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Sonochemical synthesis of magnetic responsive Fe_3O_4@TMU-17-NH_2 composite as sorbent for highly efficient ultrasonic-assisted denitrogenation of fossil fuel

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ABSTRACT

In this work, a novel magnetic responsive composite was fabricated by encapsulation of Fe_3O_4 nanoparticles into an amino-functionalized MOF (TMU-17-NH_2) under ultrasound irradiation. The prepared materials were characterized by several techniques such as elemental analyses, PXRD, FT-IR, N_2 adsorption, TGA and ICP. This composite has been applied to the adsorptive removal of nitrogen-contain compounds in model liquid fuel. The prepared composite demonstrates very good performance for the removal of NCCs. The maximum adsorption capacity of IND and QUI over prepared composite calculated 375.93 and 310.18 $mg \cdot g^{-1}$ at 25 °C, respectively. The composite material is magnetically separable and reusable for several times.

1. Introduction

The air pollution which causes irreparable and harmful effects on the human health and ecosystem, has aroused public concerns in recent centuries. Crude oil naturally contains a high concentration of nitrogen-containing compounds (NCCs) and sulfur-containing compounds (SCCs), such as indoles, sulfides, thiols and their derivatives [1–3]. These compounds are one of the main causes of air pollution. With increasing population in recent years, many countries impose strict provisions for diesel fuel quality, especially the sulfur content of gasoline and diesel fuel. The fuel quality is highly influenced by the amount of SCCs and NCCs. Therefore, according to the strict regulations, these compounds have to be removed completely from fuels [4,5]. Deep desulfurization of liquid fuel to give ultra-clean fuel usually performed with hydrodesulfurization (HDS) process in high pressure and high-temperature. Also, NCCs are commonly removed by this procedure that is kinetically slow multistep process [6–8]. NCCs adversely influence on HDS process and catalyst lifetime. Nevertheless, NCCs firstly should be removed before beginning the HDS process for removing the SCCs, if we want to decrease the energy consumption and increase the performance [9–11]. In order to overcome these problems, the adsorptive denitrogenation (ADN) process is one of the useful methods that can be employed for the removal of NCCs from diesel fuel [12]. Adsorption can play an important role in removing contaminant materials from liquid fuels. Adsorptive removal is based on the capability of a porous material to adsorb the hazardous compounds from fuel [13–15]. ADN technique is regarded as the most promising and economical process to remove NCCs from fuel because ADN perform in mild conditions and does not need hydrogen, high temperature and high pressure [16,17]. Much investigation on ADN for liquid fuels has been performed with various types of porous adsorbents such as zeolites, activated carbon, ion exchange resins, meso-silicas, silica–zirconia cogel, Ti-HMSs, activated aluminas, Ni-based adsorbents and NiMOs [17–20]. Metal organic frameworks (MOFs) are a new class of porous martial which composed of metal ions or cluster and organic compound as a linker. These materials show ultrahigh porosity, high stability in various medium, flexibility and easy design [21].

The ultrasound approach as an attractive and efficient method employed for acceleration of the chemical processes [22,23]. When the liquid contact with high-intensity ultrasonic irradiation, shock waves lead to acoustic cavitation in the medium. The formation and subsequent violent collapse of bubbles can create high temperature (up to 5000 K) and pressure (up to 1000 atm)

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localized spots in the liquid. The oxidative desulfurization performed in the biphasic system including extraction solvent and oil that ultrasound waves can be disperse emulsion-like of biphasic system [24]. Appling the ultrasonic power combined with the adsorption method was very efficient in shortening the removal time of NCCs by enhancing the dispersion of sorbent and adsorbates in solution and effective interactions among them.

In adsorptive removal, the surface area of sorbent is an important factor in adsorption capacity. Ahmed and coworker were firstly studied the removal of indole from model fuel over MOFs that functionalized by amino groups [25]. Also, Ahmed et al. investigated adsorptive denitrogenation of model fuels with MIL-101 (Cr) that impregnated with phosphotungstic acid [26].

In this work, we have successfully reported a facile method for preparation of magnetic sorbent with the encapsulation of Fe_3O_4 in metal organic frameworks. This type of sorbent can be easily separate in the reaction medium by an external magnetic field that is very important for industrial purpose. In presence study, for the first time, a novel composite of Fe_3O_4 nanoparticles that encapsulate in cages and the pores of TMU-17-NH_2 prepared and applied for deep denitrogenation of model fuels. This MOF is a two-fold interpenetrated metal-organic frameworks.

2. Experimental

2.1. Material and method

All of the reagents that used in this study, were analytical grade and no further purification required. Elemental analyses (carbon, hydrogen, and nitrogen) were performed with an ECS4010 CHNSO made in Costech. Italy. The powder X-ray diffraction patterns (PXRD) were recorded by using a D_8 ADVANCE diffractometer with monochromated Cu-k_α radiation (λ = 1.54056 Å). Nitrogen adsorption isotherms that performed with a Micromeritics ASAP 2000 over P/P_0 = 0.0–1.0 applied to surface area investigation prepared material. FT-IR spectra were obtained by a Jasco 3600 FT-IR spectrometer using the KBr disk technique at room temperature. Thermogravimetric analyses (TGA) of the materials were obtained by a TGA-50 Shimadzu thermo-balance. The gas chromatography-mass spectrometer (GC–MS) (Agilent 7890/5975C-GC/MSD; HP-5 137 MS column, 30 m × 250 μm i.d × 0.25 μm) used to characterize the oxidized sulfur-containing compounds An ICP-Spectro ciros M CCD spectrometer was employed to determination of Fe_3O_4 amount encapsulated in MOFs. A vibrating sample magnetometer (LAKESHORE-7304, USA) was employed for magnetization measurements of prepared samples at ambient temperature. Ultrasound waves generated by an ultrasound bath (Sonic 6mx, 37 kHz with a maximum power output of 240 W, Polsonic, Warsaw, Poland.

2.2. Preparation of sorbent

Safarifard et al. solvothermally synthesized The TMU-17-NH_2 that reported in the previous paper [27]. TMU-17-NH_2 is a two-fold interpenetrated three-dimensional porous Zn(II)-based MOF. This MOF has been synthesized with 1,4-bis(4-pyridyl)-2,3-diaza-2,3-butadiene (4-bpdb), and amino-1,4-benzenedicarboxylate (NH_2-BDC), as organic linker. In order to preparation of magnetic composite, Fe_3O_4 nanoparticles were encapsulated in TMU-17-NH_2. Encapsulation of Fe_3O_4 nanoparticles in TMU-17-NH_2 was performed by ultrasound irradiation for the first time and employed ultra-deep denitrogenation of fossil fuel. In order to fabricate the Fe_3O_4@TMU-17-NH_2, a suspension of Fe_3O_4 nanospheres (100 mg) in DMF was prepared under ultrasound irritation and added to a mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.297 g, 1 mmol), 4-bpdb (0.119 g, 0.5 mmol) and 1,4-benzenedicarboxlic acid (H_2BDC) (0.181 g, 1 mmol) in 15 ml DMF as solvent. Then the mixture was transferred into the ultrasonic bath in ambient temperature and atmospheric pressure. After 10, 20 and 30 min under ultrasound irradiation with 37 kHz frequency and 240 W output power, products were separated by a magnet, washed with DMF three times and dried in an oven.

2.3. General procedures for the adsorption experiments

Ultrasonic-assisted adsorption of indole (IND) or quinoline (QUI) from fossil fuel was investigated to find the optimum conditions. The sorbent was dried overnight at 100 °C under vacuum before use in removal experiments. The model fuel that is a solution of IND or QUI with the desired concentration, prepared using n-octane (each at a concentration of 10,000 ppm). The batch experiments for optimization of conditions were performed with working solutions that prepared to step by step dilution of the stock solutions. Typically, an exact amount of the sorbent (10 mg) was put in model fuel (10 mL) having a fixed concentration (1000 ppm). Obtained mixture was mixed well with a shaker and maintained for a fixed time (10 min to 12 h) at room temperature in an ultrasonic bath. After adsorption, the sorbent was separated from the mixture with a magnet. The concentrations of NCCs in solution were analyzed with GC analysis. The amount of NCCs adsorbed onto sorbent was calculated by flowing Eq. (1) [28]:

$$q_t = (C_i - C_f) \times \left(\frac{V}{m}\right) \quad (1)$$

where q_t is the adsorbed amount in time t (mg/g), C_i and C_f are NCC concentrations in the liquid phase, before and after adsorption, respectively. m (g) is the mass of the adsorbent and V the volume, in *mL*.

In order to investigate the regeneration of the sorbent, adsorption experiments with the used adsorbents were performed by a simple physical method. NCC can be removed by solvent washing for several times and sonication. The used sorbents were regenerated with DMF and sonication for 5 min.

3. Results and discussion

3.1. Characterization of the prepared composite

The prepared materials were characterized by several techniques such as elemental analyses, PXRD, FT-IR, N_2 adsorption, TGA and ICP.

The following results were obtained from elemental microanalysis for prepared TMU-17-NH_2: Zn(NH_2-BDC)(4-bpdb)].2DMF, calculated (%): C, 51.23; H, 4.62; N, 16.23. Found (%): C, 51.46; H, 4.84; N, 14.98. These results are in good agreement with the reported data in proviso paper [27] and confirm that the MOF was successfully prepared.

The PXRD patterns of the synthesized TMU-17-NH_2, Fe_3O_4@TMU-17-NH_2 demonstrate in Fig. 1. The comparison between PXRD of TMU-17-NH_2 and as-synthesized MOF was indicated that TMU-17-NH_2 prepared with ultrasound irradiation (Fig. 1(a)). These results were indicated that the Fe_3O_4 nanoparticles encapsulate into cages of TMU-17-NH_2 under ultrasound irradiation. The PXRD patterns of prepared composite were compared with the original MOF and demonstrated that the main peaks of Fe_3O_4 nanoparticles were appeared in the PXRD patterns of composite. An explicit change in relative intensities can be seen at 30–70°. Therefore, the preparation of the expected composite was confirmed by PXRD studies. Also, it was observed that TMU-17-NH_2 and Fe_3O_4@TMU-17-NH_2 approximately have the similar structure