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Thermal energy storage of HFO-1336-mzz(Z)/MOF-200 and MM/MOF-200 nanofluids: A molecular simulation study

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ABSTRACT

The mutual conversion of heat energy and surface energy during the adsorption and desorption of working fluids on the surface of nano-porous materials can improve the heat storage capacity for energy storage. In this paper, the energy storage properties of two industrial fluids, HFO-1336mzz(Z) and Hexamethyldisiloxane(MM),with MOF-200 nanoparticle, were investigated by means of molecular dynamics simulations and grand canonical Monte Carlo simulations. It shows that the adsorption capacity of HFO-1336mzz(Z) in MOF is higher than that of MM. Moreover, the increment ratio of thermal energy storage properties of HFO-1336mzz(Z)/MOF-200 mixture is better than that of MM/MOF-5 mixture.

Keywords: energy storage; working fluid;metal organic framework; molecular simulation

1. INTRODUCTION

Energy plays an important role in human survival and development [1]. Due to global warming and environmental pollution [2], the demand for renewable energy is increasing each year [3]. In fact, many renewable energies, including solar energy, geothermal energy, waste heat from gas turbine, and exhaust gas from industry, need to be utilized [4-7]. Generally, Organic Rankine cycle (ORC) is one of most effective ways to make use of low-grade energy, which adopts organic compounds as working fluids in the Rankine cycle [8]. The ORC cycle efficiency is relatively low because of the low temperature of hot reservoir for low-grade energy [9].

Usually, adding a certain amount of nanoparticles to the working fluids can improve their heat transfer ability [10]. Choi et al. [11] proposed the concept of nanofluid. Besides, McGrail et al. [12] proposed to use Metal-Organic Heat Carrier (MOHC) nanofluids, the organic working fluid mixed with metal organic framework (MOF) nanoparticles to form the nanofluid, to enhance the efficiency of ORC.

MOFs are highly crystallized by metal ions or metal clusters and organic ligands through the coordination bond or intermolecular interactions, possessing good thermal stability, high specific surface area and strong adsorption affinity for adsorbates [13]. Zheng et al. [14] showed that adsorption isotherms of fluorocarbon HFC-134a in MOFs and this fluorocarbon/MOF combination has the potential to be one of the most promising working pairs for use in adsorption cooling applications.

However, the pore structure scale in MOFs is too small, and it is difficult to study the adsorption characteristics of working fluids in MOFs by conventional experimental and theoretical methods[15]. With the rapid development of computer technology, molecular simulation technology has been widely used in scientific research now [16]. García et al. [17] screened 40 experimentally available MOFs for their application in adsorption air-conditioning using low-GWP working fluids by molecular simulations, so as to provide guidance for determining the best MOFs/working fluids pair. It has been obtained that MOF-200 has a good adsorption effect on fluids because of its large pore size and high BET and Langmuir surface areas. Siloxanes are considered to be one of the most suitable mediums and high temperature ORC working fluids [18], because of their good thermal stability. What's more, with the aim of reducing utilization of fluorocarbons, some low-GWP working fluids are being proposed. HFO-1336mzz(Z) is a promising hydrofluoroolefin used in ORC system

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because of its environmentally friendly features and good thermal performance [19].

In conclusion, the thermal energy storage performance of HFO-1336mzz(Z) and MM in MOF-200 working pairs is investigated by Grand Canonical Monte Carlo (GCMC) simulation associated with adsorption theories and Molecular Dynamics (MD) simulation here.

2. METHOD AND COMPUTATIONAL DETAILS

The enthalpy of MOHCs (Δh_{MOHCs}) consists of the enthalpy of pure organic fluid (Δh_{Fluid}), the energy of MOF nanoparticles ($\left(\int c_p dT\right)_{MOF}$), and the enthalpy of desorption ($\Delta h_{desorption}$) of fluid molecules[12, 20, 21]. Thus, the thermal energy storage in MOHCs can be calculated

$$h_{MOHCs} = (1-x)\cdot h_{Fluid} + x\cdot\left(\int c_p dT\right)_{MOFs} + x\cdot h_{Fluid} \quad (1)$$

And it can be written as,

$$h_{MOCHs} = h_{Fluid} + x\cdot\left(\left(\int c_p dT\right)_{MOFs} + h_{desorption} - h_{Fluid}\right) \quad (2)$$

where x is the mass fraction of MOF in MOHCs, and c_p is the heat capacity of MOF. It can be concluded that the MOHCs is able to store more thermal energy than the pure fluid since the sum of thermodynamic energy change of MOFs particles and desorption heat of fluid in MOFs is larger than the enthalpy change of working fluids.

2.1 Computational model

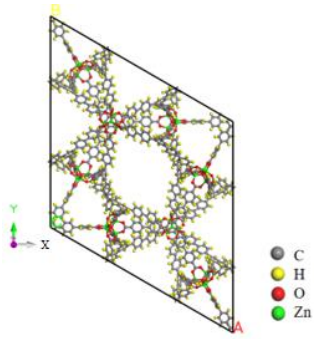

Fig. 1. MOF-200 structure

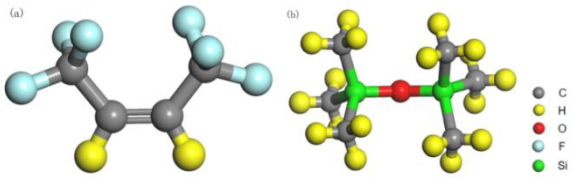

Fig. 2. Molecular model of HFO-1336-mzz(Z) and MM

The MD calculation model of GCMC adsorption model was established by 1×1×1 unit cells of MOF-200 (including 720 carbon atoms, 104 oxygen atoms, 432 hydrogen atoms and 32 Zn atoms) in the simulation box (X: 52.022 Å, Y: 52.022 Å, Z: 42.316 Å , α=β=90° , γ=120°) ,as shown in Fig. 1. And the fluid, HFO-1336mzz(Z) is shown in Figure 2(a), MM is shown in Figure 2(b). The MD simulations and GCMC simulations are performed by Materials Studio. The COMPASS force field is applied to describe the interactions of atoms[22]. Ewald method is employed to calculate the long-range Coulombic interactions. The periodic boundary conditions are applied in X, Y and Z directions.

2.2 MD computational details

In MD simulations, the internal energies of MOF-200 nanoparticles at different temperatures (290 K, 310 K, 330 K, 350 K 370 K and 390 K) are computed in NVT ensembl. The timestep is set as 1 fs and the system equilibrated for 100 ps to obtain the internal energy. The Berendsen method is employed to control the temperature[23].

2.3 GCMC computational details

The GCMC simulations are carried out to calculate the adsorption isotherms (290 K, 310 K, 330 K, 350 K 370 K and 390 K) of HFO-1336mzz(Z) and MM in MOF-200 nanoparticles (the structure shown in Fig. 1). The pressure is calculated from 1 to 2000 kPa. The method chooses Metropolis, mainly for general small molecule or particle adsorption. The fugacity is calculated by the Peng-Robinson equation. Here, the balanced process is 2000000 cycles and the production is 3000000 cycles. The periodic boundary conditions are applied in X, Y and Z directions.

3. RESULTS AND DISCUSSION

3.1 Internal energy of MOF-200

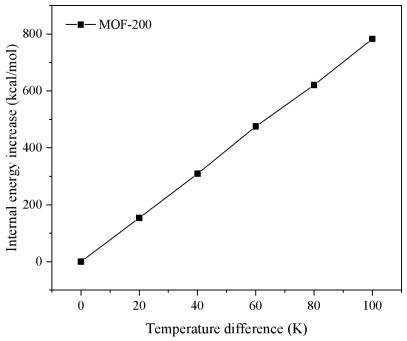

Fig. 3. Variation of the relative change of the thermodynamic energy of MOF-200 with temperature

Previous works had proved that it can obtain reliable thermodynamic performance parameters by MD [24-26]. The internal energy of MOF-200 at different temperatures is shown as Fig.3. Actually, the internal energy of MOF-200 linearly increases as the temperature arises. Compared with the MOF-5 [21], MOF-200 has smaller density and larger volume.

3.2 Adsorption isotherm

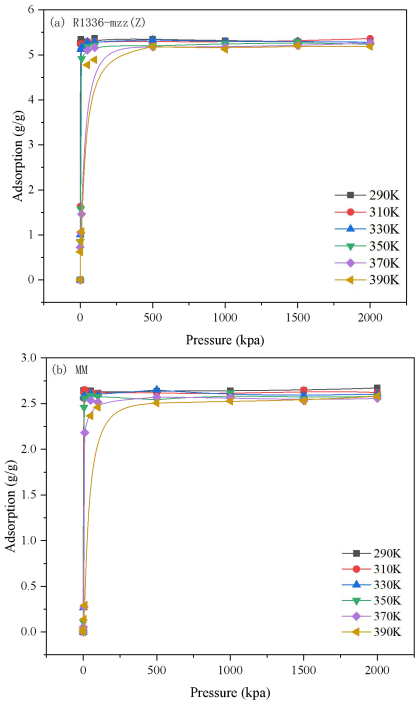

Fig. 4. Adsorption in MOF-200 at different temperatures (a) HFO-1336mzz(Z) (b) MM

Figure 4 depicts the adsorption isotherms of refrigerants including HFO-1336mzz(Z) and MM in MOF-200 at different temperatures, in which symbols represent the results measured in the present GCMC simulations. The adsorption decreases with temperature for all the studied adsorbates. At the same temperature, the adsorption capacity increases gradually with the increase of pressure, but the increasing trend slows down until saturation. It can be seen that the saturation adsorption capacity of HFO-1336mzz(Z) in MOF-200 is higher than that of MM at the same temperature.

3.3 Thermal energy storage

The relationship between thermal energy storage and temperature difference of HFO-1336mzz(Z)/MOF-200 and MM/MOF-200 mixture are illustrated in Fig. 5. It shows that adding MOF-200 nanoparticles to HFO-1336mzz (Z) and MM can change their energy storage characteristics, and the energy storage effect increases with the increase of the mass fraction of nanoparticles. Fig. 5 shows that the energy storage enhancement effect of MOF-200 nanoparticles on HFO-1336mzz(Z) is better than that on MM.

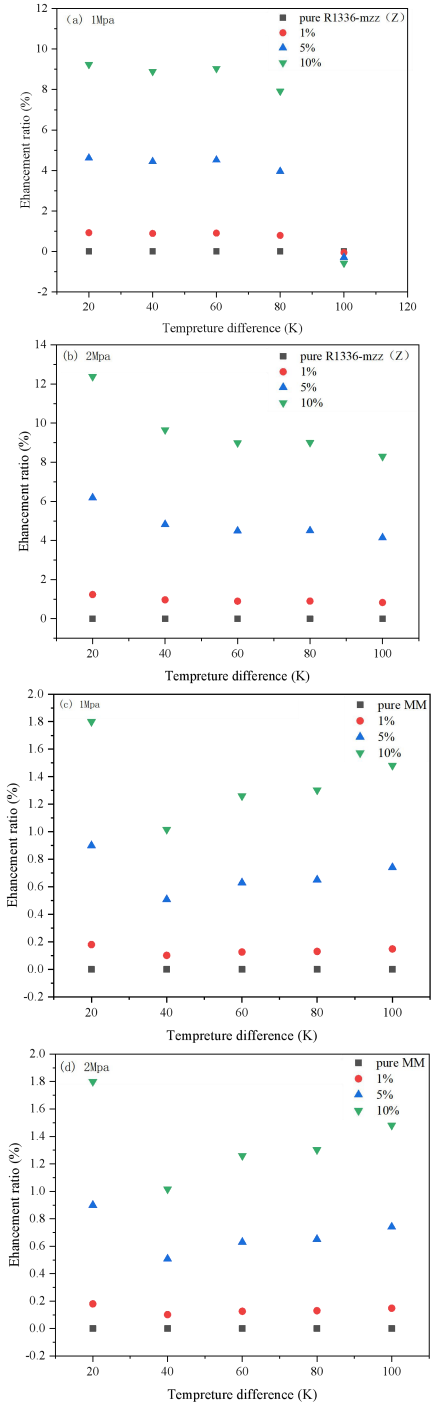

Fig. 5. The relationship between thermal energy storage and temperature difference of MOHCs at pressure of 1Mpa,2Mpa

4. CONCLUSION

In this study, molecular simulations including MD and GCMC methods are applied to investigate the energy storage properties by the adsorption of working fluids, HFO-1336mzz(Z) and MM, in MOF-200. The results could draw the following conclusions.

The saturation adsorption capacity of HFO-1336mzz(Z) in MOF-200 is higher than that of MM at the same temperature. The MOF-200 nanoparticle is more conducive to enhance the thermal energy storage capacity of HFO-1336mzz(Z) than that of MM. And the energy storage enhancement effect of MOF-200 nanoparticles on HFO-1336mzz(Z) is better than that on MM.

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