Talanta 99 (2012) 944–950

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

# Evaluation of isostructural metal–organic frameworks coated capillary columns for the gas chromatographic separation of alkane isomers

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## ARTICLE INFO

*Article history:*
Received 13 June 2012
Received in revised form
22 July 2012
Accepted 25 July 2012
Available online 2 August 2012

*Keywords:*
Metal–organic frameworks
Stationary phase
Gas chromatography
Alkane isomers
Separation

## ABSTRACT

Isostructural metal–organic frameworks (MOFs) MIL-100(Fe) and MIL-100(Cr), which have identical organic linker and Mobil Thirty-Nine zeolitic type, but different metal ions, were exploited as stationary phases for capillary gas chromatographic separation of alkane isomers. MIL-100(Fe) coated capillary column showed great capability and high efficiency for the gas chromatographic separation of alkane isomers without the need of temperature-programming, while MIL-100(Cr) coated capillary column gave poor performance for the separation. The separation performance of MIL-100(Fe) coated capillary column was even better than commercial HP-5MS and GS-GasPro capillary columns. The determined McReynolds constants, adsorption enthalpies and entropies showed that MIL-100(Fe) coated capillary column gave relatively weaker interaction with alkane isomers than MIL-100(Cr) coated capillary column. The relative standard deviations of repeatability for C7 alkane isomers on MIL-100(Fe) coated capillary column were 0.06–0.16%, 1.1–1.5%, 2.8–3.0% and 2.1–2.4% for retention time, half peak width, peak height and peak area, respectively.

## 1. Introduction

Metal–organic frameworks (MOFs) are a new class of hybrid inorganic–organic microporous crystalline materials self-assembled straightforwardly from metal ions with organic linkers via coordination bonds. Their unique characters such as diverse structure topology, tunable pore size, permanent nanoscale porosity, high surface area, good thermostability, and uniform structured cavities, have made MOFs intriguing in hydrogen storage, catalysis, sensing, drug delivery, adsorption and separation [1–5].

Porous-layer open-tubular (PLOT) columns are popular in GC separation owing to their greater efficiency, faster separation, and fewer amounts of stationary phases than the packed columns [6]. However, currently available materials for PLOT columns are limited to a few kinds of nanoparticles such as alumina, carbon, silica, molecular sieve, and several porous polymers [6]. The high surface area, diverse structure and pore size, and good thermostability of MOFs provide a splendid future as novel coatings of PLOT columns for wide applications. Recently, great endeavors have been made to utilize MOFs as stationary phases for gas chromatography (GC) [7–11], especially for PLOT GC [12–15]. Studies of isostructural MOFs with identical metal ion but different pore apertures (e.g., ZIF-7 and ZIF-8) [12] and organic linkers with different functional groups (e.g., IR-MOF-1 and IR-MOF-3) [14] have been carried out. However, to our knowledge, there have been no reports on the effect of metal ion in isostructural MOFs on chromatographic separation so far, although such study should be beneficial for screening appropriate MOFs as stationary phases for chromatography.

Here we evaluated isostructural metal–organic frameworks MIL-100(Fe, Cr) coated capillary columns for the gas chromatographic separation of alkane isomers. The separation of alkane isomers is of great importance in petroleum and petrochemical industries [16–18]. To demonstrate the proof-of-concept, we chose MIL-100(Fe) and MIL-100(Cr) as stationary phases to separate alkane isomers. Although there are few reports involving the role of open metal sites in isostructural MOFs $M_2$(dhtp) (M=Mg, Mn, Co, Ni, Zn) on the adsorption of small molecules[19–24], isostructural MOFs MIL-100(Fe, Cr) has not been investigated for the role of metal ion in separation. MIL-100(Fe) and MIL-100(Cr) have different metal ions, but identical organic linker and Mobil Thirty-Nine (MTN) zeolitic type [25, 26], which contains two types of mesoporous cages of internal diameters of 25 and 29 Å, accessible through microporous pentagonal and hexagonal windows of 5.5 and 8.6 Å (Fig. S1 in the Supplementary Data).

In this work, a systematic study on the separation of alkane isomer on isostructural MOFs MIL-100(Fe, Cr) coated capillary columns was carried out. These isostructural MOFs coated capillary columns exhibited different separation performances. To get insight into the interaction between target analytes and

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http://dx.doi.org/10.1016/j.talanta.2012.07.063

MIL-100(Fe, Cr), McReynolds constants, adsorption enthalpies and entropies were measured and analyzed. Commercial GS-GasPro and HP-5 MS capillary columns were used for comparison to highlight the outstanding separation performance of MIL-100(Fe) coated capillary column. The intrinsic value of this designed study lies not only in exploring two kinds of novel stationary phases, but also in providing a new angle view for screening the most appropriate MOFs as stationary phase for GC.

## 2. Experimental section

### 2.1. Materials and chemicals

All the chemicals used are at least of analytical grade. Ultrapure water (18.2 MΩ cm) obtained from a WaterPro water purification system (Labconco Corporation, Kansas City, MO, USA) was used throughout this work. Fe° (Aladdin Reagent Co. Ltd., Shanghai, China), $CrO_3$ (Aladdin Reagent Co. Ltd., Shanghai, China), trimesic acid (Aladdin Reagent Co. Ltd., Shanghai, China), hydrofluoric acid (Aladdin Reagent Co. Ltd., Shanghai, China), and $HNO_3$ (Guangfu Fine Chemical Co. Ltd., Tianjin, China) were used for the synthesis of MIL-100(Fe) and MIL-100 (Cr). 2,2-dimethybutane, 2,3-dimethybutane, 2-methypentane, 2,2-dimethypentane and heptane were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). 2,2,3-trimethybutane was purchased from TCI Development Co. Ltd (Shanghai, China). 3,3-dimethypentane and 2,3-dimethypentane were purchased from Alfa Aesar (Ward Hill, MA, USA). 2-methyhexane was purchased from Across (Geel, Belgium). Cyclohexane, hexane and ethanol were purchased from Guangfu Fine Chemical Co. Ltd. (Tianjin, China). Fused silica capillary (20-m long × 0.25-mm i.d.) was purchased from Yongnian Optic Fiber Plant (Hebei, China).

### 2.2. Synthesis of MIL-100(Fe) and MIL-100(Cr)

MIL-100 (Fe) was synthesized according to Yoon et al. [27]. Typically, Fe° (112 mg, 2.0 mmol), trimesic acid (300 mg, 1.3 mmol), hydrofluoric acid (160 μL, 4.0 mmol), $HNO_3$ (75 μL, 1.2 mmol), and $H_2O$ (10 mL, 555.6 mmol) were loaded in a Teflon-lined bomb. The Teflon-lined bomb was then sealed, placed in an oven at 150 °C for 24 h. The obtained orange product was recovered by filtration and washed with ultrapure water. The as-synthesized MIL-100(Fe) was further purified by keeping in ultrapure water at 80 °C for 5 h, then in ethanol at 60 °C for 3 h, and recovered by filtration, washed with fresh ethanol. The solid was finally dried under ambient conditions. Thus, highly purified MIL-100(Fe) was obtained.

MIL-100(Cr) was synthesized according to Latroche et al. [28]. Typically, $CrO_3$ (250 mg, 2.5 mmol), trimesic acid (525 mg, 2.5 mmol), hydrofluoric acid (100 μL, 2.5 mmol), and $H_2O$ (12 mL, 666.7 mmol) were introduced into a Teflon-lined bomb. Then, the Teflon-lined bomb was sealed, and placed in an oven at 220 °C for 4 days. The green product was treated in the same way for MIL-100(Fe) to obtain highly purified MIL-100(Cr).

### 2.3. Characterization of MIL-100(Fe) and MIL-100(Cr)

The X-ray diffraction (XRD), thermal gravimetric analysis (TGA) and $N_2$ adsorption were employed to characterize the prepared MIL-100(Fe) and MIL-100(Cr). The XRD patterns were recorded with a D/max-2500 diffractometer (Rigaku, Japan) using $Cu_{K\alpha}$ radiation ($\lambda$=1.5418 Å). TGA experiments were performed on a PTC-10A thermal gravimetric analyzer (Rigaku, Japan) from room temperature to 650 °C at a ramp rate of 10 °C $min^{-1}$. BET surface area was measured on an ASAP 2010 micropore physisorption analyzer (Micromeritics, Norcross, GA, USA) using nitrogen adsorption at 77 K in the range $0.02 \leq P/P_0 \leq 0.20$.

The MIL-100(Fe, Cr) coated capillary columns were characterized by scanning electron microscopy (SEM). The capillaries were cut to expose the inner wall for SEM measurement. These SEM images were recorded on a Shimadzu SS-550 scanning electron microscope (Kyoto, Japan) at 15.0 kV.

### 2.4. Capillary pretreatment and preparation of MIL-100(Fe, Cr) coated capillary columns

Fused silica capillary (20-m long × 0.25-mm i.d.) was treated according to the following recipe before coating: the capillary was washed sequentially with 1 M NaOH, ultrapure water, 0.1 M HCl, ultrapure water, and finally ethanol. The capillary was dried with a nitrogen purge at 120 °C overnight.

The MIL-100(Fe) crystals were coated into the inner wall of the pretreated capillary columns by a dynamic coating method as follows [6]: MIL-100(Fe) was dispersed into ethanol, and sonicated for 3 h to prepare 6 mg $mL^{-1}$ homogenous suspension. 0.2-mL suspension was filled into the capillary column (20-m long × 0.25-mm i.d.), and then pushed with $N_2$ at a velocity of 18 cm $min^{-1}$ to leave a wet coating layer on the inner wall of the capillary column. To avoid acceleration of the solution plug near the end of the column, a 1-m long buffer tube (0.25-mm i.d.) was attached to the capillary column end as a restrictor. After coating, the capillary column settled for 2 h for conditioning under nitrogen. Further conditioning of the capillary column was carried out using a temperature program including three steps: 40 °C for 10 min, ramp from 40 °C to 250 °C at a ramp rate of 1 °C $min^{-1}$, and 250 °C for 30 min. The procedure was repeated for five times. Thus, MIL-100(Fe) (6 mg $mL^{-1}$) coated capillary column was obtained.

The MIL-100(Cr) crystals were coated into the inner wall of the pretreated capillary columns in the same way. Finally, MIL-100(Cr) (2 mg $mL^{-1}$)-coated, MIL-100(Cr) (6 mg $mL^{-1}$)-coated and MIL-100(Cr) (10 mg $mL^{-1}$)-coated capillary columns were obtained.

### 2.5. GC measurements

All GC separations were performed on an Agilent 7890A/5975C GC system fitted with a flame ionization detector (FID) (Agilent, Santa Clara, CA, USA). Data acquisition and processing were controlled by ChemStation software. Hydrogen and air flow were maintained at 30 and 400 mL $min^{-1}$, respectively. The inlet and detector temperatures of GC were both set at 250 °C. High purity nitrogen (99.999%, BOC Gases Co. Ltd., Tianjin, China) was employed as a carrier gas. The split ratio is 10:1. The commercial GS-GasPro (20-m long × 320-μm i.d.) and HP-5 MS capillary column (30-m long × 250-μm i.d.) from Agilent Technologies were employed for comparison.

### 2.6. Calculation of the adsorption enthalpies and entropies of alkane isomers on MIL-100(Fe) and MIL-100(Cr)

Adsorption enthalpy ($\Delta H$) and entropy ($\Delta S$) for the interaction between the analytes and the stationary phase were calculated from the van't Hoff equation (Eq. (1)) [29,30]

$$\ln k' = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln \Phi \tag{1}$$

where $k'$ is the retention factor, $R$ is the gas constant, $T$ is the absolute temperature, and $\Phi$ is the phase ratio. The phase ratio, $\Phi$, is defined as the volume of the stationary phase divided by the volume of the mobile phase. A phase ratio of $8.05 \times 10^{-3}$ based on a 0.5-μm stationary phase film thickness was calculated for the capillary columns. The value of $k'$ was calculated according to Eq. (2)

$$k' = (t - t_0)/t_0 \tag{2}$$

where $t$ is the retention time for the analyte and $t_0$ is the column void time.

## 3. Results and discussion

### 3.1. Characterization of MIL-100(Fe) and MIL-100(Cr)

The successful synthesis of MIL-100(Fe) and MIL-100(Cr) was confirmed by comparing the experimental X-ray diffraction (XRD) patterns with the simulated one (Fig. S2a in the Supplementary Data). The thermal gravimetric analysis (TGA) curves show that MIL-100(Fe, Cr) frameworks were stable up to about 280 °C (Fig. S2b in the Supplementary Data). The first weight loss at 100 °C arose from the departure of free water molecules inside the pores, while the second loss resulted from the escape of water molecules which interacted with the metal ions. The gaseous $N_2$ sorption isotherms (Fig. S3 in the Supplementary Data) on fully evacuated samples are between type I and type IV with slight secondary uptakes, indicating the existence of micro- and mesopores. The estimated BET surface areas of the as-prepared MIL-100(Fe) and MIL-100(Cr) were 2040 and 2153 $m^2\,g^{-1}$, respectively. Particle size distributions of MIL-100(Fe) and MIL-100(Cr) were investigated (Fig. S4 in the Supplementary Data). The average diameter of MIL-100(Fe) is 899.1 nm and the effective diameter is 607.0 nm; the average diameter of MIL-100(Cr) is 638.9 nm and the effective diameter is 569.0 nm. The average particle sizes of both MIL-100(Fe) and MIL-100(Cr) are much smaller when the alcohol suspensions of them are sonicated, but the diameters increased as time passed, especially for MIL-100(Fe).

### 3.2. Separation of alkane isomers on MIL-100(Cr) and MIL-100(Fe) coated capillary columns

The MIL-100(Fe) coated capillary column offered high resolution and selectivity for the separation of alkane isomers within 5 min without the need for temperature-programming (Fig. 1a, b). However, MIL-100(Cr) coated capillary gave a poor separation performance: not only the alkane isomers were not baseline separated even the elution time was approximately three times long as that on MIL-100(Fe) coated capillary column, but also the peaks were broad and tailing (Fig. 1c, d). In addition, MIL-100(Fe) coated capillary column gave much smaller half peak widths, and much larger theoretical plate numbers for C6 alkane isomers than MIL-100(Cr) coated capillary column (Fig. S5 in the Supplementary Data).

To reveal whether the poor separation of alkane isomers on MIL-100(Cr) coated capillary column was caused by technical factors or not, the effects of temperature and coating thickness were studied (Fig. 2). Increase of the separation temperature from 70 to 110 °C on MIL-100(Cr) (6 mg $mL^{-1}$) column improved the peak shape to some extent (Fig. 2b), but reduced the selectivity and resolution (Fig. 3). The results indicate that baseline separation of alkane isomers is impossible in the studied temperature range.

Furthermore, capillary columns with different thickness of MIL-100(Cr) coatings were fabricated with various concentrations of MIL-100(Cr) ethanolic suspensions to evaluate the effect of the coating thickness on separation. Change of the concentration of MIL-100(Cr) ethanolic suspension resulted in different thickness

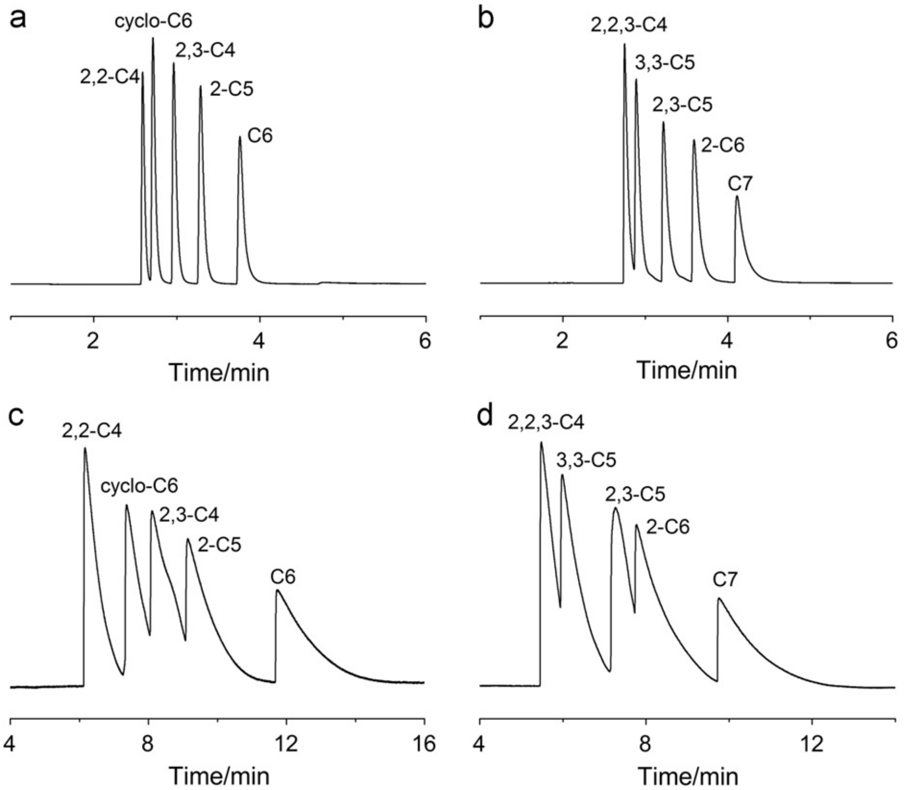

**Fig. 1.** Chromatograms on MIL-100(Fe) (6 mg $mL^{-1}$) (a, b) and MIL-100(Cr) (6 mg $mL^{-1}$) (c,d) coated capillary columns (20 m × 0.25 mm i.d.): (a, c) C6 group: 2,2-C4 (2,2-dimethybutane), cyclo-C6 (cyclohexane), 2,3-C4 (2,3-dimethybutane), 2-C5 (2-methypentane), and C6 (hexane) under a $N_2$ flow rate of 1.0 mL $min^{-1}$ at 80 °C and (b, d) C7 group: 2,2,3-C4 (2,2,3-trimethybutane), 3,3-C5 (3,3-dimethypentane), 2,3-C5 (2,3-dimethypentane), 2-C6 (2-methyhexane) and C7 (heptane) under a $N_2$ flow rate of 1.0 mL $min^{-1}$ at 110 °C.

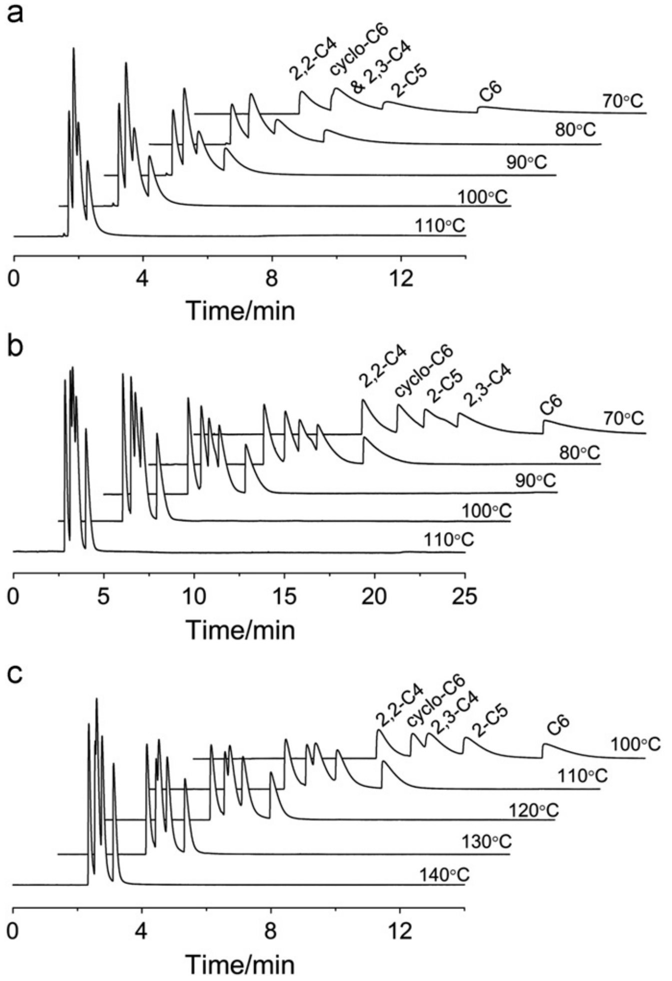

**Fig. 2.** Chromatograms of C6 group on MIL-100(Cr) coated capillary column ($20\,\mathrm{m} \times 0.25\,\mathrm{mm}$ i.d.) at various temperatures under a $N_2$ flow rate of $1.0\,\mathrm{mL\,min^{-1}}$. Concentration of MIL-100(Cr) suspension used to prepare MIL-100(Cr) coated capillary ($\mathrm{mg\,mL^{-1}}$): (a) 2, (b) 6, and (c) 10.

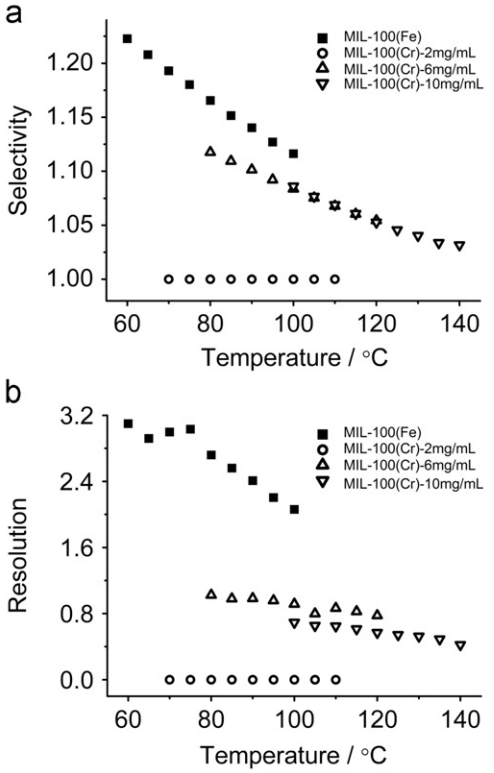

**Fig. 3.** Effect of temperature on: (a) selectivity and (b) resolution of cyclohexane and 2,3-dimethybutane on MIL-100(Fe) ($2\,\mathrm{mg\,mL^{-1}}$), MIL-100(Cr) ($2\,\mathrm{mg\,mL^{-1}}$), MIL-100(Cr) ($6\,\mathrm{mg\,mL^{-1}}$), and MIL-100(Cr) ($10\,\mathrm{mg\,mL^{-1}}$) coated capillary columns.

**Table 1**
McReynolds constants for MIL-100(Fe, Cr) coated capillary columns at 100 °C.

| MOFs | *X* [a] | *Y* [a] | *Z* [a] | *U* [a] | *S*[a] |
|---|---|---|---|---|---|
| MIL-100(Fe) | −45.8 | −2.6 | 56.4 | 27.0 | −104.6 |
| MIL-100(Cr) | −32.5 | 97.9 | 44.6 | 43.7 | −42.1 |

[a] *X* refers to benzene, which is related to weak dispersion forces and polarizability character of the phase; *Y* represents *n*-butanol, which indicates the hydrogen-bonding ability of the phase; *Z* represents 2-pentanone, whose behavior relates to the polarizability and part of the dipolar character of the stationary phase; *U* refers to nitropropane, which is related to the electron donor, electron acceptor, and dipolar character of the phase; the *S* term, from pyridine, a strong proton acceptor and polar molecule, indicates the acidic character of the phase.

of MIL-100(Cr) coatings on the inner walls of capillary columns (Fig. S6 in the Supplementary Data), but the selectivity and resolution of alkane isomers were not improved significantly (Fig. 3), and thus baseline separation of alkane isomers was still impossible on these MIL-100(Cr) coated capillary columns (Fig. 2a, c). Therefore, the poor separation of alkane isomers on MIL-100(Cr) coated capillary column cannot be attributed to the effects of separation conditions such as separation temperature and the thickness of the MIL-100(Cr) coatings.

The remarkable difference of the separation performance between MIL-100(Fe) and MIL-100(Cr) most likely originated from the nature of MIL-100(Fe) and MIL-100(Cr). MIL-100(Fe) and MIL-100(Cr) have identical organic linker and Mobil Thirty-Nine (MTN) zeolitic type, but different metal ions, which should be responsible for the different separation performances. As most widely used system for classifying chromatographic stationary phases, McReynolds constants were used to describe the polarity of the MIL-100 columns using benzene, 1-butanol, 2-pentanone, 1-nitropropane, and pyridine as test solutes [13,31]. The McReynolds constants for MIL-100(Fe, Cr) are summarized in Table 1. The larger McReynolds constants of MIL-100(Cr) coated column indicate that MIL-100(Cr) shows stronger hydrogen-bonding ability than MIL-100(Fe) (See the *Y* term in Table 1).

According to the molecular simulation studies by Nicholson and Bhatia[32], besides the van der Waals interaction between alkane and the framework of MOFs, the hydrogen atom of alkane can form H-bond with the framework oxygen of the organic linkers, which also contributes to the total binding energy. Compared with Cr(III), Fe(III) has smaller radius and stronger electrostatic Coulomb interaction with the framework oxygen. Therefore, MIL-100(Fe) gives less partial negative charges on the framework oxygen, in turn weaker C–H…O bonds between CH group of alkanes and the framework oxygen than MIL-100(Cr).

To get further insight into the different separation performances between MIL-100(Fe) and MIL-100(Cr), thermodynamic parameters (Table 2) for the separation of alkanes on MIL-100(Fe) and MIL-100(Cr) coated capillary columns were calculated from van't Hoff plots (Fig. S7 in the Supplementary Data). For all of the alkanes tested, MIL-100(Cr) coated capillary column gave larger negative enthalpy changes than MIL-100(Fe) capillary column, indicating stronger energetic interaction between alkanes and MIL-100(Cr). Besides, MIL-100(Cr) coated capillary offered larger negative entropy changes for all the alkanes than MIL-100(Fe) coated capillary column, suggesting that the alkane moleclues

**Table 2**
Enthalpy and entropy changes for the gas chromatographic separation of alkane isomers on MIL-100(Fe) and MIL-100(Cr) coated capillary columns.

| Alkane isomers | MIL-100(Fe) column | | MIL-100(Cr) column | |
|---|---|---|---|---|
| | $-\Delta H$ (kJ mol$^{-1}$) | $-\Delta S$ (J mol$^{-1}$ K$^{-1}$) | $-\Delta H$ (kJ mol$^{-1}$) | $-\Delta S$ (J mol$^{-1}$ K$^{-1}$) |
| 2,2-Dimethybutane | $28.1 \pm 0.4$ | $35.6 \pm 1.2$ | $40.7 \pm 0.5$ | $62.7 \pm 0.3$ |
| Cyclohexane | $29.4 \pm 0.5$ | $38.7 \pm 1.4$ | $42.7 \pm 0.5$ | $66.5 \pm 0.4$ |
| 2,3-Dimethybutane | $31.4 \pm 0.4$ | $43.3 \pm 1.2$ | $44.4 \pm 0.5$ | $70.4 \pm 0.3$ |
| 2-Methypentane | $33.9 \pm 0.4$ | $49.0 \pm 1.1$ | $46.1 \pm 0.5$ | $74.1 \pm 0.4$ |
| Hexane | $37.1 \pm 0.5$ | $56.1 \pm 1.3$ | $48.9 \pm 0.5$ | $79.8 \pm 0.5$ |
| 2,2,3-Trimethybutane | $34.7 \pm 0.5$ | $46.3 \pm 1.4$ | $45.4 \pm 0.1$ | $66.4 \pm 0.3$ |
| 3,3-Dimethypentane | $36.0 \pm 0.5$ | $49.0 \pm 1.4$ | $46.9 \pm 0.2$ | $69.4 \pm 0.6$ |
| 2,3-Dimethypentane | $38.4 \pm 0.5$ | $54.0 \pm 1.4$ | $48.5 \pm 0.4$ | $71.7 \pm 0.9$ |
| 2-Methyhexane | $40.7 \pm 0.5$ | $58.9 \pm 1.3$ | $50.7 \pm 0.3$ | $76.8 \pm 0.8$ |
| Heptane | $43.1 \pm 0.5$ | $63.6 \pm 1.3$ | $53.8 \pm 0.5$ | $82.9 \pm 1.2$ |

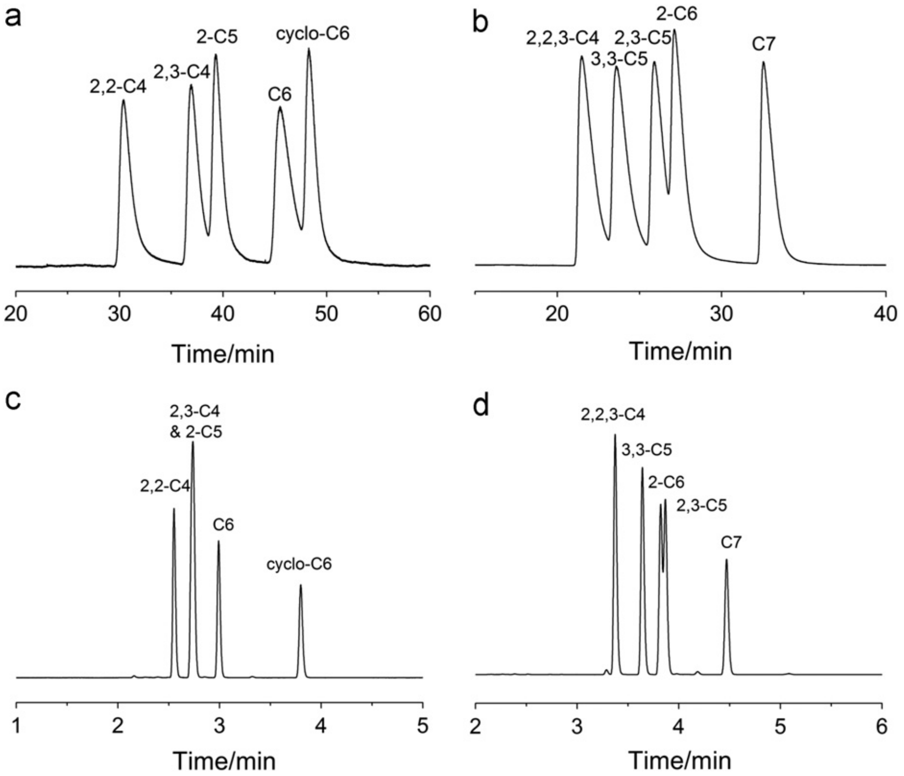

**Fig. 4.** Chromatograms on GS-GasPro capillary column (20 m × 0.32 mm i.d.) (a, b) and HP-5MS capillary column (30 m × 0.25 mm i.d.) (c, d): (a) C6 group under a $N_2$ flow rate of 1.0 mL min$^{-1}$ at 80 °C, (b) C7 group under a $N_2$ flow rate of 1.0 mL min$^{-1}$ at 110 °C, (c) C6 group, and (d) C7 group under a $N_2$ flow rate of 1.0 mL min$^{-1}$ at 40 °C.

lost more freedom, adsorbed more tightly and restricted to a higher degree in MIL-100(Cr). Both larger negative enthalpy and entropy changes on MIL-100(Cr) coated capillary column resulted in stronger interaction of the alkane molecules with the stationary phase and loss of more freedom during separation, leading to longer retention time, tailing chromatographic peak, and lower resolution on MIL-100(Cr) coated capillary column. The less negative enthalpy and entropy changes on MIL-100(Fe) coated capillary column are beneficial for gas chromatographic separation of alkane isomers.

### *3.3. Advantages of MIL-100(Fe) coated capillary over commercial GC capillary columns for the separation of alkane isomers*

Commercial GS-GasPro and HP-5MS capillary columns were employed for comparison to highlight the outstanding separation performance of MIL-100(Fe) coated capillary column. GS-GasPro capillary column is a PLOT column, coated with silica-based adsorbents. Separation of C1–C12 hydrocarbons is one of its typical applications. However, both C6 and C7 groups cannot be baseline separated on GS-GasPro capillary column (Fig. 4a, b). The elution time is very long, 50 min for C6 group and 35 min for C7 group. Different separation temperatures are helpless for efficient separation (Fig. S8 in the Supplementary Data). HP-5MS capillary column is an excellent non-polarity column coated with (5%-phenyl)-methylpolysiloxane. Even though HP-5MS column gives symmetrical chromatographic peaks of the alkane isomers (Fig. 4c, d), 2,3-dimethybutane and 2-methypentane eluted simultaneously while 2,3-dimethypentane and 2-methyhexane overlapped seriously. Decrease of temperature to 26 °C (the lowest temperature our GC could reach) and the velocity of $N_2$ to 0.1 mL min$^{-1}$ can not improve the separation performance of HP-5MS (Fig. S9 in the Supplementary Data). In contrast, the MIL-100(Fe) coated capillary column gave high resolution and selectivity for the separation of alkane isomers within 5 min (Fig. 1a, b). The above results show obvious advantages of the MIL-100(Fe) coated capillary column over commercial GS-GasPro and HP-5MS capillary columns for the separation of alkane isomers.

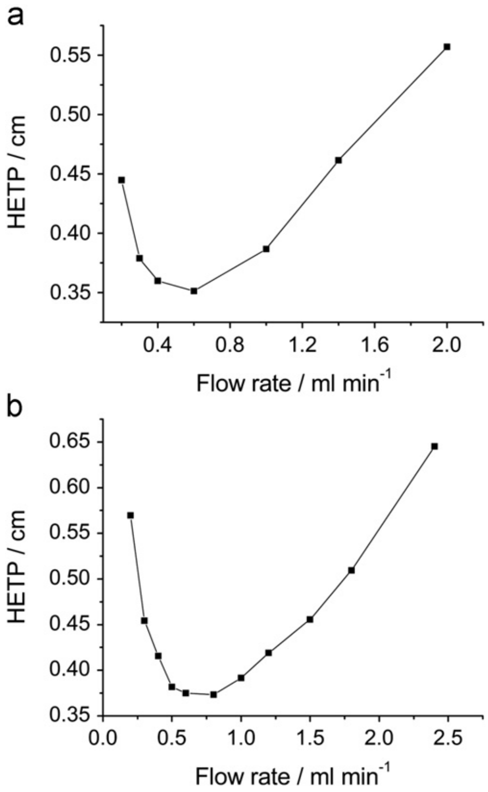

**Fig. 5.** Van Deemter plots for 2,2-dimethybutane (150 mg) on: (a) MIL-100(Fe) coated capillary column at 80 °C and (b) HP-5MS capillary column at 40 °C.

### 3.4. Figures of merit of MIL-100(Fe) coated capillary column

The van Deemter plots of the MIL-100(Fe) coated capillary column and HP-5MS column were measured by employing 2,2-dimethybutane as the test molecule at 80 °C and 40 °C under a $N_2$ flow of 1 mL min$^{-1}$. MIL-100(Fe) coated capillary column gave smaller height equivalent to a theoretical plate (HETP) than HP-5MS column (Fig. 5).

The ability for quantitative and qualitative analysis on MIL-100(Fe) coated capillary column was further investigated by changing the mass of the analytes. An increase of the injected target mass resulted in a linear increase of chromatographic peak area response in the range of 0–120 ng (Fig. 6). No significant effect of analyte mass on retention time was observed, resulting in stable retention factor in the studied range. This feature of MIL-100(Fe) coated capillary column is favorable for its application to quantitative analysis. Besides, MIL-100(Fe) coated capillary column has good reproducibility. The relative standard deviation (RSD) of repeatability for C7 alkane isomers on MIL-100(Fe) coated capillary column is 0.06–0.16%, 1.1–1.5%, 2.8–3.0% and 2.1–2.4% for retention time, half peak width, peak height and peak area (Fig. S10, Table S1 in the Supplementary Data), respectively.

## 4. Conclusions

In summary, isostructural metal–organic frameworks MIL-100(Fe, Cr) coated capillary columns were evaluated for the gas chromatographic separation of alkane isomers. MIL-100(Fe) coated column offers excellent features for capillary gas chromatographic separation of alkane isomers with excellent repeatability, whereas MIL-100(Cr) coated capillary column gives poor separation performance. Baseline

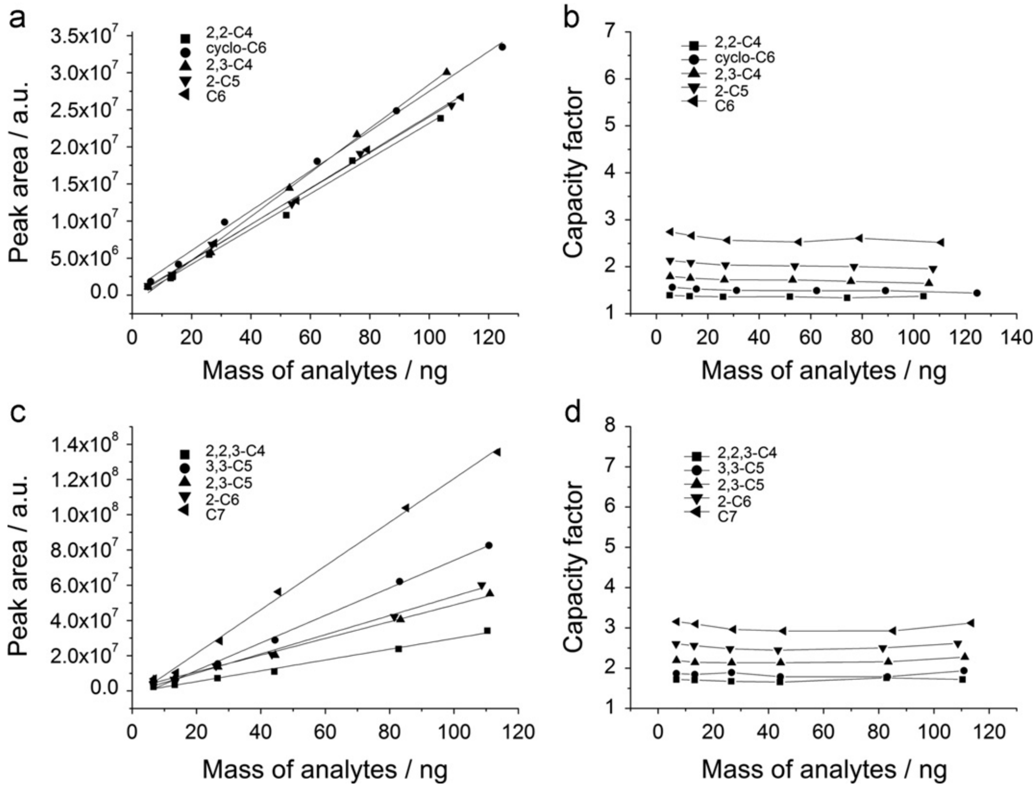

**Fig. 6.** Effect of analyte mass on peak area response and retention factor on MIL-100(Fe) coated capillary column under 80 °C at a $N_2$ flow rate of 1.0 mL min$^{-1}$.

separation of C6–C7 alkane isomers has been achieved on MIL-100(Fe) coated capillary column only within 5 min without the need for temperature-programming, better than the commercial GS-Gaspro and HP-5MS capillary columns. The MIL-100(Fe) coated capillary column is promising for the separation of alkane isomers. The easy synthesis of MOFs and facile fabrication of capillary columns coated with only tiny amount of MOFs in conjunction with their diverse structures and unique properties make MOFs attractive and cost-effective as novel stationary phases in capillary gas chromatography. However, it is imperative to evaluate the long term stability of MOFs coated PLOT columns for their practical applications.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grants 20935001 and 21077057) and the Fundamental Research Funds for the Central Universities.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.07.063.

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