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Separation of C_5-Hydrocarbons on Microporous Materials: Complementary Performance of MOFs and Zeolites

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Abstract: This work studies the liquid-phase separation of the aliphatic C_5-diolefins, mono-olefins, and paraffins, a typical feed produced by a steam cracker, with a focus on the seldomly studied separation of the C_5-diolefin isomers isoprene, *trans*-piperylene, and *cis*-piperylene. Three adsorbents are compared: the metal−organic framework MIL-96, which is an aluminum 1,3,5-benzenetricarboxylate, and two zeolites with CHA and LTA topology. All three materials have spacious cages that are accessible via narrow cage windows with a diameter of less than 0.5 nm. The mechanisms determining adsorption selectivities on the various materials are investigated. Within the diolefin fraction, MIL-96 and chabazite preferentially adsorb *trans*-piperylene from a mixture containing all three C_5-diolefin isomers with high separation factors and a higher capacity compared to the reference zeolite 5A due to a more efficient packing of the trans isomer in the pores. Additionally, chabazite is able to separate *cis*-piperylene and isoprene based on size exclusion of the branched isomer. This makes chabazite suitable for separating all three diolefin isomers. Its use in separating linear from branched mono-olefins and paraffins is addressed as well. Furthermore, MIL-96 is the only material capable of separating all three diolefin isomers from C_5-mono-olefins and paraffins. Finally, the MOF $[Cu_3(BTC)_2]$ (BTC = benzene-1,3,5-tricarboxylate) is shown to be able to separate C_5-olefins from paraffins. On the basis of these observations, a flow scheme can be devised in which the C_5-fraction can be completely separated using a combination of MOFs and zeolites.

1. Introduction

In chemical industry the largest fraction of production costs is related to the separation and purification of product streams, mainly due to the high energy demand of these unit operations. An increase of their efficiency is therefore a direct way to produce cheaper compounds. In the field of separation and purification, distillation is the most common unit operation but becomes energetically unfavorable and unpractical when boiling points are close or when the mixture's constituting compounds are unstable or reactive at elevated temperature. Distillation under reduced pressure and cryogenic distillation are potential but expensive solutions.[1,2] One of the most interesting alternative technologies is separation by adsorption, which can be applied in both liquid and gas phases. Separation is then obtained by a difference in interaction of the compounds with a bed of porous material, whereby kinetic effects like shape selectivity as well as enthalpic or even entropic factors can be the driving forces.[3] In liquid-phase adsorption processes, product stream concentrations are much higher than in the gas phase and elevated temperatures are not strictly necessary as compounds are not to be vaporized. This may solve the problem of potential side reactions, at least if the adsorption bed is not reactive itself.

There are plenty of challenging liquid-phase separations, such as the separation of xylenes or that of *cis*- and *trans*-olefins.[4−10] Besides continuous efforts to find optimal adsorbents for these well-studied separations, it is also interesting to focus on feeds that are nowadays not yet separated in industry. The pure molecules that could be obtained from such feeds might have applications that can only be developed as soon as processes are available to obtain the individual compounds with high purity at reasonable cost. In this work the relatively unexplored adsorptive separation of C_5-hydrocarbons is investigated. All of the C_5-hydrocarbons mentioned in Scheme 1 are obtained as a mixture from the outlet of a steam cracker. The boiling points of these compounds are in an interval between 30 and 45 °C, making further separation by distillation difficult. Three main fractions are distinguished: paraffins, mono-olefins, and diolefins. First, these three fractions are to be separated in order to obtain in a next step the pure individual isomers from each fraction. This often implies a separation of *cis*- and *trans*-isomers

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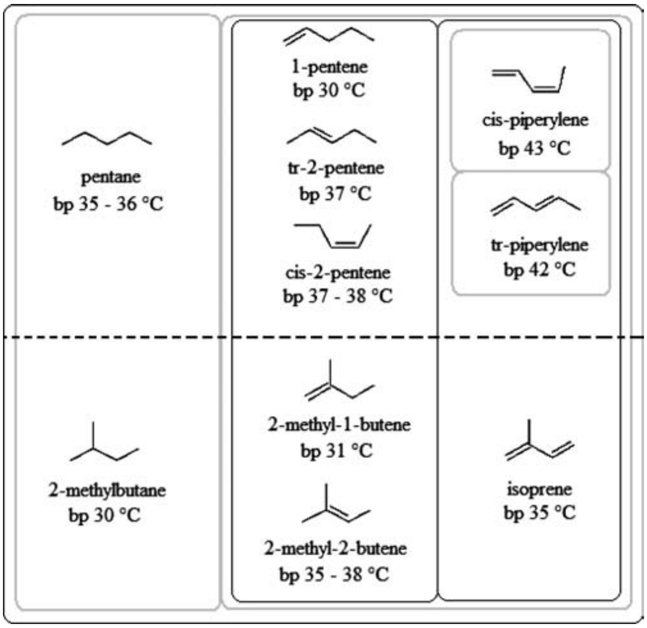
10.1021/ja9088378

Scheme 1. Molecular Structures and Boiling Points of the Compounds of the C_5-Fraction Discussed in This Paper[a]



[a] Subgroups of interest for separation are indicated by rectangles.

or of linear and branched isomers. Pure compounds obtained from the mono-olefin fraction can be used as starting materials in the synthesis of polymers for the production of rubbers, lubricants, etc.[5,11,12] The C_5-alkadiene fraction contains isoprene (branched) and *cis/trans*-piperylene (linear). These isomers are commercially important: isoprene is an important industrial monomer for the production of synthetic rubbers and resins;[5,13] piperylenes, currently produced in smaller amounts, have applications in the production of adhesives and glue polymers in envelopes and diapers.[5,14] At this moment isoprene can only be separated from both piperylenes by a series of extractive distillation steps in which a polymerization inhibitor should be present to avoid side reactions at the high temperatures applied.[5,15]

We have recently shown that a novel class of microporous adsorbents, the metal−organic frameworks (MOFs), has high potential for performing a number of challenging separations in liquid phase, for instance, of C_8-alkylaromatics, naphthalenes, functionalized aromatics, and *cis/trans*-mono-olefins.[17−19] Literature also reports on other liquid-phase adsorption applications of MOFs, for instance, in the field of desulfurization.[20,21] MOFs are hybrid materials composed of metal atoms and organic linkers. The connections in their lattices are provided by using polyfunctional ligands. Aromatic polycarboxylic acids seem to be essential elements of robust and stable MOF lattices.[22−25] The large variety in MOF topologies and structures gives rise to an enormous diversity of interactions that may come into play in their channels or cages.[26] In recent literature it has become clear that MOFs should be seen as complementary rather than competitive when compared with zeolites.[27] With respect to the separation of molecules of different size and/or length, zeolites and MOFs containing cages interconnected via small windows were shown to possess interesting properties leading to remarkable separation efficiencies.[28−30]

In this work, the performance of some cage-containing MOFs and zeolites will be compared for separations in the liquid phase using single-compound and competitive experiments either in static batch conditions or in dynamic conditions on a small column filled with adsorbent. The separation of isoprene, *trans*-piperylene, and *cis*-piperylene is performed on the metal−organic framework MIL-96 and on the two inorganic zeolite materials chabazite and zeolite 5A.[25] MIL-96 is also tested for the separation of the C_5-diolefins from the other C_5-compounds. Some other separations of the compounds mentioned in Scheme 1 will be performed as well. Chabazite will be used for separating linear and branched olefins or paraffins. Finally, for the separation of olefins from paraffins, the metal−organic framework $[Cu_3(BTC)_2]$ (BTC = 1,3,5-benzenetricarboxylate or trimesate) will be applied.[24]

2. Experimental Section

Both MOFs discussed in this paper were synthesized according to the literature.[25,31] For MIL-96, 1.314 g of $Al(NO_3)_3 \cdot 9H_2O$ and 0.105 g of H_3BTC are dissolved in 5 mL of water. The mixture is transferred into a Teflon-lined steel autoclave that is heated at 483 K for 24 h. The white powder is washed with water and activated by drying overnight at 473 K. High-silica chabazite was synthesized following an adapted synthesis procedure based on the literature and was calcined.[32] Zeolite 5A was purchased from Union Carbide. Both zeolites were activated by overnight drying at 473 K. For the electrochemical synthesis of $[Cu_3(BTC)_2]$, typically 5.3 g of 1,3,5-benzenetricarboxylic acid (H_3BTC) and 1 g of methyltributylammonium methyl sulfate are dissolved in 50 g of ethanol by stirring at 55 °C.[31] Two Cu electrodes are immersed in this solution and connected to a power source (0.2 A, 17 V). The reaction takes place for 3 h, whereafter the obtained blue crystals are washed three times

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with ethanol and dried overnight at 383 K to provide activated [$Cu_3(BTC)_2$]. All materials were characterized by XRD and additionally by thermogravimetric analysis (TGA) on both MOFs. More XRD and TGA data of the materials are provided in the Supporting Information. Their structure and phase purity were confirmed by comparison with the literature.[25,31−33] N_2-physisorption resulted in similar BET surfaces for MIL-96, chabazite, and zeolite 5A of, respectively, 625, 630, and 610 ± 10 m^2/g and pore volumes of 0.20, 0.22, and 0.19 ± 0.01 mL/g, respectively. For [$Cu_3(BTC)_2$] N_2-adsorption revealed a BET surface of 1200 m^2/g and a pore volume of 0.40−0.47 mL/g.

Liquid-phase batch adsorption experiments were carried out at 298 K in 1.8 mL glass vials filled with 0.025 g of adsorbent and a binary solution of olefins in heptane, toluene, or 1,3,5-triisopropylbenzene (TIPB) as a solvent following a literature procedure.[17,19] Uptakes were directly calculated from GC output data. Selectivities $\alpha_{i,j}$ were calculated using eq 1

$$\alpha_{ij} = \left(\frac{q_i}{q_j}\right) \times \left(\frac{c_j}{c_i}\right) \qquad (1)$$

with q_i and q_j being the amount (mol g^{-1}) of compounds i and j adsorbed per gram of MOF and c_i and c_j the concentration (mol L^{-1}) of compounds i and j present in the external liquid phase.[3] Breakthrough chromatographic experiments were performed following a literature procedure.[17] Average selectivities were calculated using eq 1 in which the adsorbed amounts q were calculated by integration of the curves (eq 2)

$$q = \int_0^t u \times (C_{\mathrm{in}} - C_{\mathrm{out}})\, \mathrm{d}t \qquad (2)$$

with u being the volumetric flow rate of the feed (L min^{-1}) and C_{in} and C_{out} the concentration (mol L^{-1}) of the adsorbate in the liquid feed and eluent, respectively. Regeneration of the column is performed by flushing the column with typically 150 mL of pure solvent at the same temperature and pressure as during adsorption.

Gas-phase adsorption at a low degree of pore filling was studied using the pulse chromatographic technique using a 30 cm column (0.22 cm internal diameter) packed with MIL-96 pellets (500−630 μm). Measurements were performed between 423 and 473 K. Adsorption equilibrium Henry constants were calculated from the first moment of the chromatographic response curves. Adsorption enthalpies were obtained from the temperature dependence of the Henry adsorption constants.[34]

3. Results and Discussion

In order to be of relevant use in liquid-phase separations, it is essential that adsorbents can be prepared in sizable amounts and at reasonable cost. Zeolite 5A, chabazite, MIL-96, and [$Cu_3(BTC)_2$] are materials that can be readily synthesized from easily accessible compounds like H_3BTC and Al, Cu, or Si compounds, although for high-silica chabazite a less accessible template molecule like *N*,*N*,*N*-trimethyladamantammonium hydroxide is needed for synthesis.[35]

The aluminum trimesate MIL-96, along with materials like [Cu(hfipbb)(H_2hfipbb)$_{0.5}$] (hfipbb = 4,4′-(hexafluoroisopropylidene)bis(benzoic acid)) and the Dy-based MOF-76, is one of the few examples of MOFs with small cage windows (<0.6 nm) and large cages.[30,36] The MIL-96 structure contains three types of cages. Of these cages only the A- and B-types are accessible for larger molecules. They both have a trigonal bipyramidal shape and an estimated minimal cavity free diameter of 0.88 nm (Figure 1). Each B-type cage is connected to 6 A-type cages by windows consisting of 14 atoms; hence, a molecule has to zigzag through both types of cages when passing through the framework. The cage windows have a diameter of 0.25−0.35 nm in the as-synthesized material. After thermal activation, one water molecule, bridging two μ_3-Al-octahedra, is removed per window.[25] This increases the window diameter with approximately 0.2 nm, which should be large enough for at least some of the C_5-compounds to enter.

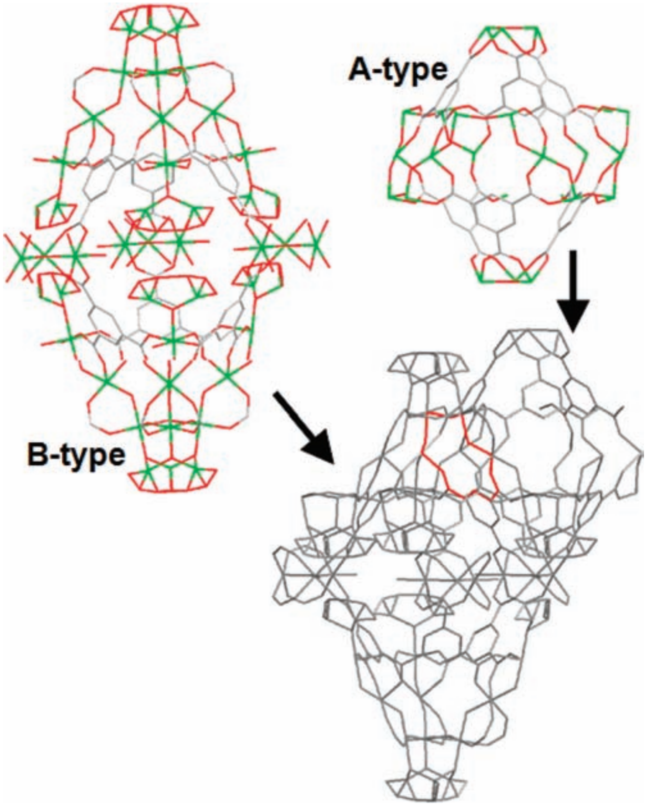

Figure 1. A- and B-type cages of MIL-96 (Al = green; O = red; C = gray; pore window highlighted in red in the dark gray composite drawing).

Chabazite and zeolite 5A are zeolites containing cages interconnected via eight-ring windows (thus containing 16 atoms) with diameters of 0.4−0.45 nm.[3,32] The cages in chabazite have a free diameter of ca. 0.9 nm. In order to avoid potential side reactions on acidic sites, it is preferable to use a chabazite with a high Si/Al ratio and hence with few acid sites; a high-silica chabazite with a Si/Al ratio of 15 was selected. A similar material has already been applied for the separation of mono-olefins.[32] Zeolite 5A has been chosen as a reference material as LTA zeolites have been extensively studied in the literature for the separation of olefins and paraffins.[3] Zeolite 5A is reportedly the LTA zeolite that is most accessible for olefins because of its wider cage windows of 0.43 nm. As preliminary experiments have shown that the uptake of C_5-diolefins on zeolites 3A and 4A from an alkane background was essentially zero, only zeolite 5A has further been considered as a reference material.

Finally, the well-known MOF [$Cu_3(BTC)_2$] is studied for separating olefins from paraffins. The paddlewheel Cu dimer subunits of this MOF are connected by trimesate linkers into a three-dimensional network containing three types of cages. Only the A- and B-type cages, with respective minimal diameters of ca. 1.2 and 1.0 nm, are large enough to accommodate C_5-

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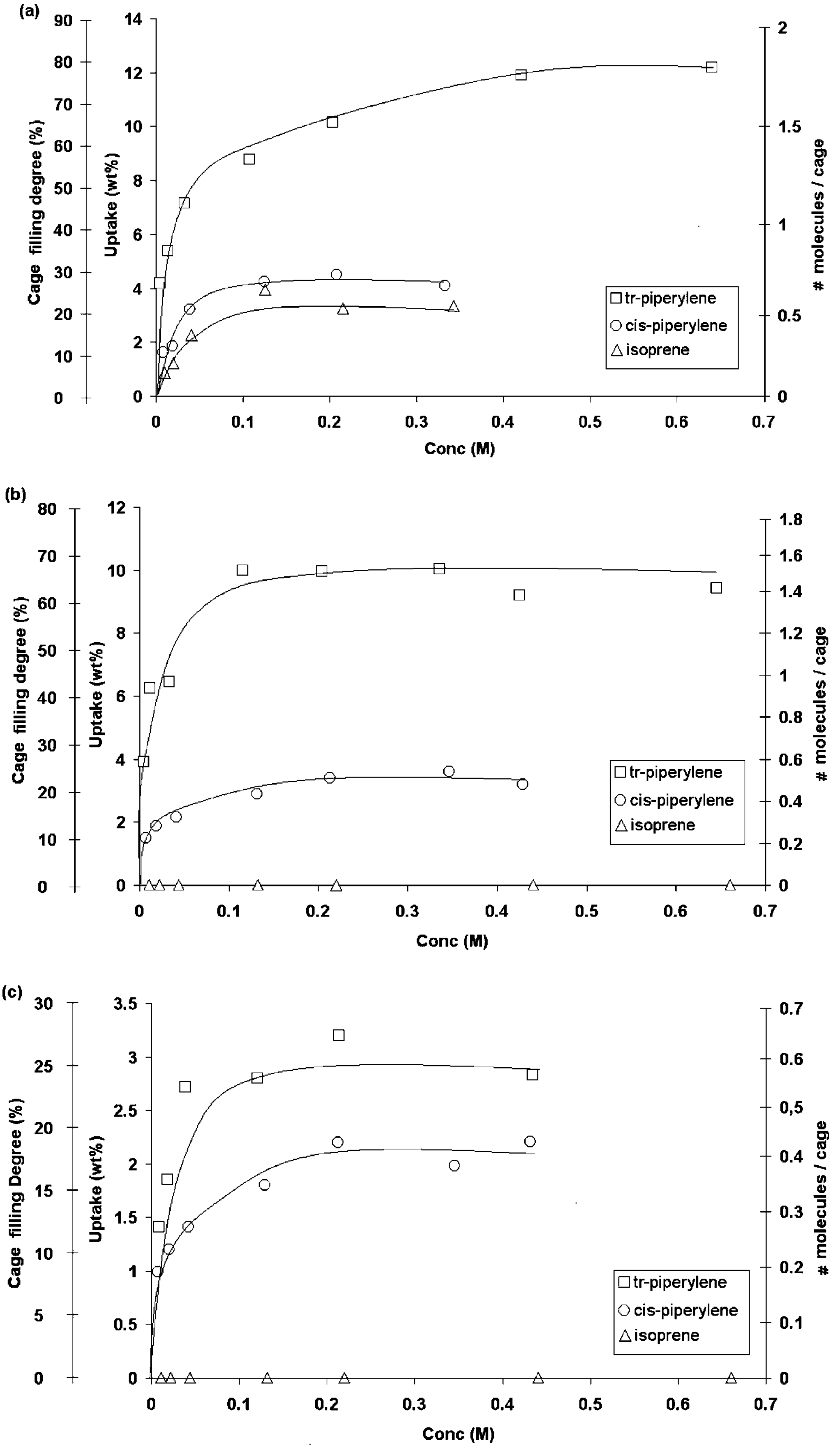

Figure 2. Single-compound adsorption isotherms of isoprene, *trans*-piperylene, and *cis*-piperylene from a heptane solution on (a) MIL-96, (b) chabazite, and (c) zeolite 5A measured in batch mode: uptake (wt %), cage filling degree (%), and number of molecules per cage (right axis) as a function of equilibrium bulk-phase concentration.

hydrocarbons. After activation, free ligation sites on the Cu atoms are present in the B-type cages.[37]

3.1. Separation of Diolefins. In order to screen the separation potential of both zeolites and MIL-96 for the different C_5-diolefins, single-compound batch adsorption isotherms were measured using heptane as a solvent (Figures 2a-c).[3,17] Analogous tests were performed with solvents that are too large to penetrate inside the pores of chabazite, zeolite 5A, or MIL-96, like toluene or 1,3,5-tri-isopropylbenzene (TIPB). These tests resulted in virtually identical diene uptakes as those obtained in heptane. Hence, it can be concluded that there is no significant competition of heptane during diene adsorption. For all three materials there is a strong preference for the slimmest isomer *trans*-piperylene. Besides the uptake values (wt %), Figure 2 also shows a hypothetical degree of cage filling, calculated using the pore volumes measured by N_2-physisorption and the density of the pure liquids at room temperature. Uptake values and the pore filling degree reach their highest values for *trans*-piperylene. The bulkier *cis*-piperylene is preferred less than *trans*-piperylene, and isoprene is taken up only by MIL-96.

In order to understand the mechanisms determining adsorption selectivities in these materials, it is of interest to evaluate the number of molecules per cage. In the case of MIL-96, a unit cell ($(Al_{12}O(OH)_{18}(H_2O)_3)_2(Al_2(OH)_4)_2[btc]_{12}$) contains two B-type cages and two A-type cages.[25] The uptake of *trans*-piperylene eventually reaches a plateau at approximately 12 wt %. This closely matches the theoretical value of 13.2 wt % that is expected for 2 molecules of C_5H_8 per A- and per B-type cage (Figure 2a). Occupation of both A- and B-type cages by two molecules of *trans*-piperylene is reasonable in view of the similar size of both cages, resulting in eight molecules of *trans*-piperylene per unit cell. Considering the shape of these cages (Figure 1), packing more than two of such molecules inside one cage seems increasingly difficult. For *cis*-piperylene and isoprene uptake on MIL-96, similar calculations result in a maximal pore filling with 0.6 and 0.5 molecules per cage, respectively. It seems that steric constraints prevent adsorption of more than one molecule of *cis*-piperylene or isoprene per cage. Therefore, a more efficient packing of the slimmer *trans*-piperylene seems to be the primary cause for its larger uptake. Steric constraints playing a crucial role in adsorption is also illustrated by comparing the adsorption of *trans*-1,3-pentadiene to that of *trans*-1,3-hexadiene in the MIL-96 cages. Even though *trans*-1,3-hexadiene is just one methylene group larger than *trans*-piperylene, it is hardly taken up by the structure (<1 wt %). A similar behavior has already been reported in the literature for adsorption in the cages of $[Cu(hfipbb)(H_2hfipbb)_{0.5}]$: while linear C_2-C_4-paraffins are taken up, slightly larger C_5-paraffins are not adsorbed as they sterically cannot fit into the cages because of their length.[30]

In a next step, the adsorption enthalpies of the C_5-diolefins at low degree of pore filling were measured by gas-phase pulse chromatography. The obtained values are similar and amount to approximately from -52 to -54 kJ mol^{-1} (Table 1). Low-coverage Henry equilibrium constants vary in the order isoprene $\approx$ *cis*-piperylene > *trans*-piperylene with differences of less than 20% between the extremes. While in the gas phase *trans*-piperylene is preferred least, it is remarkable that it is preferred most in liquid-phase adsorption. This corroborates the idea that strong packing effects govern the order of preference at a high degree of pore filling as encountered in the liquid phase.

Table 1. Zero-Coverage Adsorption Enthalpies (ΔH), Pre-Exponential Factors of the Van't Hoff Equation (K_0), and Henry Adsorption Constants at 423 K (K') of C_5-Alkadienes on MIL-96[a]

	ΔH (kJ/mol)	K_0 (mol kg^{-1} Pa^{-1})	K' at 423 K (mol kg^{-1} Pa^{-1})
cis-piperylene	-53.0	1.28×10^{-10}	4.42×10^{-4}
trans-piperylene	-54.6	0.72×10^{-10}	3.94×10^{-4}
isoprene	-52.1	1.61×10^{-10}	4.26×10^{-4}

[a] Experiments have been performed in the gas phase at temperatures between 423 and 473 K in a 30 cm column (internal diameter of 0.22 cm) filled with 500−640 μm pellets of MIL-96.

For *trans*-piperylene adsorption on chabazite, the observed saturation level is 10 wt % or 69% effective pore filling. This is somewhat below the uptake calculated for the theoretical adsorption of two molecules of *trans*-piperylene per cage, which is 12.4 wt %, but well above one molecule per cage (Figure 2b). As in the case of MIL-96, this indicates that efficient packing in the cages is causing the elevated adsorption of *trans*-piperylene. In previous work, it was found that with C_1-C_3 *n*-alkanes, a maximum of about 10−11 carbon atoms can be packed inside the chabazite cages. However, only one *n*-pentane molecule could be adsorbed per cage.[38] Apparently, although *trans*-piperylene also contains 5 carbon atoms, it is packed in a much more efficient way, probably because of $\pi-\pi$-stacking effects. *cis*-Piperylene, with only 24% effective pore filling, cannot be packed that efficiently and is only adsorbed at one molecule per cage or less.

In the case of zeolite 5A, the filling of the supercages levels off at much less than one linear C_5-diolefin per cage, corresponding to an average pore-filling degree of ~24% (Figure 2c). This is remarkably low as the cages themselves are in principle large enough to accommodate several molecules. It could be argued that the paraffinic solvent is adsorbing as well in the cages, as reported before.[40] However, if a solvent which is not able to enter the pores is used, for instance toluene, similar diene uptakes were observed. On the other hand, the Ca^{2+} cations could play an important role. These are typically located at site I, near the six rings in the corners of the large cages. Diolefins are likely strongly or even irreversibly adsorbed on these ions. This can lead to an at least partial blocking of the cages in the outer layers of the crystals, preventing further uptake of diolefins, which explains the low adsorption capacity. A strong adsorbate−cation interaction is anyhow undesirable when considering regeneration of the adsorbent. Combined with the fact that the uptake capacity of zeolite 5A is much smaller than that of MIL-96 and chabazite, the focus will be on the latter two adsorbents for the further evaluation of the separation of C_5-diolefins.

The separation of diolefins on both MIL-96 and chabazite was examined in competitive batch experiments using a heptane solution containing all three isomers (Figure 3a and 3b). The use of a ternary mixture of 50% isoprene, 31% *trans*-piperylene,

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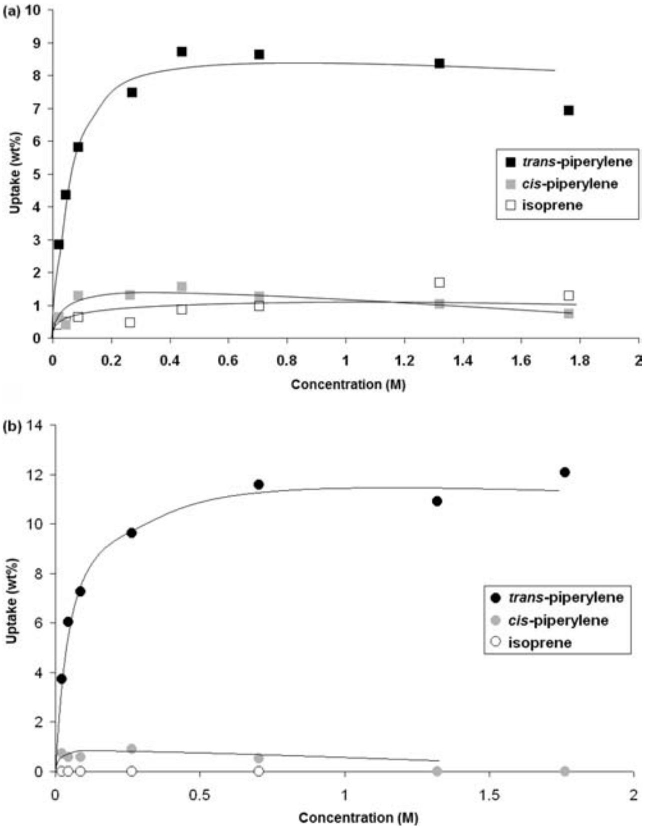

Figure 3. Competitive batch adsorption experiments on (a) MIL-96 and (b) chabazite: uptake (wt %) from a heptane solution containing 50% isoprene, 31% *trans*-piperylene, and 19% *cis*-piperylene as a function of total equilibrium bulk-phase concentration. The concentrations are based on the sum of the equilibrium concentrations of each individual compound after adsorption.

Table 2. Separation Factors of *trans*-Piperylene over *cis*-Piperylene measured in Competitive Batch Experiments on MIL-96 and Chabazite at Total Equilibrium Concentrations of the Ternary Mixture of 50% Isoprene, 31% *trans*-Piperylene, and 19% *cis*-Piperylene between 0.09 and 1.32 M in Heptane

	0.09 M	0.44 M	0.70 M	1.32 M
MIL-96	3.7	3.7	4.1	9.5
chabazite	12	18	>20	>20
zeolite 5A	3.8	4.3	4.1	3.4

and 19% *cis*-piperylene provides a quick first screening of the separation potential and the total uptake capacity of the adsorbents. Total maximal diolefin uptake measured is approximately 13 wt % both on MIL-96 and chabazite, which corresponds to a filling of ~95% of their available cage space. Compared to single-compound experiments, similar saturation levels of 10−12 wt % are reached for *trans*-piperylene in these competitive conditions; for *cis*-piperylene much lower uptakes are observed. Separation factors between *trans*-piperylene and *cis*-piperylene at total equilibrium concentrations of the ternary mixture between 0.09 and 1.32 M are given in Table 2. For MIL-96, these separation factors tend to increase with increasing concentration to reach a high value of ca. 10 at the highest concentration, while in similar experiments with zeolite 5A this separation factor is invariant with concentration (Table 2). The increase in selectivity is consistent with the assumption of packing effects forwarded above. Molecules that fill up the cage space more efficiently maximize the number of adsorbate−framework interactions. As competition for available cage space becomes stronger with increasing concentrations, separation factors increase.[17,39] Even larger separation factors between *trans*- and *cis*-piperylene are measured on chabazite. Again, selectivity increases with concentration (Table 2). This confirms that for this material packing effects are playing an important role in selectivity as well, as already suggested by analysis of the single-compound isotherms. No uptake of isoprene is observed on chabazite: the methyl side group prevents isoprene molecules to pass through the narrow cage windows. In contrast, MIL-96 is able to adsorb isoprene in competitive conditions (Figure 3a), although the uptake of this compound only reaches values between 1.0 and 1.5 wt %. Uptakes of isoprene on MIL-96 are quite similar to those for *cis*-piperylene in competitive conditions (Figure 3a).

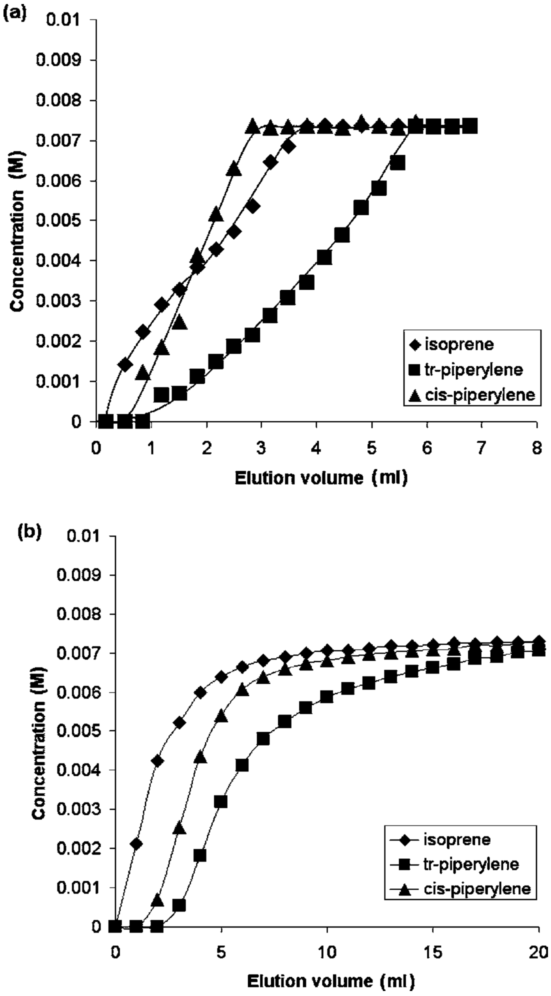

Figure 4. Breakthrough experiments of an equimolar 0.021 M heptane mixture of isoprene, *trans*-piperylene, and *cis*-piperylene on an 8 cm column filled with (a) MIL-96 and (b) chabazite at 298 K and a flow of 0.5 mL/min: effluent concentrations as a function of elution volume. Curves have been corrected for dead volume.

The observation that separation factors increase with increasing concentration incited us to simulate a realistic separation in a continuous-flow setup using 8 cm columns packed with adsorbent and placed in an HPLC apparatus. In a breakthrough experiment a 0.021 M equimolar heptane solution containing isoprene, *trans*-piperylene, and *cis*-piperylene was pumped

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Table 3. Uptake (wt %) at Different Initial Concentrations of an Equimolar Mixture of a Mono-Olefin and a Mixture of Diolefins on MIL-96 in a Pentane Background[a]

0.09 M	1-pentene	*cis*-2-pentene	*trans*-2-pentene	2-methyl-2-butene	2-methyl-1-butene
diolefin mixture	0 7	0 7	0 7	0 8	0 7

0.70 M	1-pentene	*cis*-2-pentene	*trans*-2-pentene	2-methyl-2-butene	2-methyl-1-butene
diolefin mixture	0 12	0 10	0 10	0 11	0 12

[a] The mixture of diolefins is composed of 50% isoprene, 31% *trans*-piperylene, and 19% *cis*-piperylene. The total uptake of diolefins is given as the summed uptake of the three individual diolefins in the bottom line; the uptake (wt %) of the corresponding mono-olefin is given in the top line.

through the adsorbent bed at a flow rate of 0.5 mL/min. Figure 4a shows the breakthrough profiles of this ternary C_5-diolefin isomer mixture using a column packed with MIL-96. All compounds elute relatively shortly after elution of the dead volume. The elution order nicely corresponds to the results of the competitive batch experiments, with the preferred *trans*-piperylene retained most strongly on the MIL-96 column. The amount of each compound adsorbed on the column was calculated via integration of the corresponding breakthrough profiles. From these values an average separation factor of 3.1 has been obtained between *trans*-piperylene and isoprene. The amounts of isoprene and *cis*-piperylene adsorbed on the column are similar, which shows that MIL-96 does not discriminate between these compounds in dynamic conditions either. A striking feature of Figure 4a is the fact that the curves of isoprene and *cis*-piperylene are crossing. Such behavior is indicative of differences in diffusion between these compounds when passing through the adsorbent bed.[3,41] The breakthrough of isoprene takes place during a much larger time interval compared to the breakthrough of *cis*-piperylene. Isoprene diffuses more slowly through the narrow cage windows between the A- and B-type cages due to the presence of its side chain, while the slimmer *cis*-piperylene can diffuse faster in and out of the cages. The fact that the breakthrough curve of isoprene has an inflection point rather than a purely sigmoidal shape could be explained by the fact that the faster desorbing *cis*-piperylene is retarding the desorption of the more sterically hindered isoprene, thus affecting its concentration profile.

For chabazite, no isoprene is adsorbed at all, resulting in the immediate elution of this compound from the column (Figure 4b). Shortly thereafter, *cis*-piperylene is found in the column outlet, followed by *trans*-piperylene. This elution order is in agreement with the results from the batch experiments. The separation factor of *trans*-piperylene vs *cis*-piperylene has a value of 2.3. Both MIL-96 and chabazite columns were easily regenerated by flushing the column with 100 mL of pure heptane solvent.

3.2. Separating Diolefins from Other Olefinic and Paraffinic Fractions. Of the three adsorbents tested, only MIL-96 is capable of adsorbing all C_5-diolefin isomers from an aliphatic solvent in significant amounts. When pentane is used as a solvent instead of heptane, similar results as in Figures 2a and 3a are obtained, showing that MIL-96 is able to discriminate between C_5-diolefins and their paraffinic counterparts. Another important issue is the separation of diolefins not only from paraffins but also from mono-olefins (Scheme 1). Competitive batch experiments were performed on MIL-96 using a mixture of one C_5-diolefin and one C_5-mono-olefin in pentane as a solvent (Table 3). In none of these experiments uptake of mono-olefins was observed, while the uptakes of the diolefins were quasi identical to the values from the single-compound experiments on MIL-96, as shown in Figure 2a. The similarity of the results when using heptane or pentane suggests that the affinity of MIL-96 for paraffins is much lower than that for diolefins, resulting in little or no competitive uptake of paraffins in the cages. Preferential uptake of diolefins over alkanes or mono-olefins is not caused by a larger interaction strength, as low coverage adsorption enthalpies measured in the gas phase for pentane and 1-pentene reached values almost identical to those of the dienes in Table 1. Perhaps entropic effects could be responsible for the observed exclusion of paraffins and mono-olefins. It is possible that due to the presence of three or more sp^3-hybridized carbon atoms in mono-olefins and paraffins, the entropy loss due to the loss of degrees of freedom of rotation within the cages is too large for adsorption of mono-olefins and paraffins to occur, especially when more rigid and compact conjugated systems like diolefins are already present in the cages.

3.3. Separating Linear and Branched C_5-Isomers. As discussed above, chabazite and zeolite 5A are capable of separating linear from branched diolefins via size exclusion of the branched compounds. Their capability to separate linear from branched C_5-mono-olefins and paraffins has also been evaluated (Scheme 1). As it is well known that zeolite 5A is capable to perform these separations, only chabazite was tested. Competitive batch adsorption experiments of pentane vs 2-methylbutane, 1-pentene vs 2-methyl-1-butene, and 2-pentene vs 2-methyl-2-butene were carried out (Figure 5). In order to exclude any interference by solvent competition, toluene was used as a solvent rather than heptane, since it is definitely too large to pass through the 0.35 nm cage windows. Figure 5 clearly shows that linear olefins and paraffins are adsorbed on chabazite, while branched isomers are excluded. The potential of chabazite for separation of linear and branched mono-olefinic isomers was confirmed in a continuous setup using toluene as a solvent (Figure 6). No 2-methyl-2-butene is adsorbed on chabazite, resulting in its elution on the dead volume, while 1-pentene is clearly retained on the column. As with the diolefin separations, the chabazite column was easily regenerated by flushing with 100 mL of solvent.

3.4. Separating C_5-Olefins from Paraffins. Finally, we also briefly engaged in investigating the potential of MOFs for the separation of C_5-olefins from paraffins (Scheme 1). It has been recently proven that C_4-olefins and paraffins can be separated in the vapor phase on $[Cu_3(BTC)_2]$.[42] In this work we focus on

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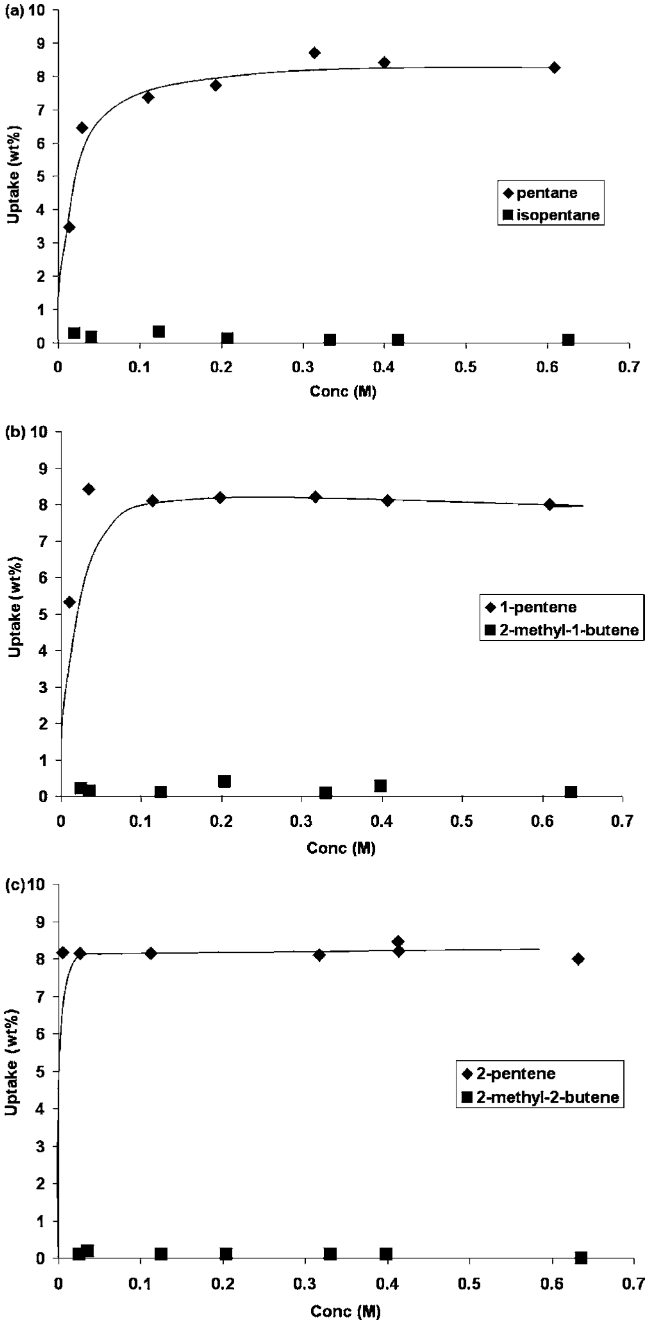


Figure 5. Competitive batch adsorption experiments on chabazite: uptake (wt %) of (a) pentane and 2-methylbutane, (b) 1-pentene and 2-methyl-1-butene, and (c) 2-pentene (*cis*:*trans* ratio of 30:70) and 2-methyl-2-butene as a function of equilibrium bulk-phase concentration using toluene as a solvent.

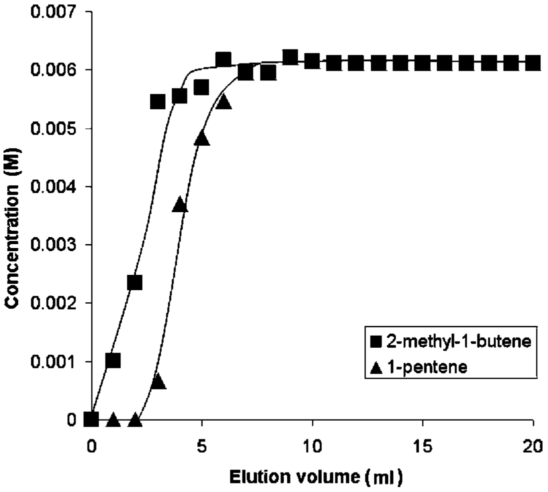


Figure 6. Breakthrough curve of an equimolar 0.016 M mixture of 1-pentene and 2-methyl-1-butene in heptane on an 8 cm column filled with dried chabazite at 298 K and a flow of 0.5 mL/min. Curves have been corrected for dead volume.

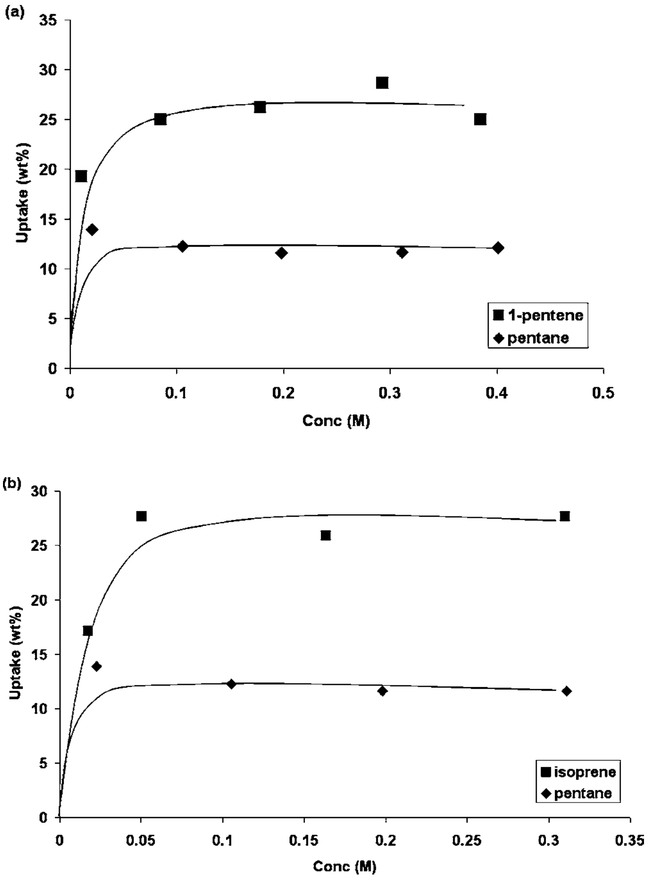
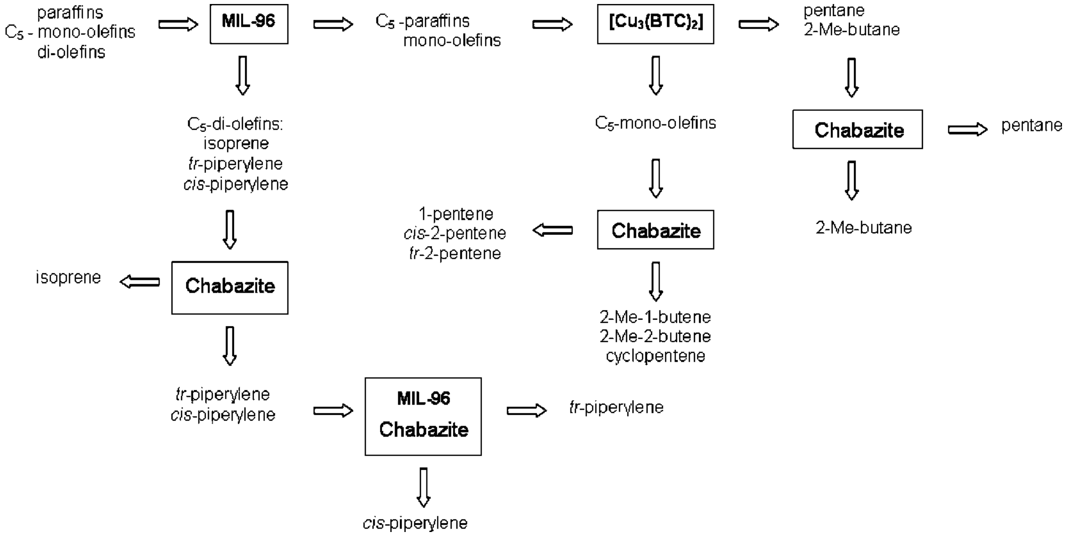


Figure 7. Competitive batch adsorption isotherms on [$Cu_3(BTC)_2$]: uptake (wt %) of (a) 1-pentene and pentane and (b) isoprene and pentane as a function of equilibrium bulk-phase concentration.

separation in the liquid phase, where higher extra-crystalline concentrations are present. Again, a nonpenetrating solvent was used, in this case the bulky TIPB. This solvent was preferred over toluene as the latter may be taken up by the large cages and windows of [$Cu_3(BTC)_2$]. Figure 7 shows a preferential uptake of 1-pentene and isoprene over the linear pentane. Other competitive experiments have been performed between pentane and 2-methyl-2-butene, cyclopentene, or piperylene, resulting in similar adsorption isotherms (not shown). A maximal uptake value of 26−32 wt % is reached when the material is saturated with either one of the olefins, while the uptake of pentane is reaching saturation levels of no more than 8−14 wt %. This selectivity seems to be much larger than that observed during the reported vapor-phase adsorption of isobutene and isobutane.[42] Most probably this discrepancy is due to the different concentrations used in the two types of experiments. For instance, differences in adsorption behavior have also been observed between the liquid- and vapor-phase adsorption of

Scheme 2. Suggested Flow Scheme for the Separation of the C_5-Cut from a Steam Cracker



xylenes on MIL-53.[18,43] The preferential uptake of olefins on $[Cu_3(BTC)_2]$ is obviously due to the interaction of the double bond with the free ligation site on the Cu atom in the B-type cages, while paraffins do not have this functional group.[19] Separation factors calculated from Figure 7 vary between 2.8 and 3.5 at saturation levels.

With this successful separation of olefins from paraffins, the most relevant separations of compounds in Scheme 1 have been performed on either a zeolite or a MOF. Scheme 2 nicely summarizes these separations in a flow diagram. It is obvious that in order to make all separations feasible a combination of both inorganic zeolite adsorbents as well as metal−organic frameworks is indispensable.

Conclusion

The metal−organic framework MIL-96 has for the first time successfully been applied to a complex liquid-phase separation, viz. the adsorptive separations of C_5-hydrocarbons, with a focus on the separation of isoprene, *cis*-piperylene, and *trans*-piperylene. The cage structure of MIL-96, together with the narrow cage windows, strongly contributes to its separation capabilities, and this earmarks this material as a high potential candidate for numerous other small molecule separations. Together with a high-silica chabazite zeolite, MIL-96 was compared to the reference material zeolite 5A. Both MIL-96 and chabazite were found to have higher uptake values for the C_5-diolefins. Although MOFs offer in theory a chemically more diverse environment to the adsorbate than zeolites, it seems that in this case the same mechanisms determining adsorption selectivity are operative, as is, for instance, clear in the stacking of *trans*-piperylene in the cages of MIL-96 and chabazite. The separations presented in this paper have been alternatively summarized in a flow scheme (Scheme 2). The combined use of MOFs and zeolites for the liquid-phase separation of the C_5-hydrocarbon fraction into individual product streams shows that their performance should be seen as complementary rather than competitive.

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Supporting Information Available: X-ray powder diffraction patterns, TGA profile, and SEM pictures of MIL-96. This material is available free of charge via the Internet at http://pubs.acs.org.

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