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Effective adsorptive removal of indole from model fuel using a metal-organic framework functionalized with amino groups

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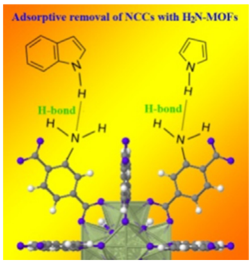
HIGHLIGHTS

- Removal of indole from model fuel was firstly studied over MOFs having $-NH_2$.
- MOFs with $-NH_2$ show much improved adsorption capacity for indole.
- The enhanced adsorption capacity can be explained with H-bonding.
- The MOFs with $-NH_2$ group can be used many times by simple washing.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrogen-containing compounds (NCCs) should be removed from fuels because of the negative effect of NCCs on the environment and catalyst stability. NCCs are composed of basic materials such as quinoline (QUI) and neutral materials such as indole (IND). The NCCs can be removed by various methods including adsorption. Compared with basic NCCs, neutral NCCs are more difficult to remove through adsorption due to their less affinity toward adsorbents. In this report, adsorption of IND (as one of the representative neutral NCCs) was studied over the metal-organic frameworks (MOFs), UiO-66 and UiO-66-NH_2, which contain terephthalate and aminoterephthalate linkers, respectively. In spite of the reduced porosity of UiO-66-NH_2, the adsorption capacity of IND was improved upto 46% when compared with pristine UiO-66. Therefore, the additional amino group in the MOF imparts extra adsorption capability on the MOF. For a detailed investigation, adsorption of other NCCs such as QUI, pyrrole, and methylpyrrole was studied. The improved adsorption of IND over amino-functionalized MOFs could be attributed to the improved interaction of IND with the MOF via H-bonding because of the $-NH_2$ group. In addition to this remarkable improvement in IND adsorption, UiO-66-NH_2 could be regenerated several times for the adsorption of IND by simple solvent washing.

1. Introduction

Energy and environment are two major concerns for human beings in this century. With increasing population and the limited fossil fuels but higher energy demand, fuels with much contaminants (S, N, and metals) and high viscosity will be utilized over the next several decades [1–3]. Therefore, various efforts have been devoted to remove sulfur-containing compounds (SCCs) or nitrogen-containing compounds (NCCs) from fuels because of the negative effects of SCCs and NCCs on the environment and catalyst lifetime [4–6].

Between these two types of contaminants, SCCs are usually removed effectively by the hydrodesulfurization (HDS) process. However, before removing the SCCs by HDS, NCCs should be removed first because NCCs adversely affect both for the catalyst and the HDS process. NCCs are conventionally removed by

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the hydrodenitrogenation (HDN) process, which requires a large amount of expensive hydrogen, high temperature, and pressure; these make it an energy-intensive and costly process. Moreover, unlike HDS, HDN is a kinetically slow multistep process [4,5,7]. Hence, the development of new removal techniques is of great importance.

One of the techniques that can be applied for the removal of NCCs from fuel is adsorptive denitrogenation (ADN) because ADN does not require hydrogen, high temperature and high pressure [4–6]. So far, several adsorbents such as activated carbon [4,8,9], Cu(I)-Y zeolites [10], ion exchange resins [11], meso-silicas [12,13], silica–zirconia cogel [14], Ti-HMSs [15], activated aluminas [16], Ni-based adsorbents [16], and NiMOs [17] have been used for ADN.

In recent times, nanoporous materials [18–22], including metal-organic frameworks (MOFs) [23–26], are one of the fastest growing fields of research among materials scientists. Porous MOFs have a lot of potential applications due to their comparatively high surface area and different types of functional sites as well as modifiability. They have a wide range of applications, including adsorption, separation, and catalysis [23–26]. For several years, they have been successfully used for the removal of different types of hazardous materials using different processes, which include adsorptive desulfurization (ADS) [27–29] and ADN [30]. MOFs show an easy tunability for their structural modification including changing the linkers or imparting the functionality by special or specific linkers containing specific functional groups [31–33]. One of promising MOFs is UiO-66 (UiO stands for the University of Oslo) [34], which contains metal clusters of zirconium linked by terephthalate derived from terephthalic acid. By using amino-functionalized terephthalic acid, i.e., 2-amino-terephthalic acid, NH_2-UiO-66 containing $-NH_2$ groups as functional moieties can be obtained [35]. NH_2-UiO-66 and UiO-66 can be regarded as analogous MOFs [36] having the same structure but different linkers. By this procedure, some additional advantages can be obtained from MOF materials, and the ability of these types of modifiability is a general character for most of the MOFs. Moreover, no additional operational step is required to improve the functionality of the MOF by changing linkers.

Indole (IND) and its derivatives are very common NCCs that occur naturally in fossil fuels. IND and its derivatives are neutral compounds and hence show less activity toward adsorbents, especially the acidic ones [37–40], compared with basic NCCs such as quinoline (QUI). Therefore, IND and its derivatives show less adsorption compared with other prominent (especially basic) NCCs in fuel, e.g., QUI and its derivatives. Until now, the successful removal of IND via adsorption was accomplished only through ordinary van der Waals attraction force by improved surface area [41] or a special interaction of π-complexation [42]. However, one of the problems associated with the π-complexation is that only a few active species such as Cu(I) and Ag(I) show the capability of such adsorption. Moreover, preparation of this type of materials is not cost effective (because of multistep processes) and the adsorbents were generally unstable [42]. To get very high surface area of adsorbents for the adsorption of neutral NCCs via van der Waals attraction also has limitations because it is difficult to increase the surface area beyond a certain value.

In this report, for the first time, we established an adsorptive method for IND (as an example of representative neutral NCCs) removal from the model fuel through the interaction between $-NH_2$ groups in MOFs and IND. A plausible explanation was also suggested based on the concept of H-bonding between the adsorbate and the adsorbent through the adsorptions of IND, pyrrole (PYR), and methylpyrrole (MPYR). The MOF with amino group, UiO-66-NH_2, showed remarkable adsorption capacity for IND with ready recyclability.

2. Experimental

2.1. Chemicals and synthesis of adsorbents

n-Octane (C_8H_{14}, 97%) and terephthalic acid (TPA, 99.0%) were purchased from Junsei Chemical Company. Hydrochloric acid (HCl, 35.0%) was obtained from OCI Company Ltd. QUI (98.0%), IND (98.0%) and zirconium chloride ($ZrCl_4$, 99.5%) were obtained from Sigma–Aldrich Co. PYR (99.0%), MPYR (99.0%) and 2-amino-terephthalic acid (NH_2-TPA, 99.0%) were procured from Alfa Aesar. All the chemicals in this study were used without further purification. The synthesis of the MOF, UiO-66, was carried out solvothermally under conventional electric heating following a previous report [43] with a few modifications. The detailed procedure for the synthesis of the MOF is as follows: $ZrCl_4$ (1.129 g), TPA (1.626 g), HCl (1.009 g) and DMF (27.04 g) were mixed in a molar ratio of 1:2:2:76. The mixture was then transferred to a 100 mL Teflon-lined autoclave and heated in an electric oven for 24 h at 180 °C. For UiO-66-NH_2, a mixture of NH_2-TPA and with a specific molar ratio was used instead of TPA. The MOFs with different aminoterephthalate compositions were denoted as UiO-66-NH_2(x), where x stands for the molar percent of NH_2-TPA in the mixture of TPA and NH_2-TPA. For this study, we prepared UiO-66-NH_2(100), UiO-66-NH_2(67), and UiO-66-NH_2(33) along with UiO-66. After the synthesis, the MOFs were filtered, washed, and purified by mixing with DMF and heating at 150 °C for 5 h. For 1 g of MOF, 50 mL of DMF was used in the purification process. The purified MOFs were then filtered and dried in a vacuum oven at 150 °C for 12 h to remove the remaining DMF.

2.2. Characterization

X-ray powder diffraction patterns (XRD) were obtained using a D2 Phaser diffractometer (Bruker, with CuKα radiation). The N_2 adsorption analyses of the adsorbents were carried out at −196 °C using a surface area and porosity analyzer (Micromeritics, Tristar II 3020) after evacuation at 150 °C for 12 h. The Fourier transform infrared (FTIR) spectra were recorded with a resolution of 2.0 cm^{-1} on a Jasco Model FTIR-4100 device equipped with an attenuated total reflectance (ATR) accessory.

2.3. General procedures for the adsorption experiments

Stock solutions (each at a concentration of 10,000 ppm) of the model fuel were prepared separately for the adsorbates (IND, QUI, PYR and MPYR) by dissolving them in *n*-octane. Solutions of varying concentrations were prepared by successive dilution of the stock solutions. A solution containing a fixed concentration of IND, QUI, PYR, and MPYR (1000 ppm each) was used to determine the adsorption capacities at various adsorption times. To obtain the maximum adsorption capacities of the adsorbents, several solutions with different concentrations (300–1800 ppm) of IND were prepared using the same solvent. Prior to adsorption, the adsorbents were dried in a vacuum oven at 150 °C for 12 h and stored in a desiccator. For each adsorption experiment, an exact amount of the adsorbent (∼5.0 mg) was added to the model fuel (∼5.0 mL) and stirred magnetically for a predetermined time (15–240 min) while maintaining the adsorption temperature at 25 °C. After adsorption, the solution was separated from the solid using a syringe filter (PTFE, hydrophobic, 0.5 μm) and analyzed with a GC (DS Science, IGC 7200) equipped with a flame ionization detector (FID).