



# Synthesis, characterization, and CO<sub>2</sub> adsorption properties of metal-organic framework NH<sub>2</sub>-MIL-101(V)

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## ARTICLE INFO

### Article history:

Received 22 November 2019  
Received in revised form 17 January 2020  
Accepted 21 January 2020  
Available online 22 January 2020

### Keywords:

Porous materials  
Composite materials  
Metal-organic frameworks  
CO<sub>2</sub> adsorption

## ABSTRACT

NH<sub>2</sub>-MIL-101(V), an amine-functionalized vanadium-based metal-organic framework (MOF) material, was successfully synthesized using a solvothermal strategy. The obtained material was characterized by X-ray diffraction (XRD), N<sub>2</sub> adsorption-desorption isotherms, Fourier transformed infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and transmission electron microscopy (TEM) techniques. The CO<sub>2</sub> and N<sub>2</sub> adsorption properties of the material were measured using the Micromeritics ASAP 2020 apparatus under ambient conditions. Compared to the previously reported method for synthesizing this MOF, we performed synthesis under a lower reaction temperature. Despite this, pure-phase NH<sub>2</sub>-MIL-101(V) nanocrystals with diameters of 40–60 nm were achieved. The synthesized sample had a large specific surface area (2340 m<sup>2</sup>/g), denoting a substantial enhancement to the literature value of the corresponding analogue. In addition, the NH<sub>2</sub>-MIL-101(V) possessed a high CO<sub>2</sub> uptake of 1.9 mmol/g at 25 °C and a pressure of 100 kPa and exhibited high CO<sub>2</sub>/N<sub>2</sub> selectivity as well as moderate CO<sub>2</sub> isosteric heat of adsorption.

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## 1. Introduction

Metal-organic frameworks (MOFs) have emerged as a new class of fully crystalline porous materials constructed by metal ions/clusters and organic linkers via metal-ligand bonds. Because of their diverse topological structures, pore dimensions, and chemical functionalities, MOFs have attracted attention in various research fields, especially in catalysis and separation [1,2]. According to preliminary statistics, more than 10,000 MOFs with different structures have been reported in the literature [3]. Among these, the Cr-based MIL-101 (MIL stands for Matériel Institut Lavoisier) has attracted significant attention for catalysis and separation purposes due to its three-dimensional structure, large specific surface area, fully accessible uniform porosity, and its robust thermal and chemical stability [4,5].

The amine-functionalized MIL-101(Cr), MIL-101(Fe), and MIL-101(Al) have also been successfully synthesized by hydrothermally reacting the organic linker 2-aminoterephthalic acid (NH<sub>2</sub>-BDC) with the corresponding metal precursors [3,6,7]. However, other isostructural MOFs containing trivalent metal vanadium as metal nodes have not been examined in depth. Given that the supported vanadium oxide-based catalysts are widely applied in the chemical

industry and the vanadium species is the active center of many biological enzymes, the synthesis of vanadium-based MOFs is an interesting subject for materials chemists [8–12]. To the best of our knowledge, there is currently only one report on the synthesis of NH<sub>2</sub>-MIL-101(V) [12]. The synthesized NH<sub>2</sub>-MIL-101(V) exhibited low X-ray diffraction (XRD) crystallinity and a rather low specific surface area (1623 m<sup>2</sup>/g), which could be attributable to the diversity and complexes of vanadium clusters that can form during MOF synthesis, resulting in difficult outcoming pure-phase NH<sub>2</sub>-MIL-101(V).

We report the reproducible synthesis of an amine-functionalized MIL-101(V) material using a solvothermal method. We were able to fabricate pure-phase NH<sub>2</sub>-MIL-101(V) nanocrystals with a relatively large specific surface area simply by lowering the synthesis temperature. The adsorption properties of the synthesized NH<sub>2</sub>-MIL-101(V) sample were evaluated in terms of single-component adsorption. The results showed that NH<sub>2</sub>-MIL-101(V) is a promising candidate for the effective removal of CO<sub>2</sub> from N<sub>2</sub>.

## 2. Experimental

NH<sub>2</sub>-MIL-101(V) nanocrystals were synthesized using a solvothermal method. In a typical procedure, NH<sub>2</sub>-BDC (0.5616 g, 3.1 mmol) was dissolved in DMF (10 mL) to form a clear solution. Following this, VCl<sub>3</sub> (0.9989 g, 6.35 mmol) was mixed with the

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above solution. To accelerate the dissolution of  $VCl_3$ , the mixture was stirred at 25 °C for 30 min, followed by sonication for 15 min. The solution was transferred into a Teflon-lined autoclave (50 mL). The autoclave was sealed and heated to 120 °C in an oven and held at this temperature for 24 h without stirring. After spontaneously cooling to room temperature, the resultant green precipitate was collected by filtration, washed with DMF (30 mL) and ethanol (30 mL) three times, and dried in a flowing nitrogen atmosphere for 12 h. MIL-101(V) nanocrystals were synthesized using the same method, but using BDC as the organic ligand.

### 3. Results and discussion

The crystal structures of the synthesized MIL-101(V) and  $NH_2$ -MIL-101(V) were determined using XRD. The results revealed

that the XRD patterns of MIL-101(V) and  $NH_2$ -MIL-101(V) were almost identical to the simulated patterns of MIL-101(Cr) (Fig. 1A) [4,5], and no impurity phase was observed, demonstrating the successful synthesis of pure-phase MOFs. Fig. 1B displays the  $N_2$  adsorption–desorption isotherms of the synthesized MOFs. Both isotherms exhibited the characteristic steps of the typical MIL-101 structure [3]. The Brunauer–Emmet–Teller (BET) specific surface areas of the MIL-101(V) and  $NH_2$ -MIL-101(V) were 2623 and 2340  $m^2/g$ , respectively.

To analyze the chemical composition and bonding configuration of the synthesized MOFs, the samples were characterized by XPS (Fig. 2 and Fig. S1 in the Supporting Information). From the survey spectrum in Fig. 2A, the sample was found to contain C, O, N, and V elements. In Fig. 2B, the deconvolution of the C 1s peak resulted in three peaks of 284.8, 286.1, and 288.6 eV, corresponding to the

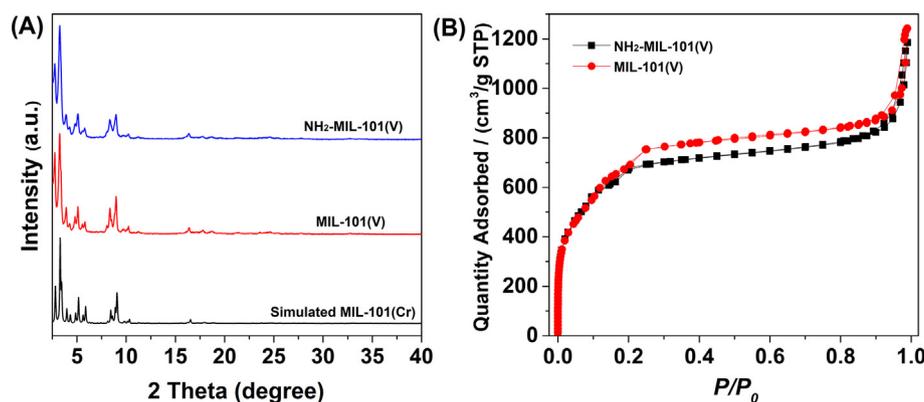


Fig. 1. (A) XRD patterns of simulated MIL-101(Cr), synthesized MIL-101(V) and  $NH_2$ -MIL-101(V), and (B)  $N_2$  adsorption isotherms at  $-196$  °C of synthesized MIL-101(V) and  $NH_2$ -MIL-101(V).

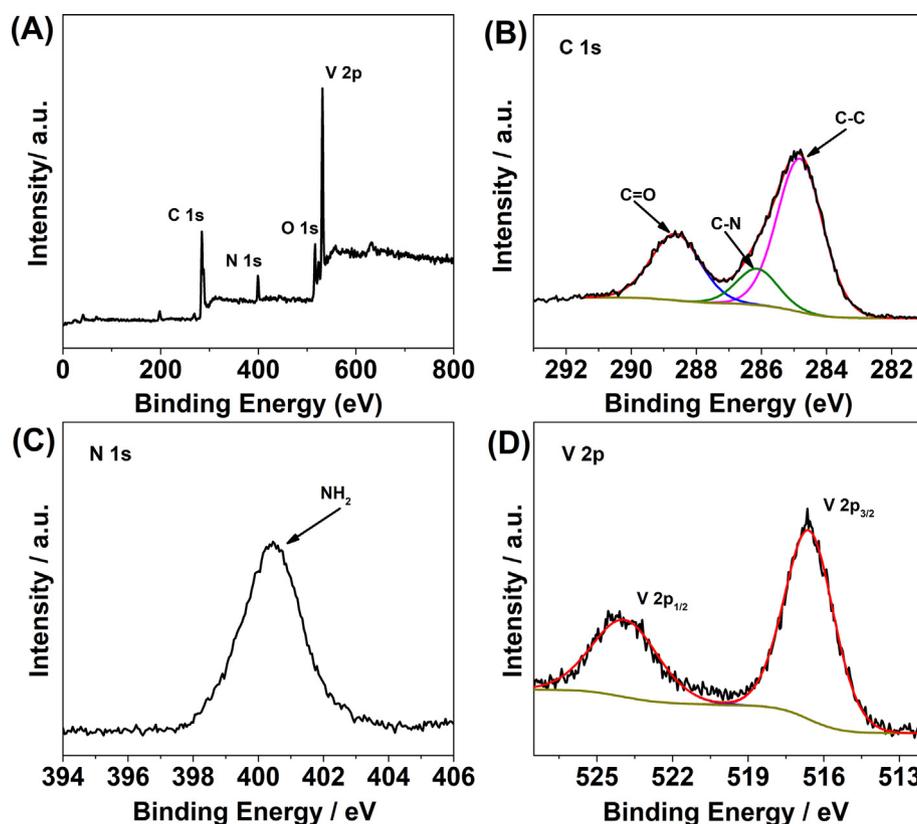
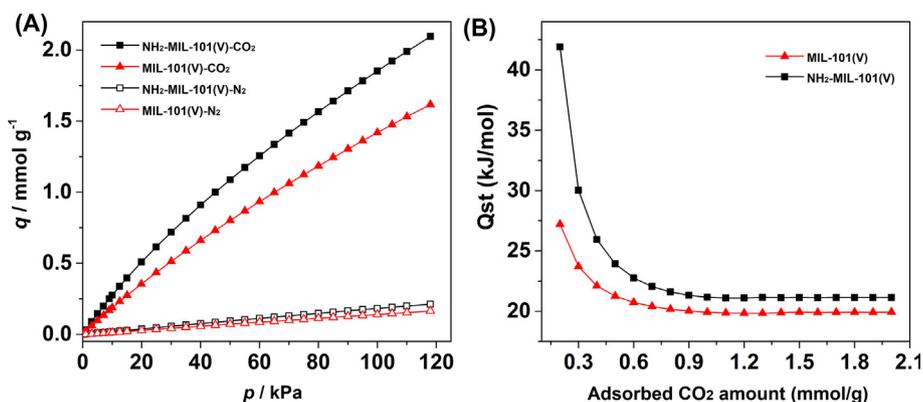


Fig. 2. XPS spectra of  $NH_2$ -MIL-101(V): (A) survey spectrum, (B) high resolution of C spectrum, (C) high resolution of N spectrum, and (D) high resolution of V spectrum.

**Table 1**  
Comparison of synthesis temperature and BET specific surface area of MIL-101 based samples.

Sample	Temperature (°C)	$S_{\text{BET}}$ (m <sup>2</sup> /g)	Reference
MIL-101(V)	120	2623	This work
NH <sub>2</sub> -MIL-101(V)	120	2340	This work
MIL-101(V)	150	2118	12
NH <sub>2</sub> -MIL-101(V)	150	1623	12
NH <sub>2</sub> -MIL-101(Al)	130	2100	3
NH <sub>2</sub> -MIL-101(Fe)	110	2476	6



**Fig. 3.** (A) Comparison of the adsorption isotherm data of CO<sub>2</sub> and N<sub>2</sub> on NH<sub>2</sub>-MIL-101(V) and MIL-101(V) at 25 °C, and (B) the corresponding isosteric heat of adsorption for CO<sub>2</sub> on NH<sub>2</sub>-MIL-101(V) and MIL-101(V).

C–N (or C–C), C–O, and C=O groups [13], respectively. The peaks in the N 1s region at 400.4 eV could be attributed to the N of the amine functionality stretching out or protruding into the cavities, similar to that reported for NH<sub>2</sub>-UiO-66(Zr) [14]. In Fig. 2D, the spectrum of V 2p showed that the two peaks at 516.6 and 524.0 eV were V 2p<sub>3/2</sub> and V 2p<sub>1/2</sub>, respectively, which indicated the presence of V (III) in NH<sub>2</sub>-MIL-101(V) [10]. The SEM and TEM images revealed that the synthesized NH<sub>2</sub>-MIL-101(V) comprised nanocrystals with a diameter size of 40 to 60 nm (Fig. S2). The synthesized materials were also characterized using FTIR, and EDX mapping (Figs. S3–S7). All characterizations showed that the MOFs were prepared successfully.

The synthesis temperature and BET specific surface area of NH<sub>2</sub>-MIL-101(V) and the isostructural analogues reported in the literature are compared in Table 1 and Table S1. In this study, synthesis was performed under a lower temperature relative to the synthesis of NH<sub>2</sub>-MIL-101(V) reported in the literature [12]. Nevertheless, the specific surface area of NH<sub>2</sub>-MIL-101(V) synthesized in this study was larger than the corresponding sample, as well as other isostructural analogues, such as NH<sub>2</sub>-MIL-101(Al). This likely resulted from the pure-phase MOF that was obtained in this study, while there were heterocrystalline phases that are not part of the NH<sub>2</sub>-MIL-101(V) structure in the cases reported in the literature [12].

The adsorption isotherms of CO<sub>2</sub> and N<sub>2</sub> on NH<sub>2</sub>-MIL-101(V) and MIL-101(V) at 0, 15 and 25 °C are compared in Fig. 3A and Fig. S8 and Table S2. 1.9 mmol/g of CO<sub>2</sub> uptake was achieved in the synthesized NH<sub>2</sub>-MIL-101(V) at 25 °C and 100 kPa, which was higher than the adsorption capacity (1.4 mmol/g) of MIL-101(V) under an identical condition. The N<sub>2</sub> uptake at 25 °C was less with MIL-101(V) (0.14 mmol/g) than the uptake amounts by the NH<sub>2</sub>-MIL-101(V) sample (0.18 mmol/g). Therefore, the selectivity of CO<sub>2</sub> over N<sub>2</sub> in NH<sub>2</sub>-MIL-101(V) was as high as 10:1. CO<sub>2</sub> was more strongly adsorbed than N<sub>2</sub> in NH<sub>2</sub>-MIL-101(V) because of the significantly stronger quadrupole moment of CO<sub>2</sub> compared to N<sub>2</sub> [14]. Fig. 3B shows the corresponding isosteric

heat of CO<sub>2</sub> adsorption as a function of CO<sub>2</sub> loading amounts, which decreased sharply with the coverage (45–22 kJ/mol) for NH<sub>2</sub>-MIL-101(V) and 35–20 kJ/mol for MIL-101(V), respectively. At nearly zero surface coverage, CO<sub>2</sub> molecules are preferably adsorbed onto the free-standing amino group of NH<sub>2</sub>-MIL-101(V) by virtue of chemical interaction, resulting in the formation of a carbamate species [15,16]. As CO<sub>2</sub> loading increases, these sites become saturated and the interaction between CO<sub>2</sub> and adsorbent is mainly regulated by dispersion [17,18].

#### 4. Conclusions

A pure-phase NH<sub>2</sub>-MIL-101(V) material based on vanadium and containing amine groups was successfully synthesized via a solvothermal route. The synthesized NH<sub>2</sub>-MIL-101(V) had a large BET specific surface area and amine-functionalized groups and exhibited high CO<sub>2</sub> adsorption capacities (1.9 mmol/g at 25 °C and 100 kPa) and high selectivity against N<sub>2</sub>.

#### CRediT authorship contribution statement

**Fumin Zhang:** Conceptualization, Project administration, Supervision, Writing - review & editing. **Qionghao Xu:** Investigation, Methodology, Writing - original draft. **Li Fang:** Methodology, Writing - original draft. **Weidong Zhu:** Project administration, Supervision, Writing - review & editing. **Yanghe Fu:** Writing - original draft. **Qiang Xiao:** Writing - original draft.

#### Conflict of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgments

The authors would like to give thanks for the financial support provided by the National Natural Science Foundation of China (No. 21576243) and the Zhejiang Provincial Natural Science Foundation of China (Nos. LY18B060006 and LY18B030006).

### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2020.127402>.

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