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Adsorption and Coadsorption of 2-methylpentane and 2,2-dimethylbutane in a ZSM-5 Zeolite

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Abstract. In this paper we present the major results of a thermodynamic and structural study of the adsorption of 2-methylpentane (2MP) and 2,2-dimethylbutane (22DMB) on a ZSM-5 zeolite under isothermal and isobaric conditions. A thermodynamically inconsistent behavior is observed with 22DMB at constant pressure: the adsorbed amount increases as the temperature of the zeolite increases from 343 to 443 K. We suspect that this particular phenomenon is the result to the monoclinic/orthorhombic phase transition undergone by the zeolite. This flexibility of the zeolite framework seems to have a significant effect on the separation of both isomers by selective adsorption. Coadsorption experiments show that the ZSM-5 zeolite has a poor selectivity for 2MP with respect to 22DMB when the structure is orthorhombic whereas it is very selective in the monoclinic structure. However the selectivity decreases sharply as the filling increases. The presence of 22DMB molecules located at the intersections of the channels probably obstructs the adsorption of 2MP.

Keywords: coadsorption, ZSM-5, 2-methylpentane, 2,2-dimethylbutane, phase transition

1. Introduction

The adsorption of n- and iso-paraffins in MFI zeolite is of great interest in the petrochemical industry. As new legislative standards on pollutants emission impose to remove toxic aromatic compounds in gasoline, it is necessary to increase the content of highly branched alkanes in the detriment of linear and mono-branched ones in order to keep a high octane number. This requires the development of a separation process of isomers of the C_6–C_{10} alkanes cut. Selective adsorption on MFI zeolite is a good way to perform this separation. Indeed, with its microporosity composed of interconnected straight and zig-zag channels of mean diameter close to the size of the alkanes molecules, the ZSM-5 zeolite is a good candidate. It is the reason why the adsorption of alkanes on these materials has been extensively studied in the last decade. Experimental works (Cavalcante and Ruthven, 1995; Denayer et al., 1998; Millot et al., 1999; Zhu et al., 2001; Jolimaître et al., 2001) as well as molecular simulations (Shenk et al., 2001; Krishna et al., 2002) have been used to study the adsorption of alkanes on ZSM-5 zeolites at the equilibrium. Usually, these approaches consist in determining the single adsorption isotherms and in predicting the adsorption isotherms of mixtures by means of thermodynamic model as for instance the Ideal Adsorption Solution Theory or by Monte Carlo simulation. However, the adsorption of alkanes under isobaric conditions has never been studied and only very limited data on adsorption equilibria of alkanes mixtures are reported. Moreover the mechanisms of adsorption and separation of alkanes by adsorption on MFI zeolites are very complex and need still to be more elucidated. This paper

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is devoted to the adsorption of 2-methylpentane (2MP) and 2,2-dimethylbutane (22DMB) on a ZSM-5 zeolite under constant vapor pressure or constant temperature. A particular attention has been paid to the effect of the structural change of the adsorbent on adsorption properties and the adsorption selectivity of 2MP with respect to 22DMB has been measured for an equimolar mixture at constant temperature.

2. Experimental

The zeolite was a template-free H-form ZSM-5 (Si/Al = 500). This zeolite is manufactured without binder by Zeolist International. The C_6 alkanes isomers were provided by Prolabo with specified purities over 99% and were stocked with a 4A zeolite to keep them dried. The adsorption-desorption isobars are determined by thermogravimetry under a saturation vapor pressure of 5.5 kPa and for temperature ranging from 298 to 673 K. The mass of zeolite was of about 15 mg. The adsorption isotherms of single components and equimolar mixture are measured at 348, 413 and 443 K in the pressure range 10^{-3}–10 kPa by using a home made manometric device coupled with a gas phase chromatograph. About 500 mg of zeolite were used for these experiments. The accuracy on the adsorbed amount is better than 0.01 molec $\cdot$ uc^{-1}, the accuracy on temperature is about 0.1 K and the one on pressure is about 1%. The interaction of 22DMB with the zeolite under constant vapor pressure was followed by "in situ" XRD by means of a specific chamber of diffraction constructed in house (Gérard et al., 1998). XRD patterns were recorded under the same isobaric conditions as for thermogravimetry and by using the Co K_α radiation. About 40 mg of zeolite were needed. Prior each adsorption experiment the zeolite was outgassed "in situ" at 673 K under dynamic vacuum for 12 h. For each adsorption experiment, the time, which was required to reach the thermodynamic equilibrium indicated by an adsorbed amount constant with time, varied from few hours up to 10 days according to the temperature and the isomer.

3. Results and Discussion

3.1. Adsorption-Desorption Isobars of Single Components

Adsorption-desorption isobars are shown on Fig. 1. They are determined as follows: after outgassing under vacuum at 673 K with an heating rate of about 1 K $\cdot$ min^{-1},the sample is slowly cooled down to 298 K. The adsorbent is then submitted to the saturation vapor pressure. This step corresponds to the first adsorption. Once the adsorption equilibrium is reached i.e. when a plateau of mass is observed, the desorption branch is drawn by increasing step by step the temperature up to 673 K. Additional adsorption-desorption cycles are then performed by changing the temperature. With 2MP the adsorption-desorption isobar is perfectly reversible. At 300 K the relative pressure p/p_s is of 0.18. Usually, filling of micropores is complete under such a relative pressure. It is not the case here because let assume the adsorbate as a liquid, 5 molecules adsorbed per unit cell (molec $\cdot$ uc^{-1}) at this temperature correspond to a volume of 0.112 cm^3 $\cdot$ g^{-1} while the microporous volume of the ZSM-5 determined by nitrogen adsorption at 77 K is of 0.165 $cm^3 \cdot g^{-1}$. 2MP does not occupy the total free microporous volume contrary to hexane, which completely fills the micropores in the same conditions (Lemaire et al., 2002). With 22DMB the adsorption capacity at 300 K is lower than

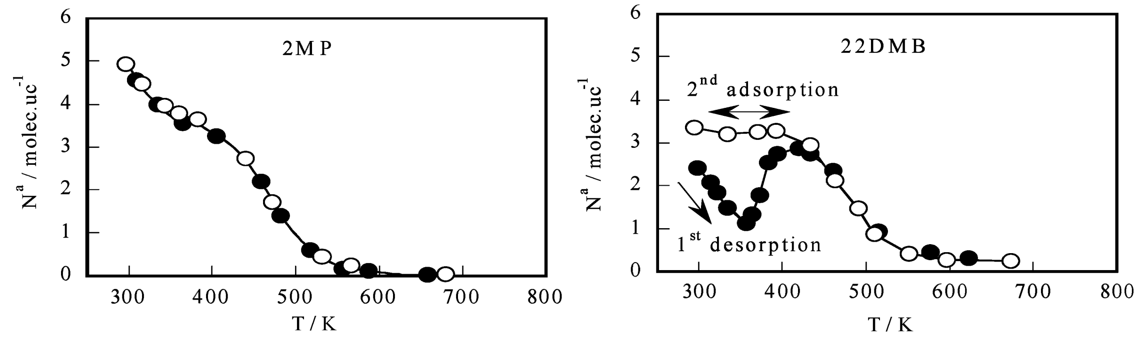

Figure 1. Adsorption-desorption isobars of 2MP and 22DMB on the ZSM-5 zeolite at 5.5 kPa (open circles: adsorption; full circles: desorption).

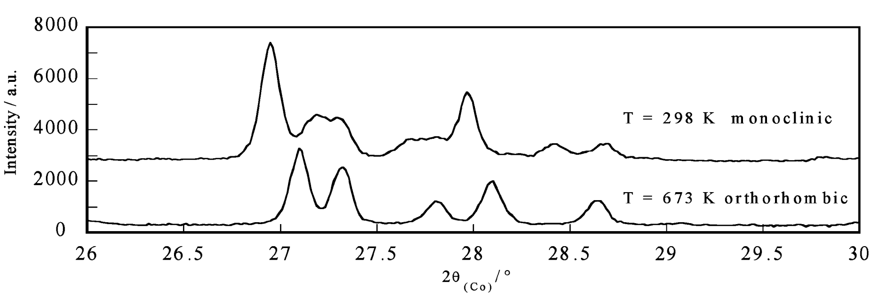

Figure 2. XRD patterns of the ZSM-5 zeolite under constant vapor pressure of 22DMB ($p = 5.5$ kPa) at 298 and 673 K. The monoclinic and orthorhombic structures are clearly identified by the evolution of the XRD massif in the 26–30°2θ angular domain (Mentzen et al., 1993).

that obtained with 2MP and a special behavior is observed during the first desorption. Indeed, the adsorbed amount increases when the temperature increases from 343 to 443 K. Above this last temperature the adsorbed amount decreases as expected and if several adsorption-desorption cycles are then performed the process is reversible. The same behavior is also observed when the sample is just outgassed under vacuum at room temperature. This singular phenomenon is thermodynamically inconsistent and has never been observed on ZSM-5 zeolite. On the other hand, the "in situ" XRD experiments performed on the ZSM-5 zeolite under constant vapor pressure of 22DMB (Fig. 2) show that the zeolite undergoes a monoclinic-orthorhombic phase transition in the range of temperature 343–353 K. Other authors have already observed this phase transition under air (Mentzen et al., 1993). We suspect that the singular behavior exhibited on the isobar is linked to this structural change. Indeed, it seems that the monoclinic-orthorhombic phase transition makes more accessible the channels to the multi-branched isomer. The orthorhombic structure then appears as a phase more favorable to the adsorption of 22DMB than the monoclinic structure. The isobaric singularity is not observed during the following adsorption-desorption cycles because starting from the orthorhombic phase the 22DMB molecules have no difficulty to enter into the channels and then remain adsorbed even if the structure becomes monoclinic when decreasing the temperature.

3.2. *Adsorption Isotherms of Single Components*

The adsorption isotherms of single components (Fig. 3) have type I of the IUPAC classification and the adsorption capacities are in good agreement with those given in the literature (Cavalcante and Ruthven, 1995; Zhu et al., 2001). As expected, the adsorption capacity of 2MP decreases as the temperature increases. Nevertheless, with 22DMB we observe that the adsorption capacity above 4 kPa becomes higher at 413 K than at 348 K. This result is obviously inconsistent from a thermodynamic point of view and could be considered as an effect of the framework flexibility. Indeed, the

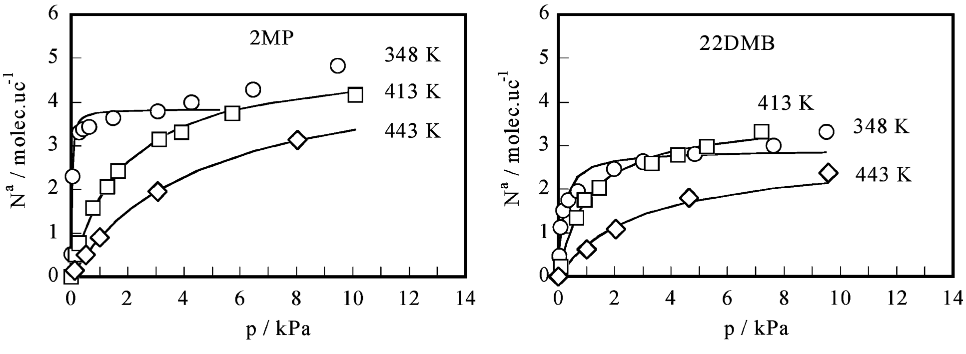

Figure 3. Adsorption isotherms of 2MP and 22DMB on the ZSM-5 zeolite at 348, 413 and 443 K (open symbols: experience; solid lines: Langmuir model).

Table 1. Langmuir parameters and enthalpies and entropies of adsorption deduced from the dimensionless constant $K_{(T)} \cdot K_L$ is the Langmuir constant expressed in kPa^{-1} and $p^\circ = 101.325$ kPa.

	T/K	N_s^a(molec · uc^{-1})	$K_{(T)} = K_L p^\circ$	$\Delta_{\text{ads}}H^\circ$(kJ · mol^{-1})	$\Delta_{\text{ads}}S^\circ$(J · K^{-1} · mol^{-1})
2MP	348	3.8	4458	−73	−137
	413	5.0	57		
	443	4.9	26		
22DMB	348	2.9	555	−36	−50
	413	3.6	96		
	443	2.8	34		

monoclinic-orthorhombic phase transition might not to be completely undergone at 348 K and a major part of the zeolite is still in the monoclinic structure. On the contrary, at 413 K the entire zeolite is in the orthorhombic structure. The decrease of the adsorption capacity induced by thermodynamic effect should be compensated by an increase caused by the structural change. This should be a competition between enthalpic and entropic effects. The adsorption isotherms are fitted with the Langmuir model. The Langmuir parameters and the enthalpies and entropies of adsorption determined by applying the van't Hoff relation to the Langmuir constants are given in Table 1. It may be noted that a poor fit is obtained with 2MP at 348 K. This is due to the fact that the adsorption isotherm exhibits a substep at a filling of 4 molec · uc^{-1}, as predicted by the Monte Carlo simulations (Shenk et al., 2001). Our adsorption isotherm does not show this complete substep because the range of pressure investigated is not large enough but one can discern that the beginning takes place. The single site Langmuir model cannot reproduce this substep and a better fit could be obtained by using a double site Langmuir model (Lemaire et al., 2002). Moreover the value of N_s^a found with the 22DMB is lower at 348 K than at 413 K. This could be still with the fact that the structure is monoclinic at this temperature and then less favorable to the adsorption of 22DMB. The adsorption enthalpies and entropies are of the same order of magnitude as those given by other authors (Cavalcante and Ruthven, 1995; Jolimaître et al., 2001; Millot et al., 1999) and are lower with 22DMB than with 2MP. This means on the one hand that the adsorbate/adsorbent interactions are weaker with the di-branched isomer and on the other hand that this molecule is less "frozen" in the channels. Both results agree with the hypothesis that 22DMB molecules should be located at the intersections between the straight and the zig-zag channels where the free space is largest whereas 2MP molecules should be rather adsorbed in the channels.

3.3. *Adsorption Isotherms of the Binary Mixture*

The total $N_t^a = f(p)_T$ and partial $N_i^a = f(p)_T$ adsorption isotherms of the binary mixture are given on Fig. 4. The amount of mixture adsorbed at 348 K lies between those of single components in the whole range of investigated pressure. The partial amount of 2MP adsorbed is largely higher than that of 22DMB indicating that the adsorption process is in favor of the adsorption of the

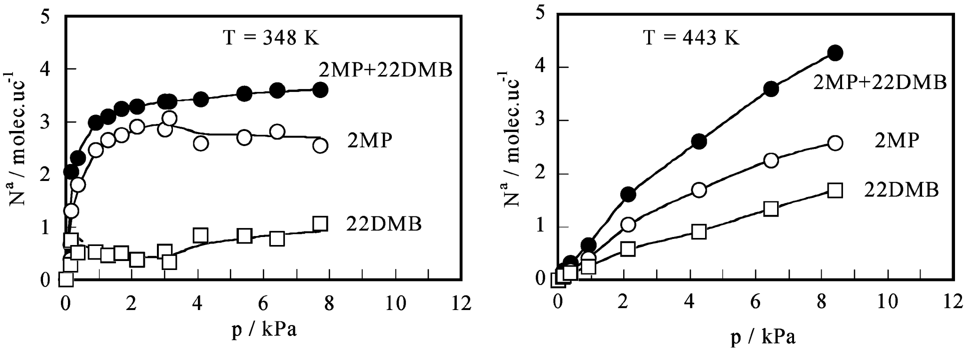

Figure 4. Total and partial adsorption isotherms of the 2MP+22DMB equimolar mixture on the ZSM-5 zeolite at 348 and 443 K.

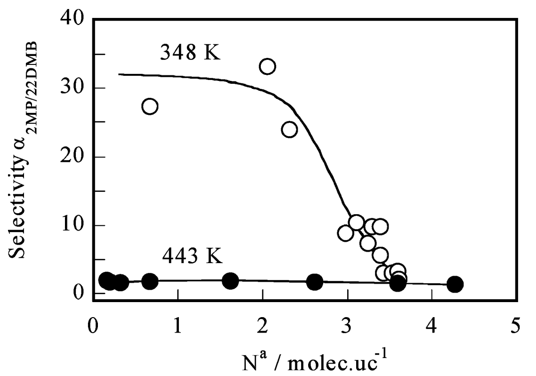

Figure 5. Dependence of the filling on the adsorption selectivity of 2MP with respect to 22DMB of the ZSM-5 zeolite at 348 and 443 K.

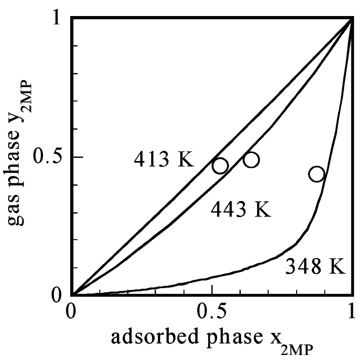

Figure 6. $x - y$ diagram for the adsorption of 2MP + 22DMB on the ZSM-5 zeolite under the pressure of 2 kPa (solid line: IAST; open circles: experiment).

mono-branched isomer. Figure 5 shows the adsorption selectivity of 2MP with respect to 22DMB as a function of the total filling. We recall that this selectivity is defined by: $\alpha_{2MP/22DMB} = x_{2MP} \cdot y_{22DMB}/y_{2MP} \cdot x_{22DMB}$, where x_i and y_i are the mole fractions of component i at the equilibrium in the adsorbed phase and in the gaseous phase respectively. For filling lower than 2 molec.uc^{-1}, the selectivity is greater than 30 and seems almost constant. Nevertheless, when the total filling exceeds this value i.e. when the amount of 22DMB reaches about 0.5 molec·uc^{-1} we observe a sharp decrease of the selectivity. Moreover, for pressure higher than 3 kPa which corresponds to a total filling of 3.5 molec·uc^{-1}, a slight decrease of the adsorbed amount of 2MP and an increase of that one of 22DMD is observed: 2MP is replaced by 22DMB (Fig. 4). Shenk et al. (2001) explain this substep by packing effects of the molecules in the channels, which they call "configurational entropy effect. At 443 K the adsorption process shows a poor selectivity. Indeed, the selectivity is of about 2 and is almost independent of the filling (Fig. 5). It may be noted that the adsorbed amount of mixture exceeds that ones obtained with the single components (Figs. 3 and 4). For example, 4.1 molec · uc^{-1} of mixture are adsorbed at 8 kPa against 3.2 and 2.3 for 2MP and 22DMB respectively. This could mean that some additional adsorption sites come into play in the adsorption process of mixture compared to the adsorption of single components. Moreover, although the partial isotherms of 2MP at 348 and 443 K display different shapes, the adsorbed amount of 2MP at 443 K is quite the same that at 348 K and 22DMB is more adsorbed at 443 K than at 348 K. This could be still explained by the competition between enthalpic effects and zeolite phase transition in the range of temperature 343–353 K. At 443 K the zeolite has the orthorhombic structure and the adsorption process should be then less selective for 2MP because this structure seems more favorable to the adsorption of 22DMB than the monoclinic one. The same observations and interpretations can be deduced from adsorption isotherms of the mixture at 413 K.

The coadsorption equilibria of 2MP and 22DMB on the ZSM-5 zeolite can be determined by using the well-known Ideal Adsorbed Solution Theory (IAST) (Myers and Prausnitz, 1965). In our predictions, the calculation of the spreading pressure is performed by numerical integration of the adsorption isotherms of single components rather than by using the Langmuir equation in order to have the best accuracy. As shown on Fig. 6, the IAST allows a good prediction of the selectivity when the filling is not too high. The sharp decrease of the selectivity when the temperature increases from 348 to 443 K is even well predicted. However, as the total filling exceeds 2 molec · uc^{-1} the prediction is not so good because the IAST cannot predict the displacement of 2MP by 22DMB.

4. Conclusion

The major result of this work is to show that the ZSM-5 zeolite exhibits a very special behavior with 22DMB under isobaric conditions. We suspect that the monoclinic-orthorhombic phase transition undergone by the ZSM-5 zeolite near 343 K is the cause of this phenomenon. This is still an assumption that one must carefully consider. Our results must be more analyzed and complementary experiments must be performed to confirm it. However this hypothesis is rather relevant to explain the strange results of adsorption that we have found in this work. It seems that the framework flexibility of the ZSM-5 zeolite has a significant effect on the adsorption properties of 22DMB. The adsorption of this isomer appears less confronted to steric constraints in the orthorhombic phase than in the monoclinic phase. The phase transition probably induces a modification of the channel geometry, which is certainly slight but enough to make the channels more accessible to 22DMB. This effect of the framework flexibility is detectable with the 22DMB because this isomer has a molecular size very close to the pore opening of the zeolite. It is insignificant with the mono-branched isomer as well as with *n*-hexane, which have a smaller size. The coadsorption equilibria of 2MP and 22DMB on the ZSM-5 zeolite are consequently influenced by this structural effect. In the monoclinic structure the ZSM-5 zeolite is very selective for 2MP whereas it exhibits a poor selectivity in the orthorhombic structure. Moreover the selectivity decreases sharply at high filling due to the displacement of 2MP by 22DMB. The di-branched isomer, which is located at the intersections of the straight channels and the zig-zag channels, probably obstructs the adsorption of 2MP. These results are of great importance for the determination of the operating conditions of *n*- iso-paraffins separation process using a ZSM-5 zeolite as selective adsorbent.

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