Selective Adsorption of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans by the Zeosils UTD-1, SSZ-24, and ITQ-4

Ralph Jäger,[a] Andreas M. Schneider,[a] Peter Behrens,*[a] Bernhard Henkelmann,[b] Karl-Werner Schramm,[b] and Dieter Lenoir[b]

Abstract: Zeosils are microporous solids with a pure silica framework. Due to their hydrophobic properties, zeosils are ideal host materials for the adsorption of hydrophobic guest molecules. We tested zeosils with different pore diameters (UTD-1, SSZ-24 and ITQ-4 as well as CIT-5) for the selective adsorption of the polychlorinated dibenzo-*p*-dioxins and dibenzofurans. This group of highly toxic substances contains 210 congeners that possess similar chemical properties, but differ in their size and shape. In the experiment, polychlorinated dibenzo-*p*-dioxins and dibenzofurans were extracted from fly ash of a waste incinerator, adsorbed on amorphous silica, then thermally desorbed and flushed over a sequential arrangement of the zeosils at elevated temperature by a stream of nitrogen. ITQ-4 with the smallest pore diameter was placed first, followed by SSZ-24 and, finally, by UTD-1 with the largest pore diameter. After the experiment, the zeosils were analysed for their contents of the different congeners. The results show that the sorption of the congeners occurs selectively and that it is governed by the size and the shape of the dioxin molecules, which in turn depend on the number of chlorine atoms and the pattern of chlorine substitution (regioisomers). Geometrical reasoning as well as molecular dynamics calculations on the zeosil structures and on the dioxin molecules were helpful in rationalising the results. This work represents an especially complex case of the molecular sieving effect and may lead to a selective on-line monitoring of the concentrations of dioxin molecules in waste gases of industrial combustion processes. The size- and shape-selective sorption of dioxin molecules may also bear some resemblance to the molecular recognition process that occurs in nature at the aryl hydrocarbon receptor.

Keywords: absorption · dioxins · molecular sieves · zeolite analogues · zeosils

Introduction

Dioxins and related compounds, that is, polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), are a class of highly toxic and persistent pollutants. PCDD/Fs are tricyclic aromatic ethers. Figure 1 shows their general formula. Altogether this class comprises 210 compounds. Table 1 summarises the number of congeners for the different degrees of chlorination.[1]

The toxicity of the dioxins varies with the number of chlorine atoms and with their substitution pattern. Only 17 of the altogether 210 congeners are especially toxic. The most toxic isomer is the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and, in general, all PCDD/Fs substituted in the positions 2, 3, 7 and 8 show higher toxicities than others.[1] 2,3,7,8-Tetra-

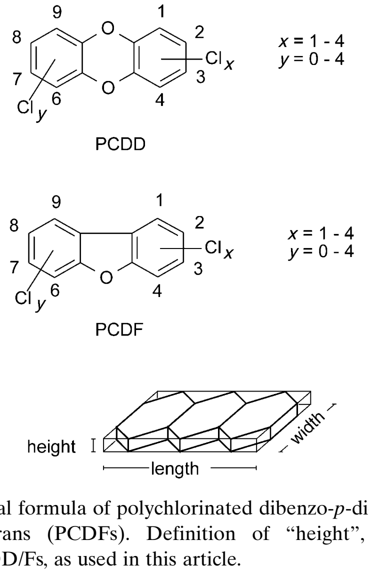

Figure 1. General formula of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). Definition of "height", "length" and "width" of PCDD/Fs, as used in this article.

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[a] Dr. R. Jäger, Dr. A. M. Schneider, Prof. Dr. P. Behrens
Institut für Anorganische Chemie, Universität Hannover
Callinstr. 9, 30167 Hannover (Germany)
Fax: (+49) 511-762-3006
E-mail: Peter.Behrens@mbox.acb.uni-hannover.de

[b] B. Henkelmann, Dr. K.-W. Schramm, Prof. Dr. D. Lenoir
Institut für Ökologische Chemie
GSF-Forschungszentrum für Umwelt und Gesundheit
Ingolstädter Landstr. 1, 85764 Neuherberg (Germany)

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Table 1. Abbreviations and number of congeners for differently substituted PCDD/Fs.

Chlorine substitution	Number of PCDDs		Number of PCDFs	
mono	MCDD:	2	MCDF:	4
di	DiCDD:	10	DiCDF:	16
tri	TriCDD:	14	TriCDF:	28
tetra	TCDD:	22	TCDF:	38
penta	PCDD:	14	PCDF:	28
hexa	HxCDD:	10	HxCDF:	16
hepta	HpCDD:	2	HpCDF:	4
octa	OCDD:	1	OCDF:	1
Σ		75		135

chlorodibenzo-*p*-dioxin is a known human carcinogen, and other dioxins are likely human carcinogens. Dioxins also adversely affect the development of fetuses, the endocrine and immune system. The different toxicities in living beings can be ascribed to the different affinities to a receptor system, the aryl hydrocarbon receptor (AhR).[1e,2] Although current research on the specifity of the congener–receptor relation focuses on electronic interactions,[3] the stereochemical fit, regulated by the size and the shape of the molecule, will also have a strong influence. By crystal structure analysis the unsubstituted dibenzo-*p*-dioxin and the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin[4a] as well as the corresponding furan[4b] were shown to be nearly planar. Different substitution patterns influence the lengths and the widths of the molecules, whereas their height is fairly constant (for a definition of the length, width and height of dioxin molecules as used in this paper, see Figure 1).

A major source of dioxins is industrial combustion processes, especially in waste incinerators. The regulations on dioxin emissions are strict and complex. Today, adsorption by materials based on activated carbon is the standard method for the removal of dioxins from waste incinerators. Activated carbon has a high adsorption capacity[5] and a high affinity for dioxins;[6] it is also a relatively cheap sorbent material. However, there are also disadvantages as the fire hazard due to the formation of hot spots, the adsorption of water, difficulties in the regeneration of active carbon and, therefore, in the waste disposal of the highly contaminated adsorbent material.[7]

Consequently, a variety of different materials has been tested as sorbents for dioxins: γ-Al_2O_3,[6] clays as bentonite and laptonite[6] as well as pillared clays,[8] a variety of zeolites[5,6,9,10] and, recently, also carbon nanotubes.[11] Among the zeolites tested were synthetic zeolite Y,[6] natural zeolite clinoptilolite,[6] a volcanic rock called phonolite containing 45% zeolite[9] and the zeolite Wessalith DAY.[10] The last zeolite is a Y-type zeolite from which the framework aluminium atoms have been removed post-synthetically. Wessalith DAY consists of a faujasite-type framework of pure silica, which contains, in addition to the crystallographically defined micropores, also mesopores. The application of a pure silica zeolite is advantageous due to the fact that pure silica frameworks are strongly hydrophobic and excellent sorbents for unpolar organic substances as dioxins.

Zeolites belong to the class of microporous solids[12] and are applied in a number of industrially important sorption and separation processes.[13] The separation of molecules can be influenced by electronic interactions, but is typically governed by size and shape considerations, which is why zeolites (and other similar substances) are called “molecular sieves”. Apart from the separation of small molecules (as in the separation of air into N_2 and O_2), a variety of mixtures of larger organic molecules can be separated over zeolites, the most prominent example possibly being the separation of branched and unbranched alkanes. However, separation attempts on a mixture as complicated as that liberated by typical dioxin sources have not been reported so far.

Whereas dealuminated Wessalith DAY is an effective sorbent for dioxins,[10] it is not well-suited for separation purposes, due to the ill-defined pore system of micro- and mesopores. However, there exists a class of zeolite-type solids with a pure silica framework, the so-called zeosils.[14] Their framework is generated by structure-directed synthesis by using organic or organometallic compounds as structure-directing agents.[15–17] Therefore, their structure is regular and their pore systems are well-defined.

In the work presented here, we have used three zeosils with different pore diameters for the selective sorption and separation of PCDD/Fs. Figure 2 shows the structures of UTD-1 (framework type DON for the variant synthesised in a fluoride medium),[18] SSZ-24 (AFI)[19] and ITQ-4 (IFR).[20] All three of them possess one-dimensional pore systems. Their static pore diameters[21] (Figure 2) have been chosen to fall into the size regime of the width of dioxin molecules. Due to the large number of congeners and the similar chemical properties of PCDD/Fs, analytical investigations of dioxins are very complex and time-consuming. A separation into different size groups by molecular sieving could simplify the

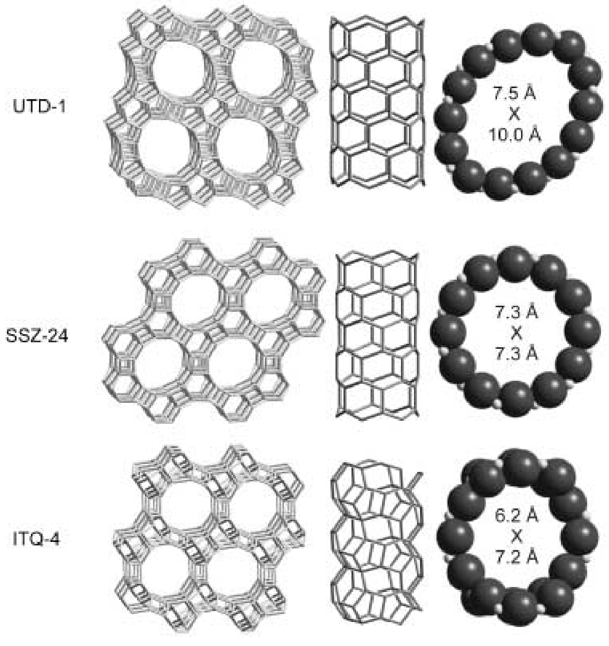

Figure 2. Crystal structures and pore sizes of zeosils. On the left the framework topologies are shown. In the central column the topologies of the channels are shown. Oxygen atoms are omitted for clarity. On the right, the arrangements of the Si and O atoms around the circumference of the channels are shown and the static pore diameters are given.

analysis of dioxins. Such a procedure would also be of special interest, as the selection due to size and shape should bear some similarity to the biological selection exerted by the AhR receptor.

Results and Discussion

The separation experiments were carried out with an arrangement as shown in Figure 3. A dioxin-loaded nitrogen stream passes in sequence over the zeosils ITQ-4 (with the smallest pore diameter), SSZ-24, and, finally, over UTD-1 (with the largest pore diameter). The sorption experiments took place at a temperature of 300 °C.

Figure 3. Schematic set-up of the sorption experiments.

The sequence of the zeosils in this experimental arrangement was of course chosen according to the principles of size- and shape-selective sorption. In order to rationalise the results of the selective sorption experiments described further below, it is therefore necessary to first investigate the relevant geometric parameters. With regard to the shape of the zeosil pores, it is clear that for noncircular ones the largest open diameter of the aperture is relevant. Due to the flat shape of the PCDD/F molecules, it is evident that it is the width of the molecules that is decisive as to whether these molecules can enter a pore system, whereas the length and the height are unimportant. Size considerations are more complicated. In addition to purely geometrical calculations, we have also carried out molecular dynamics investigations on the zeosil frameworks as well as on the dioxin molecules.

Size considerations for zeosil pores: The pore diameters given in Figure 2 are static diameters derived from structural analysis. As the sorption experiments were carried out at 300 °C, the dynamics of the zeosil frameworks at 300 °C were calculated with the molecular modelling program Cerius^2 from MSI. The distances of opposite oxygen atoms in the circumferences of the pores were determined and are plotted in Figure 4. For the symmetric pore of SSZ-24 it is evident that the most probable diameter of the channel is 7.3 Å. The diameter distribution follows a Gaussian function. Accordingly, 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 determine the largest dioxin molecules that can be sorbed based on size considerations and are thus most relevant. Thus, the dynamic pore diameters are 7.0 ± 0.4 Å for ITQ-4 and 10.6 ± 0.6 Å for UTD-1.

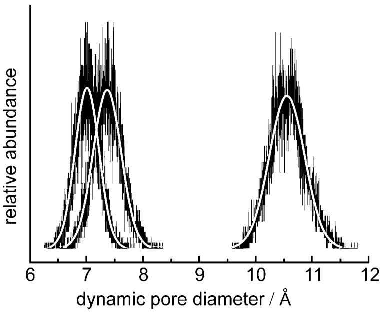

Figure 4. Pore diameters of ITQ-4 (left), SSZ-24 (centre), UTD-1 (right) according to molecular dynamics calculations.

These values correspond to the usual definition of the effective pore diameter.[21] However, the flat dioxin molecules can also use an orientation whereby they make use of the additional space provided by the indentations between the oxygen atoms; that is, the peripheral atoms of the dioxin molecules do not point directly at the oxygen atoms, but nestle between two of them (Figure 5). When the PCDD/F molecules acquire such an orientation, the relevant pore diameter is larger than the effective pore diameter by approximately 0.2–0.4 Å. Because the covalent radius of hydrogen is smaller than that of chlorine, this nestling effect is more pronounced for those PCDD/Fs with hydrogen atoms in positions 1, 4, 6 and/or 9 than for PCDD/Fs which exhibit chlorine atoms in these positions.

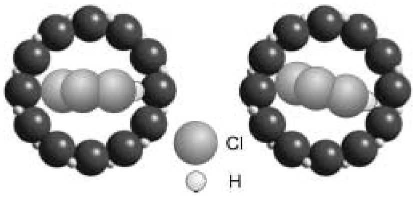

Figure 5. Schematic depiction of the "nestling" effect which takes into account that molecules entering a zeosil channel may make use of the indentations between the framework oxygen atoms surrounding a pore. In the orientation shown on the left-hand side, there is overlap between a dioxin molecule (e.g., 1,2,3-dibenzodioxin) and the pore wall, whereas in the orientation on the right-hand side, the molecule can enter the channel.

Size considerations for dioxin molecules: In a first approximation, dibenzo-*p*-dioxin molecules can be grouped into three size classes according to the chlorine substitution pattern (Figure 6). Basically, PCDD molecules of the first group do not possess any chlorine substituents in the positions 1, 4, 6 and 9; the width of these "slim" molecules is around 7.4 Å. Molecules of the third group carry chlorine atoms in these positions on opposing sides of the aromatic systems; these "fat" molecules have a width of about 9.9 Å. The molecules of the intermediate group possess widths which lie in between, at approximately 8.6 Å.

Some refinements can be applied to this simple model. For some specific substitution patterns of PCDDs and PCDFs, arrangements can be found which reduce the width of these molecules and may allow them to pass a small zeosil channel. As an example, Figure 7 shows 1,2,6-

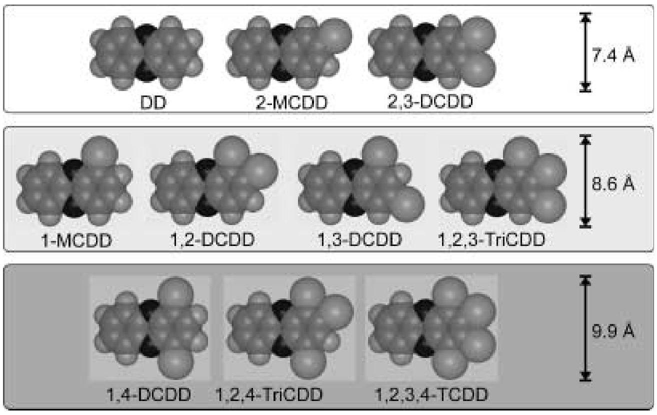

Figure 6. Distinction of dibenzo-*p*-dioxin molecules into three different size classes (shown by way of example for chlorine substitution in positions 1, 2, 3 or 4).

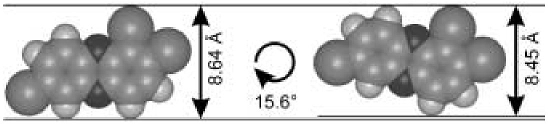

Figure 7. The effective width of 1,2,6-TriCDD, a member of the second group of medium-sized dioxins, is reduced from 8.64 Å to 8.45 Å by a rotation by 15.6° versus the orientation shown on the left-hand side.

TriCDD, a member of the second group of medium-sized dioxins: By a rotation by 15.6°, the effective width is reduced from 8.64 Å to 8.45 Å, that is, by 2.2%. The largest reductions in width are obtained for 1-MCDD, 1,2-DCDD, 1,6-DCDD, 1,7-DCDD, 1,2,6-TriCDD, 1,2,7-TriCDD and 1,2,6,7-TCDD, that is, molecules in which the positions 3,4,8 and 9 are not chlorinated.

The mentioned widths are estimated by taking the distance between the centres of the atoms at positions 1 and 4 and adding the corresponding effective ionic radius for hydrogen (1.20 Å) or chlorine (1.81 Å).[22] Using the values given by Nyburg et al.[23] for nonspherical atoms bonded to carbon atoms (H: 1.01 Å, Cl: 1.58 Å), the calculated sizes for the PCDD/F molecules decrease by approximately 0.4 Å.

For some of the PCDD/F molecules, molecular dynamics were also calculated at 300 °C. The variation of the distance measured between the atom at the 1-position and that at the 4-position, plus the corresponding effective radii for the atoms at these positions, is shown in Figure 8 for 2,3-DCDD, 1,2-DCDD and 1,4-DCDD, as representatives for the three size classes. In a similar way, the dynamic size of some PCDFs dibenzofuranes was obtained (Figure 9). The results are summarised in Table 2. They show that in extreme conformations the width of dioxin molecules is reduced by approximately 0.2 Å.

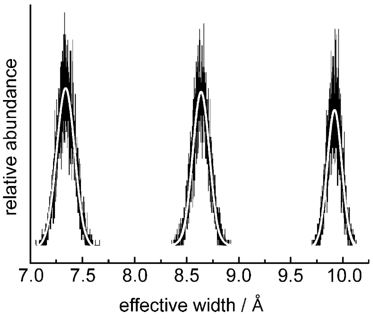

Figure 8. Molecular dynamics calculations on dibenzo-*p*-dioxins. Shown is the variation of the distance measured between the atom at the 1- and 4-positions, plus the corresponding effective radii for the atoms at these positions. Left: 2,3-DCDD; centre: 1,2-DCDD; right: 1,4-DCDD.

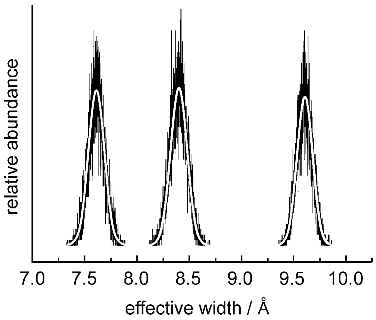

Figure 9. Molecular dynamics calculation on dibenzofurans. Shown is the variation of the distance measured between the atom at the 1- and 4-positions, plus the corresponding effective radii for the atoms at these positions. Left: 2,3-DCDF; centre: 1,2-DCDF; right: 1,4-DCDF.

Table 2. Results of molecular dynamics calculations for selected dibenzo-*p*-dioxin and dibenzofuran molecules. The average width corresponds to the distance measured between the atoms at the 1- and 4-positions, plus the radii for the atoms at these positions. The values are given for effective ionic radii (w_e)[22] and for nonspherical radii (w_n).[23] The half-width of the distribution is also given.

Congener	w_e [Å]	w_n [Å]	half-width [Å]
2,3-DCDD	7.34	6.96	0.20
1,2-DCDD	8.65	8.23	0.19
1,4-DCDD	9.94	9.48	0.17
2,3-DCDF	7.72	7.34	0.18
1,2-DCDF	8.51	8.09	0.19
1,4-DCDF	9.74	9.28	0.17

Finally, Figure 10 compares the dimensions of the zeosil pores and of three representatives of the different size classes for PCDD and PCDF molecules, respectively. The upper limit for the zeosil pores is calculated based on the static pore diameter, adding the half-width of the pore-width distribution from the molecular dynamics calculation and 0.3 Å as an average for the nestling effect, which is due to the fact that the peripheral atoms of the dioxin molecules may point in between the oxygen atoms of the framework. The lower size limit for the PCDD/F molecules is calculated from the static width obtained by employing the (smaller) radii for nonspherical atoms[23] and subtracting the half-width of the size distribution as obtained by the molecular dynamics calculations. The reduction in width due to rotation, which applies only to some congeners with specific substitution patterns and can attain values up to 0.2 Å, is not included here.

According to this theoretical comparison, the PCDD/F of the smallest group fit into all three zeosils used and should

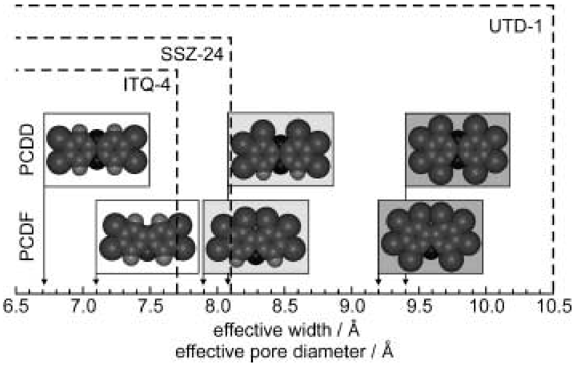

Figure 10. Comparison of the relevant pore diameter of the zeosils ITQ-4, SSZ-24 and UTD-1 with the widths of selected PCDD and PCDF molecules (see text). Upper row: 2,3,7,8-TCDD, 1,2,3,7,8,9-HxCDD and OCDD; lower row: 2,3,7,8-TCDF, 1,2,3,7,8,9-HxCDF and OCDF.

in the experimental setup used become sorbed on ITQ-4. The PCDD/F of the medium group should fit into SSZ-24 and UTD-1. The sorption of PCDD/Fs on SSZ-24 represents a borderline case and it will be especially interesting to investigate this experimentally. The members of the third group, and even the largest of them, should become sorbed on UTD-1.

Studies of selective sorption: After the sorption experiments, the zeosils were recovered, extracted and digested. The combined extracts were treated to obtain the sorbed dioxins, which were then analysed by using conventional procedures (see Experimental section). The final step is a chromatographic analysis for which some isomers have identical or very similar retention times. These were discarded from the following analysis in which we use only those peaks of the chromatograms that are unequivocally ascribed to one single congener.

All the PCDD/Fs of the group of small molecules should become adsorbed on ITQ-4, whereas the larger ones should pass this stage of the sorption experiment. Figure 11 shows the contents of those mono- to tetrachlorinated PCDD/Fs, which belong to the group of slim molecules, in the different zeosils. The tri- and tetrachlorinated dibenzo-*p*-dioxins and dibenzofurans of this group are adsorbed nearly completely on ITQ-4, whereas, unexpectedly, the mono- and dichlorinated PCDD/F molecules are only partially adsorbed on this zeosil. Part of them pass this zeosil and travel on to the SSZ-24 stage and is sorbed there. This deviation from the expected sorption behaviour can be ascribed to the high volatility of the low chlorinated PCDD/F molecules. For example, 2-MCDD has a melting point (T_m) of 87–90 °C and a boiling point (T_b) of 298–316 °C.[24] Thus, the low chlorinated PCDD/F molecules cannot enter the pores of ITQ-4 (or are sorbed and become desorbed again), but condense on SSZ-24 (due to a temperature gradient in the oven, the temperature should be somewhat lower at this stage). This problem could in principle be solved by using a more sophisticated, specially adapted temperature profile within the oven.

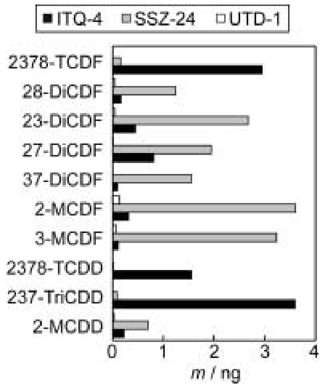

Figure 11. Contents of those mono- to tetrachlorinated PCDD/Fs, which belong to the first group of slim molecules, in the different zeosils.

Figure 12 shows the contents of PCDD/F molecules belonging to the group of medium-sized entities in the different zeosils. As can be read from Figure 10, these molecules have sizes located at the borderline of the pore size of SSZ-24. In fact, the experiments show that SSZ-24 finely differentiates between different members of the group of medium-sized PCDD/F molecules. Figure 12 is subdivided into several diagrams. The diagrams on the left-hand side show these PCDD/F species that become sorbed on SSZ-24, the figures on the right-hand side contain those which cannot enter the pore system of SSZ-24. The two upper diagrams present the PCDD molecules under discussion, the four lower ones the PCDF species. In Figure 13, PCDD and PCDF molecules representative of both subgroups are shown. In general, those molecules that are not sorbed on SSZ-24 appear to be bulkier than those that can enter the pores of this zeosil. In fact, the experimentally observed differentiation of the group of medium-sized molecules into two subgroups can largely be traced back to differences in the substitution patterns: PCDD congeners that are not chlorinated at the 4- and 6-positions become adsorbed on SSZ-24, whereas those which contain chlorine atoms at the 1- and 6-positions are not. However, there are some exceptions to this simple rule. Especially puzzling is the fact that 1,2,3,7,8,9-HxCDD is sorbed into SSZ-24, whereas 1,2,3,7,9-PCDD evidently does not fit into the pores of this zeosil, although the additional chlorine substitution at the 8-position of the former does not change the relevant dimensions. Similar simple substitution pattern rules also govern the differentiation of the PCDF species: those not substituted simultaneously in the 4- and 6-positions are mainly adsorbed by SSZ-24 (with the exception of 3,4,6,7-TCDF, which also has a puzzlingly high concentration on ITQ-4), whereas the congoners that possess chlorine atoms in the 1- and 6-positions are not (with two exceptions: 1,2,3,6,7-PCDF and 1,2,6,7-TCDF). The simultaneous substitution at the 4- and 6-positions is especially crucial in the case of PCDFs, because these chlorine atoms decorate the large angle between the two benzene rings of the PCDF entity and thus increase the width of PCDFs significantly. This crucial role is nicely illustrated by a pair of PCDF molecules: although highly chlorinated, 2,3,4,7,8-PCDF becomes adsorbed on SSZ-24 (due to its special substitution pattern), 2,3,4,6,7,8-HxCDF cannot enter the pores of SSZ-24 (see Figure 13, bottom row).

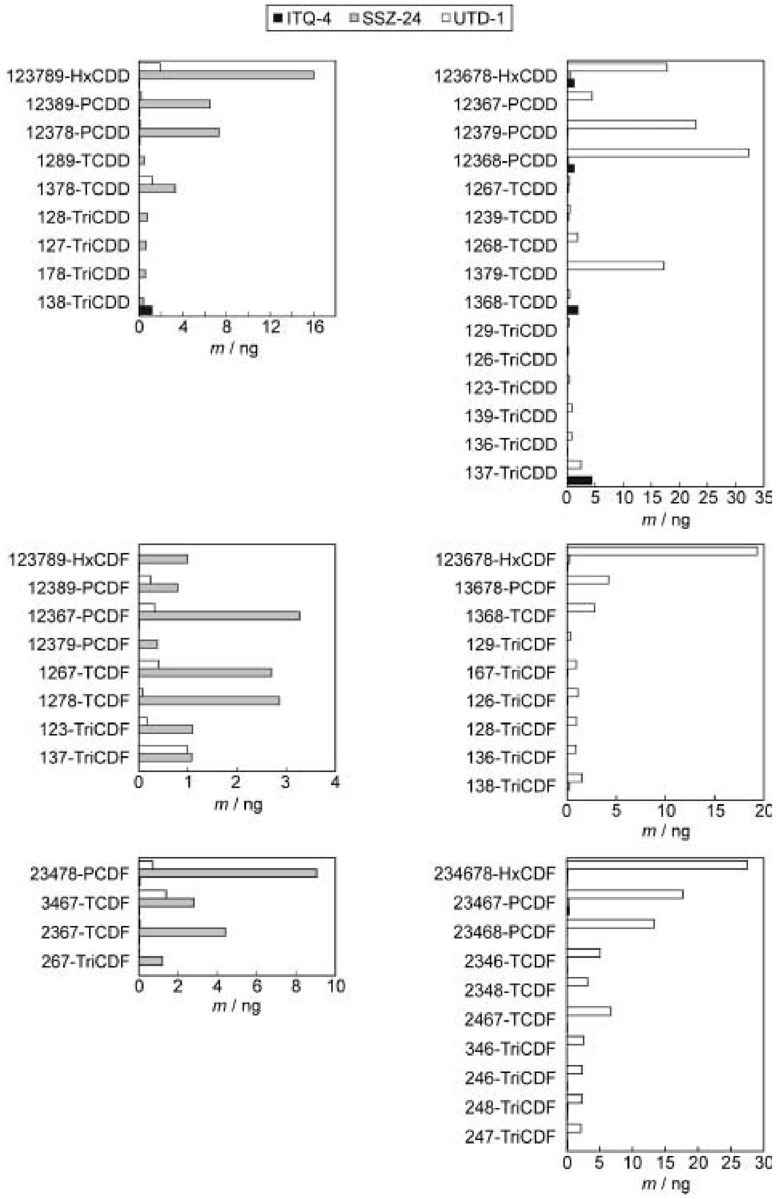

Figure 12. Contents of the PCDD/Fs belonging to the group of medium-sized molecules in the different zeosils. The upper two diagrams display the PCDDs; the central row shows PCDFs substituted at the 1-position, and the bottom row those PCDFs not substituted at the 1-position. Left column: PCDD/Fs that are sorbed on SSZ-24; right column: PCDD/Fs that are not.

Finally, the PCDD/Fs of the group of "fat" molecules all become adsorbed on UTD-1 (Figure 14). Small amounts of highly chlorinated isomers found on SSZ-24 and ITQ-4 are probably due to condensation of these molecules at the outer surface of these zeosils, as a result of their very low volatility.

We did not find dioxins in the gas stream after the passage through the zeosil arrangement, that is, all dioxins were adsorbed on the molecular sieves.

The last fact is in line with earlier findings that zeolites[5,6,9] and dealuminated zeolites[10] are excellent sorbents for dioxin molecules (provided that their pore openings are large enough). This should be all the more true for zeosils with their pronounced hydrophobic properties. None of these previous investigations, however, made use of the molecular sieving properties of zeolites. Our work shows that these properties can be favourably exploited even on such a complex class of molecules as dioxins. Most of the separations are highly efficient (only few congeners are sorbed in significant amounts on more than one zeosil).

In general, the distribution of PCDD/Fs can be explained by shape and size considerations, if—in addition to purely static diameters—several effects (dynamics of the zeosil frameworks and the organic molecules, possibility of "nestling" orientations, specific substitution patterns of dioxin molecules, use of radii for nonspherical atoms) are taken into account. Some deviations of the sorption behaviour from this purely geometric model can be ascribed to the differences in volatility of the PCDD/Fs. Due to the large range this property spans (2-MCDD: $T_m = 87$–$90\,°C$, $T_b = 298$–$316\,°C$; OCDD: $T_m = 318$–$332\,°C$, $T_b = 510\,°C$),[24] it is difficult to find an optimum temperature for the sorption experiments. By increasing the temperature, highly volatile PCDD/Fs will be even more prone to pass that zeosil in which they should become sorbed and will be transferred to the subsequent stage in the arrangement of zeosil sorbents; whereas, upon decreasing the temperature, the danger arises that congeners of low volatility can condense on the outer surfaces of the primary stages of the arrange-

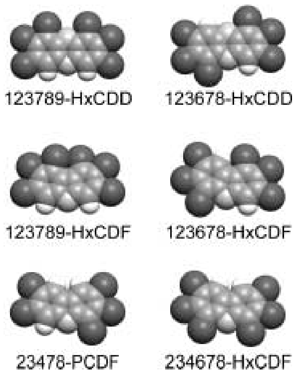

Figure 13. Comparison between PCDD/F molecules that are sorbed on SSZ-24 (left-hand side) and those which are not retained on SSZ-24, but are sorbed only by UTD-1 (right-hand side). The most highly chlorinated congener of each of the six diagrams of Figure 12 is shown.

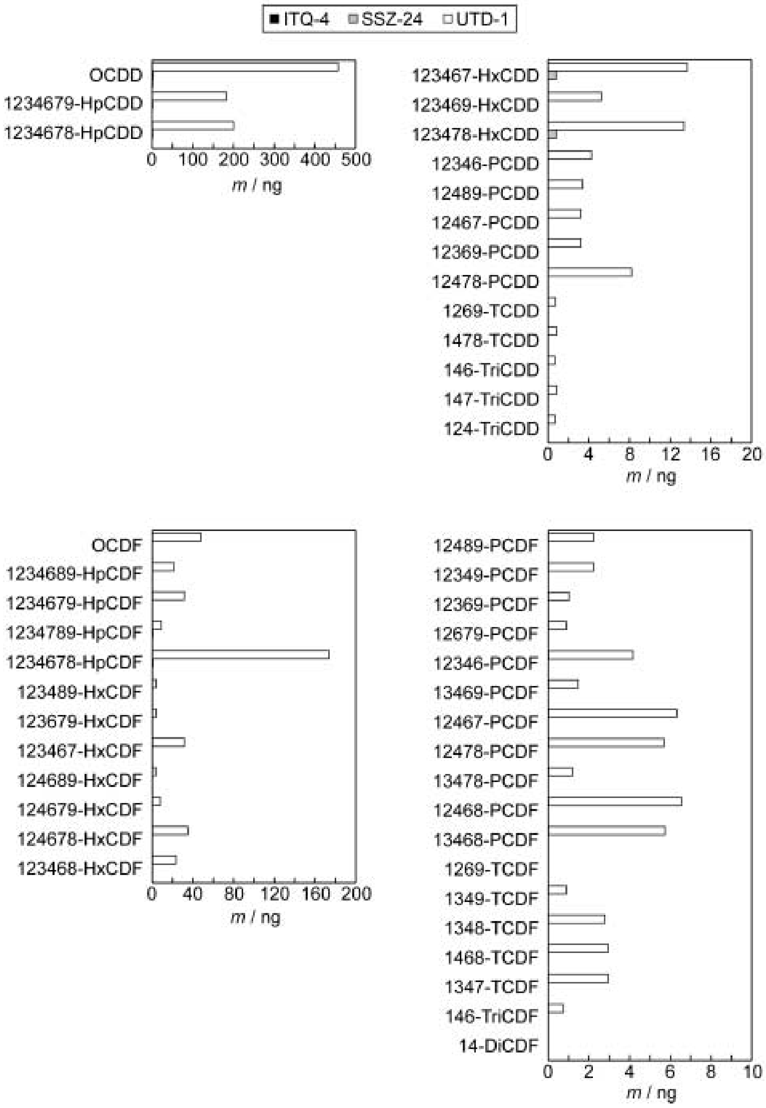

Figure 14. Contents of the PCDD/Fs belonging to the group of "fat" molecules in the different zeosils. The upper two diagrams display the PCDDs, the lower two the PCDFs.

ment. A possible solution to this problem could be the integration of a zeosil with pore characteristics that are especially well suited to sorb the highly volatile dioxin molecules, so that the volatility of these PCDD/Fs is overcome by an increased sorption enthalpy.

The possibility of condensation of PCDD/Fs on the outer surface of zeosils was verified in an accompanying test experiment (carried out at 240 °C). For this purpose, silicalite-1 with the MFI structure type[25] was introduced as a sorbent. As expected, the pores of this zeosil with its three-dimensional channel system of ten-membered ring apertures are too small for the sorption of even the smallest dioxins. However, the highly chlorinated dioxins with low volatility (e.g., OCDD and the HpCDDs) condense on this zeosil to a large extent.

In addition to these deviations from the geometrical model, which can be ascribed to differences in volatility, there are puzzling results for a few other dioxin molecules. These cannot be explained at the moment. In view of the large number of PCDD/F congeners and their chemical similarity, however, it must be stated that zeosils have clearly demonstrated their power in separation tasks. Especially noteworthy is the fine-tuned discrimination between molecules of very similar size, shape and chemical properties displayed by SSZ-24. This zeosil separates the species of the group of medium-sized molecules into two subgroups, whereby the smaller ones are sorbed on SSZ-24, while the larger become sorbed only at the last stage, UTD-1. There, they are found together with all the molecules of the group of large dioxin species. Of course, it would be interesting to separate the PCDD/Fs sorbed on UTD-1 into the two different size classes. The zeosil CIT-5 should be able to accomplish this task. CIT-5 is a zeosil with pores circumscribed by 14-membered rings.[26] The pores, however, are deformed, so that the static pore diameter of CIT-5 falls in between that of SSZ-24 and UTD-1, and thus also between the groups of medium-sized and large PCDD/F molecules. However, when we replaced SSZ-24 with CIT-5 in an experiment similar to the one described here, we obtained an unexpected result. This zeosil adsorbed all those molecules which had passed the ITQ-4 stage. In other words, CIT-5 was also able to adsorb the PCDD/Fs of the large group; therefore the sorption behaviour of this zeosil is similar to that of UTD-1. This result contrasts also with the behaviour of these two zeosils in the sorption of 1,3,5-triisopropylbenzene, a molecule with a kinetic diameter of 8.5 Å. This large molecule is sorbed by UTD-1, but not by CIT-5.[27] Possibly, a zeosil with 13-membered ring pores would be able to accomplish the intended separation. No such zeosil, however, has been described so far, and, in general, large rings with an odd number of tetrahedra (>6) seem not to be favoured. Only SSZ-23 with a nine-membered ring is known.[28]

Finally, the deviations from the sorption behaviour expected on the basis of size and shape considerations could also have another reason. We are not able to exclude the possibility that some assignments of PCDD/F molecules to the peaks in the chromatograms obtained in the analytical work-up of dioxins could be wrong.

Conclusion

This work has shown that the separation of a complex class of hydrophobic substances as the dioxins is possible with high efficiency by using a judiciously chosen arrangement of zeosils. Our choice of zeosils has been optimised during several experiments, guided by size and shape considerations as well as by molecular dynamics calculations.[29] However, it has also become clear that the separation characteristics of our sorption system could be further improved if zeosils with some certain pore characteristics were available (e.g., a zeosil sorbing the PCDD/Fs of high volatility with large specifity, or a zeosil separating the large species of the group of medium-sized molecules from those of the group of large molecules). Therefore, the ongoing search for new zeosil structures is worthwhile, especially in the field of frameworks with large and ultra-large pores.[30] Eventually, a system of microporous sorbents might become available which mimics the recognition characteristics of natural molecular recognition systems as receptors or enzymes, where it is known that geometric factors as size and shape play an important role, too.[1e,2] Such a system could be of interest also for the separation of other hydrophobic, ecologically important substances, for example, those mimicking sexual hormones.

The preparation of the zeosils used in the present work is very expensive, mainly due to the valuable structure-directing agents used in their synthesis.[15–17] This precludes their application as large-scale sorbents in technical processes, as it does for recently introduced carbon nanotubes[11] for similar reasons. However, the separation of zeosils might improve current analytical techniques. The simplest approach to exploit the efficient selective sorption could be the pre-separation of dioxin congeners before the application of the current techniques of dioxin analytics. A zeosil, or a combination of them, might possibly also be used as a chromatographic material, although the morphology of the zeosil particles would have to be adapted.

The most interesting application, however, would be an on-line monitoring of dioxin concentrations. This aim has proven elusive so far.[1e] Bein et al.[31] have shown that is possible to anchor small zeolite crystallites onto a quartz micro balance (QMB) and have thus prepared sensor devices that react with the selectivity of a zeolite to very small mass signals, transducing them into electrical ones. Three such QMBs equipped with ITQ-4, SSZ-24 and UTD-1 zeosil crystals, respectively, exposed on-stream to a dioxin-containing gas flow, could yield data for a semi-quantitative on-line analysis of PCDD/Fs. Branching the gas flow into three streams for the three QMBs, the ITQ-4-QMB would give the amount of small dioxin molecules, the SSZ-24-QMB would add up the concentrations of small and medium-sized PCDD/Fs, and the UTD-1-QMB would record the total dioxin contents. Also, a simple single ITQ-4-QMB operated at a temperature slightly higher than in the experiments described here (so that low chlorinated, highly volatile PCDD/Fs would not become sorbed at all) would probably mainly monitor the contents of the most toxic congener 2,3,7,8-TCDD. In real gas streams, additional substances will be present and might complicate the proposed approaches. Water, present in many gas streams to a large extent, would not be a problem due to the strongly hydrophobic nature of the zeosils. In exhaust gas streams from waste incinerators, other small organic molecules and $HgCl_2$ are present. To eliminate these substances, a preceding sorption stage of the zeosil silicalite-1, which is known to sorb small organic molecules[13] as well as inorganic[32] ones, could be helpful.

Experimental Section

Synthesis of the zeosils: The zeosils were synthesised according to literature procedures[33–35] that were slightly modified to yield larger homogeneous batches of materials. Template removal was achieved by calcination at 600 °C in air for several hours; in addition UTD-1 was treated with diluted hydrochloric acid in order to remove cobalt oxide remaining in the pores from the oxidation of the structure-directing agent, the decamethylcobalticinium cation.

Sorption experiments: In the sorption experiments, an extract of the fly ash of the municipal waste incineration München-Süd (July 18, 1991) was used as PCDD/F source. The fly ash was extracted with toluene by means of an accelerated solvent extraction (ASE 200, Dionex) apparatus at 200 °C and 140 bar. The standard clean-up for PCDD/F was performed with an acidic column (SiO_2/H_2SO_4 (44 %)) and an alox column. The PCDD/F cocktail was dissolved in dichloromethane and after addition of internal and external standards, the concentrations of PCDD/Fs were determined by GC/MS. 0.5 mL of the PCDD/F extract were given to 1.15 g of amorphous silica. The impregnated solid obtained after evaporation of the dichloromethane represents the PCDD/F source.

In the sorption experiment arrangement, a glass tube was placed vertically in an oven and was flushed by a stream of nitrogen (12 $mL\,min^{-1}$) from the lower end. The gas stream first passed the desorption stage of the PCDD/F source, which was placed in the centre of the glass tube. Upon heating the glass tube to 300 °C, the PCDD/Fs were desorbed and then flushed over the sequential arrangement of zeosils for adsorption. In this arrangement, 0.53 g ITQ-4, 0.37 g SSZ-24 and 0.55 g UTD-1 were used. The gas stream finally bubbles through a bottle filled with toluene. The toluene solution was also analysed for dioxins, but no PCDD/Fs were found there. 0.43 g of the loaded ITQ-4, 0.26 g of the loaded SSZ-24, 0.53 g of the loaded UTD-1 and 1.03 g of the silica of the PCDD/F source were recovered from the glass tube after the experiment.

Analysis for the PCDD/Fs: The analysis followed the usual methods for the analysis of dioxins, involving isotopic dilution, gas-chromatographic separation and mass-spectroscopic detection.[36] An internal isotopic standard consisting of 2,7-, 2,3,7-, 2,3,7,8-, 1,2,3,7,8-, 1,2,3,4,7,8-, 1,2,3,6,7,8-, 1,2,3,7,8,9-, 1,2,3,4,6,7,8- and 1,2,3,4,6,7,8,9-$^{13}C_{12}$-PCDD as well as 2,3,7,8-, 1,2,3,7,8-, 2,3,4,7,8-, 1,2,3,4,7,8-, 1,2,3,6,7,8-, 1,2,3,7,8,9-, 2,3,4,6,7,8-, 1,2,3,4,6,7,8-, 1,2,3,4,7,8,9- and 1,2,3,4,6,7,8,9-$^{13}C_{12}$-PCDF was used. Concentrations were in the range from 100 to 1000 $pg\,\mu L^{-1}$.

The recovered substances were first extracted and then digested in order to gather all the dioxins sorbed. Before the extraction, the internal standard (10 μL) was added. The extraction took place at the ASE with a mixture of acetone and hexane at 150 °C and 200 bar (four subsequent extractions, first two times for ten minutes and then two times for sixty minutes). Due to the purity of the zeosils and the PCDD/F cocktail used as dioxin source, the usual clean-up procedure necessary for solid samples could be reduced. The samples were eluted over a mini-alox column (Olson). Then, 10 μL of an external $^{13}C_{12}$-1,2,3,4-TCDD standard were added.

After the extraction, the residual zeosil samples and the residual PCDD/F source were digested with hydrofluoric acid (40 %) in teflon-lined steel autoclaves at 70 °C overnight. The solutions obtained were neutralised with sodium hydroxide. Then, the internal standard (10 μL) was added and the mixture was stirred with toluene (80 mL) overnight. The toluene phase was separated from the water phase with a separatory funnel and dried over sodium sulfate. For the clean-up, a mini-alox-column (Olson) was used and the $^{13}\mathrm{C}_{12}$-1,2,3,4-TCDD external standard (10 µL) was added.

The isomer-specific PCDD/F separation was performed using a gas chromatograph Agilent 6890 from Hewlett Packard equipped with a Restek Rtx-2330 column. The isomer-specific detection of PCDD/F was performed using a mass spectrometer MAT 95S from Finnigan.

Structural and molecular modelling: Modelling calculations were performed on Silicon Graphics Octane and Silicon Graphics O2 workstations. Computational results were obtained using software programs from Accelrys. Energy minimisation and dynamics calculations were performed with the Discover program using the COMPASS force field. Graphical displays were generated with the Cerius^2 molecular modelling system.

As starting structures and for comparison, the global minimum-energy conformations of the dibenzo-*p*-dioxins and dibenzofurans were determined for the undisturbed molecules by gas-phase minimisations. For this purpose, a quenched dynamics (QD) calculation was performed at elevated temperature. Quenching was performed every 100th step by employing a combination of a steepest descent, a conjugate gradient and finally a Newton-Raphson minimiser.

The molecular dynamics (MD) simulation was carried out at 450 K for 100 ps (step width 0.001 ps, relaxation time 1 ps, n,p,T = constant) in order to determine the effective width of the molecules. In general, the effective width is the distance between the atom centres of substituents connected to C1 and C4 plus the effective atomic radii of the substituents ($r_{\mathrm{eff}}(\mathrm{H}) = 1.2$ Å, $r_{\mathrm{eff}}(\mathrm{Cl}) = 1.8$ Å, see Figure 6). However, this value may be reduced by a rotation (see Figure 7). The effective width was calculated for every 100th frame of the MD trajectory.

The effective pore diameters of the silica host materials were determined in a similar way. As a starting model, the lattice parameters and atomic positions of the zeosil structures as described in the literature were used. However, the space-group symmetry of the host structures was reduced to *P*1 to avoid artefacts. The conditions chosen for the MD calculations of the zeosils were the same as for the organic molecules with a relaxation time of 0.1 ps. The effective pore diameter was calculated as the distance between the atomic cores of opposite oxygen atoms minus two times the effective ionic radius of the oxygen anion ($r_{\mathrm{eff}}(\mathrm{O}) = 1.4$ Å).

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