STUDY ON SURFACE ENERGY PARAMETERS AND MORPHOLOGY OF PROMISING ADSORBENT MATERIALS

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(次世代吸着剤の表面形状及び表面エネルギーに関する研究)

区　　分　Category： 甲

論 文 内 容 の 要 旨

Thesis Summary

The demand for adsorption technologies is rapidly rising in various applications due to its applicability in utilizing low-temperature heat sources (industrial waste heat or solar heat) and environmentally friendly refrigerators (H_2O, CO_2, NH_3, CH_4O, etc.). The application area includes but not limited to refrigeration & heat pumping, water production & treatment, air conditioning & thermal comfort, and thermal energy storage. The critical component of the adsorption technologies is the porous materials, known as adsorbents. The morphological features of the adsorbents require to have some distinctive features like high surface area, meso or microporosity, and optimum affinity towards refrigerants to become suitable for the adsorption-based systems. Many promising adsorbents (silica gel, activated carbons, metal-organic frameworks) are already synthesized having the mentioned features; still, there is no clear breakthrough in adsorption systems found. One of the reasons behind this is the existing gap between material science (MS) and applied thermal engineering (ATE). This research gap predominantly depends on the existence of the intermediate characterization technique, which supposes to relate the morphological features with the adsorption phenomenon. Recently, it is found that the surface energy of the adsorbents plays a vital role in developing a universal model for all eight major types of isotherms. Therefore, it is assumed that surface energy might be the predicted intermediate characterization technique that can mitigate the existing gap up to some reasonable level between MS and ATE.

The surface energy is a distinctive feature of adsorbents, which is rarely measured; indeed, it carries essential information for the adsorption process. The surface morphological characterization alone does not provide the full feature of a surface; it is vitally required to measure the surface activities which can be performed by surface energy measurements. From the above perspective, this thesis emphasizes the novel characterization techniques that can employ in developing promising adsorbents for adsorption-based systems. The research stresses several factors, firstly, extracting the morphological and surface activity information of the promising adsorbents using novel characterizing techniques. Secondly, finding a thermodynamic relationship between surface activities with the texture properties. Finally, it includes the synthesis and characterization of metal-organic frameworks to enhance the performance of adsorption chillers, which concludes with an insight of the enhancement from the surface energy point of view.

At first the three-dimensional morphological features are extracted using an atomic force microscopy (AFM) equipment, which is further employs to calculate the surface porosity information. Additionally, a novel approach is developed to measure the adsorbent surfaces to generate height images.

Secondly, the surface energy analysis in the infinite dilution was performed by the Inverse Gas Chromatography (IGC) technique to measure the dispersive and specific components for various promising silica gels (RD silica gel, Chromatorex, Home silica gel, and B-type silica gel). From the experiment the dispersive component is found dominating, and the highest value was observed for RD granular silica gel. It is predicted that the higher the surface energy in the infinite dilution, the higher will be the adsorption uptake because surfaces contain high energy sites that might contribute significantly to the adsorption process. These results led to further experiments on the activated carbon-based adsorbents, which exhibits high surface energy (>200 mJ m^{-2}) than the silica gels (<100 mJ m^{-2}).

The next experiments conducted on the activated carbons (Maxsorb III, WPT-AC, H_2-treated Maxsorb) were slightly different from that of silica gels. Here, the measurement of isosteric heat and isotherms in the Henry region were targeted to calculate the energetic behaviors of a single component adsorbate-adsorbent system (ethanol-activated carbon pair) in terms of enthalpy and entropy. A thermodynamic trend is established between the specific entropy and the Henry's law constant including the pore volume of adsorbents, and one can predict the isosteric heats and adsorbent-pore-size for activated carbon + ethanol system by extending the proposed linear trend, which is predicted to significantly contribute in tailoring the adsorbent materials for the design of adsorption bed with a minimal or maximum driving force depending on the types of heat transformation applications. However, the improvement mostly depends on the modification of the pores and surface area, which might limit the tailoring efficiency. In addition, from the previous two experiments, it is predicted that, creating charge disparity inside the adsorbents might increase the specific surface energy which has a possibility to improve the total surface energy. In that case, metal-organic frameworks are promising due its exceptional interior decoration and tailoring capability, so that, the predicted charge disparity can be implemented.

A rigorous review on promising MOFs and their modification were performed to select the suitable MOF for adsorption chiller applications. After synthesizing a wide variety of MOFs (Aluminium Fumarate, MIL-101 (Fe), MIL-100(Fe), MOF-74 (Co), MOF-74(Ni), CAU-10H, HKAUST-1), aluminum fumarate was selected for analysis and modification. A modified protocol was used to synthesis a tailored MOF which is developed in our laboratory (SMOF) to enhance the yield and water adsorption uptake. The SMOF is then doped with various concentration metal ions (Fe, Co) to observe the variation on water adsorption isotherms. Interestingly found that the newly synthesized SMOF exhibits significantly high uptake and shifts the water adsorption isotherms towards the lower pressure region. Both the findings are crucial for the development of adsorption chillers; the analysis shows that SMOF improves the specific cooling efficiency (SCE) up to 150%.

To deliver an insight into the improvement, the surface energy of the SMOFs was conducted in the lower pressure region. A comparison of surface energy components between the SMOFs reveals that the dispersive surface energy of the doped SMOFs was significantly improved. However, the doped ions only contributed to tailoring the morphological properties. Further studies on finite dilution will reveal much interesting information which will help to synthesize next generation adsorbents.