



The high efficient separation of divinylbenzene and ethylvinylbenzene isomers using high performance liquid chromatography with Fe-based MILs packed columns



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ABSTRACT

The baseline separation of divinylbenzene (DVB) and ethylvinylbenzene (EVB) isomers was achieved using HPLC with MIL-53(Fe) and MIL-100(Fe) packed columns respectively when hexane/dichloromethane (100:0) used as mobile phase, at flow rate of 0.5 mL min⁻¹, room temperature, and monitored with a UV detector at 254 nm. The two Fe-based MILs packed columns showed different separated performances, analytes had short retention time on MIL-100(Fe) compared to MIL-53(Fe), but selectivity of DVB isomers (*m*-DVB and *p*-DVB) was lower, which was mainly due to the differences of the pore size and structure of MILs. Moreover, the results of calculated thermodynamic parameters showed that the separation of DVB and EVB isomers was not only controlled by enthalpy change (ΔH), but also controlled by entropy change (ΔS). The head-to-tail stacking was the main reason for the separation according to the mechanism of the DVB and EVB isomers on Fe-based MILs packed columns.

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1. Introduction

As one of key materials for preparation of cross-linked styrene polymers [1], which are utilized in the manufacturing of ion-exchange resins, divinylbenzene (DVB) is commonly produced through dehydrogenation of diethylbenzene (DEB) isomers. So pure *m*- and *p*-DVB are not easily available but consist of *m*- and *p*-ethylvinylbenzene (EVB) as by-products due to their close boiling temperature. However, the proportion of *p*-DVB can impact the quality of ion-exchange resins [2]. It is emergency to separate commercial DVB. Currently, the main separation method of DVB and EVB isomers is rectification except the limited absorption separation and gas chromatography separation [2,3]. From an industrial standpoint, the large-scale separation methods have proven to be inefficient [2]. As an important separation method, the high performance liquid chromatography (HPLC) separation is widely used for separation of complicated chemical or environmental substances [4–8].

Metal-organic frameworks (MOFs) are synthesized via the self-assembling combination of organic ligands and inorganic metals or metal-oxo units (secondary building units, SBUs) using strong bonds to form a permanent, porous open crystalline framework [9,10], and having been attracted much attention in the last decades because of their unique characters [11–14], such as uniform structural cavities, tunable pore size, high surface area, good thermal and chemical stability [15–17]. So MOFs can be used as stationary phase for liquid chromatogram [18–20]. Among them, the MIL (Material of Institute Lavoisier) family synthesized via combination of carboxylate and trivalent metal center has particularly attracted a great deal of attention [21]. Specially, the structure of MIL-53(Fe) is flexible, i.e. “breathing effect”; it can adapt its pore size according to the guest species, but it doesn't lose its crystallinity or break bond. MIL-100(Fe), a crystalline three-dimensional iron (III) trimesate based on μ_3 -oxo-centered trimers of Fe^{III} octahedra, has open metal sites, and possesses two-types of mesoporous cages (25 and 29 Å) and accessible windows (5 and 9 Å). These excellent properties make Fe-based MILs suitable for being used in the field of HPLC separation. Yan et al. [22] found MIL-53(Fe) packed column has obvious advantages over MIL-53(Al, Cr) packed columns, and it achieved separation of xylene, chlorotoluene and dichlorobenzene

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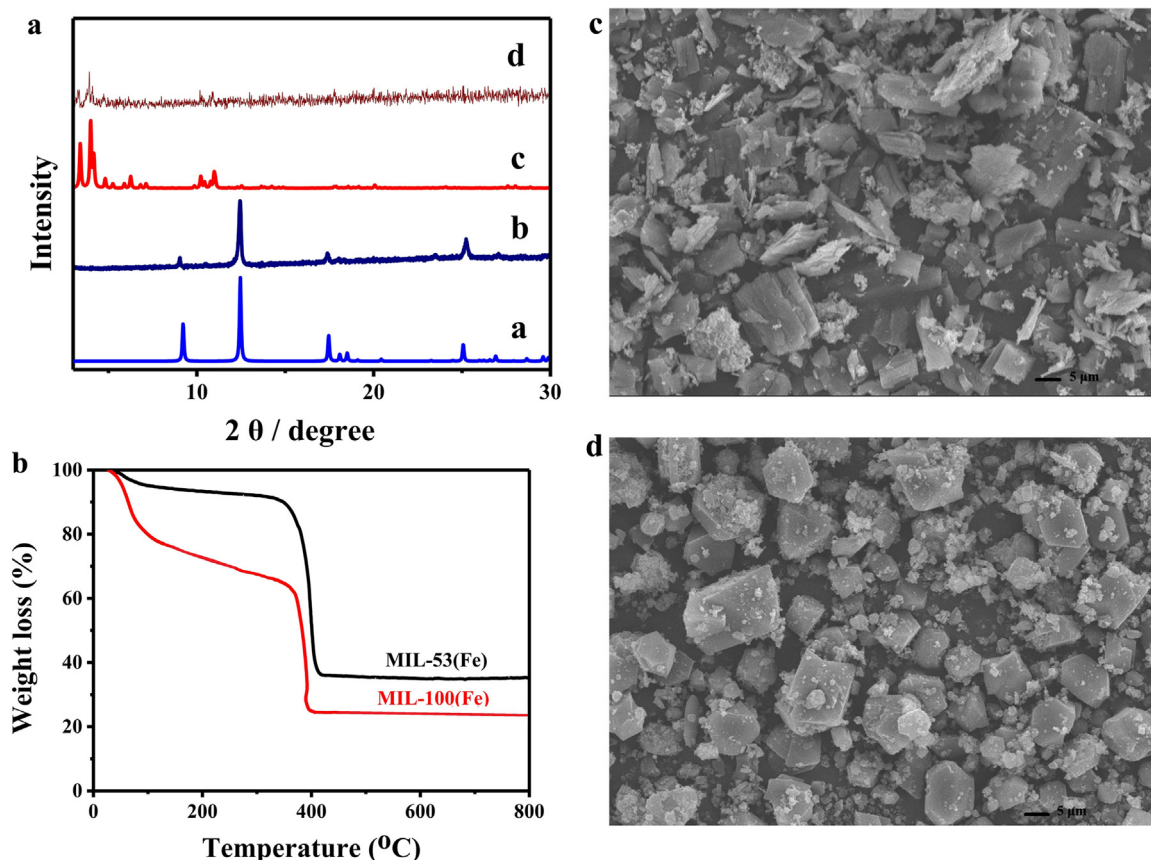


Fig. 1. Characterizations of the synthesized Fe-based MILs: (A) the simulated XRD patterns of MIL-53(Fe) (a) and MIL-100(Fe) (c), the synthesized MIL-53(Fe) (b) and MIL-100(Fe) (d); (B) TGA of the synthesized MIL-53(Fe) and MIL-100(Fe); (C) SEM image of the synthesized MIL-53(Fe); (D) SEM image of the synthesized MIL-100(Fe).

[22,23]; some aromatic compounds were also separated using MIL-100(Fe) packed column [24]. Their separation mechanisms mainly are stacking effect, hydrogen bonding. And the open metal sites of MIL-100(Fe) also play an important role [22–24]. Because both DVB and EVB belong to aromatic compounds, it is possible for their isomers to be separated using HPLC with Fe-based MILs columns.

So, in this work, a systematic study on the separation of the DVB and EVB isomers using Fe-based MILs packed columns was firstly carried out. The effects on the separation, such as the structure of MILs, organic ligand and Fe active sites were explored. In order to investigate the interaction between the isomers and Fe-based MILs, absorption enthalpies and entropies were measured and analyzed.

2. Experimental

2.1. Material and chemicals

All chemicals and reagents used were at least of analytical grade. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Iron ions, diethylbenzene (DEB), and *N,N*-Dimethylmethanamide (DMF) were purchased from Fuchen Chemical Reagent (Tianjin, China). Terephthalic acid and trimesic acid were purchased from Shanghai Aladdin Chemistry Co. Ltd. (Shanghai, China). Nitric acid, HF and ethanol were purchased from Beijing Chemical Works (Beijing, China). Divinylbenzene (DVB) was purchased from Alfa Aesar (Shanghai, China). Ultrapure water (18.2 MΩ cm) was obtained from MilliQ Advantage A10 system (Millipore, Molsheim, France).

Hexane and dichloromethane (DCM) were purchased from Fuchen Chemical Reagent (Tianjin, China). Methanol (MeOH) was purchased from Fisher Scientific (USA).

2.2. Apparatus

The X-ray diffraction (XRD) patterns of Fe-based MILs were obtained by a Bruker D8-Focus Bragg-Brentano X-ray powder diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178$), thermal gravimetric analysis (TGA) of MIL-53(Fe) and MIL-100(Fe) were performed on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of 2°C min^{-1} under a N_2 atmosphere. Scanning electron microscope (SEM) images were recorded on a ShimadzuSS-550 scanning electron microscope at 15.0 KV. The BET was measured on a Micromeritics ASAP2020 surface area by using N_2 absorption at 77 K.

The HPLC separation was performed on SHIMADZU LC-16 liquid chromatograph equipped with quaternion pump, column oven, variable wavelength detector, and manual injector (SHIMADZU, Japan). A KH-100B ultrasonic cleaner (Kunshan, China) was used for ultrasonic treatment. HY-HPLC-M chromatographic column packing instrument (Singapore Hydratech Industries, Beijing, China) was used to prepare the MILs packed columns.

2.3. Synthesis and characterization of Fe-based MILs

MIL-53(Fe) was synthesized according to previous studies [22,25]. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mmol), terephthalic acid (10 mmol), and DMF (50 mL) were loaded in a Teflon-lined steel autoclave at 150°C for three days. Then solid was washed with deionized water and dried in air.

MIL-100(Fe) was hydrothermal synthesized according to Férey et al. [26] Iron ions, trimesic acid, nitric acid, HF and H_2O (1.0: 0.67: 0.6: 2: 277) were introduced into a Teflon-lined steel autoclave at 150°C for 12 h. The light orange solid was filtered, and washed

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