**Adsorption of elemental mercury from waste gases**

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**Highlights**

* Thermodynamics of physical adsorption from 25 to 100 °C
* Determination of isosteric heats of adsorption
* Fitting of diffusion coefficients by mathematical modelling
* Investigation of chemical adsorption by temperature programmed desorption experiments

**1. Introduction**

Sources of mercury pollution such as coal-fired power plants, cement plants and waste incineration plants are subject to tightening of regulatory limits. In addition, a stronger focus is given to mercury emission from discontinuous processes e.g. in metal refining or crematoria. While in continuous processes, established technologies like absorptive gas scrubbing or flue gas adsorption are applied, for discontinuous emissions only fixed-bed adsorption with activated carbon is suitable from an economic point of view. For the design and optimization of such processes, a good knowledge of the adsorption thermodynamics and kinetics is necessary. Measurement of mercury adsorption is difficult because mercury is toxic, adsorbs chemically on the surface of many materials (e.g. metal surfaces of pipes and valves) and reproducible supply of mercury vapor requires thorough experimental care. Accordingly, only few data of mercury adsorption has been published.

The aim of this work is to better understand the mechanisms involved in the adsorption of mercury. This understanding particularly applies to the interactions of mercury with the surface of the adsorbents and the influence of the pore size distribution on equilibrium and kinetics.

**2. Methods**

The adsorption of Hg0 from a N2 carrier gas stream is studied on commercial activated carbons. Single and cumulative breakthrough curves are measured in a fixed bed at temperatures of 25 °C to 100 °C and mercury concentrations of 50 to 1000 μg/m3. From the measured adsorption isotherms isosteric heats of adsorption are determined. In addition, desorption experiments are conducted to distinguish the contributions of physisorption and chemisorption. A dynamic simulation of experimental breakthrough curves yields diffusion coefficients which are discussed with respect to the concentration and temperature dependence of diffusion mechanisms in mercury physisorption. For detailed investigation of mercury chemisorption temperature programmed desorption (TPD) experiments employing activated carbon loaded with mercury are carried out. During the experiments, the adsorbents are heated from 30 to 500 °C with a constant heating rate of 5 °C/min.

**3. Results and discussion**

The activated carbons AC 01 and AC 02 are good examples to investigate in detail the dynamics and equilibria during pure mercury physisorption. The measured equilibrium isotherms almost show Henry behavior. A significant increase in capacity is observed when temperature decreases and/or concentration increases. This pronounced temperature and concentration dependence is typical for physisorptive adsorption mechanisms. The calculated isosteric heats of adsorption of Hg0 only amount to 50 % of the enthalpy of evaporation. This shows that the adsorption of Hg0 is exothermic, but the interactions of mercury with the surface of the activated carbon are significantly weaker than the interactions between mercury atoms in the condensed mercury phase. This phenomenon can be explained by the strong forces in liquid mercury. At room temperature, liquid mercury forms strong van-der-Waals clusters, whose bonding energies lie between dispersion interactions and covalent bonds [1]. The experimental breakthrough curves can be described by dynamic simulations with good accuracy. The results demonstrate that surface diffusion is the rate-determining diffusion process. Surface diffusion of Hg0 on the activated carbons exhibits no concentration dependence but a strong dependence on temperature typical for activated processes.

Both, physisorptive and chemisorptive mechanisms play a role in mercury adsorption on non-impregnated activated carbons AC 03 and AC 04. Ultimate analysis proves a high oxygen content of AC 03 and a high chlorine content of AC 04. The type and number of oxygen-containing functional groups are determined by Boehm titration. It is assumed in literature that the presence of oxygen-containing functional surface groups and chlorine favors chemisorption [2,3,4]. Therefore, TPD experiments are carried out to investigate the desorption kinetics and to obtain information on the surface chemistry of chemisorbed mercury. For AC 03, concentration peaks are detected in the temperature range from 120 to 350 °C, which can be assigned to individual functional oxygen groups. The results for AC 04 show a single peak at 420 °C and above. The reaction order and adsorption enthalpy can be determined by dynamic simulations.

**4. Conclusions**

The physisorptive and chemisorptive adsorption and desorption behavior of four commercial activated carbons was systematically investigated by experimental measurements and dynamic simulations.

**References**

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