



Review

Aluminum metal–organic frameworks for sorption in solution: A review

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ABSTRACT

This Review covers the progress of research on sorption on aluminum metal–organic frameworks, Al-MOFs in the liquid phase within the recent 5 years and the relevant earlier reports. Al-MOFs show the versatility in the structure, an exceptional chemical and structural stability at the elevated temperatures, in air, water and organic solvents, high capacity and selectivity in the sorption, separations, purification, heterogeneous catalysis, sensing. This focused critical Review includes the research on the following aspects of Al-MOFs: 1) their activation and thermal stability; 2) stability in water and aqueous solutions; 3) sorption of organic dyes, miscellaneous organic and inorganic compounds in water; 4) stability in organic solvents, and sorption of organic compounds of various classes e.g. N-heterocyclic and S-heterocyclic compounds from liquid fuels, and 5) the industrial-scale synthesis and emerging large-scale applications. The perspectives and limitations of a wide industrial use of Al-MOFs are outlined. The particular focus is on the mechanisms of activation and molecular interactions with the adsorbate during the sorption/desorption: the π - π , Lewis and Brønsted acid-base interactions, ionic, coordination and hydrogen bonding, “breathing”, sterical match between the “guest” molecule and nanopores in Al-MOFs, and non-specific interactions. The current knowledge gaps are highlighted and the unexplored application niches are revealed.

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Abbreviations: 1,2DMI, 1,2-dimethylindole; 2MI, 2-methylindole; AAS, atomic absorption spectroscopy; ABDC, 2-aminobenzene-1,4-dicarboxylate; AFM, atomic force microscope; ASA, *p*-arsanilic acid; ATR-FTIR, attenuated total reflectance Fourier transformed infrared spectroscopy; BDC, benzenedicarboxylic acid; BET, the Brunauer–Emmett–Teller method to determine the pore size and volume; BT, benzothioephene; BTC, benzenetricarboxylic acid; CBZ, carbazole; CUS, coordinatively unsaturated site; C_0 , the initial concentration in solution; DBT, dibenzothiophene; DFT, density functional theory; DI, deionized water; DVS, dynamic vapor sorption analyzer; EPR, electron paramagnetic resonance; FESEM, field emission scanning electron microscope; GI-WAXS, grazing incidence wide angle X-ray scattering; IND, indole; LUMO, the lowest unoccupied molecular orbital; MAS, magic-angle spinning; MB, Methylene Blue dye; MD, molecular dynamics simulations; MG, Malachite Green dye; MO, Methyl Orange dye; MOF, metal–organic framework; NAP, naphthalene; NMR, nuclear magnetic resonance; NMCBZ, N-methylcarbazole; PL, photoluminescence; PNP, *p*-nitrophenol; PSM, post-synthetic modification of MOFs; ROX, roxarsone; q_m , the Langmuir constant; QUIN, quinoline; Q_0 , the highest adsorbed amount; RH, relative humidity; RhB, Rhodamine B dye; RT, room temperature; SEM, scanning electron microscopy; TEM EDS, transmission electron microscopy with energy dispersive spectroscopy; TGA, thermogravimetric analysis; URPh, phenylurea; UV-Vis DRS, UV-Vis diffuse reflectance spectroscopy; v/v , volume content in the binary mixture, vol%/vol%; XPS, X-ray photoelectron spectroscopy; VT-PXRD, variable temperature powder XRD.

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1. Introduction

MOFs are well-ordered, 3-D nanostructured coordination polymers, which contain metal cations and the structure-building organic linkers. Aluminum MOFs (Al-MOFs) demonstrate high capacity and selectivity in the sorption, separations, purification of water and air, heterogeneous catalysis, sensing. Fig. 1 shows the growth of the number of publications on Al-MOFs (the Scopus search, “aluminum OR aluminium AND metal–organic frameworks” through “Article title, Abstract, Keywords”).

The growing interest to Al-MOFs is reflected in a book chapter of 2014 on their synthesis and structure [1] and a review of 2012 on their transition from research lab to industry [2]. A recent review in *Comptes Rendus Chimie* [3] presents a large overview of Al-MOFs from the structural standpoint, including their inorganic building units. A review in *Coord. Chem. Rev.* [4] discussed heterogeneous catalysis by various MOFs including Al-MOFs. To our knowledge, there is no review article on sorption/desorption on Al-MOFs in solution, sorption capacity and selectivity, their molecular mechanisms and sorbent regeneration.

This Review Article provides a critical analysis and systematization of the published reports on sorption/desorption of various organic and inorganic compounds on microporous and mesoporous Al-MOFs in the liquid phase and the associated chemical mechanisms. While the focus is on research papers reported within the recent 5 years when an explosive growth of interest to Al-MOFs has occurred, the publications prior to 2013 are also covered as needed. The sorption/desorption in water and the non-aqueous media are discussed for the following classes of compounds of major industrial and environmental interest: organic dyes, hydrocarbons, aromatic N-heterocyclic and S-heterocyclic compounds,

miscellaneous organic and inorganic industrial products and by-products, the biologically active large molecules, and common environmental pollutants. The mechanisms of thermal activation and stability of Al-MOFs and the effects of post-synthetic modification (PSM) are discussed. The stability of Al-MOFs in the liquid water, water vapor, and organic solvents is critically analyzed. The following mechanisms of sorption/desorption are covered: 1) ionic interactions, 2) the π - π interactions, 3) coordination bonding, 4) Lewis acid-base interactions, 5) Brønsted acid-base interactions, 6) hydrogen bonding, 7) “breathing” and its effects on sorption capacity and selectivity, 8) sterical match between the size of the “guest” molecule and nanochannels in Al-MOFs, and 9) non-specific interactions. The topic of primary interest is how the structure of Al-MOF and the PSM translate into the higher sorption capacity, the better selectivity, and the capability of the multi-cycle regeneration of the “spent” sorbent. As the research on Al-MOFs has approached maturity, understanding the functional performance and molecular mechanisms is expected to translate into the applications which directly benefit the mankind. The gaps in the knowledge are highlighted, and the unexplored research and application niches are revealed.

2. Studies of thermal activation and framework flexibility of Al-MOFs

2.1. Thermal activation, stability and mechanisms

The importance of activation of MOFs has been recognized early [5], and today virtually every paper describes the activation at an elevated temperature in vacuum or air to remove organic precursors, solvents, and water. The activated MOFs are routinely characterized by powder XRD, the total BET surface area, and the DFT pore size distribution [6]. Of a particular interest is the *in-situ* analysis during the activation, Table 1. The variable temperature powder XRD (VT-PXRD) and thermogravimetric analysis (TGA) are used most often.

In Al-MOFs, the Al^{3+} cations in an octahedral environment form a variety of structures with isolated AlO_4 units, Al clusters, or infinite chains of octahedra with shared corners or edges. The ^{27}Al NMR spectrum provides a fingerprint of coordination state of the Al-containing cluster [16]. The ^{27}Al NMR spectrum is very sensitive to the H-bonding between the —OH groups connected to Al atoms and water molecules in the nanopores, as seen by comparison of the spectra of MIL-53(Al) in the hydrated (the narrow-pore, *np*) and activated or dehydrated (the wide-pore, *wp*) forms [16]. The magic-angle spinning (MAS) solid state ^1H and ^{27}Al NMR spectroscopy was used to determine the molar fraction of 2-aminobenzene-1,4-dicarboxylate (ABDC) linker in the activated mixed-linker MIL-53(Al) also containing benzene-1,4-dicarboxylate (BDC), by the intensity of signal of —NH₂ group [8]. For an activated Al-MOF, the ^1H MAS NMR spectra showed a strong signal at chemical shift $\delta = 7.6$ ppm from the protons in the CH groups of benzene ring, and no signals due to protons in the —COOH groups.

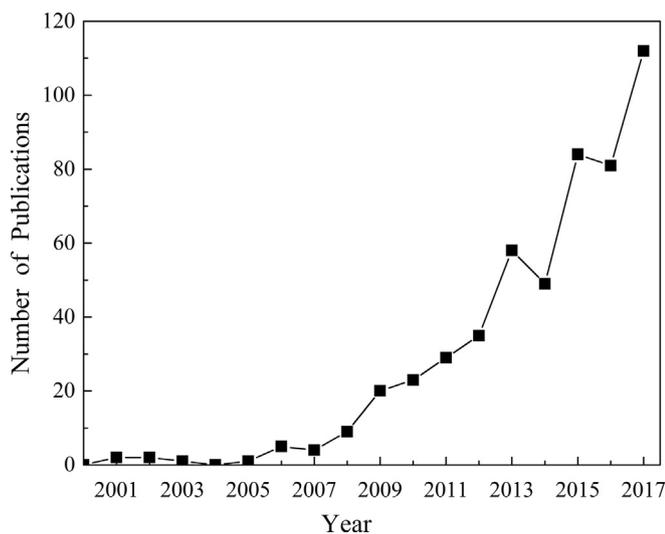


Fig. 1. Growth in the annual number of publications on Al-MOFs.

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