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Synthesis and adsorption performance of a modified micro-mesoporous MIL-101(Cr) for VOCs removal at ambient conditions

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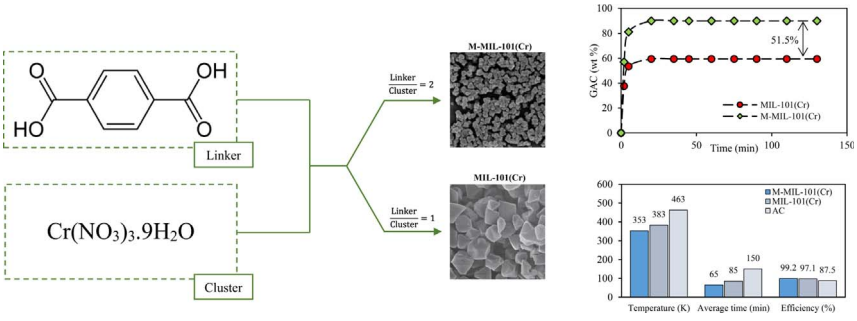
HIGHLIGHTS

- A new modified M-MIL-101(Cr) was successfully synthesized.
- Extra-high surface area (4293 m^2/g) and pore volume (2.42 cm^3/g) were obtained.
- M-MIL-101(Cr) exhibited higher VOCs adsorption capacity.
- The regeneration of M-MIL-101(Cr) was obtained at low temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, dynamic adsorption behavior of different gaseous volatile organic compounds (VOCs) on a new modified M-MIL-101(Cr) was investigated with a great emphasis on gasoline adsorption. The M-MIL-101(Cr) was synthesized, along with comprehensive purification procedures, using a new linker to cluster molar ratio (2:1 instead of 1:1) and different modulators (i.e. HF and HNO_3). All prepared adsorbents were characterized by XRD, FTIR, FE-SEM and N_2 adsorption-desorption at 77 K. The results showed that surface area and pore volume of the M-MIL-101@Free (i.e. modified MIL-101(Cr) with using any modulator) which were 4293 m^2/g and 2.43 cm^3/g, greatly elevated up to 37.2% and 71.6% against the MIL-101@HNO_3 (i.e. the best case of usual MIL-101(Cr)). The dynamic adsorption behavior of various VOCs (i.e. gasoline, n-pentane, n-hexane, n-heptane, benzene, toluene and xylenes), dispersed into an air stream at atmospheric conditions, was studied using an in-house made apparatus. The M-MIL-101@Free greatly exhibited high adsorption capacity for all selected VOCs which was approximately 1.9–2.5 times more than MIL-101@HNO_3. Furthermore, the M-MIL-101@Free possessed maximum gasoline uptake of 90.14 wt%, which was enhanced by 116% (41.7 wt%) and 260% (25 wt%), compared to MIL-101@HNO_3 and commercially activated carbon. Besides the prominent adsorption capacity of M-MIL-101@Free, it was also succeeded to be regenerated in 23.5% shorter time, 7.8% lower temperature and 2.1% higher efficiency versus the MIL-101@HNO_3 after 4 cycles.

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1. Introduction

Nowadays, the growing trend of industrialization, air pollution and hazardous materials emission, have become some of the main challenges of humans which can unprecedentedly threaten their health and environment. Volatile organic compounds (VOCs), as a major source of air pollution, have widely attracted scientists and legislators during the past two decades [1,2]. VOCs are defined as a sub-branch of biogenic or anthropogenic compounds and are categorized as a main group of hazardous materials and air pollutants [3,4]. These compounds not only can intensify ozone layer depletion and greenhouse effect, but also can seriously harm human health and cause irreversible defects during long-lasting exposure [5]. Despite the deduction of international protocols (e.g. Multi-effect protocol at Gothenburg and VOC protocol at Geneva) to retrain the detrimental effects of VOCs, a growing trend of VOCs emission has been being recorded [6,7]. Hence, VOCs removal from indoor/outdoor atmosphere has drawn worldwide attention as an indispensable issue.

In order to eliminate VOCs from an air stream and atmosphere, various separation technologies have been developed, including adsorption [8], absorption [9], condensation [10], catalytic oxidation [11], photocatalytic reaction [12] and membrane separation [13]. Although each technique has its particular privileges, adsorption has been known as the most economical, energy efficient and convenient technique with endurable lifetime [14,15]. Therefore, adsorption is the only promising choice for VOCs capture from the indoor/outdoor environment at room temperature and atmospheric pressure, particularly when a low concentration of pollutants is presented in feed streams and an ultra-trace level is desired at the final products [4,16,17].

Among various design parameters of an adsorption process, choosing a suitable type of adsorbent can be named as the most crucial one, depending on the properties of carrier gas and pollutants and their molecular sizes. Commercial adsorbents, such as activated carbons [18–21], silica gels [22] and zeolites [23–25], have been extensively used for adsorptive removal of hazardous compounds and VOCs. However, these adsorbents highly suffer from poor adsorption capacity, high energy demand and low regeneration efficiency [3]. Hence, in recent years, a great number of papers have focused on novel carbon-based adsorbents (e.g. biochar [26], graphene [27], porous carbon [28] and multi-walled nanotube [29]) to find a superior alternative to commercial adsorbents.

Although recent developments have notably improved carbon-based adsorbents' adsorption capacity for VOCs, there are still some disadvantageous, such as high regeneration temperature, low energy efficiency and flammability [3,4]. Accordingly, metal-organic frameworks (MOFs), especially MIL-101(Cr), have been extensively developed and studied as a new substitute for carbon-based adsorbents [4,30] with ultra-high surface area, pore volume and porosity [31,32].

There are a great number of researches dealing with VOCs adsorption (e.g. benzene, toluene, xylene and linear hydrocarbons) by MIL-101(Cr) [33,34]. Nevertheless, improving the textural properties of MIL-101(Cr) for VOCs capture and other atmospheric pollutants have been the core of pioneer studies. Jia et al. [35] synthesized a hybrid composite consisting MIL-101(Cr) and phosphotungstic acid for removing aromatics and sulfur compounds from fuels. They displayed that the new hybrid structure has a higher adsorption capacity compared to the virgin MIL-101(Cr). Sun et al. [36,37] reported that the adsorption capacity of their new synthesized MIL-101(Cr)/graphene oxide composite increased by 25–29% for n-alkanes (C_5-C_8). Qin et al. [38] worked on a palladium doped MIL-101(Cr) to enhance toluene removal at low partial pressure. They showed that the new MIL-101(Cr) structure, with the optimal amount of palladium, is able to increase toluene adsorption capacity approximately 450% and 16% at $P/P_o = 1$ and 0.06, respectively. Besides the synthesizing innovate MOF structures for higher VOCs adsorption measured by static isotherms, recently, a low number of works have expended their efforts on dynamic adsorption behavior (breakthrough curves) of VOCs at ambient conditions (P = 1 bar, T = 298 K and saturated concentration of VOCs in an air stream). Bahri et al. [39] and Vellingiri et al. [40] reported the breakthrough curves of toluene for diverse types of MOFs under ambient conditions (P = 1 bar and T = 298 K). They considered different levels of humidity which could close the experimental conditions to an indoor environment one. Zhu et al. [41] tried to increase the selectivity of MIL(Cr) for benzene over water by replacing a new type of linker with two benzene rings. The published breakthrough curves authenticated 58% enhancement in benzene adsorption at 60% RH and 1 bar.

Although with the recent improvements in the synthesis of novel hybrid and doped MOF structures with high adsorption capacity for VOCs removal from air streams, there are still some significant barriers (e.g. high capital cost and energy consumption) to their commercialization. Herein, a modified MIL-101(Cr), denoted as M-MIL-101(Cr), was synthesized with a new linker to cluster ratio. Both dynamic adsorptive capacity (DAC, i.e. adsorption capacity at different time steps) and equilibrium adsorption capacity (EAC) of diverse VOCs on the M-MIL-101(Cr), with a great emphasis on gasoline adsorption, were measured using a specialized in-house apparatus at 1 bar and 298 K. The kinetic behavior of VOCs on M-MIL-101(Cr) were modeled by pseudo-first order, pseudo-second order and fractal-like pseudo-first-order kinetic models. Moreover, the diffusion mechanism of VOCs on M-MIL-101(Cr) was completely investigated by kinetic curves and the general diffusion model. The main purpose of this research was to introduce the M-MIL-101(Cr) as a promising and inexpensive adsorbent for the purification of air streams saturated with gasoline vapors (against previous works which were related to a single component of VOC family) with exceptional adsorption capacity, high regeneration efficiency and low energy consumption at ambient conditions.

2. Materials and methods

2.1. Materials

All chemicals obtained from commercial vendors (reagent grade) and used without additional purification. Chromium nitrate nonahydrate ($Cr(NO_3)_3{\cdot}9\ H_2O$, Sigma-Aldrich, 97%), 1, 4-benzene dicarboxylic acid (H_2BDC, Merck, 98%), hydrofluoric acid (HF, Merck, 40%) and nitric acid (HNO_3, Merck, 65%) were used in the synthesis of MIL-101(Cr) and M-MIL-101(Cr). All solvents, such as methanol (MeOH, Merck, 99.9%), ethanol (EtOH, Merck, 99.9%), N, N-dimethylformamide (DMF, Merck, 99.8%), ammonium fluoride (NH_4F, Sigma-Aldrich, 99.99%) and dionized (DI) water were used as received. Normal Pentane, normal heptane, normal hexane, benzene, toluene and xylene were purchased from Merck Company (> 99.7%) as VOC samples without further treatment. In addition, commercially activated carbon (AC) was supplied by NORIT Company.

2.2. Synthesis and post-synthesis methods

2.2.1. Synthesis of conventional MIL-101(Cr)

As mentioned in previous works, physicochemical and textural properties of microwave products are very similar to hydrothermal one [42]. Most of the reported works have been concentrated on hydrothermal method although microwave method has advantages as well as limitations [43]. The major disadvantages of microwave synthesis is high cost for devoted microwave reactors and its scale up [44]. MIL-101(Cr) was hydrothermally synthesized on the basis of the reported procedure by Ferey et al. [45]. Typically, $Cr(NO_3)_3{\cdot}9H_2O$ (4 g, 10 mmol) and H_2BDC (1.66 g, 10 mmol) were dissolved in DI water (2650 mmol, 48 mL) and stirred for 15 min using a magnetic mixer. Then, a suitable modulator (10 mmol of HF or HNO_3) was gradually added to the mixture and stirred vigorously for further 15 min. The acquired suspension was poured into a Teflon-lined stainless steel autoclave and transformed in an oven. The autoclave was heated with a