

Effect of nano-confinement on sorption properties of mesoporous silica

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Sorption by nanoporous media may be critically involved in many fundamental geological and geochemical processes. Yet, while previous studies often aimed at enhancing sorption efficiency of nanoporous materials through surface modification, an improved understanding of the sorption behavior due to nano-confinement effect is still needed. In this work, we used unmodified MCM-41 silica with a monodisperse pore size (3.2–4.4 nm) and a large BET specific surface area (840–880 m²/g) as a model adsorbent to study the sorption characteristics of molecules/ions on mesoporous silica.

It was found that the capillary condensation pressure of nitrogen in MCM-41 mesopores increased with the increase of pore size. The freezing point of water in mesopores could be reduced to below -60 °C, and decreased with the decrease of pore size. The degree of pore-filling by water was estimated to be close to 100%. The highest escaping temperature of ammonia in silica increased with the decrease of pore size, reaching 250 °C at the pore size of 3.2 nm. Hexadecyl trimethyl ammonium bromide (CTAB) in MCM-41 silica was difficult to be removed by water washing, but could be oxidatively decomposed at high temperature.

The Cu²⁺ adsorption capacity was found to increase with increasing suspension pH in the range from 3 to 5, and to decrease in the presence of NaNO₃. A high value (over 45) of the dimensionless partition coefficient suggests the intense metal ion-enriching effect due to the existence of nanopores. The relatively slow adsorption kinetics is interpreted as a result of film and intra-particle diffusion associated with the restricted nanopores. Thermodynamic analysis shows that the adsorption was an entropy driven, endothermic spontaneous process, possibly involving both outer-sphere and inner-sphere complexes. The superposition of the electric potentials inside mesopores may play a key role in the sorption of metal ions.