Remarkable adsorbent for phenol removal from fuel: Functionalized metal–organic framework

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HIGHLIGHTS

- Metal–organic frameworks (MOFs) were firstly applied in phenol adsorption from fuel.
- Functionalized MOFs showed remarkably enhanced adsorption for phenol via H-bond.
- Detailed adsorption mechanism was clearly shown based on adsorption results.
- Functionalized MOFs can be used for many times by simple solvent washing.

GRAPHICAL ABSTRACT
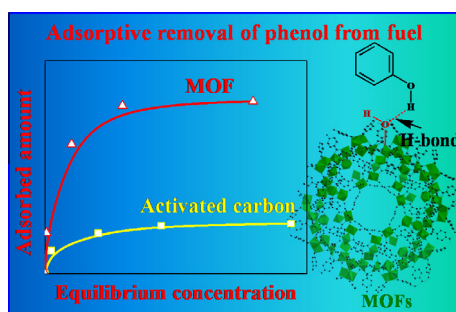
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ABSTRACT

Adsorption of phenol from a model fuel was firstly conducted over activated carbon (AC) and a typical porous metal–organic framework (MOF, MIL-101) in order to understand the possible application of MOFs in fuel purification. MIL-101 showed a remarkable phenol adsorption capacity (∼2.7 times that of AC) under the studied conditions. Moreover, the adsorption capacity enhanced further (up to ∼3.7 times of AC) after introduction of a hydroxyl group on the MOF (even though porosity of the MOF was decreased noticeably) by grafting ethanolamine (EA) on coordinatively unsaturated sites on MIL-101. The adsorption of phenol on EA-grafted MIL-101 (HO-MIL-101) is explained by H-bonding. Comparative adsorption of phenol and anisole on MIL-101 and HO-MIL-101 suggests that H-bonding occurs between the H-atom of the phenolic –OH and the O-atom of HO-MIL-101. HO-MIL-101 is recyclable after simple solvent washing, showing the potential application of MOFs, if suitably functionalized, for phenol adsorption/removal from fuel.

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1. Introduction

Phenol, which is both Brønsted acid and Lewis base, is one of the major oxygen-containing components in crude oil. Phenolics present in crude oil have come to the attention of researchers because of their industrial uses. In addition, crude oil with a high acid content causes operational problems such as corrosion of oil containers and surface deposition [1,2]. Therefore, the separation and removal of phenol from fuel is important. This separation

can provide phenol for industrial uses, and offer oxygenate-free ultrapure fuel to inhibit auto-oxidative corrosion and deposit formation inside engines [1,3].

The conventional method of phenol recovery from crude oil is chemical extraction using aqueous alkaline solutions (e.g., aq. NaOH) based on acid-base chemistry. This method has multiple drawbacks including production of toxic waste, complex flow routes, and high cost [2]. Therefore, various alternative non-aqueous methods have been studied in recent decades [4–12]. For example, a variety of chlorinated quaternary organic salts has been used to form deep eutectic solvents with phenol via H-bonding [5–8]. The Cl⁻ ion from the quaternary organic salt

provides an H-bond acceptor site for the –OH group in phenol, which efficiently separates phenol from fuel. Other separation methods have been studied using basic chemicals, which also separate phenol via H-bonding [9–11]. Materials such as choline chloride, triethylammonium hydrochloride [5], tetraethylammonium chloride [6], and 1-butyl-3-methylimidazolium chloride [7,8] have been used as second-generation reagents for phenol separation. These chlorinated chemicals, however, produce aqueous Cl⁻ which may corrode iron machinery [7,8]. Using a similar interaction mechanism, basic chemicals such as imidazole, nicotinamide, 1-methylimidazole, monoethanolamine, and monoethanolammonium formate (third-generation materials) have been used for chloride-free phenol separation [9–11]. Recently, Gao et al. [12] reported the complexing adsorption of phenol from a model oil (*n*-hexane) via H-bonding or Lewis acid–base interactions using a solid Lewis acid, such as $AlCl_3$, or solid Lewis base, such as hexamethylenetetramine or triazole, as sorbents [12]. However, the complexing adsorption is different from traditional adsorptions on surfaces since there is no porosity of the used sorbents.

Nanoporous materials have attracted a significant amount of attention in recent years due to their vast number of applications, including removal of hazardous contaminants from air, water, and fuels, and separation of commercially important organics [13–22]. Metal–organic frameworks (MOFs) are the most fascinating class of such advanced materials because of their facile synthesis, high degree of porosity, tunable pore size and shape, and easy modification [16–22]. Consequently, MOFs have already been studied extensively for adsorptive removal of sulfur- and nitrogen-containing compounds (SCCs and NCCs) from fuel, and hazardous materials from water. This method uses coordinatively unsaturated metal sites (CUSs), the acid or base functionality on the ligand, and metal centers on MOFs [23–32]. In addition, the functionality and stability of MOFs can be improved further via formation of composites with materials such as carbon nanotubes, graphene/graphite oxides, and carbon nanofibers. These MOF composites have expanded the applicability of MOFs to include gas and liquid phase adsorptions [33,34]. MOFs have also been suggested as a potential adsorbent for nonpolar solvents because of their hydrophilicity [35].

The surface properties of MOFs can be functionalized through incorporation of functional groups on the ligand, or grafting with functional organic molecules. The strategy of surface grafting has been studied extensively with chromium(III) terephthalate (MIL-101), and found to have several special applications, such as for catalysis [31,32,36,37], encapsulation of metals, Keggin polyanions and drugs [32], and water purification [38,39]. Based on these applications of surface-modified MIL-101, herein, we introduce a surface functionalizing agent, ethanolamine (EA), in which the –NH₂ group is coordinated on the CUSs of MIL-101, and the –OH group offers H-bond donor and acceptor sites for adsorbates. We investigated the adsorptive behavior of phenol on HO-MIL-101, and a possible adsorption mechanism is proposed. This is the first time that a MOF is shown to be an efficient adsorbent for the removal of phenol from a model fuel even though there are a few reports on the adsorption of phenols over MOFs from water [40–43]. Moreover, the adsorption capacity can be enhanced remarkably by surface modification of a MOF (even though porosity was decreased noticeably), and adsorption mechanism could be clearly shown with the adsorption of anisole. The molecular structures of phenol and anisole are shown in Scheme 1.

2. Experimental

2.1. Chemicals and synthesis of adsorbents

All chemicals were purchased from commercially available sources and used without further purification. Chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, 99%) was procured from Samchun chemicals. Terephthalic acid (TPA, $C_8H_6O_4$, 99%) and ammonium fluoride (NH_4F, 97%) were purchased from Junsei chemicals. Ethanol (C_2H_6O, 99.5%), toluene (C_7H_8, 99.5%), and diethyl ether ($C_4H_{10}O$, 99%) were obtained from OCI chemicals. Ethanolamine (C_2H_7NO, 99.5%) was obtained from Alfa Aesar. Phenol (C_6H_6O, 98.5%) and anisole (C_7H_8O, 99.7%) were acquired from DC Chemical Co. Ltd. and Sigma Aldrich, respectively. *n*-Octane (C_8H_{18}, 97%) was procured from Yakuri Chemical Co., Ltd.

The synthesis of MIL-101 was done using a method reported previously (summarized in the Supporting Information) [32,44]. Pure MIL-101 was functionalized following the process described earlier on grafting MIL-101 with ethylenediamine, which provided –NH₂ functionality on the MOF surface [38]. Before functionalization, MIL-101 was dehydrated at 150 °C for 12 h in a vacuum oven to produce CUSs. The TPA-free dehydrated MIL-101 (0.5 g) was suspended in anhydrous toluene (30 mL), and 1.5 mmol of EA was added to the suspension. Then the mixture was refluxed with stirring for 12 h. Unreacted EA and solvent were removed by repeated washing with ethanol and deionized water while filtering. The resulting material was dried at room temperature. The material after EA grafting on CUSs of MIL-101 was designated HO-MIL-101.

2.2. Characterization of MOFs

Powder X-ray diffraction (XRD) patterns of the synthesized MOFs were acquired by a diffractometer (D2 Phaser, Bruker, Germany) using Cu Kα radiation. The Fourier transform infrared (FT-IR) spectra of the virgin and functionalized MIL-101 MOFs were measured with a Jasco FT-IR-4100, which was in the attenuated total reflection mode (maximum resolution: 0.9 cm⁻¹). The nitrogen adsorption isotherms of selected adsorbents were measured using a surface area and porosity analyzer (Tristar II 3020, Micromeritics, USA) at −196 °C. The samples were evacuated at 150 °C for 12 h before adsorption. The surface areas and total pore volumes were evaluated with the BET and Langmuir equations, and the adsorbed amount ($P/P_0 = 0.99$), respectively.

2.3. Adsorption experiments

Stock solutions (5000 ppm) of phenol and anisole were prepared by dissolution in *n*-octane. The mother solutions were diluted to prepare solutions of desired concentration (100–2000 ppm) for the adsorption experiments. The concentration of adsorbate in these solutions was determined by absorbance (λ_{max} = 270 nm for phenol and 259.7 nm for anisole) from the UV spectra recorded using a spectrophotometer (Shimadzu UV spectrophotometer, UV-1800). Previously purified adsorbents were activated by vacuum drying at 150 °C and used for adsorption of phenol or anisole from *n*-octane. An exact amount of adsorbent (5 mg) was added to 5 mL of a known concentration of phenol or anisole, and shaken for predetermined times at room temperature. After the adsorption process was allowed to occur for a pre-set time, the solution was separated from the adsorbent with a syringe filter (polytetrafluoroethylene, hydrophobic, 0.5 μm), and the concentration of the remaining adsorbate solution was calculated from its measured UV absorbance. Adsorption experiments were
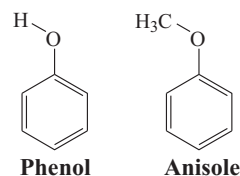
Scheme 1. Molecular structure of phenol and anisole.