

FUNCTIONALIZATION OF HKUST-1 WITH ETHYLENEDIAMINE FOR EFFECTIVE CO₂ ADSORPTION

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ABSTRACT

Metal-organic framework structure HKUST-1 was successfully modified with ethylenediamine in order to enhance the interaction between CO₂ and framework. Incorporation of amine moieties into the structure was confirmed by XRD, FT-IR and N₂ sorption isotherms. Modified materials show the decrease of the CO₂ sorption capacity, but on the other hand significant improvement of isosteric heat of adsorption.

Keywords: metal-organic framework, HKUST-1, framework functionalization, CO₂ adsorption

INTRODUCTION

Carbon capture and storage technologies have been intensively developed in the recent years. One of the main goals of emerging technologies is efficient CO₂ capture, which can later be reused for the production of different chemicals.^[1,2] In last decades metal-organic frameworks (MOFs) are receiving wide attention as an adsorbent material. MOFs are innovative microporous materials constructed by the combination of organic ligands and inorganic building units forming 3D extended crystalline porous structures. They have many key advantages such as low density, high specific surface area, pores of different shapes and dimensions, robustness and relative high chemical and thermal stability. Among various application opportunities, MOFs can be used as gas adsorbents and catalysts.

Optimization of MOFs for efficient gas adsorption, separation and catalysis aims to adopt affinities toward certain gases (e.g. CO₂), increase the capture ability at low pressures or improve the catalytic activity for organic transformation reactions.^[3-5] One of the most promising MOF for gas adsorption and catalysis is copper-based benzenetricarboxylate or HKUST-1. The metallic group in HKUST-1 involves a pair of Cu²⁺ ions coordinated by four carboxylate bridges, which are part of linker molecule, to form a paddle-wheel moiety. In the synthesized material, the fifth binding site on each Cu²⁺ ion is occupied by oxygen from solvent molecule which can easily be removed with heat treatment under vacuum, rendering the Cu²⁺ Lewis acid centres directly accessible. The open Cu²⁺ coordinative site can adsorb CO₂ molecules or act as catalytic active site.^[3,6] Open metal sites are further amenable to post-synthetic functionalization, for example with amino groups, which are known to be highly effective for CO₂ adsorption. In this study we modified HKUST-1 with ethylenediamine to improve its adsorption properties toward CO₂ framework binding interaction.

EXPERIMENTAL

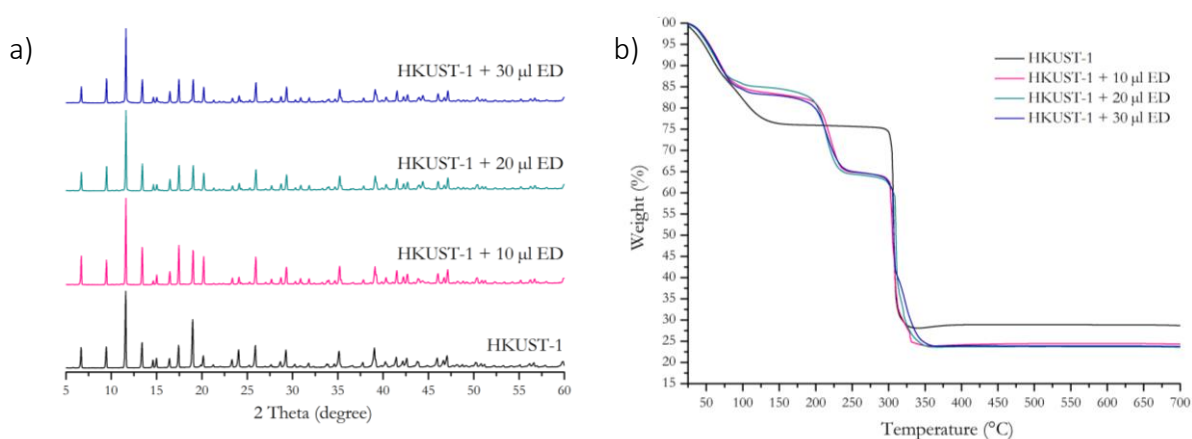
HKUST-1 was synthesized according to the procedure reported by Yang *et al.*^[3]

2.007 g of copper (II) nitrate were dissolved in 15 ml of H₂O. To this solution, 1.0 g of 1,3,5-benzenetricarboxylic acid dissolved in mixture of 15 ml C₂H₅OH and 15 ml DMF were slowly added on continuous stirring. The resulting reaction mixture was hydrothermally treated at 100 °C for 12 h. Before the functionalization, HKUST-1 was activated under vacuum at 150 °C for 16 h. Framework has been functionalized with ethylenediamine (ED) in three different molar ratios, where 10 µl, 20 µl and 30 µl of ED were dissolved in 50 ml of toluene. Suspensions were added to 0.20 g of activated HKUST-1 and stirred for 4 h under reflux at 50 °C. The functionalized product was isolated by filtration, and dried at room temperature overnight.

XRD measurements were performed on a PANalytical X'Pert PRO diffractometer using CuK α radiation ($\lambda=1.5418$ Å), IR spectra were recorded on Bruker IFS 66/S spectrometer with integration sphere, gravimetric analysis was performed on TA Instruments Q 5000 IR analyser. Porosity data based on the N₂ sorption isotherms was obtained on Micromeritics ASAP 2020, whereas CO₂ sorption capacities were monitored on manometric gas analysis system HTP-IMI Hiden Isochema Inc.

RESULTS AND DISCUSSION

Positions of diffraction peaks of as-synthesized and modified HKUST-1 with ED in three different molar ratios, agree well with the simulated XRD pattern, however intensities of some reflections in the case of modified materials differ in comparison with the parent MOF (Fig. 1a). The difference in intensities can be attributed to the presence of additional molecules located in the HKUST-1 structure. FT-IR spectrum of the modified HKUST-1 + 30 µl ED shows distinctive bands assigned to the vibrations in the ED molecule: at 3365, 1558 and 1434 cm⁻¹ for N–H stretch, at 1043 cm⁻¹ for N–C stretch and at 488 and 474 cm⁻¹ for N–Cu stretch. As expected, described bands are not present in the case of as-synthesized material.



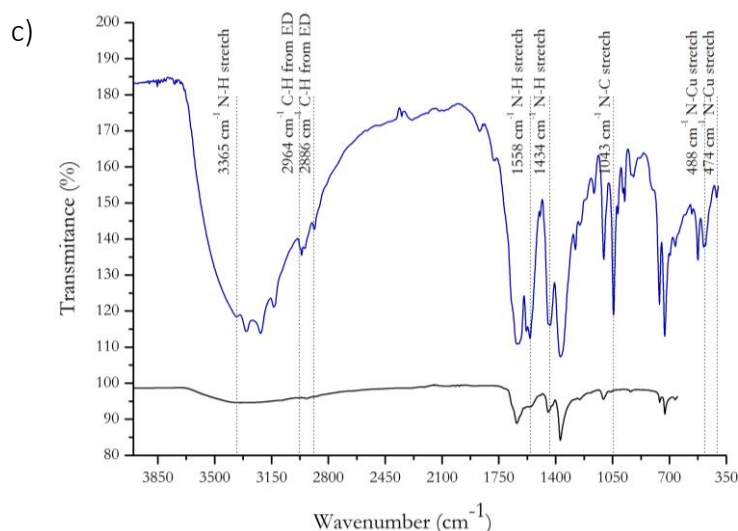


Figure 1. Powder XRD pattern of as-synthesized and modified HKUST-1 with ED in three different molar ratios (a); TGA profile of as-synthesized and modified HKUST-1 (b) and IR spectrum of HKUST-1 and HKUST-1 + 30 μ l ED (KBr) (c).

TG curves of the parent and modified MOF materials are shown in Fig. 1b. As-synthesized HKUST-1 shows two weight losses attributed to the removal of solvent moieties and decomposition of ligand in the temperature ranges 25 – 150 °C and 300 – 320 °C, respectively. On the other hand, modified materials have another distinctive step in the temperature range 200 – 250 °C which can be assigned to the removal of incorporated ED.

Table 1. Surface area, pore size, uptake and isosteric heat of adsorption for as-synthesized and modified HKUST-1+10 μ l ED and HKUST-1+20 μ l ED

Adsorbent	S_{BET} (m^2/g) ¹	D (\AA) ²	Uptake (wb%) ⁴	ΔH (kJ/mol) ⁵
HKUST-1	1809	8.6	40	14
HKUST-1 + 10 μ l ED	1467	5.9; 7.9 ³	17	22
HKUST-1 + 20 μ l ED	1406	7.5	20	15.5

¹Calculated on the basis of BET method in the relative pressure range up to 0.1; ²Determined by NLDFT method; ³pore size distribution with two maxima; ⁴measured at 25 °C, 30 bars, ⁵isosteric heat of adsorption based on the Clausius-Clapeyron calculations at surface coverages of 10 wt.%.

Figure 2a shows N₂ sorption isotherms, which all belong to type I (typical for zeolite-like microporous materials). As expected, the uptakes at saturation points and BET surface areas are decreasing with the increased loading of ED due to the decreased availability of pore volume, however the isosteric heat of adsorption is increasing, which could be favourable for further CO₂ conversion reactions.

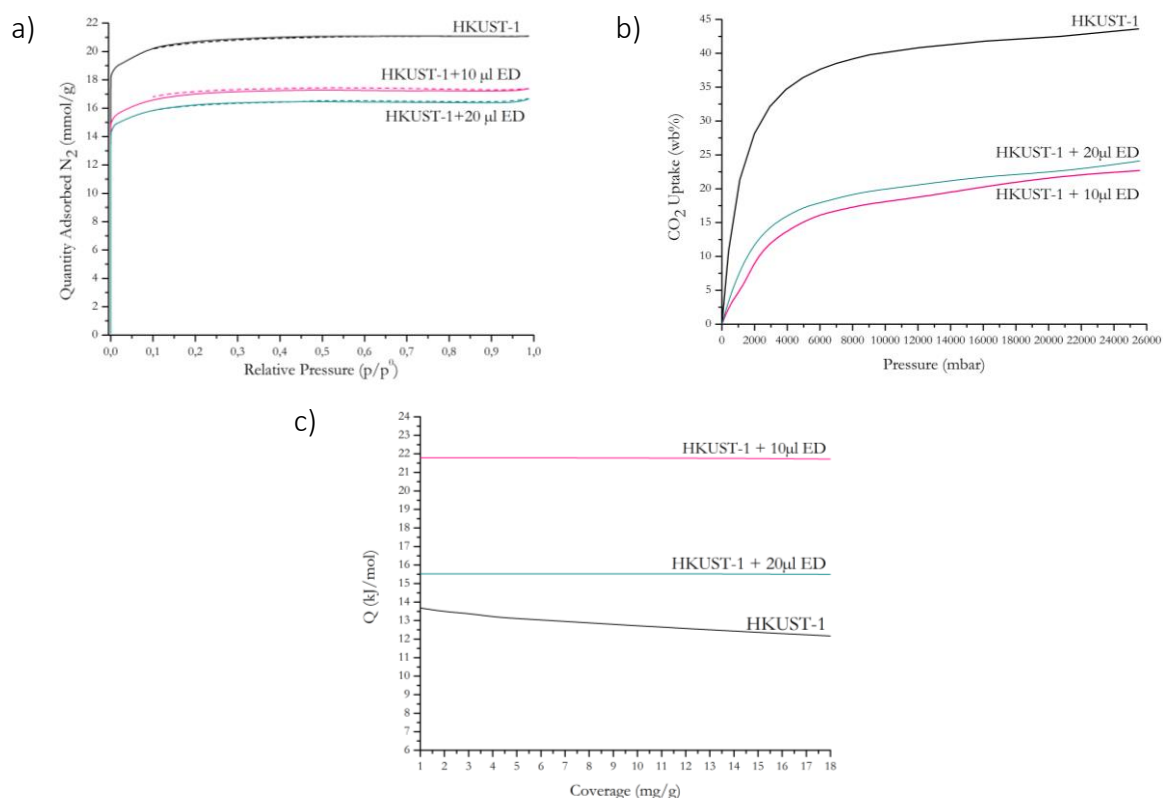


Figure 2. N₂ adsorption-desorption isotherms at 77 K of as-synthesized and modified HKUST-1 with ED (a); CO₂ CO₂ isotherm at 25 °C of as-synthesized and modified HKUST-1 with ED (b); isosteric heat of adsorption of as-synthesized and modified HKUST-1 with ED (c).

CONCLUSION

HKUST-1 metal-organic framework was modified with ED for the purposes of CO₂-to-framework interaction enhancement. In respect with the pristine HKUST-1, modification leads to the decrease of CO₂ sorption capacities due to the partial filling of the micropores with ED moieties. However, the presence of amine groups attached on the framework causes the increase of the CO₂ adsorption enthalpies.

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