## P.079. Hexane isomers sorption on the rigid framework MOF MIL-100(Cr)

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There is a huge diversity of metal-organic frameworks (MOFs) bearing different compositions, architectures, pore sizes and capacities. Depending of their structural and chemical features, the affinity between the adsorptive molecules and the framework will be modified and consequently cause a better or worse adsorption and separation capacity. A post synthetic method is a fast and easy alternative that can be used to adapt the pore size and host-guest by tuning the nature of the functional groups grafted.
In this work we studied the hexane isomers sorption on the MIL-100(Cr) [1]. The first part of the study was related to the pattern MIL-100(Cr) solid, the second dealt with the MIL-100(Cr) grafted with EtAp (Ethylamine pure) and the third with MIL-100(Cr)MEDA (Methyl ethylene diamine). The synthesis and characterization of MIL-100 (Cr), MIL-100(Cr)EtAp and MIL-100(Cr)MEDA was performed at *Institut Lavoisier de Versailles*. The separation and adsorption capacity of each MOF were evaluated through breakthrough experiments in a chromatographic system at LSRE using an equimolar mixture of four hexane isomers: n-hexane (nHEX) (RON 25), 3-methylpentane (3MP) (RON 75), 2,3-dimethylbutane (23DMB) (RON 103) and 2,2-dimethylbutane (22DMB) (RON 94) with the objective to the develop an adsorptive process to separate hexane isomers (kinetic diameter very similar) in order to improve the quality of gasoline measured by the octane number (RON).
The grafting consists on a post-synthesis substitution of a solvent molecule coordinated on the Lewis acid unsaturated metal sites (CUS) of the MOF by an amine group. In the MIL-100(Cr) (Material from *Institut Lavoisier*), grafting with ethylamine occurs through a substitution of water by ethylamine molecules. The kinetic diameter of the hexane isomers is indeed between 4.3 and 6.2 Å and the free diameters of the pentagonal and hexagonal windows at the entrance of the two types of mesoporous cages of MIL-100(Cr) are close to 5.5 Å and 8.6 Å. Coordinated water molecules point at the center of the windows. At this stage, only the pentagonal windows might lead to the isomers separation considering

the larger dimension of the hexagonal ones. So, the objective was to graft with an amine to reduce the size of the windows to improve the adsorption and selectivity of the hexane isomers. Two types of ethylamine precursors were used: pure ethylamine and an aqueous ethylamine solution (70 %; 1 mol MIL-100(Cr): 1 mol $C_2H_5$-$NH_2$ ratio). For the pure ethylamine, it is necessary to work at room temperature, due to low boiling point (15.8 °C), but as the typical grafting conditions require higher temperatures, close to 150 ºC, we increased the reaction times. Although the aqueous solution of ethylamine can be heated at 150 °C; this solution contains water, which might reduce the efficacy of the amine grafting.

Fig. 1 shows typical quaternary breakthrough curves of the hexane isomers in MIL-100(Cr) under a partial pressure of 1.6 kPa and 10 kPa at 343 K obtained at LSRE. A roll-up phenomenon of the less adsorbed components is observed meaning that there is competition for sorption of the hexane isomers in MIL-100(Cr). The increase in mixture pressure has an influence on the degree of the roll-up phenomena since the amount adsorbed increases and consequently the competition effect is also higher. We can observe significant adsorbed amounts ranging from 27 wt% at 10 kPa to 12.5 wt% at 1.6 kPa. The sorption hierarchy is here *n*HEX>3MP>22DMB>23DMB with the selectivity 3.1 for the ratio *n*HEX/22DMB and for ratio 23DMB/22DMB one reaches 1.3. These values are reasonable and might be interesting for the separation of the compounds taking into account that adsorbed amounts are here considerable. Similar results were found for the MIL-100(Cr) grafted with EtAp (Ethylamine pure) and MIL-100(Cr)MEDA (Methyl ethylene diamine).

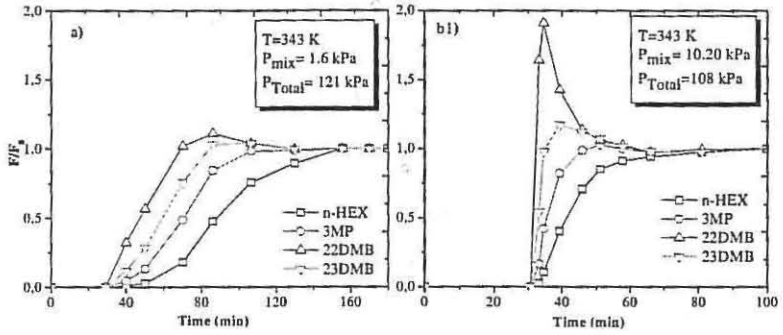


Figure 1 Quaternary breakthrough curves of the hexane isomers in MIL-100(Cr) at 343 K. (a1) pp = 1.6 kPa and (b2) pp = 10 kPa.

[1] *G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour, I. Margiolaki, A Hybrid Solid with Giant Pores Prepared by a Combination of Targeted Chemistry, Simulation, and Powder Diffraction, Angew. Chem. Int. Ed., 43 (2004) 6296-6301.*