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Pore mouth *versus* intracrystalline adsorption of isoalkanes on ZSM-22 and ZSM-23 zeolites under vapour and liquid phase conditions

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Methylbranched C_5–C_9 alkanes do not adsorb in the intracrystalline void space of ZSM-23, neither from the vapour nor the liquid phase, but are adsorbed in ZSM-22, if only from the liquid phase, and this despite the small difference in pore size.

Several successful applications of synthetic zeolites as cation exchangers, adsorbents and catalysts are based on their molecular sieving properties. The close matching of guest molecules with zeolite pores and the strong Brønsted acidity explain the successful applications in catalysis. In skeletal isomerization of normal alkanes, 10-membered ring zeolites with parallel tubular pore systems have the most pronounced shape-selective properties.[1] ZSM-22 is the exponent of this zeolite family. The platinum loaded hydrogen form of it was found to be the most selective zeolite catalyst for the conversion of *n*-alkanes into 2-methyl-branched skeletal isomers.[2] Some authors ascribed these peculiar product features to transition state shape selectivity[3] and product diffusion selectivity.[4] In addition, a new adsorption-reaction mechanism in pore mouths was proposed to explain the unique *n*-alkane reaction scheme on ZSM-22 zeolite.[5,6] According to this pore mouth mechanism, the skeletal branching step occurs in a pore opening such that the branched alkane sticks with its longest linear alkyl group inside the pore while the bulky part of the molecule remains outside. In a previous study in vapour phase[7] some of us examined micropore *versus* pore mouth adsorption using two different forms of zeolite ZSM-22. Beside the specimen with evacuated pores, a "closed" form was used having the organic template molecules inside its pores. From the similarity of adsorption parameters of iso-alkanes on open and closed zeolite, it was concluded that iso-alkanes have no access to the micropores, even when evacuated. In order to further examine the occurrence of pore-mouth adsorptions, we included ZSM-23 zeolite in our studies. ZSM-22 and ZSM-23 zeolites differ only very slightly in their pore sizes (0.46 × 0.57 nm in ZSM-22 *versus* 0.45 × 0.52 nm in ZSM-23). Pt/H-ZSM-23 is an industrial isodewaxing catalyst.[8] In this communication, we compare the adsorption parameters of linear and branched C5–C10 alkanes under liquid and vapor phase conditions on ZSM-22 and ZSM-23.

Adsorption equilibria of linear and branched alkanes in ZSM-22 and ZSM-23 zeolites were determined using the batch technique in liquid phase and the tracer chromatographic technique in vapour phase. Details on our experimental techniques and calculation methods of Henry adsorption constants and adsorption enthalpies were reported elsewhere.[7,9] The micropore volumes determined using nitrogen adsorption and the *t*-plot method of ZSM-22 and ZSM-23 are 0.087 ml g^{-1} and 0.034 ml g^{-1}, respectively. The micropore volume of closed ZSM-22 was 0.00016 ml g^{-1}, confirming the blocking of micropores with the 1,6-diaminohexane template.

Liquid phase adsorption capacities of normal and branched alkanes from their mixtures with 2,2,4-trimethylpentane serving as non-adsorbing solvent are plotted in Fig. 1. Under liquid phase conditions, ZSM-23 zeolite adsorbed *n*-hexane (C6) but did not adsorb any 2-methylpentane (2MC5), 3-methylpentane (3MC5) or 2,3-dimethylbutane (23DMC4) (Fig. 1). On closed ZSM-22, none of the linear or branched alkanes showed any uptake, similar to ZSM-23. In ZSM-22, there was uptake of monobranched isoalkanes and dimethylbranched alkanes except those with quaternary carbon atoms (2,2-dimethylbutane and 3,3-dimethylpentane). On ZSM-22, the order of the adsorbed volumes obeys the order: *n*-alkanes > monobranched alkanes ≫ doubly branched alkanes without quaternary carbon atoms. Under the batch experimental conditions, the amounts adsorbed from the liquid phase reflect only the uptake in the intracrystalline void volume of a zeolite and does not include the adsorption at the external surface or at the pore mouths. ZSM-22 and ZSM-23 have only subtle differences in pore shape and diameters. The pronounced difference in adsorption behaviour in the liquid phase shows that these two zeolites present the critical pore size for discrimination between linear and branched alkane molecules.

In liquid phase, the driving force for adsorption is much larger than under vapour phase at low alkane partial pressures. Vapour phase chromatographic conditions lead to very low zeolite loadings. Adsorption properties under these conditions represent the interaction between the adsorbed molecules and the most favorable adsorption sites of the material. Henry adsorption constants and limiting enthalpies of adsorption were determined in vapour phase experiments. The ratio of Henry constants, representing the separation factor α of a linear alkane over its 2-methylbranched isoalkane isomer on ZSM-22, ZSM-23 and some reference zeolites in vapour phase is presented in Fig. 2. ZSM-22 and ZSM-23 exhibit a very pronounced separation of these molecules. The separation on these materials is much larger than on ZSM-5 zeolite with intersecting 10-membered ring channels and the 12-membered ring zeolites Beta, Mordenite and Na-Y. The origin of the large separation factors in zeolite ZSM-23 is obvious when considering that

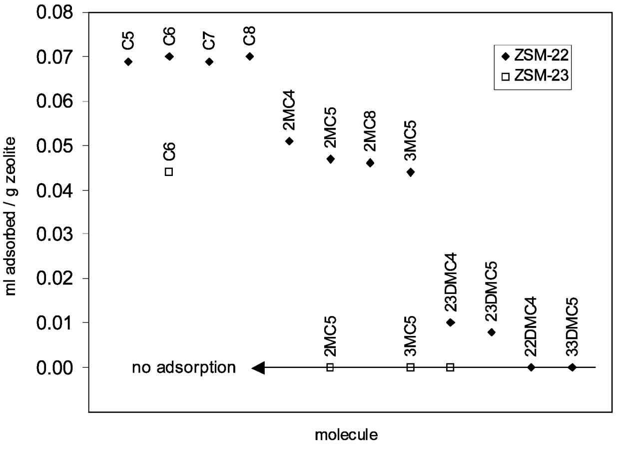

Fig. 1 Linear and branched alkane adsorption capacities of ZSM-22 and ZSM-23 in liquid phase.

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even in liquid phase, methylbranched alkanes are excluded from the pores (Fig. 1). Although zeolite ZSM-22 is capable of adsorbing monobranched alkane molecules under liquid phase conditions (Fig. 1), it exhibits very high separation factors when contacted with vapours (Fig. 2). In previous work it was shown that under vapour phase conditions on ZSM-22, adsorption entropies of isoalkanes are quite small, showing that in the adsorbed state, the molecules largely retain their mobility, which is unlikely for adsorbed positions inside the pores.[7] Low coverage adsorption enthalpies on ZSM-22 and ZSM-23 substantiate the thesis of pore mouth adsorption on these two zeolites (Table 1).

Considering that ZSM-22 and ZSM-23 both have tubular, undulated channel systems running in only one crystallographic direction without intersections,[11] the adsorption sites may be located either in the micropores or at the pore mouths. Limiting adsorption enthalpies of isoalkanes on ZSM-23 and ZSM-22 are very similar and only slightly larger than on closed ZSM-22 (Table 1). On both zeolites, limiting adsorption enthalpies of monobranched alkanes are significantly lower than for linear alkane molecules. The liquid phase experiments (Fig. 1) showed that isoalkanes do not penetrate into the pores of ZSM-23. Thus, the similarity of adsorption enthalpies of isoalkanes on ZSM-22 and ZSM-23 under vapour phase conditions (Table 1) reveals that only pore mouth adsorption occurs under vapour phase conditions on ZSM-23 as well as on ZSM-22.

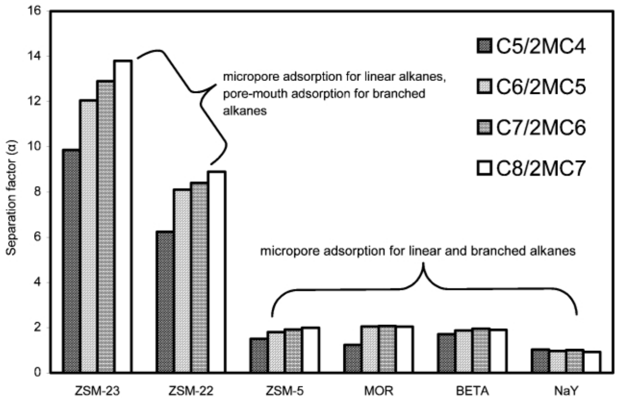

Fig. 2 Separation factors on different zeolites at 473 K. Values for the zeolites ZSM-5, MOR, BETA, NaY are calculated from tabulated values in reference 10.

Table 1 Low coverage enthalpies of adsorption on open and closed ZSM-22 and on ZSM-23 (kJ mol^{-1})

	ZSM-22 Open	ZSM-22 Closed	ZSM-23
n-Pentane	63.3	47.7	58.5
n-Hexane	77.1	58.5	71.8
n-Heptane	89.4	70.9	84.0
n-Octane	101	81.7	94.3
n-Nonane	112	92.7	106
2-Methylbutane	49.3	47.7	49.4
2-Methylpentane	60.0	59.1	61.3
2-Methylhexane	76.1	71.1	76.2
2-Methylheptane	87.3	81.0	87.9
2-Methyloctane	97.8	93.7	97.4
2-Methylnonane	107	105	107

Molecular computational simulations suggested that both linear and branched alkane molecules have access to the micropores of zeolite ZSM-22 and ZSM-23.[4,12] The present adsorption measurements show that in practice, branched alkanes enter the micropores of zeolite ZSM-22 only under liquid phase conditions. On ZSM-22 and ZSM-23 in contact with isoalkane vapour, pore mouths are the active adsorption sites. Our findings will be useful in clarifying the discrepancies between the outcome of molecular simulations and experimental adsorption measurements. It also provides a motivation for research efforts on characterisation of zeolite pore mouths.

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