Journal of Thermal Analysis, Vol. 54 (1998) 881-889

ADSORPTION OF A POLAR OR A NON-POLAR CHLOROALKENE ON A ZSM-5 ZEOLITE AT 298 K

F. Bouvier and G. Weber[*]

UMR 5613, Université de Bourgogne-CNRS, LRRS, 9, avenue Alain Savary, BP 400
21011 Dijon Cedex, France

(Received December 21, 1997)

Abstract

The physisorption of trichloroethylene and tetrachloroethylene on ZSM-5 (Si/Al = 339) zeolite was investigated at 298 K using thermogravimetry, differential microcalorimetry and X-ray diffraction. The zeolite always undergoes a monoclinic-orthorhombic structural change during the adsorption of the first molecules. An alignment of the polar trichloroethylene molecules inside all the channels of the zeolite is proposed to account for the experimental results. A phase transition of the non-polar tetrachloroethylene is suggested to produce the stepped isotherm, the steep rise in the heat curve and the high increase in the mobility of the molecules for the loading of 4 molecules per unit cell.

Keywords: phase transition, stepped isotherm, structural change, tetrachloroethylene, trichloroethylene, ZSM-5 zeolite

Introduction

Physisorption of gases (*n*-paraffins and *n*-olefines) [1] on MFI-zeolites [2] usually gives rise to type I isotherms. However, some small molecules (Ar, Kr, O_2, H_2, N_2, CO) [3] and some aromatic compounds (benzene, toluene, ethylbenzene, *p*-xylene, bromobenzene) [4–8] can interact with such hydrophobic adsorbents showing step(s) in the isotherms and in the corresponding heat curve. In the literature the existence of these steps is interpreted as the result of a phase transition of the adsorbate i.e. a change in the state of the admolecules, but also in some cases to a change in the framework symmetry of the adsorbent [7–10]. Indeed, X-ray diffraction studies showed that an ortho (orthorhombic with Pnma symmetry) – para (orthorhombic with $P2_12_12_1$ symmetry) framework symmetry change occurs during the adsorption *p*-xylene [9] and of *p*-dichlorobenzene [10] on sili-

---

[*] Author to whom all correspondence should be addressed.

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

calite when the loading increases from 4 to 8 molecules per unit cell (molec./u.c.), respectively. Moreover, molecular simulations about the adsorption of benzene or *p*-xylene on silicalite [11] indicate that such a symmetry change can account for the steep jump observed in the experimental isotherms at 4 molec./u.c. A cooperative effect between a structural change of the zeolite and a phase transition of the adsorbate may also be proposed to explain the origin of the stepped isotherms [12].

In this work the interaction of trichloroethylene and tetrachloroethylene on ZSM-5 (Si/Al=339) was investigated at 298 K using thermogravimetry, differential microcalorimetry and X-ray diffraction. The shape of the isotherms and the heat curves was examined and discussed in the light of literature data. An adsorption pathway model is proposed for each system.

Experimental

Materials

The template-free ZSM-5 zeolite with a silicon to aluminium ratio of 339 was prepared by Conteka. The powdered sample composed of spherical uniform-sized grains with a diameter averaging 2 μm contains approximately 3% of water at room temperature.

The trichloroethylene and the tetrachloroethylene distributed by Prolabo (R.P. Product) contained 0.0100 and 0.0050% of water, respectively. Therefore prior to adsorption measurements, the adsorptives were dried over a hydrophilic 3A zeolite to prevent any residual and competitive adsorption of water. Some physical properties of the two adsorptives are given in Table 1 [13].

Table 1 Physical characteristics of the adsorptives (*M*: molecular mass [13]; *d*: density at 298.15 K [13]; μ: dipole moment of the molecule [13]; *L*: length of the molecule [19]; *l*: width of the molecule [19]; p_0: saturated vapour pressure at 298.15 K [13]; $\Delta_{vap}H^{\circ}_{m}$: heat of vaporization at 298.15 K [13])

Adsorptives	Trichloroethylene	Tetrachloroethylene
$M/(\mathrm{g\ mol^{-1}})$	131.39	165.83
$d/(\mathrm{cm^3\ g^{-1}})$	1.458	1.613
μ/D	1.4*	0
L/nm	0.68	0.68
l/nm	0.66	0.66
p_0/hPa	98.28	24.72
$\Delta_{vap}H^{\circ}_{m}/(\mathrm{kJ\ mol^{-1}})$	34.54	39.68

* Value estimated by considering that the dipole moment of the molecule is the same as the dipole moment of monochloroethylene

Techniques

Thermogravimetry

The adsorption-desorption isotherms were measured at 298 K by TG using a McBain balance. About 15 mg of sample were activated in situ at 673 K under a vacuum of 10^{-2} Pa for 12 h before exposing to the pure vapour of chloroalkene controlled by the 'cold point' [14]. The adsorption branch of the isotherm was constructed by increasing the pressure step by step up to saturation ($p/p_0=1$) after the change in sample mass was less than ±0.01 mg in a 1 h period. The desorption branch of the isotherm was measured in the opposite direction, by decreasing the pressure from the saturated state of the zeolite [15].

X-ray powder diffraction

Structural data were obtained using X-ray powder diffraction with $CuK_{\alpha 1}$ radiation on a diffractometer equipped with an INEL curved counter. The diffraction patterns of the unloaded zeolite (before and after activation) or at micropore saturation were always recorded at room temperature.

Differential microcalorimetry

Energetic data were measured at 298 K using a heat flow microcalorimeter (C80-SETARAM) coupled with a volumetric equipment [16]. About 1 g of sample was activated as described above in the thermogravimetric section. The differential enthalpies of adsorption were recorded as a function of filling by admitting successive known quantities of chloroalkene vapour to the sample. Equilibrium was reached when the temperature of the sample cell was equal to the temperature of the reference cell. The adsorption isotherms obtained from microcalorimetry and thermogravimetry were found to coincide.

A kinetic approach of the adsorption phenomenon was made based on an analysis in the long time region of every heat curve recorded as a function of time for each successive amount of chloroalkene adsorbed. The transport diffusivity D which is assumed to be a constant at a given loading, was first calculated from the Fick equation in spherical symmetry [17]:

$$\ln\left(1-\frac{Q_t}{Q_\infty}\right)=\ln\left\{\frac{[6K(K+1)]}{[9(K+1)+\beta^2K^2]}\right\}-\left(\frac{\beta^2Dt}{r^2}\right)$$

Q_t, Q_∞: amount of chloroalkene adsorbed in an adsorption time t or at equilibrium, respectively,

$K=C_\infty/(C_0-C_\infty)$ with C_0, C_∞: the concentration of the chloroalkene in the gaseous phase at the initial time and at equilibrium, respectively,

β: the first positive root of the equation with $\tan\beta=3\beta/(3+K\beta^2)$.

Each corrected diffusivity D_0 was then calculated from the corresponding transport diffusivity D using the Darken correction factor:

$$D = D_0 \left| \frac{\delta \ln(P)}{\delta \ln(n)} \right|$$

Then, the curve $D_0/r^2 = f(n)$ was drawn to describe the variation of the molecular mobility as a function of the loading for a given spherical grain size.

Results and discussion

Adsorption of trichloroethylene

The adsorption-desorption isotherms of trichloroethylene on ZSM-5 (Si/Al=339) are type I-shaped (Fig. 1). The maximum amount adsorbed into micropores is 10 molec./u.c. ($p/p_0=0.25$). It is interesting to note that the total length of a chain composed of 10 molecules of trichloroethylene (68 nm) assembled end to end is in a good agreement with the total length of the channels of one unit cell (66 nm) (Table 1). It follows that the nature of the different adsorption sites (4 sites in the zig-zag channels, 4 sites in the middle of the straight channels and 4 sites in the intersection of the straight and the zig-zag channels) does not influence the arrangement of the molecules.

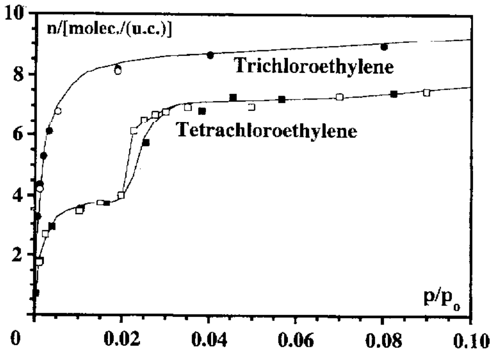

Fig. 1 Isotherms of the adsorption (close symbols) and desorption (open symbols) of tetrachloroethylene and trichloroethylene on ZSM-5 (Si/Al=339) at 298 K

Such an arrangement of the molecules in the micropores agrees with the classical shape of the corresponding adsorption heat curve shown in Fig. 2a. Indeed, the differential molar enthalpy regularly increases from 50 to 70 kJ mol^{-1} during the adsorption of the 10 molecules adsorbed per unit cell. This increase of 20 kJ mol^{-1} in the differential molar enthalpy indicates the increasing adsorbate/adsorbate interactions. The difference of 15 kJ mol^{-1} between the heat of va-

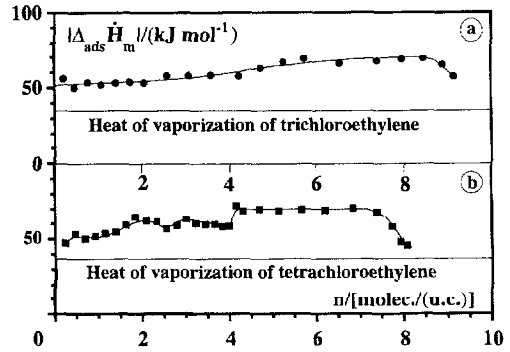

Fig. 2 Calorimetric curves of the adsorption of tetrachloroethylene and trichloroethylene on ZSM-5 (Si/Al=339) at 298 K

porization of the adsorptive and the differential molar enthalpy at zero loading of the zeolite gives an estimation of the adsorbate/adsorbent interactions which seem to be quite constant during the adsorption of the 10 molecules. As a matter of fact the adsorbed molecules with a molecular diameter very close to the pore opening of the zeolite, always interact with the micropore walls in the same way.

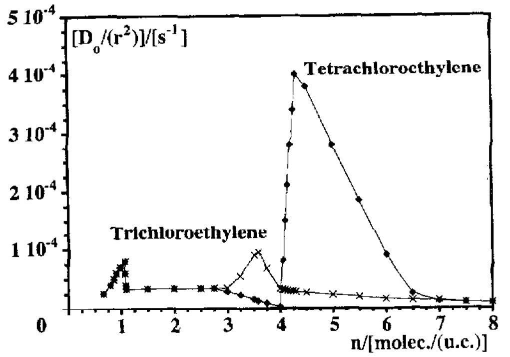

Fig. 3 Dependence of the corrected diffusivity on the number of molecules of tetrachloroethylene and trichloroethylene adsorbed per unit cell of ZSM-5 (Si/Al=339) at 298 K

As shown in Fig. 3, the mobility of the molecules is only slightly modified during the adsorption of the 10 molecules of trichloroethylene. However, two peaks of equal intensity indicate that the mobility of the molecules is maximum at a loading of 1 and 3.5 molec./u.c., respectively (Fig. 3). These two peaks may be the signature of the filling of the straight and then the sinusoidal channels different in size.

The analysis of the diffraction patterns of the unloaded zeolite and that saturated with solvent indicates that the zeolite framework undergoes a monoclinic-orthorhombic structural change during the adsorption of trichloroethylene. Moreover, this structural change occurs far below the adsorption of 4 molec./u.c.

Adsorption of tetrachloroethylene

In contrast to what was observed for the adsorption of trichloroethylene, the isotherms for the adsorption and desorption of tetrachloroethylene exhibit a quite vertical step at 4 molec./u.c. at p/p_0=0.02 [18]. The hysteresis loop associated with the step indicates the difficulty to desorb the molecules because of steric hindrance and kinetic effects. The micropores are saturated at p/p_0=0.10 and only 8 molecules are adsorbed per unit cell. The fact that the maximum amount of chloroalkene adsorbed into micropores is lower by 2 molec./u.c. for tetrachloroethylene than for trichloroethylene points out the existence of strong intermolecular interactions between the non-polar molecules.

Indeed, the heat curve in Fig. 2b shows an irregular increase of about 10 kJ mol^{-1} during the adsorption of the first four molecules per unit cell. This particular shape of the heat curve at low filling may be attributed to a successive local displacement of the non-polar molecule around an adsorption site because of attraction and repulsion interaction forces. At a loading of 4 molec./u.c., the intermolecular interactions are so strong that a stepwise increase of 10 kJ mol^{-1} is observed in the heat curve. It is worth noting that the stepwise increase in the heat curve has the same shape as the step in the adsorption isotherm. Above 4 molec./u.c., the heat curve stays quite constant up to micropore filling before decreasing to the value of the heat of vaporization of tetrachloroethylene. The horizontal part of the heat curve indicates that the four additional molecules of tetrachloroethylene are adsorbed on four energetically equivalent sites of the zeolite.

The curve of the dependence of the corrected diffusivity on the filling exhibits 2 peaks, as it was observed for the adsorption of trichloroethylene (Fig. 3). The maxima are located at the loadings of 1 and 4.3 molec./u.c., respectively. The first peak which is located at the same loading as the one already observed in the case of trichloroethylene, shows the same shape, the same intensity and the same area. The second peak located in the range of the micropore filling of about 4–6.5 molec./u.c. is four times higher than the second peak for the adsorption of trichloroethylene. The beginning of this peak is located at the same loading as the step in the isotherm and the stepwise increase in the heat curve. This indicates that the first four molecules preadsorbed on a given site jump to another more stable site because of strong intermolecular repulsion forces. The first four sites which are free again are therefore able to accommodate four additional molecules. The mobility of the molecules decreases above a loading of 4.3 molec./u.c. because of steric effects during micropore filling.

As concerns structural aspects, the zeolite undergoes a monoclinic-orthorhombic change during the adsorption of tetrachloroethylene. This structural change which has been previously observed during the adsorption of trichloroethylene occurs at a loading far below 4 molec./u.c.. Therefore, it cannot account for the existence of the step in the adsorption isotherm.

Pathway for the adsorption of trichloroethylene and tetrachloroethylene on ZSM-5

The adsorption of the first molecules of trichloroethylene or tetrachloroethylene induces a monoclinic – orthorhombic structural change of the zeolite framework far below 4 molec./u.c.. From the inspection of the curves of the variation of the corrected diffusivity as a function of the filling, such a structural change is supposed to occur as soon as the first molecules is adsorbed. Above 1 molec./u.c., the accommodation of the molecules into the channels of the zeolite depends on the strength of the adsorbate/adsorbent and adsorbate/adsorbate interactions.

For the adsorption of trichloroethylene, the molecules are self-assembled end to end to form dipole chains in the straight and sinusoidal channels of the zeolite. The molecules are supposed to migrate from the straight to the sinusoidal channels above 3 molec./u.c. because the corrected diffusivity coefficient is slightly increased at this loading. An ortho-para symmetry change of the adsorbent previously observed by van Koningsveld *et al.* [9–10] is supposed to explain such a migration of the molecules.

For the adsorption of tetrachloroethylene, the coincidence between the step in the isotherm, the stepwise increase in the heat curve and the high peak in the corrected diffusivity at 4 molec./u.c. is attributed to a phase transition of the adsorbate with a rearrangement of the molecules. Such a rearrangement is observed because the size of the non-polar molecule is very close to the pore opening of the zeolite and because of strong intermolecular forces due to the presence of chlorine atoms. To account for a micropore filling pathway with an occupation of 8 sites above the 12 available, it may be assumed that the first four molecules are preferentially localized in the channel intersection as has already been suggested for the adsorption of aromatic compounds [4–8]. At 4 molec./u.c., the intermolecular repulsions are so strong that the molecules jump from the intersections to vicinal sites located either in the sinusoidal channels or along the straight channels. With such an arrangement, four additional molecules may be adsorbed into the pores to create a more ordered and denser packing state of the molecules. Therefore the molecules self-assembled two by two into a «T» structure would give rise to chains either in the sinusoidal or along the straight channels. The first alternative i.e. the jump of the molecules from the intersections to the sinusoidal channels, seems to be more realistic than the second one because the experimental data (isotherm and heat curve) are very similar to those of *p*-xylene [4–6]. On this assumption and according to van Koningsveld's studies [9, 10], a relaxation of the first four molecules of tetrachloroethylene adsorbed at the intersections of the channels would produce an ortho-para symmetry change, inducing in turn an opening modification of the sinusoidal channels and therefore allowing the access of the molecules to the sinusoidal channels. Such a symmetry change may account for the high increase in the corrected diffusivity coefficient at a loading of 4 molec./u.c..

Conclusions

The adsorption of a chloroalkene on a ZSM-5 zeolite (Si/Al=339) is described by isotherms, whose shape depends on the polarity of the molecule. A type I isotherm is observed for the adsorption of trichloroethylene as for the adsorption of a *n*-alkane. The heat curve shows a classical shape on micropore filling. The molecules adsorbed at micropore saturation fill up the straight and sinusoidal channels of the zeolite. Dipole chains are supposed to be formed in the micropes to account for the experimental results. Concerning the adsorption of tetrachloroethylene, a stepped isotherm is observed at 4 molec./u.c. as for the adsorption of an aromatic compound whose molecular diameter is very close to the pore opening of the zeolite. The heat curve and the corrected diffusivity curve exhibit a jump too at the same loading to 4 molec./u.c. Such an accident in the curves is attributed to a phase transition of the non-polar adsorbate into a denser packing state to give sinusoidal chains in the channels of the zeolite.

The monoclinic-orthorhombic structural change cannot account for the step in the isotherm of the adsorption of tetrachloroethylene because it occurs far below 4 molec./u.c. for both adsorbates. Such a structural change which induces an increase in the mobility of the molecules may be suspected as soon as the first molecule of chloroalkene is adsorbed. On this assumption the increase in the mobility at 4 molec./u.c. for tetrachloroethylene and at 3 molec./u.c. for trichloroethylene would be attributed to the ortho-para symmetry change already observed for the adsorption of *p*-xylene and *p*-dichlorobenzene.

References

1 H. Stach, U. Lohse, H. Thamm and W. Schirmer, Zeolites, 6 (1986) 74.
2 W. M. Meier and D. H. Olson, in Atlas of Zeolite Structure Types, Butterworth-Heinemann, 1992.
3 J. P. Coulomb, P. L. Llewellyn, C. Martin, Y. Grillet, J. Rouquerol and M. D. le Van ed., in Fundamentals of Adsorption, Kluwer Academic Publishers, Boston, Massachusett 1996, p. 211.
4 C-K. Lee and A. S. T. Chiang, J. Chem. Soc., Faraday Trans., 92 (1996) 3445.
5 H. Thamm, J. Phys. Chem., 92 (1988) 193.
6 O. Talu, C.-J. Guo and D. T. Hayhurst, J. Phys. Chem., 93 (1989) 7294.
7 B. F. Mentzen and P. Gelin, Materials Research Bulletin, 30 (1995) 373.
8 P. Gelin, J. F. Dutel and B. F. Mentzen, Microporous Materials, 4 (1995) 283.
9 H. van Koningsveld, F. Tuinstra, H. van Bekkum and J. C. Jansen, Acta Cryst., B45 (1989) 423.
10 H. van Koningsveld, J. C. Jansen and A. J. M. de Man, Acta Cryst., B52 (1996) 131.
11 R. Q. Snurr, A. T. Bell and D. N. Theodorou, J. Phys. Chem., 97 (1993) 13742.
12 D. Pan and A. Mersmann, in Characterization of Porous Solids II, ed. F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing and K. K. Unger, Elsevier, Amsterdam 1991, p. 519.
13 Handbook of Chemistry and Physics, David R. Lide, Editor-in-Chief, 72nd edition 1991–1992.

14 A. Tiselius and S. Brohult, Z. Phys. Chem. Abt, A 168 (1934) 248.
15 M. H. Simonot-Grange, A. Elm Chaouri, G. Weber, P. Dufresne, F. Raatz and J.-F. Joly, Zeolites, 12 (1992) 155.
16 M. H. Simonot-Grange, O. Bertrand, E. Pilverdier, J. P. Bellat and C. Paulin, J. Thermal Anal., 48 (1997) 741.
17 J. Karger and D. M. Ruthven, in Diffusion in Zeolites and Other Microporous Solids, Wiley, New York 1992.
18 G. Weber, O. Bertrand, E. Fromont, S. Bourg, F. Bouvier, D. Bissinger and M. H. Simonot-Grange, J. Chim. Phys., 93 (1996) 1412.
19 L. Pauling, in La Nature de la Liaison Chimique et de la Structure des Molécules et des Cristaux, Seconde Edition, Presses Universitaires de France, Paris 1949.