DOI 10.5162/IMCS2018/P2GS.2

Gas Adsorption and Sensing Mechanism Studies by Measu ring Enthalpy of Porous Materials with QCM

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Abstract :
Quartz crystal microbalance (QCM) loaded with different porous materials was used as a new tool to measure adsorption isotherms for calculating adsorption enthalpy. The QCM devices enable to measure the adsorption isotherms and monitor the dynamic process for the adsorption of CO_2 on ZIF-8.,UIO-66 and SBA-15-NH_2 which represent three different adsorption mechanism. The adsorption isotherms of the CO_2 on ZIF-8 followed the Kraussius-Clapelon equation with the characteristic energy of 15.6 kJ.mol^{-1}.This adsorption enthalpy approximates the result of BET test(14.6~14.9kJ. mol^{-1}) and the Gaussian calculation software(14.8kJ), and according with previous studies about 15~20kJ.mol^{-1} (belong to physical absorption). The adsorption enthalpy of CO_2 on UIO-66 was 38~42 kJ.mol^{-1}, conforming with previous studies about 40kJ.mol^{-1} (belong to weak chemical absorption).The SBA-15-NH_2 was choose as a strong chemical adsorption on CO_2 to explore the accuracy of this method. Fortunately, the figure obtained is in keeping with the theoretical value (greater than 80 kJ mol^{-1}) . As a result, the above three adsorption enthalpy measured by QCM are consistent with that calculated from the earlier adsorption theory. This will open a new route to judge if the material is suitable for adsorptive and sensing materials.

Key words: QCM, adsorption, adsorption enthalpy, ZIF-8,CO_2

Results and Discussion

QCM transducer was employed to measure enthalpy of three different adsorption that physical adsorption, chemical adsorption and weak chemical adsorption.

Fig.1 shows the CO_2 adsorption isotherms on ZIF-8 at 273K and 287K in the pressure range from 0 to 35 bar. It can be seen that the CO_2 uptake increased drastically with pressure. Which can be attributed to the micropore adsorption.

Fig.2 shows the adsorption enthalpy (ΔH) of CO_2 on ZIF-8 determined by measuring two isotherms at 287K and 273K, and fitting the data to the virial model. The enthalpy of adsorption enthalpy (ΔH) for ZIF-8 is 14.7 kJ/mol approximately .

Fig.3 and Fig.4 were two stable configure-tions for the complex $C_4H_6N_2$ ⋯CO_2 to analog computation. The most stable conformation has the CO_2 on the imidazole ring top position (Fig.3), with C(CO_2) at a distance of 3.556 and 3.958 Å from two imidazole ring N a-toms and 4.494 Å from the methyl C atom. The stability of the conformation is caused by the quadrupole-π electron interaction between the π electrons on the imidazole ring and the electron-deficient carbon of the CO_2 molecule, as well as by the weak interaction between the methyl and CO_2 molecule. And less stable configuration has the CO_2 positioned beside the methyl group with the shortest distance O (CO_2) ⋯H (methyl) of 3.239 Å (Fig.4) because there is a hydrogen bond-like interaction between O (CO_2) and H (methyl). The simulated

Fig.5 and Fig.6 were the responses of ZIF-8 based QCM towards CO_2 in two different temperature of 273K and 287K. It is obvious that temperature cause low responses .the frequency shift represent adsorbing capacity.

Fig.7 was a fitting model from Fig.5 and Fig.6. According to the Kraussius-Clapelon equation, choose any same adsorption capacity point can calculate different enthalpy of adsorption (ΔH) about 15.6 kJ/mol.

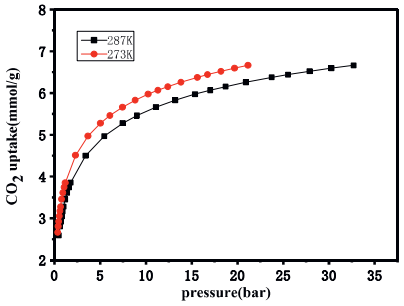

Fig.1 CO_2 adsorption-desorption isotherm on ZIF-8 at 287K and 273K

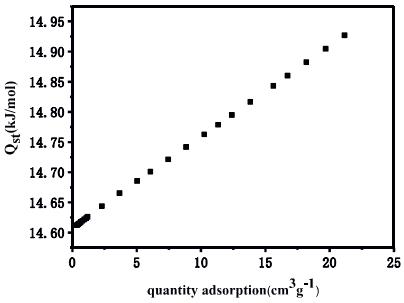

Fig.2 Dependence of enthalpy of adsorption on the a mounts adsorbed of CO_2 over ZIF-8

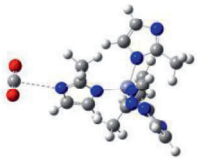

Fig.3 DFT-optimized stable configurations of the com plex $C_4H_6N_2$ ⋯CO_2 in ZIF-8 of C ⋯N

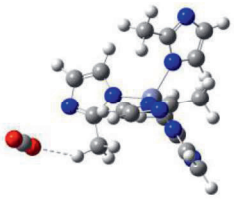

Fig.4 DFT-optimized stable configurations of the com plex $C_4H_6N_2$ ⋯CO_2 in ZIF-8 of O ⋯H

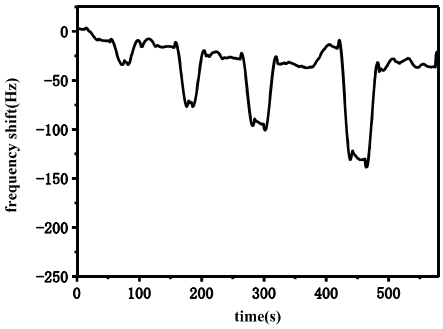

Fig.5 response curve of different concentrations of C O_2 at 287K

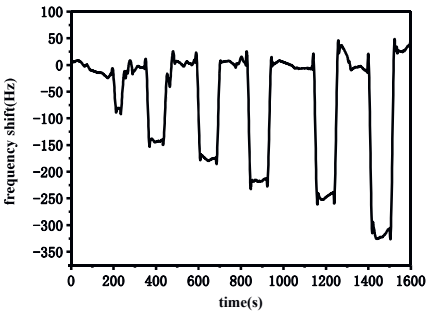

Fig.6 response curve of different concentrations of C O_2 at 273K

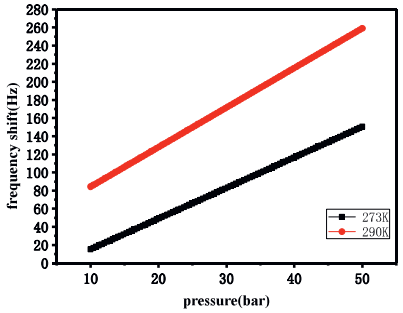

Fig.7 CO_2 adsorption isotherm on ZIF-8 at 287K and 273K fitting from QCM

Reference

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