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Activation strategies of metal-organic frameworks for the sorption of reduced sulfur compounds

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Abstract

In order to investigate the possible options to improve the pore properties of metal-organic frameworks (MOFs), the sorptive capacity of MOF-199 was assessed based on the two contrasting activation approaches (i.e., 'chemical (**C**)' and 'thermal (**T**)' activation) against four reduced sulfur (S) compounds **(**RSCs: H_2S, CH_3SH, $(CH_3)_2S$ (DMS), and CH_3SSCH_3 (DMDS)). In order to represent the pristine (**C1**) and chemically activated forms of MOF-199 (**C2**), the pores were filled by N,N′-dimethylformamide (DMF) (i.e., as synthesized) and dichloromethane (CH_2Cl_2), respectively. The corresponding counterparts for thermal treatment (150°C under 100 mL min^{-1}) were named as **T1** and **T2**, respectively. The combined effects of chemical/thermal activation were found to enhance the sorption capacity of MOF-199, while such advantage was not evident when treated by chemical activation only. Overall, the relative ordering of four different MOF-199 against diverse S compounds was found to be DMDS>CH_3SH>H_2S>DMS. The mechanism for such sorption was ascribed to two major competing interactions: a) S-Cu for lighter S and b) -CH_3 group (in S compound) and aromatic ring (in MOF ligand) for heavier S. This synergetic effect was also confirmed by both thoretially (density functional theory (DFT)) and experimentally (Fourier Transform Infrared (FTIR) spectroscopy analysis). As such, MOF-199 prepared through both chemical and thermal treatments was identified as an efficient sorbent to capture S compounds even in ambient conditions.

Keywords: *MOF-199, H_2S, CH_3SH, Sorption, Activation*

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