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SEPARATION OF HEXANE ISOMERS IN METAL-ORGANIC FRAMEWORKS

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The design of specific porous structures which can give improved performance to adsorption separation processes and catalysis is a challenging goal of solid chemistry. The chemical nature of Metal-Organic frameworks based in a hybrid skeleton that combines inorganic building bricks (or Secondary Building Units – SBU) together with organic polytopic linkers present a system with several degrees of freedom that can be explored to solve specific separation problems [1].

One of such combinations is based in the connection between the inorganic brick cluster $Zr_6O_4(OH)_4$ with the organic linker 1,4-benzenodicarboxylate (BDC) resulting in the so-called UiO-66(Zr) with chemical formula $Zr_6O_4(OH)_4(CO)_{12}$ [2]. The UiO-66 structure, easily tunable by using different length or functionalized organic linker, proved to be highly chemically and thermally stable. It possesses an important porosity (BET surface area ~1200 m^2/g) with two types of microporous cages, a large octahedral cage (diameter ~ 11 Å) and a small tetrahedral cage (diameter ~ 8 Å), which is responsible for the reverse shape selectivity of hexane isomers previously observed in this material [3].

The conventional Total Isomerization Processes (TIP) for improving the octane rating RON (Research Octane Number) of light hydrocarbons is one the first and most successful process in the application of adsorption phenomena to industrial processes. It consists in isomerizing light naphtha mainly composed by normal paraffin's to branched ones. The success of the process is in part due to the capacity of zeolite 5A to completely separate unreacted normal (nHEX) from branched paraffin's (3MP, 23DMB, 22DMB). However, TIP process suffer from the disadvantage that in the final stream there are still low RON molecules such as the mono-branched isomers of hexane (3MP). Accordingly, the discover of an adsorbent that separate di-branched (23DMB, 22DMB) paraffins from mono-branched (3MP) will have a great impact in petrochemical industry.

In this work we study the effect of the functionalization of UiO-66(Zr) architecture with three different organic ligands: 2-aminoterephthalic acid (NH_2-H_2BDC), 2-nitroterephthalic acid (NO_2-H_2BDC) and 2-bromoterephthalic acid (Br-H_2BDC) on the separation of hexane isomers by adsorption viewing the upgrading of TIP processes. The functionalized MOFs were synthesized and fully characterized applying established techniques: X-ray powder diffraction (XRPD), Infra-Red spectroscopy (IR), Thermo Gravimetric analysis (TGA) and nitrogen adsorption measurement. The potential of separation of the hexane isomers in the synthesized MOFs has been assessed by performing several screening studies in a breakthrough apparatus exploiting the effect of temperature and partial pressure, demonstrating that functionalization changes sorption behavior improving the separation between 22DMB and the other isomers. Figure 2 shows an experimental breakthrough curve performed in a bed packed with amino functionalized UiO-66 (UiO-66_NH_2) where it can be seen that this material is able to separate high RON di-branched isomers (22DMB) from the low RON parents mono (3MP) and linear (nHEX) ones.

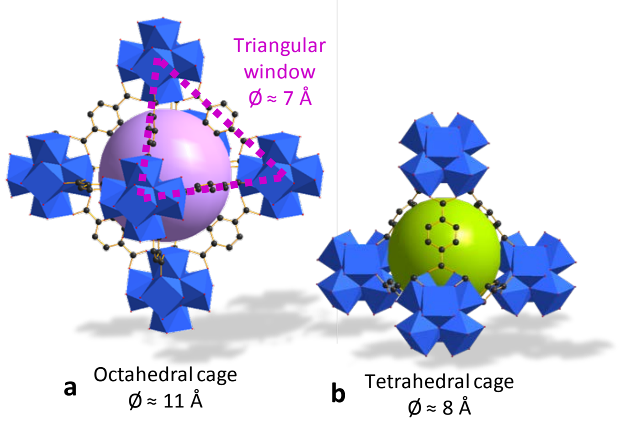

Figure 1. Octahedral and tetrahedral cages of UiO-66 structure. Zirconium polyhedra and carbon atoms are in blue and black, respectively. For a better understanding, free accessible diameters are represented through purple and green spheres, respectively.

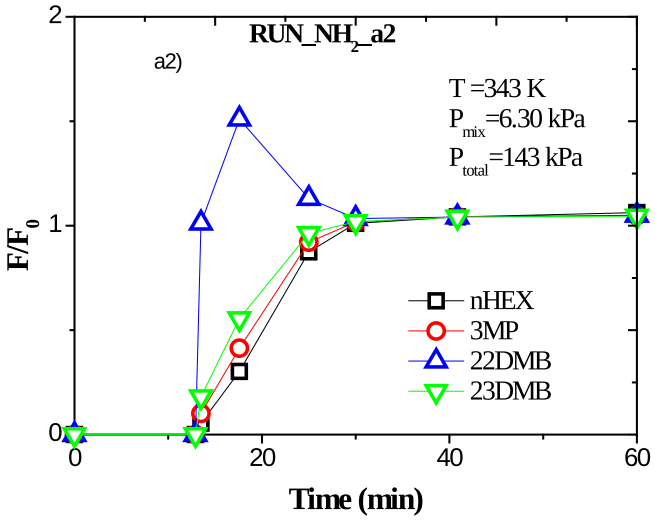

Figure 2. Experimental breakthrough curve for sorption of hexane isomers in UiO-66_NH_2.

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