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"Molecules in Confined Spaces: The Interplay between Spectroscopy and Theory to develop Structure-Activity Relationships in the fields of Heterogeneous Catalysis, Sorption, Sensing and Separation Technology"

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Editorial Highlight

Editorial Highlight: Molecules in confined spaces

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Editorial Highlight: Molecules in confined spaces

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1. Introduction

At interfaces, the properties of molecules are different from those in the bulk gas phase or bulk liquid phase. Several observations make this clear: capillary rise and contact angles, as well as wetting. These are macroscopic phenomena, which are described by thermodynamics with the surface tension or the free energy change per unit surface area as the most important thermodynamic quantity.¹ Adsorption, or the tendency of a molecule to have a higher concentration at the interface (gas/liquid, gas/solid, liquid/solid and liquid/liquid) than in the adjacent bulk phases is measured by adsorption isotherms. The physical basis for adsorption is two-fold. On one hand, the surface contains coordinatively unsaturated atoms, functional groups (*e.g.* OH), exchangeable cations and defects. On the other hand, the adsorbate consists of molecules, which are non-polar, polar or ionic. As a consequence, a multitude of interactions may take place. In the case of physisorption, these interactions are typically intermolecular, namely ion–dipole, ion–apolar, dipolar–dipolar, dipolar–apolar and apolar–apolar. In the case of chemisorption, a chemical bond is established between the surface atoms and the adsorbed molecule.

The question is now what governs the physical chemistry of molecules when they are confined in spaces of molecular dimensions. In this Editorial Highlight to the themed *PCCP* issue “Molecules in Confined Spaces”, we wish to address this fundamental question by highlighting two particular aspects. The first concerns host–guest chemistry of molecules in confined spaces with particular emphasis on the properties of water, acid–base properties of guest molecules and the ion exchange of transition metal ion complexes. The second example focuses on heterogeneous catalysis, including the aspects of molecular diffusion, reactivity, shape-selective catalysis and pore curvature effects. As will be shown by the several studies covered within this themed issue, these aspects of molecular confinement are often encountered in various fields of chemical research.

2. Host–guest chemistry in confined spaces

2.1 Water in confined spaces

In confined spaces, *i.e.* in cages and pores of molecular dimensions, all the adsorbed molecules are more or less in

interaction with the surface. This has important consequences for the physical and chemical properties of the molecules adsorbed in micro- and mesopores. One of the more spectacular examples is the swelling of clay minerals by adsorption of water.² Swelling is the separation of successive layers of a clay mineral particle by adsorption of water in the interlamellar space. In the case of Na⁺ as an exchangeable cation, mono-, bi- and three-layers of water molecules are taken up successively, resulting in basal spacings of 1.25, 1.50 and 1.78 nm, respectively. In liquid water the amount of water molecules taken up in the interlamellar space is such that the clay mineral particles fall apart in elementary layers, which diffuse randomly in the liquid water. Such a swelling does not occur with the bigger monovalent cations (*i.e.*, K⁺, Rb⁺ and Cs⁺) because of their weaker ion–dipole (H₂O) interactions, nor with divalent cations (*e.g.* Ca²⁺). In the latter case, the ion–dipole interaction cannot fully overcome the ion–surface interactions and swelling stops with two water layers in the interlamellar space.

In the monolayer hydrate of a Na⁺-smectite all the water molecules are in the hydration sphere of the Na cations and in interaction with the surface oxygen atoms of the smectite. These water molecules are highly polarized by the electrical field of the Na cations and acidic. Upon adsorption of ammonia ammonium cations are formed,³ according to eqn (1):



Now, the charge of the clay mineral is compensated by NH₄⁺. In zeolites water molecules are confined in the microporous cages and pores and swelling does not occur. However, the number of molecules per cage is small and of the same order of magnitude as the number of exchangeable cations, as illustrated by the numbers of Table 1.⁴

Highly concentrated solutions are obtained in which there is no free water. It is then not surprising that this water does not freeze upon cooling; *i.e.*, there is no clearly defined freezing point. Upon removal of water from the zeolite cages the last water molecule in the coordination sphere of the exchangeable cation might dissociate according to:

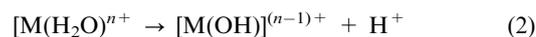


Table 1 Water and cations in the supercages of zeolites X and Y

Zeolite	Si/Al	Na ⁺ /UC ^a	H ₂ O/UC	Conc./M ^b
X	1.25	86	280	15
Y	2.50	56	280	7.7

^a UC = unit cell. ^b Equivalent molar concentration in the supercages.

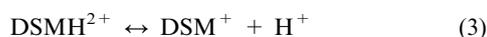
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The proton forms an acidic bridging hydroxyl group. The extent of eqn (2) increases with increasing polarizing power of the exchangeable cation M. For three-valent cations (e.g. La³⁺) eqn (2) is definitely shifted to the right. For monovalent and divalent cations a strongly polarized but not dissociated water molecule is in the first coordination sphere with characteristic OH stretching frequencies, depending on the type of cation.⁵

2.2 The concept of pH within confined spaces

Organic dye molecules are used as indicators of pH in aqueous acid–base chemistry. When such a dye molecule is adsorbed in the cages and channels of e.g. zeolites, similar acid–base equilibria are established and the “effective pH” of a cavity or pore can be estimated from the spectra of adsorbed indicators. This is exactly what has been studied by Calzaferri and coworkers for zeolite L with a one-dimensional twelve-membered ring (12MR) pore system (6). DSM⁺ was found to be an excellent indicator, because it is characterized by an intense absorption with maximum at 450 nm, as compared to the maximum of the protonated form, DSMH²⁺, at 330 nm. The pK_a of the reaction:



is 3.7. The spectra have a clear and unique isobestic point at 360 nm, which is indicative for the presence of two distinct species and thus the pH can be calculated from the spectral intensities, according to eqn (3). The results are summarized in Table 2.

One observes a relatively small variation of the pH with the lowest pH for Mg²⁺- and Ca²⁺-exchanged zeolite L. This is attributed to a contribution of water dissociation in the coordination sphere of these divalent cations (see eqn (2)). When dispersions of K⁺L are buffered at pH = 5, 6, 7 and 9 the DSM⁺ indicator reveals pH values in the same range as those of Table 2. The zeolite seems to act as a buffer, keeping the pH between 3 and 4. In the aqueous dispersion of the acidic zeolite L, H⁺L, the effective pH inside the 12MR channels, as probed by thionine, is –0.33 or equivalent to that of a 2.5 M HCl solution.⁶ These data are obtained spectroscopically on aqueous dispersions. If the system is in thermodynamic equilibrium, the chemical potential of the protons inside and outside the zeolite crystals must be equal and so is the pH. This is clearly not the case. Thus, the pH measured inside the channels of zeolite L is an effective pH, not the thermodynamic pH value.

Table 2 pH inside zeolite L crystals dispersed in water^a

Cation	pH
Li ⁺	3.45
K ⁺	3.38
Cs ⁺	3.68
Mg ²⁺	2.82
Ca ²⁺	3.10

^a The loading is 0.06 DSM⁺ per unit cell.

Eqn (3) must be rewritten as:



With $K_a = (a[\text{DSM}^{+}] a[\text{H}_3\text{O}^{+}]) / (a[\text{DSMH}^{2+}] a[\text{H}_2\text{O}])$
and a activities (5)

In eqn (5) the activity of water is explicitly taken into account, because with finite amounts of water the concentration of water in the channels of zeolite L is, according to eqn (4) not constant. The situation is similar to that in biological systems, for which the thermodynamics have been developed.⁷ It might be worthwhile to do the same for reactions involving water in micro/mesoporous systems.

2.3 Coordination chemistry of transition metal ion complexes within confined spaces

Ligands of transition metal ions might also undergo acid–base reactions in the micro/mesoporous systems of microporous and mesoporous solids. This is the case of N-containing ligands, such as ammonia, ethylenediamine (en) and histidine (his). In the preparation of the transition metal ion complexes in solution there is always excess ligand present, which, depending on the pH, might be protonated. It can therefore be exchanged together with the cationic complex.

A beautiful example is Cu(his)₂, which is prepared in solution with a his/Cu = 5.^{8–11} Upon exchange in the supercages of zeolite Y both the complexes and the protonated his ligands are exchanged. About 80% of his in the zeolite is ion-exchanged, 20% is complexed. From this an effective pH of 5 has been estimated in the supercages, to be compared with pH = 7 in the exchange solution. Thus, the effective pH in the zeolite is different from the pH of the equilibrium solution. This is similar to the observations of Calzaferri *et al.* with dye molecules.⁶

The complexes in the micro/mesopores are not necessarily the same as in aqueous solution. This is due to: (i) the effective pH, which is different from the solution pH; (ii) the competition with H₂O and surface oxygen atoms or surface hydroxyl groups for coordination; and (iii) the presence/absence of excess ligand. The first observations on these conceptual ideas^{12–15} show the stabilization of mono-complexes in the supercages of faujasite-type zeolites and of planar bis-complexes in the interlamellar space of smectites. In the latter case, the adsorption is accompanied by the loss of axially coordinated water molecules:



As a consequence, the maximum of the d–d absorption band shifts to higher wavenumbers, which is indicative for the extra-stabilization of the bis-complex on the clay surfaces. Also [Ni(en)₂(H₂O)₂]²⁺ complexes lose their axial water molecules on the clay surface turning them from pseudo-octahedral, high spin complexes in solution into diamagnetic, planar complexes on the clay surface.^{16,17} Similarly [Co(en)₂]²⁺ is planar and low spin on the clay surface.¹⁸

The stabilization of mono-complexes in the supercages of faujasite-type zeolites is confirmed by the study of Cu–his complexes. With a bis-complex in solution one finds mono- and bis-complexes in the supercages. The mono-complex is

preferred at low Cu content and the first coordination sphere of Cu is NNOO with NNO of his and one surface oxygen. The coordination sphere of the bis-complex is NNNO and surface oxygen atoms are not involved.^{8-11,19,20} Similarly with 3,3-bis(1-methylimidazol-2-yl)propionate (Mim2Pr) as a ligand mono- and bis-complexes are found in the zeolite supercages.²¹ In the mono-complex, the coordination sphere of Cu²⁺ is completed with two surface oxygen atoms.

Based on these characterization studies we can conclude that mono-complexes are preferred in zeolites and planar bis-complexes on clay surfaces. Three reasons can be advanced. (a) The chemical composition of the confined spaces (water, free ligand, protonated free ligand and complexes) is different from that of the exchange solutions. The equilibria shift accordingly. This is nicely shown by the exchange of the his complexes of Cu. The bis-complex is in a solution with his/Cu = 5, containing different types of his species. It is exchanged together with positively charged his molecules, while negatively charged and neutral his molecules are not adsorbed (or in very small amounts). The bis-complexes in the zeolite supercages will lose one his ligand to re-establish the equilibria. (b) The second reason is surface curvature. In zeolites there is not enough space in the channels and cages to stabilize planar bis-complexes. The complex has to lose one ligand to have the ideal geometry for maximum interaction with the surface. (c) The surface oxygen atoms of a zeolite have different chemical properties from those of a clay surface. The latter is a siloxane surface with little or no isomorphous substitution. The zeolite is a charged surface, due to the isomorphous substitution of Si by Al and the oxygen atoms have more coordination ability than those of the clay surface. Thus, the competition between *e.g.* H₂O and surface oxygen atoms for the coordination sites of an adsorbed transition metal ion is more in favor of the surface oxygen atoms in the case of the zeolite than in the case of clay minerals. The surface oxygen atoms of the clay surface have a lower coordination power.

3. Heterogeneous catalysis

For heterogeneous catalysis in confined spaces the central concept is shape selectivity. We distinguish reactant shape selectivity, product shape selectivity and transition state shape selectivity. The subject is treated in numerous book chapters and review papers.²²⁻²⁴ Theoretical investigations of the subject reveal the importance of adsorption of reactants, intermediates and products.²² For C₈-C₂₀ cracking the reactivity and the true activation energy are independent of the chain length of the hydrocarbon molecules. The adsorption enthalpy decreases drastically with chain length, because of the increase of van der Waals interactions. This strong adsorption puts a limit on the number of possible geometrical isomers in the adsorbed state and as a consequence the entropy of adsorption increases with chain length. Both effects compensate each other. This compensation effect is a clear function of pore size. Thus, the reactivity of n-alkanes as a function of chain length depends on the topology of the zeolites. This is a clear example of reactant shape selectivity. ZSM-11 has two straight 10-membered ring (MR) channels, while ZSM-5 has

one straight 10-MR channel and one zigzag 10-MR channel. The former adsorbs preferentially 2,4-dimethyloctane at the channel intersections, leading to isobutane upon cracking. The latter adsorbs preferentially 4,4-dimethyloctane at the intersections of the channels and this gives n-butane as the preferred cracked product. The difference in product distribution is a consequence of the difference in adsorption of the intermediates in the channel intersections. Such a phenomenon is called reaction intermediate shape selectivity. In general, zeolites form intermediates with low energy of formation in the adsorbed state. These intermediates are commensurate with the zeolite structure. The importance of the adsorption of intermediates in shape selectivity points to the importance of the thermodynamics of this adsorption process, but one cannot neglect the kinetics of the isomer formation either. Nevertheless, adsorption thermodynamics should be studied in catalytic conditions and this is what has been done by Denaeyer *et al.*^{25,26}

One can imagine that a catalytic reaction takes place at the active site. The reactants must approach the site in the right conformation for the reaction to occur. Now the geometry of the surface may come into the game in that a molecule and its environment tend to optimize their van der Waals interactions. The molecule nests itself into the zeolitic pore.²⁷ Another way to express this idea is the surface curvature effect, introduced by Derouane *et al.*^{28,29} The adsorption enthalpy of small hydrocarbons increases with decreasing pore size. As a consequence, in a zeolite with different pore sizes the small hydrocarbons tend to occupy first the pores with the smallest diameter. The center of the pore is never a stable adsorption position, except when the diameter of the molecule equals the diameter of the pore. Because the molecules adapt their configuration to the pore size and shape, they nest themselves in the pore mouth. The molecules have to overcome an energy barrier to diffuse in the pores and an equilibrium is established between the concentration of hydrocarbons outside the pores and inside the pores:

$$K_a = [\text{RH}]_i/[\text{RH}]_e \quad (7)$$

Where the subscripts i and e denote inside and outside the pores, respectively. The reaction rate constant inside the pores is then given by

$$r = k [\text{RH}]_i = k K_a [\text{RH}]_e \quad (8)$$

And the adsorption process is taken into account *via* the K_a . Also for the constraint index k_h/k_p , the ratio of the rate constants of n-hexane cracking and 3-methylpentane cracking, the difference in adsorption of both molecules has to be taken into account. For these small molecules the adsorption has little effect on the number of possible configurations in the adsorbed state. This is not the case for long chain hydrocarbons, as suggested in previous paragraphs.

With the rise of research on mesoporous materials the subject has been revived, mainly due to Haller and co-workers.^{30,31} They observed a decrease of the reduction temperature of lattice Co³⁺ and an increase of the amount reduced in Co-MCM-41 with increasing surfactant chain length, *i.e.* with increasing pore size. For V-MCM-41 the methanol oxidation

had a maximum turnover frequency (TOF) for pore sizes in the range 2.2–2.3 nm, while the formaldehyde yield was maximum for pore sizes around 2.4 nm and the yield of (CH₃)₂O for pore sizes of 2.5–2.6 nm. Co and V are substituted for Si in the structure of MCM-41. Because of the difference in size and in metal–oxygen bond length, both Co and V will be locally in a strained pseudo-tetrahedral configuration in the MCM-41 lattice. This strain might depend on the surface curvature, *i.e.* on the diameter of the pores. However, other factors come into play too and have to be investigated before definitive conclusions can be drawn. These factors are: (a) the tendency of transition metal ions to maximize their coordination number, also in ion exchange position in the cages and micropores of zeolites;³² (b) the dependence of the stability of the transition metal ions in the structure on the oxidation state; and (c) it is not clear whether the transition metal ions are in the structure of MCM-41 as isolated cations or whether they form dimeric, trimeric or polymeric structures in the MCM-41 structure.

In related studies,^{33,34} the effect of the pore curvature and chemical composition of the support oxide has been studied for the CO oxidation over supported metal nanoparticles. For this purpose, Pt nanoparticles have been loaded onto microporous (ITQ-1), mesoporous (Si-MCM-41, Si-MCM-48 and Si-SBA-15), macroporous (SiO₂) all-silica supports, as well as onto a macroporous SiO₂ support, impregnated with monovalent (Na⁺, Cs⁺) and divalent (Mg²⁺, Ba²⁺) cations, and zeolite Y ion exchanged with monovalent (Na⁺, K⁺, Rb⁺, Cs⁺) and divalent (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺) cations. It was concluded that chemical composition dominates over pore curvature and the *T*_{50%} for CO oxidation was almost entirely controlled by the basicity of the support material; *i.e.*, a more basic promoter element, such as Ba²⁺, leads to a lowering of the *T*_{50%}, regardless of the porosity of the support oxide.

4. Concluding remarks

We have briefly discussed the broad field of “Molecules in Confined Spaces” by highlighting two particular aspects, namely aqueous confined spaces with properties of water, acid–base properties and the ion exchange of transition metal complexes and non-aqueous confined spaces with special attention to diffusion, chemical reactivity and heterogeneous catalysis. It has been shown that the chemistry of aqueous confined spaces can best be treated from the viewpoint of the well-established aqueous solution chemistry. In doing so, the published data reveal three rather general characteristics of aqueous confined spaces:

(1) As in water, polyvalent cations are able to generate acidity by dissociation of water molecules under the influence of the strong electrostatic fields of the polyvalent cations.

(2) The number of water molecules in confined spaces is limited. Ions hydrated by these water molecules and dissolved molecules generate locally high molar concentrations. In reactions involving water, the amount of water cannot be considered as a constant as in dilute solution chemistry. The activity of water must be explicitly taken into account.

(3) The chemical composition of the confined spaces is different from that of the solution, due, *e.g.*, to preferential

adsorption phenomena. Equilibria shift according to this composition. This explains the preference for monocomplexes in the supercages of zeolites and for planar bis-complexes on clay mineral surfaces.

In heterogeneous catalysis a molecule diffuses within the cages and pores, is adsorbed, reacts and the related product diffuses out of the catalyst grain. Diffusion is implicitly contained in the concepts of reactant and product shape selectivities. Molecules diffusing in the pores of zeolites follow a tortuous path and eventually are adsorbed. The diffusion coefficients of these molecules will depend on the pore diameter, the path tortuosity and the adsorption processes. It is then of fundamental importance to determine diffusion coefficients in single crystals of zeolites.^{35–37} Adsorption determines the concentration of reactant molecules around the active sites. The relevant adsorption processes are then those that are measured in conditions as close as possible to the catalytic conditions of the reactants under study. Finally, the catalytic act requires the right configuration of the reactants around the active site to form the transition state complex. This is in most cases a local phenomenon, as evidenced by the success of high-level quantum-chemical cluster calculations.^{38,39} Such calculations require accurate experimental data for comparison purposes. Studies of single crystal catalysis, made possible by micro-spectroscopic techniques,^{35–37} can provide such data. Finally the single crystal catalytic data can be treated by *e.g.* periodic DFT calculations to obtain ideas about the importance of long range effects on catalysis.

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