a wide variety of MOF structures. For example, the amino-functionalization of MIL-68(In) resulted in higher sorption enthalpies for both hydrogen and CO_2 [1]. Also MIL-101(Al) and MIL-53 have been functionalized with amino moieties and were found to perform better in CO_2/CH_4 separation compared to the original material [2,3]. In the case of NH_2-MIL-53, the enhanced CO_2 separation is due to a change in the breathing properties of the material, rather than to a specific interaction between CO_2 and the amino-groups. The addition of other functional groups to the MIL-53 series also changes the structural properties of these breathing materials [4,5].

H-KUST-1 was post-synthetically modified with secondary amines functionalities [6]. These functional groups react with nitric oxide to form N-diazenium diolates. The parent material on the other hand irreversibly binds nitric oxide to its open metal sites. Morris et al. synthesized a series of five ZIFs containing different functionalized imidazole units. They showed that the symmetry and polarizability of the functionalities considerably influence the CO_2 uptake capacity [7]. A couple of $-NH_2$ containing MOFs were post synthetically modified with anhydrides and isocyanates to alter their hydrogen adsorption properties [8]. Farrusseng et al. also post synthetically modified $-NH_2$ containing MOFs, where in a first step the $-NH_2$ groups are converted into azides. By means of "click chemistry" the azide group is grafted with the desired functional group [9,10]. UiO-66 and MIL-47 were modified with a plethora of functional groups and the effects on the sorption characteristics for CO_2, water and light alkanes were investigated by us [11,12]. Addition of a methyl group to the UiO-66 framework leads to a lower amount of water adsorbed which would be beneficial for separations in humid conditions [13]. Similar hydrophobizations were done by us by fluorinating and difluorinating MIL-47 and MIL-53 structures [14,15]. Simulations performed by Torrisi et al. demonstrated that the addition of several functional groups to the MIL-53(Al) material results in a higher adsorption enthalpy for CO_2 [16,17]. Computational studies on different IRMOFs for natural gas upgrading showed that electron-donating functional group can enhance the CO_2/CH_4 selectivity [18]. A significant

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increase in Henry constant of noble gasses on IR-MOF was observed when halogen groups were added to the linkers [19]. Adding a thiol-group to Cu-BTC resulted in adsorption of Hg^{2+} from water while the unfunctionalized material did not show any uptake [20]. Mesoporous N_3-bio-MOF-100 was post synthetically modified with strain-promoted “click” chemistry. This introduced functional groups like succinimidyl ester bio conjugation moieties which would allow the coupling of bio molecules to the pore wall [21]. Cohen et al. demonstrated that ligand and metal exchange is possible via post synthetic modification. This could lead to the synthesis of otherwise very difficult or impossible materials [22].

These studies have clearly shown that fine-tuning of adsorption properties of MOFs can be achieved through the addition of chemical functionalities to the pore walls. In here, we have synthesized and studied a sulfone functionalized DUT-5 material, the so-called sulfone-DUT-5 or SO_2-DUT-5. It is composed of aluminium and 4,4′-bibenzoic acid-2,2′-sulfone (BPDC-SO_2) linkers. The parent material, DUT-5, was first synthesized by Kaskel et al. [23]. DUT-5 consists of aluminium and 4,4′-biphenyl dicarboxylate linkers. Sulfolane (a 5-membered cyclic sulfone) is a liquid, first developed by Shell Oil Company as a solvent. It is applied in the sulfinol®-X process, where it is used together with methyl diethanolamine, piperazine and water to remove hydrogen sulphide, carbon dioxide, carbonyl sulphide, mercaptans and other organic sulphur compounds from of natural gas streams [24]. In UOP’s sulfolane process, it is used as a solvent for the extraction of aromatics from hydrocarbon mixtures. In this process, the aromatic fraction is dissolved in the solvent while the aliphatic fraction is not. Subsequently, the aromatic fraction is recovered from the solvent to obtain a very pure aromatic fraction. The aromatic fraction itself is send over a distillation column to obtain the individual aromatics [25].

With these properties of sulfolane as a solvent in mind, the SO_2-DUT-5 is tested for its adsorption properties towards CO_2 and hydrocarbons, including alkanes, alkenes and aromatics. Low coverage adsorption properties were studied by inverse gas chromatography. Separation of hexane, benzene and 1-hexene was also studied at higher degree of pore filling by means of breakthrough experiments. A comparison is made with the pristine DUT-5 material.

2. Experimental

2.1. Synthesis of SO_2-DUT-5-as $(Al(OH)(BPDC\text{-}SO_2)\cdot(DMF)_{1.6}\cdot(H_2O)\cdot(CH_3OH)_{2.5})$

All starting materials were commercially available reagents of analytical grade and used without further purification. The organic ligand 4,4′-bibenzoic acid-2,2′-sulfone (H_2BPDC-SO_2) was synthesized following the reported procedure [26]. Microwave-assisted syntheses were carried out on a microwave synthesizer (Discover, CEM Inc.).

2.1.1. Method 1: solvothermal synthesis

SO_2-DUT-5-*as* was synthesized using a mixture of $Al(NO_3)_3\cdot 9H_2O$ (0.6 g, 1.6 mmol), H_2BPDC-SO_2 (0.8 g, 2.6 mmol) suspended in 60 mL N,N-dimethylformamide (DMF). The mixture was placed in a 100 ml Schlenk flask sealed and heated at 413 K for 24 h with stirring. The white powder phase was filtered off, washed thoroughly with DMF, methanol and acetone in sequences and vacuum dried. (Yield: 84.7%, 0.637 g, based on $Al(NO_3)_3\cdot 9H_2O$). C, H, N, S elemental analysis: for $Al(OH)(C14H6SO6)\cdot(C3H7NO)_{1.6}\cdot(H_2O)(CH_3OH)_{2.5}$: Calcd: C, 45.58; H, 5.42; N, 3.99; S, 5.71 (%); Found: C, 45.80; H, 5.76; N, 3.89; S, 5.73 (%). IR spectrum (cm^{-1}, KBr pellet): 3391 (br), 1666 (s), 1607 (s), 1556 (w), 1476 (w), 1432 (s), 1403 (s), 1304 (m), 1257 (w), 1179 (m), 1138 (m), 1100 (w), 1071 (w), 916 (w), 862 (w), 786 (m), 665 (w), 578 (w), 436 (w).

2.1.2. Method 2: microwave synthesis

Microwave enhanced irradiation synthesis was also used for the synthesis of SO_2-DUT-5. 0.04 g $Al(NO_3)_3\cdot 9H_2O$ and 0.053 g linker suspended in 3.3 mL DMF were heated to 423 K under microwave irradiation for 20 min with magnetic stirring. The maximum irradiation power was set to 300 W, with the ‘powermax’ active (air cooling was used during the irradiation). After completion of the reaction, white powder was collected over a membrane filter, washed thoroughly with DMF, methanol and acetone in sequences and subsequently dried at room temperature under vacuum. (Yield: 75.3%, 37.7 mg, based on $Al(NO_3)_3\cdot 9H_2O$). A reference material, DUT-5, was synthesized and activated following the reported procedure [23].

2.2. Characterisation

Fourier transform infrared (FT-IR) spectra were recorded in the region of 400–4000 cm^{-1} on a Bruker EQUINOX 55 FTIR spectrometer. Prior to analysis, pellets of the samples, diluted with KBr, were made. Elemental analyses were carried out on a Thermo Scientific Flash 2000 CHNS-O Analyzer. Thermogravimetric analysis (TGA) was performed with a Netzsch STA 449 F3 Jupiter-Simultaneous TG-DSC analyzer in the temperature range of 298–1073 K in air at a heating rate of 10 K/min for SO_2-DUT-5 and 2 K/min for DUT-5. Laboratory X-ray powder diffraction (XRPD) patterns were recorded on a Thermo Scientific ARL X’Tra diffractometer, operated at 40 kV, 40 mA using Cu-Kα (λ = 1.5406 Å). The lattice parameters were determined using the DICVOL program [27] and refined using the STOE’s WinXPow software package [28]. Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200FEG microscope with 4 nm resolution operating at 30 kV. Prior to the measurements a thin conducting layer of gold was spread on the sample to avoid charge building up on the surfaces.

Nitrogen adsorption experiments were measured at 77 K using a Belsorp mini II gas analyzer. Argon isotherms were measured with an autosorb AS-1 from Quantachrome instruments. The micropore volume was determined with the method of de boer [29] and the NLDFT method (oxygen and zeolite as parameters) was used for determining the pore size distribution [30]. The adsorbent was activated by heating up the sample at a heating rate of 1 K/min under vacuum up to 393 K and holding this temperature for 5 h.

CO_2 adsorption experiments at low pressure were conducted at 273 K with a Micromeritics Tristar 3000. CO_2 adsorption experiments at higher pressures were measured with a magnetic suspension balance (Rubotherm) at 303 K.

2.3. Inverse gas chromatography

Low-coverage adsorption properties of C_5–C_7 *n*- and iso-alkanes, C_5–C_7 1-alkenes and C_6–C_7 aromatic compounds were determined using the inverse gas chromatographic technique. A stainless steel column of 30 cm length and 1/8 inch diameter was filled with pellets of 500–630 μm. Pellets were formed by pressing the SO_2-DUT-5 or DUT-5 powder to a disk, crushing this disk and sieving the fragments to the desired fraction. The material in the column was activated by heating the column under constant helium flow to 573 K at a rate of 1 K/min and maintaining this temperature overnight. Temperature of the experiments varied from 303 to 513 K. Henry constants K' were calculated from the first order moment of the chromatogram [31]. Adsorption enthalpies, ΔH_0, and pre-exponential factors, K'_0, were calculated from the