A wet impregnation approach to synthesize MIL-101(Cr) with open metal sites and their application in the adsorption of volatile organic compounds

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Abstract. The simple wet impregnation method reported a series of MIL-101(Cr) materials doped with copper acetate paddle wheel species. Powder X-ray diffraction and SEM studies showed the MOF frameworks remained intact during wet impregnation, and SEM- EDX, XPS, and N_2 adsorption analyses confirmed the successful copper acetate loading. Volatile organic compounds adsorption capabilities of these materials were further examined, and it found that copper acetate doped MIL-101 (Cr) possesses up to 61% improvement in toluene uptake as compared to pristine MIL-101 (Cr) at a low partial pressure of $P/P_0 = 0.10$ under 298.1 K. This performance improvement is attributed to the unsaturated open metal sites introduced by molecular copper acetate with a paddle wheel structure. This study provides not only a new series of promising VOC removal MOFs with unsaturated Cu(II) open metal sites but also a simple, widely applicable method for introducing Cu(II) open metal sites into MOFs by using molecular copper species with predefined paddle wheel structure.

Keywords: Wet impregnating, molecular copper paddle wheel species, open metal sites, volatile organic compounds, MIL-101(Cr).

1. Introduction

Volatile organic compounds (VOCs), as a specific group of organic compounds, features low boiling points from about 50 ºC to about 240 ºC [1]. Common instances of VOCs produced by anthropogenic activities include formaldehyde, alkyl carbons, and aromatics [2]. They frequently pose serious threats to human health with neurotoxicity and respiratory depression [3]. It is therefore important to remove VOCs from the atmosphere.

Common VOC abatement strategies include recovery methods such as membrane separation, absorption, adsorption and condensation [4,5], and destruction methods such as photocatalytic degradation, and thermal oxidation [6,7]. Among these, adsorption-based VOC removal stands out because of its operational flexibility, compatibility with a wide range of VOC types, as well as their low cost and long lifespan [8]. Braida and others [9] investigated an adsorption-desorption scheme of charcoal and revealed the significance of the porosity and chemical functionality of the adsorbent in determining VOC removal efficiencies. For the removal of VOCs, a variety of porous materials have been utilized, including zeolites, mesoporous silica, metal oxides, and activated carbon [10]. However, they have intrinsic limitations, for instance, small pore size, and low surface area, which hinder their wide applications for VOC removal [11].

In recent years, metal-organic frameworks (MOFs), which are a rising class of porous materials, have been studied for VOC capture due to their ultrahigh porosity and desirable functionality [8]. They have shown ultra-high uptakes for VOCs [11]. For instance, MIL-101 possessed superb benzene adsorption of up to 16.5 mmol/g, representing the highest capacity among all porous materials attributed to their extra-high surface area (>3000 m^2/g), large pore size (29Å-34 Å), and coordinately unsaturated sites (CUSs) [12]. However, because of the relatively weak interaction between the MOF and the VOC molecules, VOC uptakes of MIL-101 at low concentrations, which are typically encountered under practical conditions, are not very attractive [13]. To improve its VOC uptake at low partial pressure, the introduction of external metal sites by metal ion or metal nanoparticle doping was proven to be a successful method [14]. A similar improvement of gas uptake with copper nanoparticles embedded is seen in work by other researchers [15,16]. For example, a Cu(I) doped MIL-101 was made via a one-pot in-situ hydrothermal synthesis with Cu(II) nitrate, and the material showed an 11wt% improvement in benzene uptake at low partial pressure regime, however, impure phases were observed due to the complex chemistry of copper ions under harsh hydrothermal conditions. A facile, controllable way of introducing open metal sites into MIL-101 is highly desired.

Here, a straightforward wet impregnation method was reported for introducing open metal sites to MIL-101. Cu(II) acetate with well-defined copper(II) paddle wheel structure selected comprising one open metal site on each Cu center. The gentle, simple wet impregnation approach avoided undesired side reactions of copper ions during impregnation. As a result, a sequence of copper acetate-doped MIL-101 was prepared. The toluene adsorption of these copper-doped MIL-101 materials was further tested and found that one of the copper acetate-impregnated MIL-101 showed up to 60.8% improvement at $P/P_0 = 0.1$, which is a low toluene partial pressure. This improvement is much higher than other metal-doped MIL-101 materials reported previously [15]. It was attributed to the introduction of copper open metal sites, as well as the wet impregnation approach that avoids the introduction of impurities. The results suggested that it is effective to enhance the VOC uptakes in MOFs through wet impregnation of molecular species with predefined open metal sites.

2. Experimental section

2.1. Chemical compounds

All the chemicals involved in this research were commercially sourced, and used with no further purification: chromium(III) terephthalate (MIL-101), copper acetate monohydrate [99%, $Cu(OAc)_2H_2O$] were obtained from XFNANO Materials Tech. Limited Liability Company and Rhawn Reagent Limited Liability Company.

2.2. Synthesis of $Cu(OAc)_2$/MIL-101

Copper acetate was loaded into MIL-101(Cr) through a wet impregnation approach, of which the procedures were modified according to previous literature. 0.5 grams of MIL-101(Cr) was dispersed in 5 mL of a 0.05M, 0.1M, and 0.5M $Cu(OAc)_2$ aqueous solution in 20 mL glass vials, respectively. The obtained mixtures were stirred with a magnetic stirrer gently overnight. Afterward, the solids were collected via filtration, followed by washing them with water under filtering. After drying on the filter paper, the resultant solids were placed in a warm oven of 120 °C for exactly 12 hours. The Cu acetate-containing materials obtained were designated as $Cu(OAc)_2$/MIL-101(Cr)-A, $Cu(OAc)_2$/MIL-101(Cr)-B, and $Cu(OAc)_2$/MIL-101(Cr)-C for the samples in 0.05M, 0.1M, and 0.5M $Cu(OAc)_2$ aqueous solution, respectively.

2.3. Characterisation of synthesised $Cu(OAc)_2$/MIL-101

Powder X-ray diffraction (PXRD) patterns of all samples were collected using CuKα radiation (λ = 1.5418 Å) on a D8 Advance (Bruker, German) diffractometer at 298K. With a step size of 0.0855°, the angle was manipulated within the range of 3-40° (2θ) using a fully opened 100-channel X'Celerator detector. (Operating Voltage: 40kV). The morphological properties and elemental mapping (Cr, Cu) of the samples were examined using Gemini 300 (ZEISS, German). N_2 isotherms were measured at 77K on ASAP 2460 (Micromeritics, USA). Before the measurement, all the samples were activated under a vacuum for 3 hours at a temperature of 50 °C. X-ray photoelectron spectroscopy (XPS) was carried out on ESCALAB 250Xi (Thermo Scientific, USA), which used a monochromic Al Kα X-ray source to identify the atoms on the surface of the samples. Based upon the neutral C 1s peak, all binding energies were corrected at 284.77eV, which removes the surface charging effects. The thermal stability was examined via thermal gravimetric (TG) analysis (Q600, TA, USA) by heating the samples from 30 °C to 800 °C with a speed of 10 $K \cdot min^{-1}$ in N_2 atmosphere. Toluene sorption capacities were evaluated by measuring adsorption isotherms using Autosorb IQ (Quantachrome, USA). In advance of the experiment, the samples were outgassed at 150 °C for 3 hours.

3. Results and discussion

3.1. Powder X-ray diffraction analyses of MIL-101 with different loading of copper acetate

PXRD studies examine the crystallinity of pristine MIL-101, pristine $Cu(OAc)_2 \cdot H_2O$ and $Cu(OAc)_2$/MIL-101(Cr) samples with different $Cu(OAc)_2$ loading. As presented in Figure 1, the MIL-101 diffraction peaks that were well maintained in all copper acetate-impregnated samples were observed, suggesting the wet impregnation process did not damage the MIL-101 framework integrity. Yet the diffraction peaks of Bulk $Cu(OAc)_2$ in any of the copper acetate-impregnated MIL-101 samples were not seen, which confirmed the phase purity of these materials and suggested that the copper acetate species were doped within the pores of MIL-101 rather than existing as impurities. It forms a distinct comparison to the reported Cu-doped MIL-101 materials in literature, where impurity peaks were commonly observed [17,18].

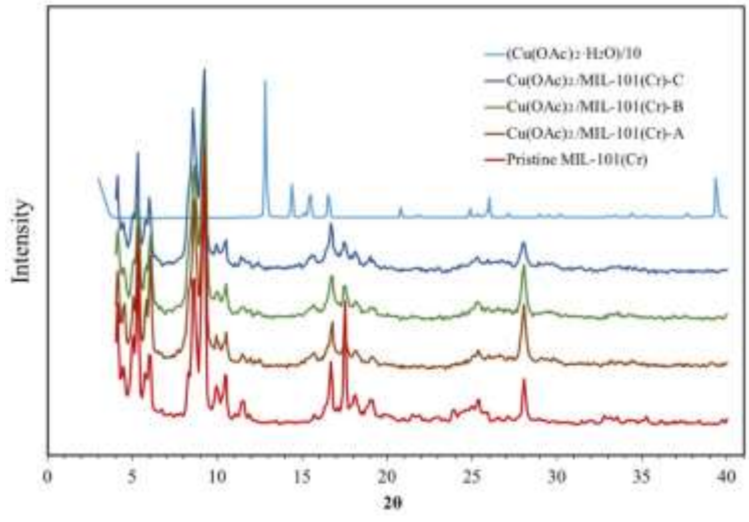

Figure 1. Color-coded X-ray diffraction patterns of $Cu(OAc)_2 \cdot 5H_2O$, $Cu(OAc)_2$/MIL-101(Cr) samples with different $Cu(OAc)_2$ loading and pristine MIL-101(Cr).

3.2. X-ray photoelectron spectroscopy analyses of MIL-101 with different loading of copper acetate

X-ray photoelectron spectroscopy, also known as XPS, was utilized to identify the valence states of the copper ions in MIL-101. Figure 2 shows the wide-scan spectra of both pristine MIL-101(Cr) and copper acetate-impregnated MIL-101(Cr) materials. The presence of Cu in all three impregnated samples can be easily identified with the characteristic peak of Cu at 935 eV on average across the three samples. High-resolution spectra of Cu $2p_{3/2}$ further confirm the valence states of Cu to be 2+. The 2+ valence of Cu ion particularly marked the success of this wet impregnation method.

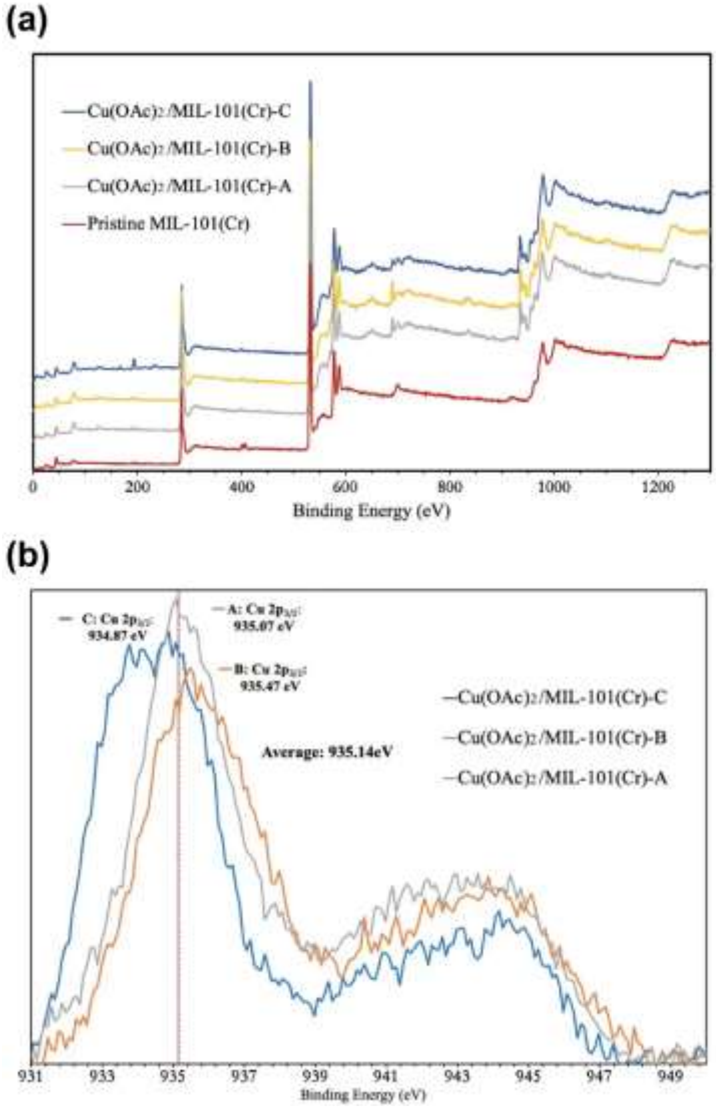

Figure 2. (a) XPS wide-scan spectra of $Cu(OAc)_2$/MIL-101(Cr) samples with different $Cu(OAc)_2$ loading and pristine MIL-101(Cr); (b) High-resolution XPS spectra of Cu-$2p_{3/2}$ and binding energy.

3.3. Scanning electron microscopy of MIL-101 with different loading of copper acetate

The morphologies of pristine MIL-101(Cr), as well as the copper acetate-impregnated MIL-101(Cr) samples, were inspected via SEM. In Figure 3, it is clear that MIL-101(Cr) were all octahedral-shaped crystals with sizes of approximately 100-200 nm. The well-preserved crystal shapes of $Cu(OAc)_2$/MIL-101(Cr) samples revealed that the MIL-101(Cr) framework has high chemical stability during impregnation.

EDX analyzed all samples to examine the copper loading in MIL-101 (Cr) crystals as well. As presented in Figure 3(c), the EDX-mapping of $Cu(OAc)_2$/MIL-101(Cr)-B showed a homogeneous distribution of Cu throughout the crystals, indicating that copper acetate was successfully doped. As shown in Table 1, Cu loadings were found to be 0.181, 0.188, and 0.755 mmol/g for $Cu(OAc)_2$/MIL-101(Cr)-A, $Cu(OAc)_2$/MIL-101(Cr)-B, and $Cu(OAc)_2$/MIL-101(Cr)-C, respectively, from the quantitative EDX analyses. This result further confirmed the successful copper acetate loading and demonstrated the feasibility of tuning product compositions by simply varying the reaction stoichiometry during the wet impregnation process.

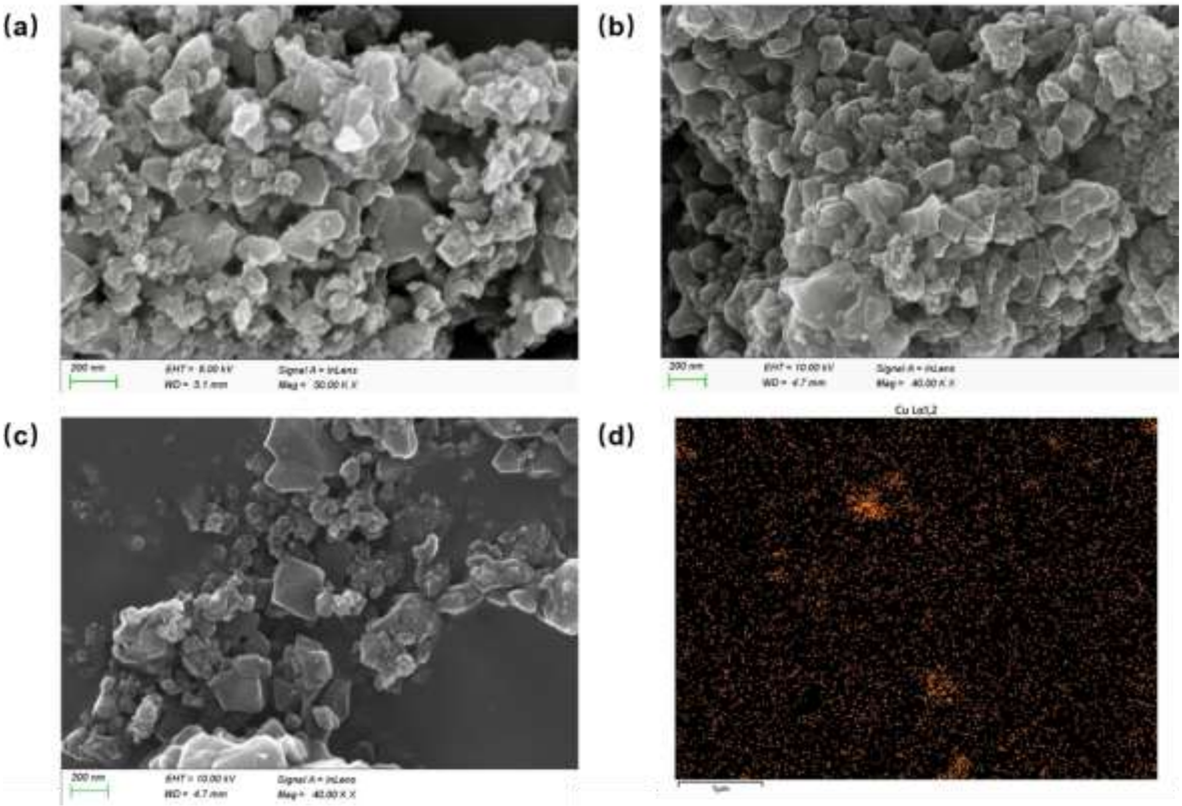

Figure 3. SEM images of (a) $Cu(OAc)_2$/MIL-101(Cr)-A; (b) $Cu(OAc)_2$/MIL-101(Cr)-B; (c) $Cu(OAc)_2$/MIL-101(Cr)-C; (d) Energy dispersive X-ray spectroscopy elemental mapping of $Cu(OAc)_2$/MIL-101(Cr)-B.

3.4. Thermogravimetric analyses of MIL-101 with different loading of copper acetate

Thermal stabilities of pristine MIL-101, pristine $Cu(OAc)_2{\cdot}H2O$, $Cu(OAc)_2$/MIL-101(Cr) samples with different $Cu(OAc)_2$ loading were studied by using thermogravimetric analyses under the N_2 atmosphere. As shown in Figure 4, both pristine MIL-101 and copper acetate-impregnated MIL-101 showed that the majority of the weight loss within 400-500°C was due to the framework decomposition, suggesting their high thermal stability. The residual weight percentage of three copper acetate doped samples is higher than that of pristine MIL-101 at 16.1%; 32.6%, 32.3%, and 35.0% for samples from A-C, respectively, which can be ascribed to the presence of copper acetate in the pores of MIL-101 and confirmed the copper acetate loading.

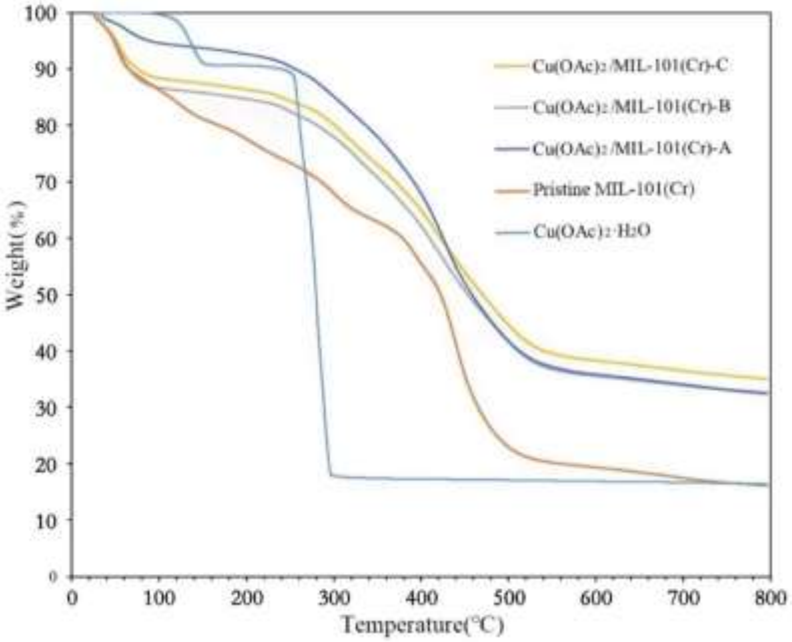

Figure 4. Thermogravimetric analysis of $Cu(OAc)_2 \cdot H_2O$, pristine MIL-101(Cr) and $Cu(OAc)_2$/MIL-101(Cr) samples with different $Cu(OAc)_2$ loading.

3.5. Gas adsorption of MIL-101 with different loading of copper acetate

By performing nitrogen adsorption-desorption tests at 77 K, the pore metrics of the copper acetate-loaded MIL-101(Cr) and the copper acetate-loaded MIL-101(Cr) were examined. Figure 5 presents the nitrogen isotherms of all four samples. It can be seen that, at a low partial pressure range ($P/P_0 < 0.3$), all isotherms displayed a sharp increase in the uptake, suggesting the rich microporosity of these materials. As shown in Table 1, lower BET surface areas were observed (1475, 1448 and 1386 m^2/g for A, B, and C, respectively) and pore volumes (0.774 cm^3/g, 0.752 cm^3/g, 0.824 cm^3/g for A, B, C respectively) in the three copper acetate impregnated samples as compared to that of pristine MIL-101 (1720 m^2/g; 0.844 cm^3/g). These were attributable to the reduced pore volume and surface area due to copper acetate impregnation.

Table 1. BET surface area, pore volume and toluene adsorption capacity data for pristine MIL-101(Cr) and $Cu(OAc)_2$/MIL-101(Cr) samples with different $Cu(OAc)_2$ loading.

	Input Cu (mmol)	Cu loaded (Cu:Cr)	BET surface area (m^2/g)	Total pore volume (m^2/g)	Toluene uptake at $P/P_0 = 0.1$ (mmol)	Toluene uptake at $P/P_0 =$ 0.95 (mmol)
MIL-101(Cr)	N/A	N/A	1720	0.8443	2.48	3.34
$Cu(OAc)_2$/MIL-101(Cr)-A	0.25	0.18147	1475	0.7744	3.99	5.37
$Cu(OAc)_2$/MIL-101(Cr)-B	0.50	0.18765	1448	0.7521	3.84	4.98
$Cu(OAc)_2$/MIL-101(Cr)-C	2.50	0.75469	1386	0.8240	3.46	4.89

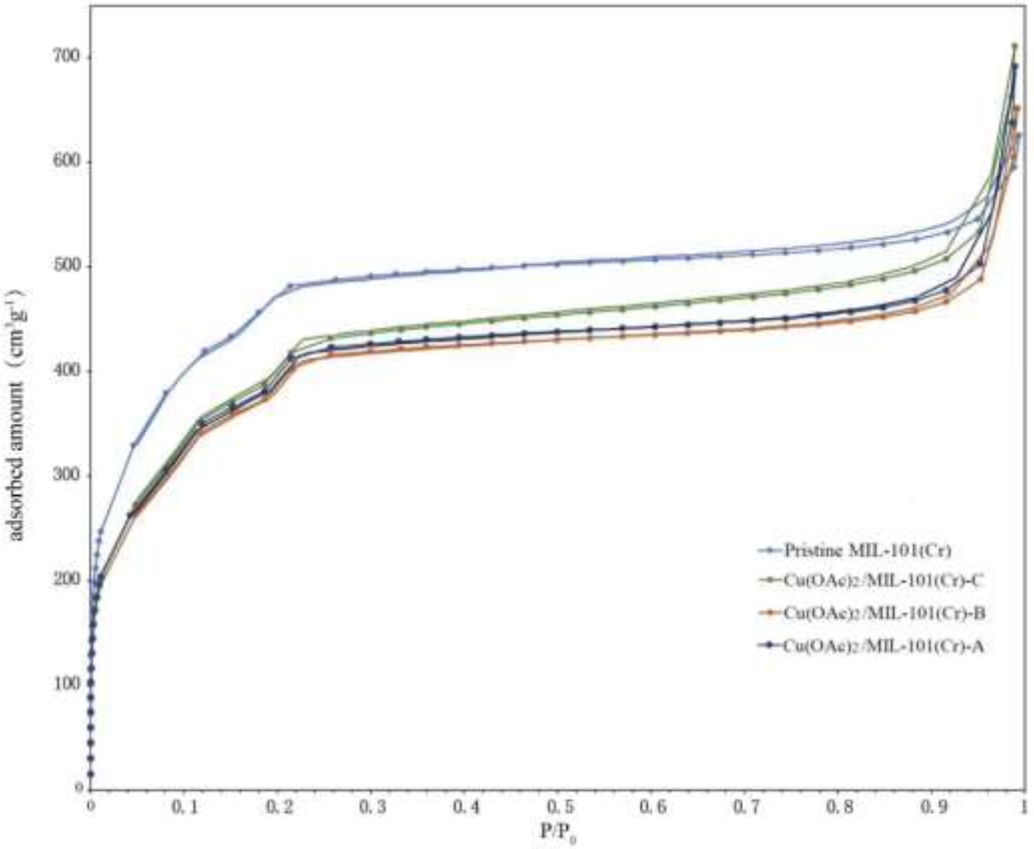

Figure 5. N_2 isotherm of pristine MIL-101(Cr), $Cu(OAc)_2$/MIL-101(Cr) samples with different $Cu(OAc)_2$ loading.

3.6. Toluene adsorption analyses of MIL-101 with different loading of copper acetate

To probe the VOC adsorption capability of copper-acetate-loaded MIL-101 materials, toluene was chosen as a representative VOC [19]. Vapor adsorption isotherms of toluene at 298 K for pristine MIL-101 (Cr), $Cu(OAc)_2$/MIL-101(Cr) samples with different $Cu(OAc)_2$ loading were measured. As shown in Figure 6, at low partial pressure ($P/P_0 < 0.1$), all four materials displayed a steep toluene uptake and then quickly reached a plateau at high partial pressure ($P/P_0 > 0.1$). However, the toluene isotherms for the three copper acetate-impregnated samples are much steeper at the low partial pressure range than that of pristine MIL-101, and the uptake increased with the increasing copper acetate loading. As a result, high toluene uptakes of 3.99, 3.84, and 3.46 mmol/g were observed at $P/P_0 = 0.1$ for $Cu(OAc)_2$/MIL-101(Cr)-A, $Cu(OAc)_2$/MIL-101(Cr)-B, and $Cu(OAc)_2$/MIL-101(Cr)-C, and these values are 60.8% greater than toluene uptakes of pristine MIL-101 (mmol/g at $P/P_0 = 0.1$). These improvements are also much higher than other copper-doped MIL-101 materials reported previously. And this can be attributed to the introduction of copper open metal sites using molecular copper acetate species with paddle wheel structure. The final results demonstrate the importance of impregnating molecular species with predefined open metal sites into MOFs for enhanced VOC uptake [15].

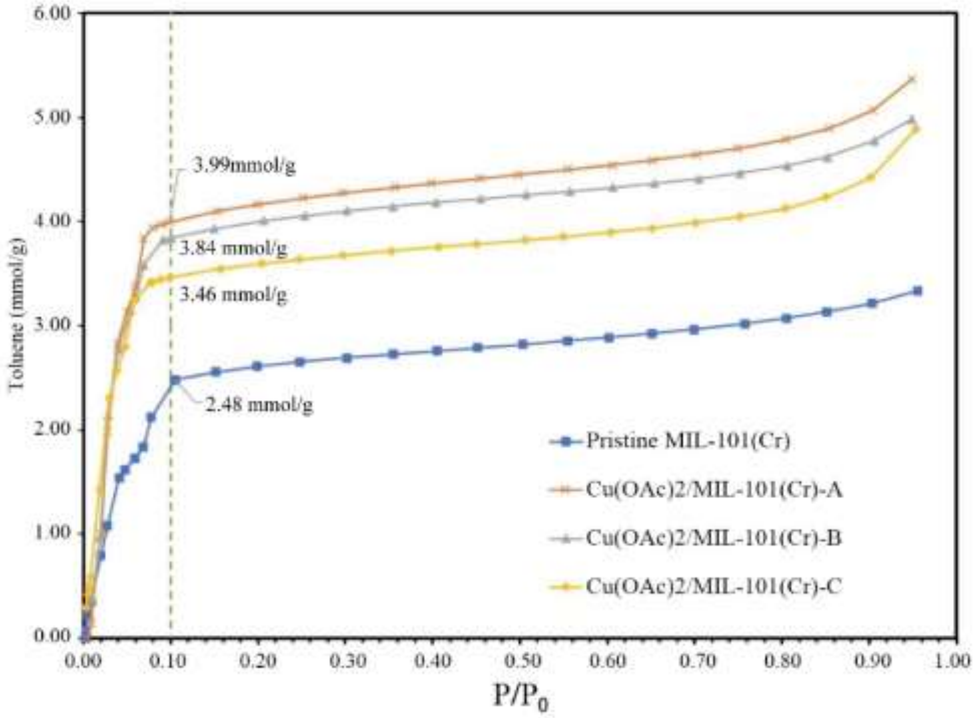

Figure 6. Toluene isotherm of pristine MIL-101(Cr), $Cu(OAc)_2$/MIL-101(Cr) samples with different $Cu(OAc)_2$ loading.

4. Conclusion

In summary, a facile approach was presented to introduce unsaturated copper open metal sites into the MIL-101(Cr) framework by simple wet impregnation with molecular copper acetate with a predefined paddle-wheel structure. the MIL-101(Cr) framework integrity was investigated during impregnation by examining their crystallinities and morphologies using XRD and SEM analyses. The successful copper acetate impregnation was confirmed by SEM-EDX and XPS studies as well. Reduced surface areas and porosity were observed in these samples with high copper acetate loading (up to a 14.2% decrease in BET surface area). However, these samples showed much-improved toluene uptake at a low partial pressure range, which was attributed to the introduction of copper open metal sites. The results obtained pointed out an effective way for enhanced VOC uptakes of MOF by impregnation molecular species with predefined open metal sites.

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