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Liquid-phase separation of benzene from saturated aliphatics by adsorption on a copper benzene-1,3,5-tricarboxylate metal-organic framework

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Copper benzene-1,3,5-tricarboxylate metal-organic framework is an effective adsorbent for the liquid-phase separation of benzene from saturated aliphatics.

The removal of aromatics from saturated hydrocarbons is of importance in the petrochemical industry.[1] For example, the mixtures of benzene and cyclohexane cannot be separated by distillation due to the only 0.6 °C difference in the boiling points of these two components. Although azeotropic distillation and extractive distillation can be used for this separation, both of the processes suffer from high capital and operation costs.[2] Adsorption techniques for the separation of benzene from aliphatics are of considerable interest.[1] The porous metal-organic frameworks (MOFs) MIL-47, MIL-53(Al) and HKUST-1, which consist of V^{IV}, Al^{III} and Cu^{II} ions or clusters and terephthalate or benzene-1,3,5-tricarboxylate ligands can adsorb xylene isomers, ethylbenzene and styrene from hexane or heptane.[3–8] In this work we used three commercially available MOFs, Basolite C300 (HKUST-1), Basolite A100 [MIL-53(Al)] and Basolite F300, for the liquid-phase separation of benzene from saturated aliphatic hydrocarbons.† HKUST-1 consists of copper paddlewheel metal clusters linked by benzene-1,3,5-tricarboxylate ligands.[9] MIL-53(Al) contains the infinite chains of octahedra formed by the coordination of Al^{III} to terephthalate and OH^- groups.[10] Basolite F300 is porous iron(III) benzene-1,3,5-tricarboxylate with an unknown structure.

The adsorption properties of the materials were investigated in static and dynamic experiments. First, the adsorption of benzene on Basolite C300, Basolite A100 and Basolite F300 was examined under static conditions using *n*-heptane as a solvent (Figure 1).‡ Basolite C300 exhibited a high adsorption capacity for benzene (0.25 g of benzene per gram of Basolite C300 at ambient temperature). The adsorption capacities of Basolite A100 and Basolite F300 were 0.12–0.14 g of benzene per gram of adsorbent under the same conditions. It can be assumed that the adsorption of benzene on Basolite A100 and Basolite F300 mainly occurs due to π–π stacking interactions with the aromatic moieties of MOFs. The adsorption of benzene on Basolite C300 proceeds due to π-complexation bonds between benzene molecules and coordinatively unsaturated copper sites in addition to adsorption *via* the stacking interaction.[1,11] Thus, the higher adsorption capacity of Basolite C300 can be explained by the coordination of benzene molecules to the copper centers of framework. MOFs displayed rapid kinetics for the adsorption of benzene from heptane solutions, the equilibrium concentration of benzene was reached in 15 min from the beginning of the experiment in the presence of Basolite C300 and in 30 min in the presence of Basolite A100 and Basolite F300.

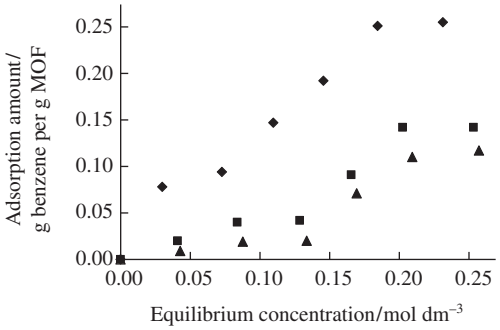

Figure 1 Adsorption isotherms of benzene on (◆) Basolite C300, (■) Basolite A100 and (▲) Basolite F300 from heptane solutions.

The breakthrough experiments were performed using a column packed with Basolite C300, Basolite A100 and Basolite F300 and 0.05 or 0.20 M solutions of benzene in *n*-heptane (Figure 2). Basolite C300 made it possible to purify a significant amount of solution before the benzene was detected in the effluent liquid. Benzene breakthrough occurred at 16 or 10 ml (g MOF)$^{-1}$ for a 0.05 or 0.20 M solution of benzene in heptane, respectively. The spent Basolite C300 can be regenerated using a heptane flow (1 ml min^{-1}) for 2 h or vacuum drying at 200 °C without loss of its adsorption capability.

A similar Basolite C300 column was used in a liquid chromatographic experiment for the separation of a mixture of benzene and cyclohexane (1 mg of benzene and 1 mg of cyclohexane in 0.1 ml of heptane) (Figure 3).§ The experimental chromatogram

† MOFs Basolite C300, Basolite A100 and Basolite F300 were purchased from Sigma-Aldrich. The BET surface areas of Basolite C300, Basolite A100 and Basolite F300 (for N_2) are 1450, 1112 and 1321 m^2 g^{-1}, respectively. HPLC-grade *n*-heptane from Panreac (99.0%) was used as the solvent.

‡ For static adsorption experiments, MOF (30 mg, activated at 200 °C in a vacuum for 2 h) was added to a solution of benzene in heptane (2 ml) containing *n*-decane (1.0 vol%). After stirring the mixture for 2 h at room temperature, the adsorbent was filtered off. The concentration of benzene in the filtered solution was determined by gas chromatography (Agilent 6890N instrument with a 19091S-416 HP 5-MS capillary column 60.0 m × 320 μm × 0.25 μm) using *n*-decane as an internal standard.

§ The breakthrough and chromatographic experiments were performed at room temperature on a 30 mm stainless steel column with an internal diameter of 4 mm (cartridge CatCart®30) filled with MOFs (100 mg) and placed in H-Cube Pro instrument (Thalesnano, Hungary) with an HPLC pump. For breakthrough experiments, a 0.05 or 0.20 M solution of benzene in heptane containing *n*-decane (1.0 vol%) as an internal standard was fed into the column at a flow rate of 0.15 ml min^{-1}. For chromatographic experiment, 0.1 ml of a heptane mixture containing benzene (1 mg) and cyclohexane (1 mg) was placed at the inlet of the column and eluted by heptane. The elution rate was 0.15 ml min^{-1}. The effluent fractions were collected every 3 min. Samples of 0.45 ml were taken directly at the column outlet, and concentrations were determined by GC analysis.

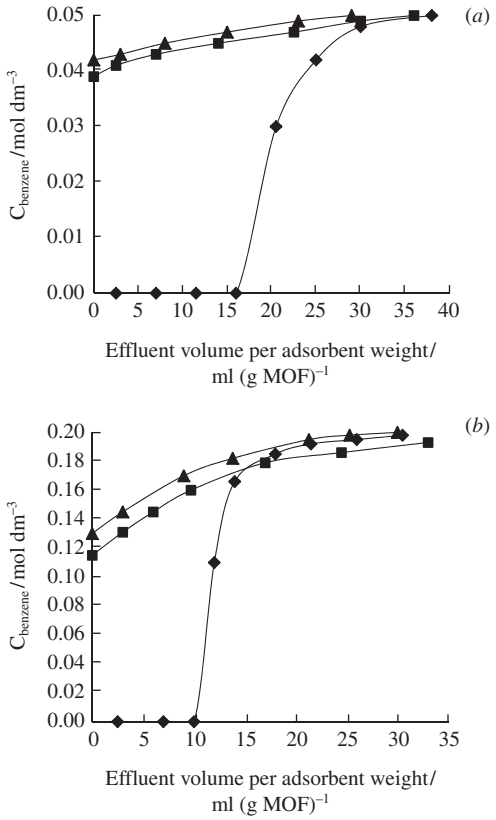

Figure 2 Breakthrough curves for (*a*) 0.05 and (*b*) 0.20 M benzene solutions in heptane for (◆) Basolite C300, (■) Basolite A100 and (▲) Basolite F300. The curves are corrected for the dead volume.

demonstrates a clear peak resolution. In contrast to Basolite C300, benzene appeared immediately when Basolite A100 or Basolite F300 was used as the adsorbent. In these cases, only a decrease in the benzene concentration was observed (Figure 2).

Thus, the MOF Basolite C300 exhibited a high adsorption capacity for benzene (0.25 g of benzene per gram of Basolite C300) from heptane solution at ambient temperature. This solid is an efficient adsorbent for the liquid-phase separation of benzene from saturated aliphatic hydrocarbons. Basolite C300 can be used as a stationary phase for the liquid-chromatographic separation of a mixture of benzene and cyclohexane. In contrast to Basolite C300, the adsorption capabilities of Basolite A100 and Basolite F300 are insufficient for the successful purification of saturated aliphatics. These observations can be explained by the formation

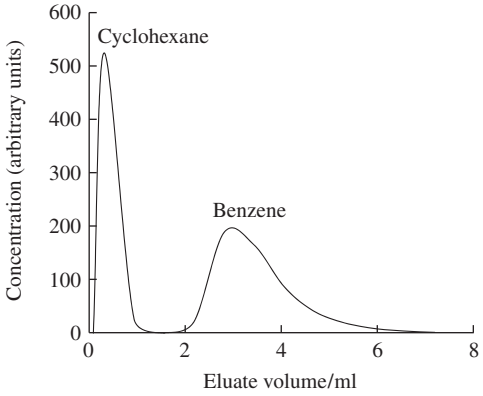

Figure 3 Chromatogram of a mixture of benzene and cyclohexane (column packed with Basolite C300; eluent, heptane).

of π-complexes between benzene molecules and coordinatively unsaturated copper sites of the framework of Basolite C300.

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