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Heat and Mass Transfer Kinetics of MOF-Coatings from Al-fumarate and CAU-10(Al)-H from IR-LTJ experiments: The Impact of Characteristic Times

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Abstract:

The metal-organic frameworks (MOFs) Al-fumarate and aluminum-isophthalate CAU-10 (CAU = Christian Albrechts University Kiel) are considered for water-based adsorption chillers because of their excellent cyclic stability and high water uptake. However, water uptake captures only the equilibrium behavior, while process performance depends strongly on kinetics. In this work, we, therefore, determine characteristic time constants for water ad- and desorption on Al-fumarate and CAU-10. The MOF coatings are studied by small-scale Infra-red Large-Temperature-Jump (IR-LTJ) experiments. Commercially available granular silica gels serve as benchmark. We show that the performance expected from the characteristic time constants depends strongly on the chosen characteristic time as well as the chosen reference in the heat exchanger: For area-specific mean power, silica gel performs best for small time constants, CAU-10 and silica gel both perform best for intermediate time constants, and Al-fumarate performs best for large time constants for the temperature triple 10/30/80 °C. For volume-specific mean powers, silica gels are outperformed by both MOF-coatings with the best results for CAU-10 at intermediate time constants. The results highlight the potential of MOF coatings for adsorption chillers.

1. Introduction

Adsorption chillers can provide environmentally-friendly cooling but are typically limited by low specific cooling power (SCP) and coefficients of performance (COP) [1]. To overcome the limitations of state-of-the-art materials like silica gels or zeolites, advanced materials are developed. Metal-organic frameworks (MOFs) provide improved equilibrium properties such as high water uptake and well-located uptake step [2]. These improved equilibrium properties allow increasing the COP.

Despite promising equilibrium properties, the MOFs MIL-101(Cr) and NH2-MIL-125 have shown poor specific cooling power SCP in granular form compared to commercial silica gel due to slow heat and mass transfer as well as low densities [3]. To also improve SCP, MOFs have been directly coated on heat exchanger surfaces with promising results [4,5]. However, benchmarking MOFs or comparing coatings with granulates is difficult.

To investigate the kinetic behavior of adsorbents, the Large-Temperature-Jump (LTJ) was developed by Aristov et al. [6] and advanced to the Infrared-LTJ (IR-LTJ) by Graf et al. [7] and Velte et al. [8]. However, different criteria have been employed to extract performance indicators from these LTJ experiments.

In this work, we perform IR-LTJ measurements of granular and coated adsorbents with water for adsorption and desorption. We then discuss two approaches to evaluate the IR-LTJ results.

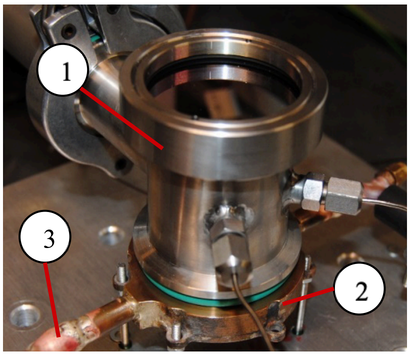

Figure 1 – Experimental IR-LTJ setup: measuring cell with IR-transparent cover (1), copper heat exchanger to control the sample temperature (2), and tubing for the heat exchanger (3).

2. IR-LTJ experiments

IR-LTJ requires less than 100 mg of the adsorbent allowing to benchmark adsorbents at an early development stage. The IR-LTJ setup (Figure 1) employs an IR-camera to monitor the temperature of the investigated adsorbent sample. The adsorbent sample is exposed to a temperature jump so that the kinetic behavior can be determined from the following step responses of pressure in the vapor phase p and temperature of the adsorbent T. The resulting change in loading X is measured indirectly from the change in vapor density in the known

volume through temperature and pressure measurements. As temperatures, we chose the commonly used triple 10/30/80 °C for evaporation, condensation/adsorption, and desorption, respectively. The refrigerant is water.
As promising adsorbents, we selected Al-fumarate [4] and the aluminum-isophthalate CAU-10 [5]. Small samples of 44 mg Al-fumarate and 35 mg CAU-10, were coated on aluminum sheets (Radius R = 15 mm) to represent the conditions in a finned heat exchanger. To resolve the impact of the coating thickness, we also investigate two thinner coatings of 22 mg Al-fumarate and 25 mg CAU-10. The reference materials for comparison are the granular silica gels "SG 123" (Grace, 0.5-1.25 mm) and "Siogel" (Oker Chemie, 0-0.71 mm) which are also placed on aluminum sheets of the same size as the MOFs. The adsorbents differ in masses, diameters/coating thicknesses, and bulk densities (Table 1) so the question remains on how to compare these adsorbents.

Table 1 – Overview of the investigated adsorbents.

Material	Supplier	Mass m_{Ads} in mg	Diameter/Thickness in µm	Bulk Density ρ_{Ads} in g/cm³
SG 123	Grace	1008	500 - 1250	0.710 ± 0.060
Siogel	Oker Chemie	436	0 - 710	0.710 ± 0.090
Al-fumarate	ISE[2]	44	181.0 ± 17.5	0.343 ± 0.036
Al-fumarate	ISE[2]	22	107.0 ± 12.0	0.291 ± 0.035
CAU-10	ISE[2]	35	112.0 ± 22.6	0.442 ± 0.091
CAU-10	ISE[2]	25	81.0 ± 11.3	0.437 ± 0.063

3. Interpretation of IR-LTJ experiments: Time constants versus mean powers

The kinetic behavior of the materials can be quantified by characteristic time constants τ as introduced by Aristov et al. [6]: The time constant $\tau_{X/X_{\mathrm{eq}}}$ (X/X_{eq} in %) is the time evolved after the applied temperature jump until the loading X has reached a specified percentage of the equilibrium loading X_{eq}.

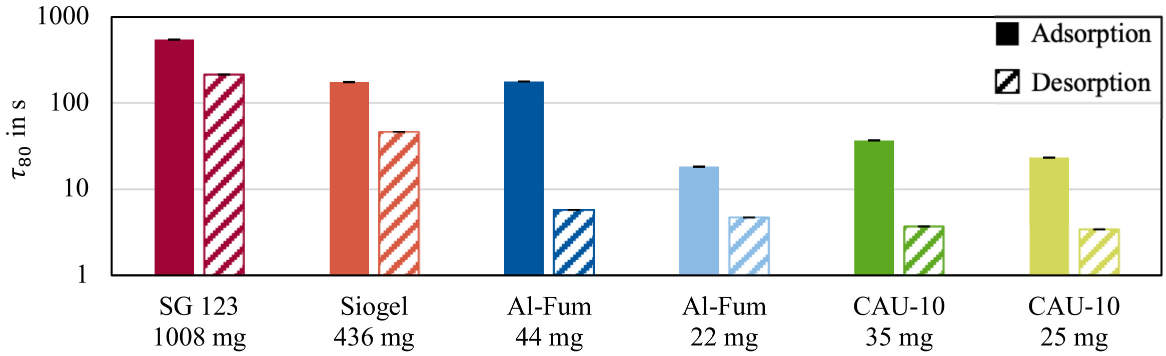

Figure 2 - Resulting characteristic times τ_{80} for 80% relative loading from the IR-LTJ for SG123, Siogel, Al-fumarate, and CAU-10-H for adsorption (filled) and desorption (hatched). Expanded measurement uncertainties are within the drawing accuracy.

The comparison of the characteristic time constants τ_{80} for 80 % relative loading in Figure 2 shows faster desorption than adsorption for all materials. MOF-coatings mostly have lower characteristic times than granular silica gels with the exception that τ_{ads} (for adsorption) of the 44 mg Al-fumarate sample is with 178 s on par with the characteristic time of Siogel (175 s). For desorption, Al-fumarate is the slower MOF (with τ_{des} = 6 s), but is still 87 % faster than the faster benchmark material Siogel (τ_{des} = 46 s). CAU-10 performs equally well as Al-fumarate for desorption and is even faster for adsorption.
However, the representation of process performance by characteristic times like τ_{80} can be misleading since the amount of adsorbed refrigerant is not included. Thus, the benefit of a high uptake capacity, which would also result in a high power density, is not considered. Based on Bendix et al. [9] and Ammann et al. [10], we, therefore, propose an alternative analysis of LTJ data by defining an area-specific mean power (Figure 3a)

$$\bar{P}_A = \frac{\Delta h_{\mathrm{evap}} \cdot m_{\mathrm{H_2O},X/X_{\mathrm{eq}}}}{A_{\mathrm{hx}} \cdot \tau_{\mathrm{ads},X/X_{\mathrm{eq}}}}, \quad [\bar{P}_A] = \frac{kW}{m^2} \tag{1}$$

with

$$m_{\mathrm{H_2O},\,X/X_{\mathrm{eq}}} = \Delta X_{X/X_{\mathrm{eq}}} \cdot m_{\mathrm{Ads}}, \tag{2}$$

and a volume-specific mean power (Figure 3b)

$$\bar{P}_V = \frac{\Delta h_{\mathrm{evap}} \cdot m_{\mathrm{H_2O},\,X/X_{\mathrm{eq}}}}{V_{\mathrm{Ads}} \cdot \tau_{\mathrm{ads},X/X_{\mathrm{eq}}}} = \frac{\Delta h_{\mathrm{evap}} \cdot \Delta X_{X/X_{\mathrm{eq}}} \cdot \rho_{\mathrm{Ads}}}{\tau_{\mathrm{ads},X/X_{\mathrm{eq}}}}, \quad [\bar{P}_V] = \frac{MW}{m^3} \tag{3}$$

where Δh_{evap} is the enthalpy of evaporation (2477 kJ/kg at 10 °C) and $m_{\mathrm{H_2O},X/X_{\mathrm{eq}}}$ is the adsorbed mass of water at varying relative loadings. Evaluating LTJ-measurements with $\bar{P}_A$ incorporates the adsorbed refrigerant mass $m_{\mathrm{H_2O},X/X_{\mathrm{eq}}}$ and the heat exchanger area A_{hx} (Eq. 1). Evaluating $\bar{P}_V$ takes into account the adsorbent volume V_{Ads} (Eq. 3) determined by the bulk densities ρ_{Ads} from Table 1. The two different mean powers lead to a more comprehensive analysis than only the time constants, but still, the choice of time constants (e.g. τ_{50}, τ_{80}, τ_{95}) strongly affects the evaluation of the LTJ-measurements (Figure 3). This effect is similar to the choice of a cycle time which affects the trade-off between SCP and COP in the full-scale adsorption chiller [11]. As adsorption seems to be slower and thus the limiting phase (cf. Figure 2), we only evaluate the adsorption phase.

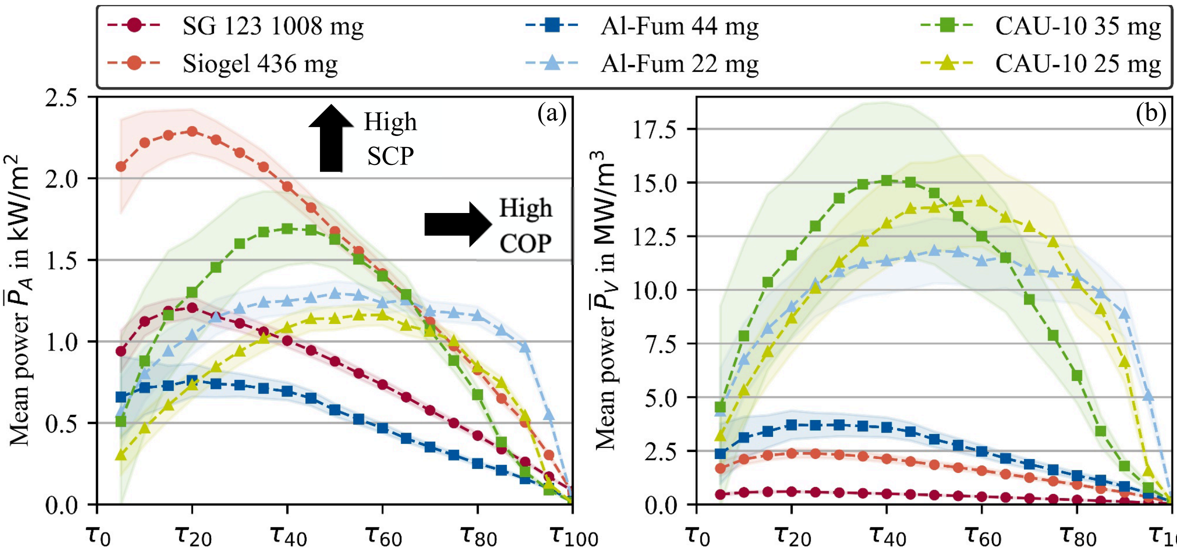

Figure 3 – Area-specific mean power $\bar{P}_A$ (a) and volume-specific mean power $\bar{P}_V$ (b) over different adsorption time constants τ_{ads} for the granular adsorbents SG 123 and Siogel as well as the MOF-coatings CAU-10 and Al-fumarate. Shaded areas represent measurement uncertainty with coverage factor k = 1 according to [12].

In Figure 3, small time constants are subject to a larger measurement uncertainty as decreasingly small pressure differences have to be detected with the indirect IR-LTJ experiment. Importantly, each adsorbent shows a distinct optimal relative loading where its mean power is maximal. The highest mean power is also provided by different adsorbents at different time constants τ_{ads} at which the LTJ-measurements are evaluated.

The highest area-specific power (Figure 3a) is provided by Siogel which is thus expected to maximize SCP. For high time constants $\tau_{\mathrm{ads}} > 75$ %, however, the thin Al-fumarate coating yields maximal area-specific mean power. Regarding coating thickness, the thick coating of CAU-10 outperforms its thin coating while Al-fumarate shows the opposite trend. Additional research is needed to optimize coating thickness and to study limits on heat and mass transfer.

In Figure 3b, the volume-specific mean power of the adsorbents also depends on the chosen time constant τ_{ads}. Here, all MOF-coatings outperform the two silica gels with the best results for CAU-10. In contrast to Figure 3a, the volume-specific mean power not only accounts for the adsorbed mass but also for the volumes of the adsorbents (cf. Eq. 3).

While the observations only hold for the chosen temperature triple of 10/30/80 °C, the findings clearly show the importance of the chosen time constant τ_{ads} and the reference for the mean power.

4. Conclusion

The equilibrium properties of new materials are not sufficient to determine the overall performance of adsorption chillers. For this reason, we determine and compare characteristic times for ad- and desorption of Al-fumarate and

CAU-10 coatings to two commonly used granular silica gels by performing IR-LTJ-experiments for the refrigerant water. Our results show that the MOF-coatings can compete with classical granular silica gels with respect to area-specific chilling power and outperform the silica gels with respect to volume-specific chilling power. For the temperature triple 10/30/80 °C, the area-specific mean power is maximal at low relative loadings for Siogel; at intermediate relative loadings for the thick coating of CAU-10 as well as Siogel, and at high relative loadings for the thin coating of Al-fumarate. For the volume-specific mean power, all MOF-coatings outperform the silica gels with the best results for CAU-10. Thus, to exploit the advantages of MOF-coatings over granular silica gels, a dedicated adsorber design is required: An adsorber with the same available heat transfer area for granular and coated materials will not provide higher cooling power for MOF-coatings.

These results indicate the complex trade-offs between kinetic and equilibrium properties, between granulates and coatings as well as between heat transfer area and adsorbent volume. Additional insight could be gained by varying the temperature triple and the coatings' thicknesses. The presented approach shows that such studies should cover the full range of time constants. To study all resulting trade-offs including SCP and COP, heat exchanger metal mass needs to be incorporated into the analysis. For such an analysis the kinetic behavior should be employed as the basis for predictive dynamic models to determine the performance of full-scale adsorption chillers as proposed by Graf et al. [3].

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