SELECTIVE ADSORPTION OF DIOXINS AND FURANS BY ZEOSILS

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Introduction

For the adsorption of the polychlorinated dibenzo-*p*-dioxins and dibenzofurans pure silica zeolites, so called zeosils were used. As the zeosils only consist of silicon and oxygen, there is no resulting ionic charge like in zeolites, that would have to be counterbalanced by cations. Because of this pure SiO_2 framework the zeosils show hydrophobic properties. This makes them an ideal host for adsorbing hydrophobic guest molecules like dibenzo-*p*-dioxins and dibenzofurans.

Methods and Materials

For the selective sorption of dibenzo-*p*-dioxins and dibenzofurans from the gas phase three zeosils with different pore diameters were chosen. Fig. 1 shows the stuctures of UTD-1 (University of Texas at Dallas-1),[1] SSZ-24 (Socal Synthetic Zeolite-24)[2] and ITQ-4 (Instituto de Tecnología Química-4),[3] all possessing one-dimensional pore systems.

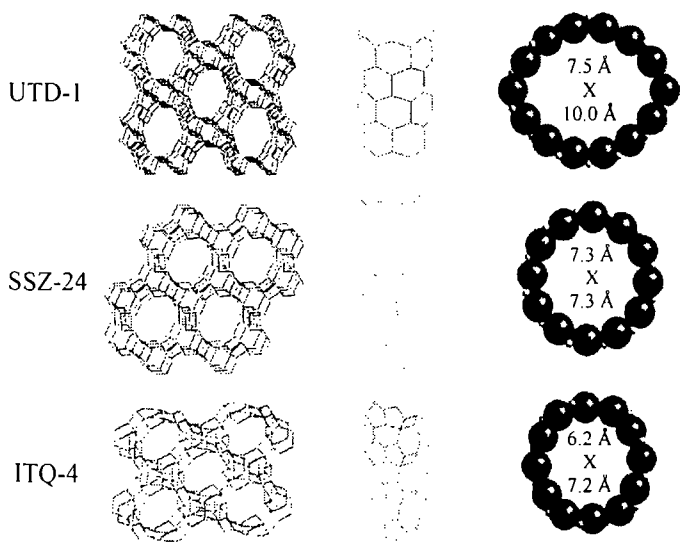

Fig. 1. Crystal structure and pore sizes of zeosils.
On the left the structural arrangement of these SiO_2 modifications is shown (oxygen atoms omitted). In the middle the channel structures are depicted (oxygen atoms omitted); and on the right, the channel diameters are given (oxygen atoms included).

Results and Discussion

The pore diameters given in Fig. 1 are static diameters. As the sorption experiments were carried out at 300 °C, the dynamics of the zeosils at 300 °C were calculated with the molecular modelling program Cerius[2] from MSI. The distance of the opposite oxygen atoms in the pores were measured and are plotted in Fig. 2. For the symmetric pore of SSZ-24 it is obvious, that the most probably diameter of the channel is 7.3 Å. The diameter distribution follows a gaussian funktion. So, the dynamic pore diameter for SSZ-24 is 7.3 ± 0.5 Å. For the oval pores of ITQ-4 and UTD-1 we obtain several different distances, the largest of which are most relevant. So the dynamic pore diameters are 7.0 ± 0.4 Å for ITQ-4 and 10.6 ± 0.6 Å for UTD-1.

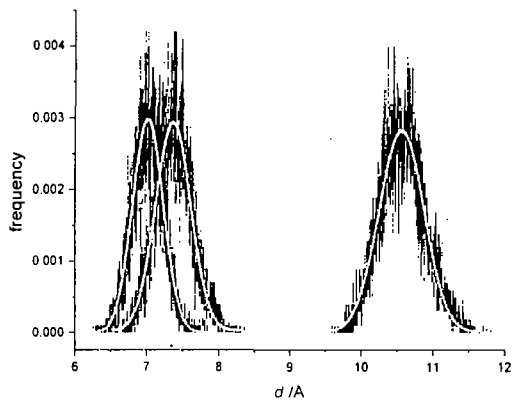

Fig. 2. Dynamical properties of the pore openings of the zeosils:
ITQ-4 left, SSZ-24 middle, UTD-1 righ

According to number and substitution pattern of chlorine atoms, dibenzo-*p*-dioxin molecules can be grouped into three size classes (Fig. 3).

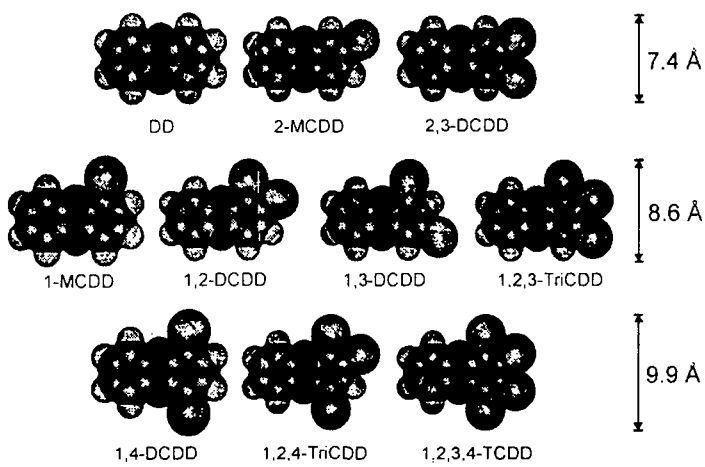

Fig. 3. Grouping of dibenzo-*p*-dioxin molecules into three different size classes (shown for chlorine substitution in positions 1, 2 ,3 and 4).

For the dibenzo-*p*-dioxins and dibenzofurans, dynamics were calculated at 300 °C, too. The results for the distance measured between the atom at position 1 and the atom at position 4 plus the corresponding van der Waals radii for 2,3-DCDD, 1,2-DCDD and 1,4-DCDD are shown in Fig. 4. In a similar way, the dynamical size of the dibenzofuranes has been obtained (Fig. 5).

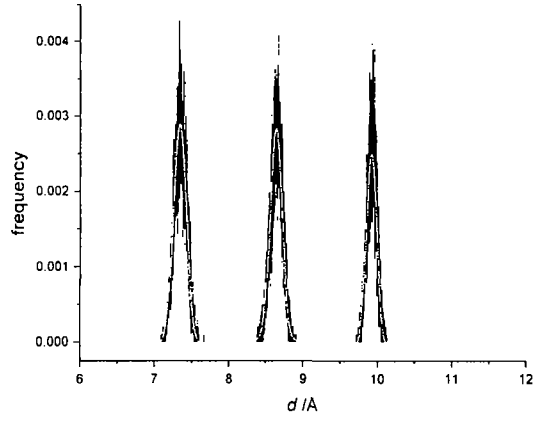

Fig. 4. Dynamical properties of the dibenzo-*p*-dioxins: 2,3-DCDD left, 1,2-DCDD middle, 1,4-DCDD right.

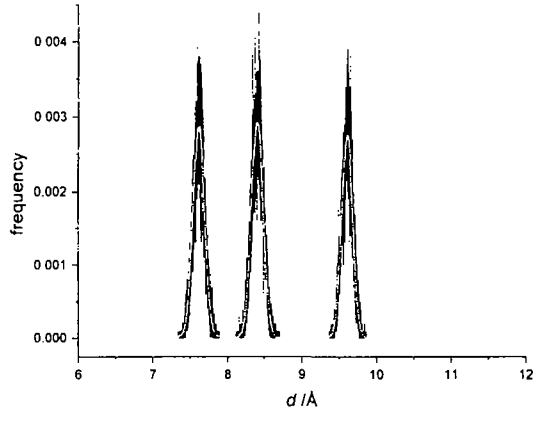

Fig. 5. Dynamical properties of the dibenzofurans: 2,3-DCDF left, 1,2-DCDF middle, 1,4-DCDF right.

In the experiments, dibenzo-*p*-dioxins and dibenzofurans were desorbed from fly ash and flushed over a sequential arrangement of zeosils at elevated temperature by a stream of nitrogen. In the arrangement of the zeosils, ITQ-4 with the smallest pore diameter was placed first, followed by SSZ-24 and finally, by UTD-1 with the largest pore diameter. The idea was to size-selectively adsorb the dibenzo-*p*-dioxins and dibenzofurans. As an example for the results obtained, the

chromatograms in Fig. 6 show the separation of the monochlorinated dibenzo-*p*-dioxins (D1) and the monochlorinated dibenzofurans (F1). For D1 the separation of 1-MCDD from 2-MCDD can be seen. For F1 the small 2- and 3-MCDF were mainly adsorbed at SSZ-24 and the larger 1- and 4-MCDF at UTD-1.

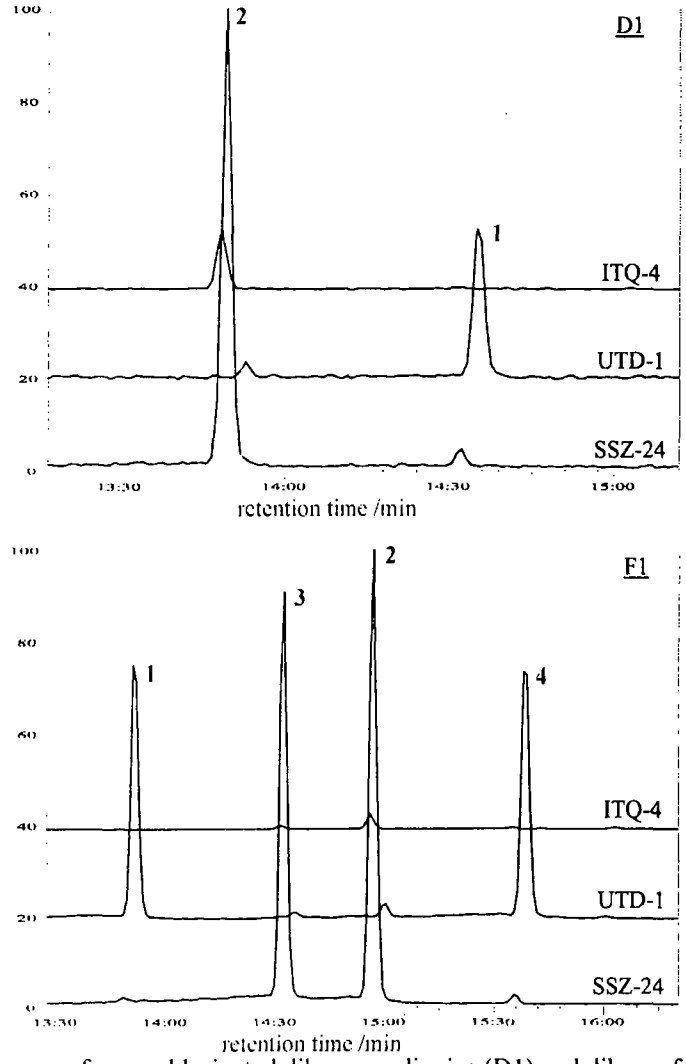

Fig. 6. Chromatograms of monochlorinated dibenzo-*p*-dioxins (D1) and dibenzofurans (F1).

References

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