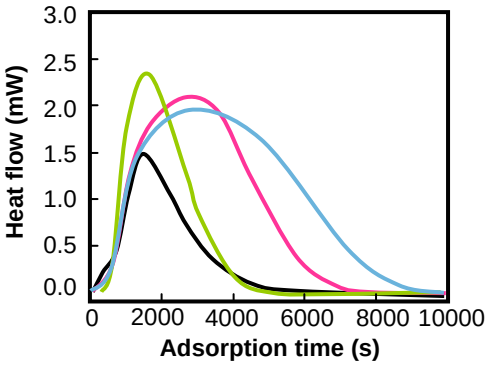
A study of the adsorption of thiophenic sulfur compounds using flow calorimetry

Reference: A study of the adsorption of thiophenic sulfur compounds using flow calorimetry, Flora T.T. Ng, Ataur Rahman, Tomotsugu Ohasi, Ming Jiang, Applied Catalysis B: Environmental 56 (2005) 127–136

Introduction: Nowadays, environment is in the middle of the concerns. In particular, many investigations are realized on the desulfurization of transportation fuels because ultra low sulfur fuel is needed for on-site or on-board use with a fuel cell system, especially in a polymer electrolyte membrane (PEM) fuel cell where the Pt electrode is readily poisoned by the S compounds. For example, the adsorption of refractory benzothiophenic type S compounds present in diesel can be studied using a liquid phase flow calorimetry technique with hexadecane as a solvent to mimic the diesel fuel and zeolites such as NaY, HY, USY and 13X as sorbents.



Heat of adsorption of sulfur compounds in hexadecane on NaY at 30 ℃. All solutions contain 1800 ppm S except 4,6-DMDBT containing 900 ppm S :
T : -39.65 J/g
BT : -31.63 J/g
DBT : -18.73 J/g
DMDBT : -12.12 J/g

Experimental

Experiments were conducted on a C80 heat-flux calorimeter at 30℃ with two identical percolation vessels, one for the sample and another for the reference.
All adsorbent samples were first ground and sieved between 250 and 500 µm particle size and then calcined in an oven at 400℃ for 6h.
For the analysis, about 250 mg of calcined zeolite sample was placed inside the vessel and the reference capsule was filled with hexadecane.
First, the zeolite was wetted by flowing hexadecane at about 4.5mL/h using a peristaltic pump what causes an exothermic heat associated with the heat of adsorption of hexadecane and wetting of the sample. Then, when the heat flow comes back near a zero value, a solution of hexadecane and sulfur-containing compound is pumped to the inlet of sample vessel at the sample flow rate.

Instrument
C80
20 to 300℃

Results

The figure shows the heat flow as a function of adsorption time for different sulfur compounds in a hexadecane solution on NaY. The concentration of Thiophene (T), Benzothiophene (BT) and Dibenzothiophene (DBT) were equivalent to 1800 ppm sulfur and the maximum achievable sulfur concentration of 4,6-dimethyldibenzothiophene (DMDBT) in the solution was 990 ppm due to its low solubility in hexadecane.
The enthalpy corresponding to the exothermic effect resulting from the adsorption capacity for these S compounds was found in the following order: T>BT>DBT>DMDBT
We can also note that, with the shape of the calorimetric curves, adsorption also strongly depends on the size of the adsorbate molecules.
Apparently, with increasing aromatic rings, very rapid adsorption occurs at the beginning of the experiments in spite of the size of the S compound. This suggests that the bulkier S compounds are adsorbed only on selected sites (pores) on the zeolites such as the supercages.

For more details ask for publication B1829