

A shape selective MOF material for the adsorptive separation of linear and branched hexane isomers

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Summary

Single and multicomponent fixed-bed adsorption of *n*-hexane (nHEX), 3-methylpentane (3MP) and 2,2-dimethylbutane (22MB) on the three-dimensional microporous metal-organic framework Zn(BDC)(Dabco)_{0.5} (BDC=1,4-benzenedicarboxylate, Dabco=1,4-diazabicyclo [2,2,2]octane) has been studied in this work. The pores system consisting in one-dimensional large channels (7.5 Å) interconnected by 3.8 x 4.7 Å narrow pores can encapsulate linear hexane and block branched hexanes. The breakthrough experiments show a highly selective sorption with respect to nHEX.

Introduction

Porous metal-organic frameworks (MOFs) have been of significant interest because of their potential applications in gas storage, separation and heterogeneous catalysis. Unlike traditional porous zeolite materials, the pores within MOFs can be tuned varying their size and functionality for specific applications. This superior feature is significantly important to develop novel functional materials for gas separation which are mainly determined by shape selectivity effects.

Taking into account the Californian ban on MTBE and the fact that oxygenate content has to be reduced in 50% of the present value; the most sustainable way to boost octane ratings in gasoline is the development of novel materials and technologies for the separation of hexane isomers. As shown in Figure 1, the kinetic diameters of nHEX, 3MP and 22MB are slightly different; thus the micropores within MOFs need to be designed with suitable pore size for such kinetic separation. The 3.8 x 4.7 Å narrow channels in microporous MOF Zn(BDC)(Dabco)_{0.5} (MOF 1) (see Figure 1) can take up the linear nHEX but block the branched 3MP and 22MB, thus the hexane isomers might be kinetically separated by fixed-bed adsorption.

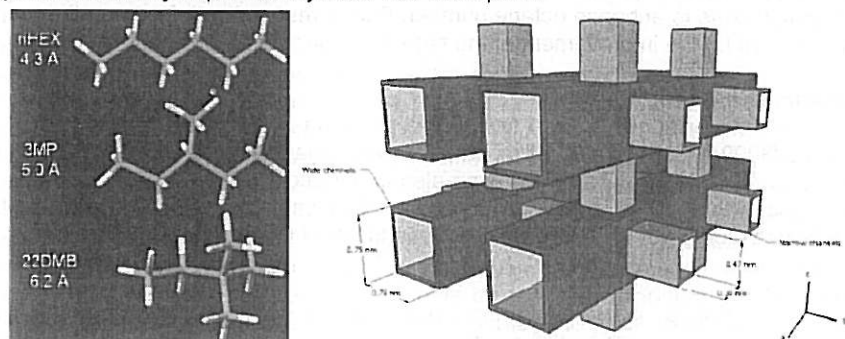


Figure 1. Three-dimensional optimized structure and kinetic diameters of hexane isomers (left); Perspective illustration of 3D intersecting channels (right).

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Experimental procedure

Adsorption equilibrium isotherms were obtained from breakthrough experiments. The adsorption column packed with crystals of MOF 1 was operated by introducing continuously a known composition of C_6 isomers in a helium stream. The procedure used for multicomponent breakthrough experiments consist in measuring the concentration history at the outlet of the packed bed in order to collect samples during the breakthrough curve. After the saturation is reached, the composition of each sample loop is evaluated by chromatography in a proper chromatographic column.

Results and discussion

In Figure 2a, we have plotted the adsorption capacities of MOF 1 for nHEX, 3MP and 22DMB. As both 22DMB and 3MP have only access to the larger channels their adsorption are significantly lower than those for nHEX. 3MP is longer than 22DMB, which leads to its slightly higher sorption capacities. The single breakthrough curve of nHEX (Figure 2b) exhibits an inflection indicating two types of interaction sites for nHEX in MOF 1, which are probably attributed to the existence of two types of channels for the access of nHEX.

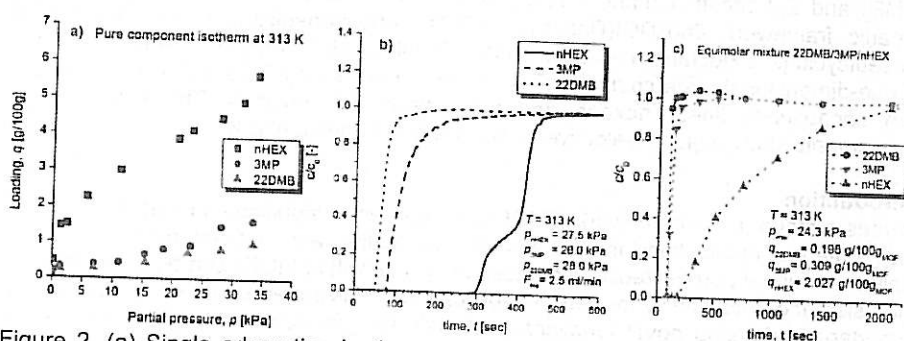


Figure 2. (a) Single adsorption isotherms at 313 K; (b) single breakthrough curve at 313 K and $p = 28$ kPa and (c) ternary breakthrough curve at 313 K and $p_{mix} = 24.3$ kPa.

The different breakthrough times following the order $nHEX \gg 3MP > 22DMB$ (Figure 2b) indicate that the adsorption strengths of the hexane isomers to MOF 1 decrease as the degree of branching increases simply because of their different van der Waals interactions with the microporous walls. The branched isomers can be readily separated from linear nHEX isomer, as shown in their ternary breakthrough curve (Figure 2c). This property is very important for its potential application in Total Isomerization Process (TIP), a process for separating branched hydrocarbons from linear components to enhance octane number. Future research will focus on the tuning of this material for the improvement of the separation degree.

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References

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