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Facile loading of Cu(I) in MIL-100(Fe) through redox-active Fe(II) sites and remarkable propylene/propane separation performance

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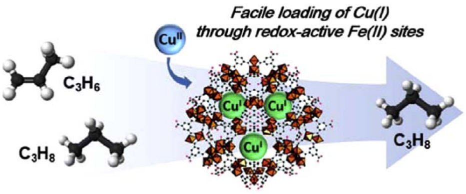
GRAPHICAL ABSTRACT



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ABSTRACT

A novel Cu(I) loading method, which includes the reduction of $CuCl_2$ to CuCl without an external reducing agent and high-temperature calcination, was developed using the redox properties of coordinatively unsaturated Fe(II) sites in MIL-100(Fe). The successful loading of Cu(I) ions and their redox-couple reactions are supported by various methods such as TEM/EDS, XPS, PXRD, and ICP-AES techniques, as well as N_2 adsorption isotherms at 77 K. Compared to Cu loaded into isostructural MIL-100(Al) devoid of redox active sites, Cu(I)-loaded MIL-100(Fe) exhibits higher C_3H_6/C_3H_8 selectivity and superior air stability. This indicates that the Fe(II) sites in MIL-100(Fe) act as antioxidants that protect the resultant Cu(I) species, as well as reducing agents for $CuCl_2$. Remarkably, in the typical pressure-swing adsorption (PSA) range (1–5 bar), the Cu(I)-loaded MIL-100(Fe) exhibits a large C_3H_6 working capacity as well as very high C_3H_6/C_3H_8 selectivities that are superior to those of the benchmark adsorbents, zeolite-13X and HKUST-1. Moreover, this material is easily regenerated under mild conditions and exhibits good separation performance under dynamic mixed-flow conditions. This facile method for loading Cu(I) can be applied to other adsorbents containing redox-active sites.

1. Introduction

Separation of olefin-paraffin mixtures is one of the most important and challenging issues in the petrochemical industry due to their similar physicochemical properties [1–3]. For over 70 years, their separations have been performed by cryogenic distillation, which is one of the most energy-intensive processes [4]. Although adsorptive separation is considered to be a promising energy-saving alternative, its success depends on the development of a highly efficient adsorbent [4]. Over the last few decades, numerous adsorbents, including zeolites and Ag(I)- or Cu(I)-loaded porous materials, have been screened in order to find a suitable adsorbent for these separations [4,5]. However, none of the materials developed so far satisfy all of the criteria for olefin adsorbents, such as high selectivity, large working capacity, and

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adsorption cyclability. This is mainly due to the limited surface areas and/or excessively strong adsorption sites within the constricted pores of these materials.

Recently, metal-organic frameworks (MOFs) have emerged as potential adsorbents for various gas separations because of their extremely high surface areas and tailorable pores [6–10]. Until now, several MOFs with unsaturated metal sites, such as M-MOF-74 [11,12] and HKUST-1 [13], have been prepared that exhibited considerable olefin selectivities as well as large olefin adsorption capacities. However, due to excessively strong adsorptions within small pores (6–12 Å), the abovementioned benchmark MOFs showed poor olefin working capacities under typical pressure-swing adsorption (PSA) conditions. The working capacity is the uptake at high pressure (e.g., 5 bar) minus the uptake at the desorption pressure (e.g., 1 bar). Hence, a strategy for creating olefin-selective adsorption sites with modest adsorption strengths within the large pores of MOFs needs to be developed.

The doping of the insides of MOF pores with transition metal ions has been recently studied for potential applications such as catalysis [14–16] and desulfurization [17–20]. Transition metal ions, such as Ag(I), Cu(I), Pt(II) and Pd(II), typically form strong π-complexes with the π-orbitals of gas or liquid molecules [21–24]. Among them, the Cu(I) ion is considered to be one of the most attractive candidates due to its low cost and ready availability [25–29]. Nevertheless, there have been very few reports on Cu(I)-loaded MOFs for olefin/paraffin separations [25].

Since MOFs have lower thermal stabilities than conventional zeolite-based support materials, it is important to develop a facile method for Cu(I) loading that does not require high-temperature calcination. Moreover, since Cu(I) ions are oxidized to Cu(II) under atmospheric conditions, the development of a Cu(I)-loaded adsorbent that is chemically stable to oxidation during the separation process is challenging.

Among the MOFs reported so far, MIL-100(Fe) is a promising material because of its high surface area ($> 2000\ m^2/g$), good hydrothermal stability, and facile synthesis scale-up [30]. This MOF has two types of mesoporous cages (29 and 25 Å), which are accessible through microporous windows (9 and 5 Å, respectively). While coordinatively unsaturated Fe(III) sites are created by heating the as-synthesized form above 373 K, a certain portion of Fe(III) is reduced to Fe(II) by heating at higher temperatures [31]. We reasoned that these redox-active Fe(II) sites could be utilized for the incorporation and stabilization of Cu(I) species. In this study, we successfully developed a novel Cu(I) loading method involving the facile reduction of $CuCl_2$ to CuCl, as well as the stabilization of the resultant Cu(I) ions through the redox properties of the Fe(II) sites in MIL-100(Fe) (Scheme 1). This Cu(I) loading method is facile because it does not require an external reducing agent and/or high-temperature calcination. Remarkably, the resultant Cu(I)-loaded MIL-100(Fe) exhibits good air stability as well as excellent propylene/propane separation performance.

2. Experimental

2.1. Materials

1,3,5-Benzenetricarboxylic acid (H_3BTC, 98%) and iron powder (Fe^0, ≥99%) were purchased from Alfa Aesar. Copper(II) chloride ($CuCl_2$, 99%), ammonium fluoride (NH_4F, ≥98%), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, ≥98%) and trimethyl 1,3,5-benzenetricarboxylate (Me_3BTC, ≥98%) were obtained from Sigma-Aldrich. Nitric acid (HNO_3, 60%), ethanol (EtOH, 99.5%), and dichloromethane (DCM, 99.5%) were provided by Daejung Chemical Co. Hydrofluoric acid (HF, 48–51%) was purchased from J.T. Baker.

2.2. Adsorbent syntheses

MIL-100(Fe) was synthesized and purified according to reported methods [31–33]. The molar amounts of the reagents in the reaction mixture were: 1.0 Fe^0: 0.67 BTC: 0.6 HNO_3: 2.0 HF: and 277 H_2O (BTC = 1,3,5-benzenetricarboxylic acid). The mixture was loaded into a Teflon-lined stainless-steel autoclave and stirred at ambient temperature for 30 min. The autoclave containing the reaction mixture was progressively heated to 433 K and kept at that temperature for 12 h, after which the autoclave was slowly cooled to room temperature. The resultant light-orange slurry was filtered and washed with deionized water. The obtained sample was immersed in hot water at 353 K for 3 h and then hot ethanol at 333 K for 3 h to remove any residual unreacted ions. The solid was finally further purified with 38 mM aqueous NH_4F at 343 K for 3 h. The highly purified MIL-100(Fe) was dried overnight at 353 K in air.

MIL-100(Al) was synthesized and purified in a similar manner to that reported [34]. The molar amounts of reagents in the reaction mixture were: 1.0 $Al(NO_3)_3 \cdot 9H_2O$: 0.667 Me_3BTC: 2.0 HNO_3: 300 H_2O (Me_3BTC = trimethyl-1,3,5-benzenetricarboxylate). The reaction was carried out in a Teflon-lined stainless-steel autoclave at 433 K for 12 h. The resulting product was filtered and washed several times with ethanol and then dried overnight at 353 K in air.

The Cu(n)@MIL-100(Fe) materials were prepared by mixing MIL-100(Fe) and an aqueous solution of $CuCl_2$ at several different $CuCl_2$/MIL-100(Fe) weight ratios (n = 0.2, 0.4, 0.6, and 0.8). The mixture was sonicated for 30 min at room temperature. The water (solvent) was subsequently removed at 338 K using a rotary evaporator. The samples obtained in this manner were then washed and filtered using dichloromethane (DCM) to remove any $CuCl_2$ located on the outer surfaces. The obtained Cu(n)@MIL-100(Fe) materials were finally dried in an oven at 333 K for 12 h, and then degassed under vacuum at 523 K for 8 h to afford the Cu(I)-loaded MIL-100(Fe) materials. For comparison, Cu(0.6)@MIL-100(Al) was prepared using the same method.

2.3. Adsorbent characterization

Powder X-ray diffraction (PXRD) patterns were recorded with an Ultima IV instrument (Rigaku Co., Japan) using Cu Kα radiation (λ = 1.54 Å) between 2θ values of 3° and 60° in 0.02° steps at a rate of 1 step s^{-1}. Transmission electron microscopy/energy dispersive X-ray spectroscopy (TEM/EDS) images were collected using a JEM-ARM 200F spectrometer (JEOL Ltd, Japan). X-ray photoelectron spectroscopy (XPS) data were obtained using a K-Alpha XPS spectrometer (Thermo, U.K.) equipped with a monochromated Al X-ray source (Al Kα line: 1486.6 eV).

The BET surface areas and total pore volumes of the MOFs were calculated from their N_2 adsorption isotherms at 77 K, which were obtained on a Tristar 3020 surface area and porosity analyzer (Micromeritics Instruments, USA). The specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) model in the linear range, as determined using the consistency criteria [35–37]. The total pore volumes were calculated at P/P_0 = 0.99. The pore size distributions were determined by the Horvath-Kawazoe (H-K) method after obtaining N_2 adsorption isotherms at 77 K using a 3Flex analyzer (Micromeritics, USA). Approximately 100 mg of sample was used for each measurement. Prior to any measurement, the MIL-100 and Cu(n)@MIL-100 samples were degassed under vacuum at 523 K for 8 h.

2.4. C_3H_6 and C_3H_8 adsorption isotherms

The adsorption isotherms for C_3H_6 and C_3H_8 at 323 K were also measured using the Tristar 3020 instrument (Micromeritics Instruments, USA) augmented with a specially designed air circulation system (Protech Korea Instruments, Korea) for maintaining constant temperature. High-pressure adsorption isotherms for C_3H_6 and C_3H_8 at 323 K were measured on a BELSORP-HP instrument (Microtrac-BEL Corp., Japan). Prior to any adsorption measurement, the MIL-100 and Cu(n)@MIL-100 samples were degassed under vacuum at 523 K for 8 h.