Self-organization of extraframework cations in zeolites

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Structural properties of a series of mordenite and ZSM-5 zeolites with different framework Al distribution modified with oxygenated extraframework Ga, Zn, Al, Cu and Fe complexes were investigated by means of periodic density functional theory calculations. It is demonstrated that mononuclear oxygenated and hydroxylated cationic metal complexes in high-silica zeolites tend to self-organize into binuclear complexes. In the cases of Ga- and Fe-modified zeolites, it is shown that the catalytic activity of the most stable binuclear extraframework cations is much higher than that of the hypothetical very reactive mononuclear counterparts. This is due to a weaker binding of reaction intermediates and easier regeneration of the initial active complexes in the course of the catalytic reaction. The formation of multiple-charged binuclear oxygenated metal species in zeolites is a general phenomenon. It does not require a specific distribution of the equivalent number of negative framework charges that compensate for the positive charge of the cationic complexes. The location and the stability of cationic complexes in zeolite micropores are mainly determined by the coordination properties of the metal centres.

Keywords: zeolites; self-organization; catalysis; density functional theory calculations

1. Introduction

Zeolites and related materials are useful microporous matrices for creating well-defined isolated active sites in a controlled environment. These materials are extensively applied as selective catalysts for a wide variety of chemical processes (Weitkamp & Puppe 1999; Cejka et al. 2010). Their broad applicability results from the possibility to fine-tune their chemical and topological properties towards optimal performance for a particular chemical reaction. Zeolites are crystalline microporous materials containing cavities and channels of a molecular size with their framework composed of silicon-occupied oxygen tetrahedra.

By substituting some of the lattice silicon with other elements, well-defined catalytic sites can be created within the zeolitic micropores. This can readily result in highly efficient single-site catalysts. Important examples of such

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materials are the Lewis acidic Ti- and Sn-substituted zeolites. The introduction of highly dispersed Sn or Ti centres into the zeolite framework generates strong Lewis acidic single sites within the walls of the zeolite channels. The titanium-modified materials are able to selectively catalyse epoxidation of olefins with hydrogen peroxide (Corma & Garcia 2002; Boronat et al. 2006 and references therein). The introduction of isolated tetrahedrally coordinated Sn centres into the framework of a large-pore BEA zeolite gives rise to an unprecedented glucose isomerization activity (Román-Leshkov et al. 2010; Nikolla et al. 2011). The resulting catalytic system has recently been proposed as a key component of a process for the conversion of carbohydrates to a potential biorenewable platform molecule—5-hydroxymethylfurfural (Román-Leshkov et al. 2007).

The second approach is based on the utilization of more common zeolitic materials, in which the tetrahedral lattice silicons are substituted with aluminium. This generates a negative charge on the framework oxygens, which is compensated by extraframework cations. When the negative charge is compensated by protons, strong Brønsted acid sites are created within the zeolite channels. By replacing the protons with other species such as metal cations or cationic metal complexes, the catalytic properties of zeolites can be greatly varied. For example, the introduction of the Lewis acidic Zn or Ga cations into high-silica zeolites (Hagen & Roessner 2000; Bhan & Delgass 2008) induces dehydrogenation activity. Modification of zeolites with reducible Cu (Groothaert et al. 2005; Vanelderen et al. 2011) or Fe species (Panov et al. 1993; Zecchina et al. 2007) leads to uniquely selective oxidation catalysts, which are able to convert benzene to phenol and methane to methanol. The presence of extraframework Al (EFAI) species enhances the performance of zeolites in acid-catalysed reactions.

The chemical reactivity of such catalysts depends strongly on the type of metal introduced and the structure of the cationic complexes. The spatial separation of the reactive cationic species can be controlled by varying the density of framework aluminium. This together with the well-defined microporous structures renders zeolites as very attractive materials for the synthesis of tunable single-site heterogeneous catalysts. This can be achieved by using the surface organometallic chemistry approach (Copéret et al. 2003; Gajan & Copéret 2011; Rascón et al. 2011). In essence, this approach involves the use of the surface of a solid as a ligand to coordinate reactive metal centres. Well-defined catalytic sites are introduced by reacting a suitable metal-containing precursor with the surface hydroxyl groups or by selective substitution of other charge-compensating cations under controlled conditions. Similar to homogeneous catalysts, the coordination properties and the chemical composition of the thus formed surface species can be further modified by various chemical and thermochemical treatments.

As an example, the group of Gates replaced acac ligands in the coordination sphere of molecular transition metal precursor complexes with a crystalline zeolite. In this way, well-defined Rh- (Kletnieks et al. 2007; Liang et al. 2009) and Ir-containing (Lu et al. 2011a,b) zeolite catalysts were obtained for acetylene cyclotrimerization and ethene hydrogenation, respectively. Efficient site isolation was ensured by the very low density of framework Al in the parent dealuminated faujasite zeolite and low concentration of the introduced transition metal species. The isolated nature of the active sites provided molecular-level insight into the reaction mechanism and the role of both the solid support and the nature of the
complexes in the catalytic cycle. More important is that the fundamental insights obtained by using these single-site materials allowed design rules to be formulated for improved catalysts (Lu et al. 2011b).

Ultimately, the quantitative and selective substitution of all original charge-compensating cations (H$^+$ or Na$^+$) by well-defined catalytic sites is desired. Among the methods explored, the most frequently employed ones involve chemical vapour deposition of volatile and reactive precursors ranging from elemental metals to organometallic compounds onto the hydrogen form of zeolites.

For example, by reacting bridging hydroxyl groups in high-silica zeolites with vapours of metallic Zn (Kazansky & Serykh 2004; Kazansky & Pidko 2005a; Pidko & Kazanski 2005) and Cd (Serykh 2005) at a high temperature, their quantitative replacement by bare Zn$^{2+}$ and Cd$^{2+}$ cations at the zeolitic exchange sites was achieved. However, owing to the inhomogeneous distribution of pairs of framework aluminium, a substantial variation in the chemical reactivity of the introduced cationic species was observed.

It is often assumed that the position of the negatively charged aluminium-occupied oxygen tetrahedra ([AlO$_2$]$^-$) in the zeolite lattice defines, to a large extent, the location of the extrazeolitic cationic species. This model readily applies for univalent cations (e.g. H$^+$, Na$^+$, NH$_4^+$, etc.), which compensate the charge via their direct interaction with the [AlO$_2$]$^-$ lattice units. For cations with higher charge, this model requires close proximity of several framework aluminium substitutions. This requirement is generally not fulfilled by high-silica zeolites.

A useful and generally accepted structural model includes the presence of extrazeolitic oxygen-containing anions that coordinate to the metal (M), resulting in the formation of more complex cationic species with a formal charge +1 such as [M$^{3+}$=O$^2-$]$^+$, [M$^{2+}$−OH]$^+$, etc. An alternative ‘charge-alternating’ model involves indirect compensation of polyvalent cationic species by distantly placed lattice anionic sites. This concept has been put forward to rationalize the experimental findings for Zn- and Cd-modified high-silica zeolites (Pidko & van Santen 2007a,b). In these materials, only some of the M$^{2+}$ cations (M = Zn or Cd) directly interact with anionic zeolitic sites. A substantial fraction of the introduced cationic species is located in the vicinity of a single framework [AlO$_2$]$^-$ unit, while the other anion required for the overall charge neutrality is located at a longer distance, where it does not directly interact with the extraframework positive charge.

High-temperature reaction of acidic forms of zeolites with metal chlorides and oxides has also been proposed for the synthesis of well-defined microporous catalysts. For example, selective modification of high-silica zeolites by isolated mononuclear Cu$^+$ (Spoto et al. 1994; Kazansky & Pidko 2005b; Pidko & Kazansky 2005), ReO$_3^+$ (Lacheen et al. 2006, 2007) as well as dimeric [O=Zr−O−Zr=O]$^{2+}$ (Lacheen & Iglesia 2007) species has been reported. The lack of control over the modification procedure along with the uncertainties in the structural characterization of the resulting materials constitutes the major drawbacks of these approaches for the formation of single-site catalysts.

A more attractive method involves the formation of well-defined grafted organometallic precursors in the zeolite voids that can be subsequently transformed to different reactive complexes by selecting the appropriate post-synthetic activation procedure. In general, this approach involves a protolysis of metal–carbon bonds by zeolitic Brønsted acid sites that results in grafted species.
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with a general formula $[M-(R)_n]^+$. For example, chemical vapour deposition of trimethyl gallium $(\text{Ga(CH}_3)_3)$ onto the acidic form of high-silica ZSM-5 zeolite yields well-defined dispersed $\text{Ga(CH}_3)_2^+$ species compensating the negative charge of the zeolite framework (Hensen et al. 2005, 2007). A similar procedure has been used for introducing well-defined Fe (Long et al. 2007) and Zn (Almutairi et al. 2012) precursors into zeolites by reacting ferrocene and dimethylzinc, respectively, with zeolitic Bronsted acid sites. The grafted organometallic precursors are then decomposed to produce the desired well-defined catalytic species. This is usually done by high-temperature hydrogenolysis or oxidation. It is generally assumed that the reaction proceeds stoichiometrically with the preservation of site isolation. This assumption is particularly crucial when deducing the state of the reactive centres in the oxygen-treated catalysts that often demonstrate enhanced reactivity.

The direct oxidative elimination of the organic ligands is accompanied by water formation, which can result in hydrolysis of the metal complexes and thus cause the formation of hydroxylated mononuclear and clustered species in the zeolite voids. As a consequence, resolving the structure of complexes after oxidation is not always straightforward. Although usually the formation of isolated oxygenated $(\text{M=O}^+)$ or hydroxylated $(\text{M=OH}^+)$ mononuclear cationic complexes is proposed, such species may undergo self-organization into more complex multi-nuclear species driven by the excessive basicity of the terminal oxygen-containing ligands and the Lewis acidity of the cationic centres. As a result, various O- and OH-bridge structures can be formed with chemical properties and catalytic reactivity very different from their mononuclear counterparts.

Here, we will illustrate the importance and the general applicability of the self-organization phenomenon when applied to oxygen-containing cationic species in zeolites. By using periodic density functional theory (DFT) calculations, the structural properties, stability and reactivity of different extraframework cationic species in high-silica zeolite matrices will be analysed.

2. Self-organization of oxygenated extraframework complexes

We first consider the formation of oxygenated extraframework complexes in single-site Ga-modified high-silica zeolites. The well-defined grafted $\text{Ga(CH}_3)_2^+$ species formed by chemical vapour deposition of trimethylgallium onto acidic zeolites can be selectively converted into the catalytically active $\text{Ga}^+$ ions (Hensen et al. 2005, 2007). The oxygenation of these sites by a reaction with nitrous oxide leads to a pronounced enhancement of the alkane dehydration activity (Rane et al. 2006). Only a stoichiometric amount of $\text{N}_2\text{O}$ is consumed per Ga. This observation together with the relatively low density of grafting sites in the original zeolite $(\text{Si/Al}=20)$ originally led to a proposition that the species responsible for the enhanced catalytic activity are the isolated mononuclear gallyl ions, $\text{GaO}^+$. However, subsequent computational efforts to identify a plausible reaction mechanism to explain the increase of the alkane dehydrogenation activity by these oxygenated extraframework complexes were not successful (Pidko et al. 2007).

We used periodic DFT calculations to follow the formation of these complexes in a high-silica zeolite matrix with mordenite topology (Pidko et al. 2008,
Periodic mordenite models modified with extraframework cations were constructed by substituting two framework Si atoms with Al in a supercell obtained by doubling the monoclinic unit cell along the c-axis. The Si/Al ratio in this zeolite model was 23. Three different Al distributions in the framework were considered (figure 1a), resulting in three distinct models denoted below as MOR-I, MOR-II and MOR-III. In MOR-I, both anionic \([\text{AlO}_2]^−\) lattice units are part of a single eight-membered ring connecting the main channel and the side-pocket of mordenite \(r(\text{Al}_f−\text{Al}_f) = 7.86\,\text{Å}\). Although crystallographic positions of the Al substitution in MOR-II are exactly the same as those in MOR-I, the Al atoms in this case are located in the opposing eight-membered rings in the main channel \(r(\text{Al}_f−\text{Al}_f) = 8.74\,\text{Å}\). In model MOR-III, the Al ions are located in five- and six-membered rings of the zeolite wall distant from the side-pocket \(r(\text{Al}_f−\text{Al}_f) = 7.52\,\text{Å}\).

The stability of the initial \(\text{Ga}^+\)-containing mordenite models is almost independent of the distribution of framework Al in the zeolite. Stoichiometric oxidation of the \(\text{Ga}^+\) sites with \(\text{N}_2\text{O}\) to isolated \(\text{GaO}^+\) species is slightly
exothermic. The DFT-computed reaction energies range from $-27 \text{ kJ mol}^{-1}$ for MOR-I to $-50 \text{ kJ mol}^{-1}$ in the case of the MOR-III model. The coordination properties of the Ga centres in these gallyl ions are very similar for all models.

From an inorganic chemistry perspective, the tridentate coordination of Ga$^{3+}$ cations and the presence of terminal O ligands are not the most stable configuration (Robinson 2003). Indeed, these complexes can be very strongly stabilized by their self-organization into an almost square–planar [Ga($\mu$-O)$_2$Ga]$^{2+}$ cluster. The formation of such species lowers the total energy by 437, 291 and 67 kJ mol$^{-1}$ for models MOR-I, MOR-II and MOR-III, respectively (figure 2). The very strong stabilization in the case of the MOR-I model is associated with the formation of an almost perfect tetrahedral environment of both Ga centres in the binuclear cluster within the side-pocket of mordenite. The lower energy gains owing to the self-organization of isolated GaO$^+$ in zeolites MOR-II and MOR-III are due to the unfavourable location of the binuclear cation along the zeolite channel. Because of the associated geometrical constraints, the favourable tetrahedral coordination of Ga centres with the lattice oxygen ions cannot be formed. Furthermore, although the distance between the framework...
Al ions in the MOR-III model is the shortest (approx. 7.5 Å) among the models considered here, the shape of the channel and the specific location of framework [AlO2]− units do not allow both cationic Ga centres in [Ga(m-O)2Ga]2+ to directly coordinate to both anionic sites. This further decreases the relative stability of the Ga2O2/MOR-III structure.

These findings already demonstrate the importance of the formation of a favourable coordination environment for the stability of extraframework cations in zeolite. Furthermore, the results obtained for the MOR-III zeolite model suggest that the compensation of the excessive Lewis acidity and basicity present in the initial monomeric species can be more important than direct charge compensation of the resulting bulkier multiple-charged cationic complex.

The total energy of MOR-II and MOR-III models with [Ga(m-O)2Ga]2+ ions notably decreases by 30 and 49 kJ mol−1, respectively, when the complex adopts the favourable tetrahedral coordination similar to the one realized in Ga2O2/MOR-I. In both cases, the extraframework cations are indirectly charge compensated. In Ga2O2/MOR-II SP, only one of the Ga centres interacts directly with a single [AlO2]− anionic lattice site. The other [AlO2]− unit required for the overall charge neutrality is located 5.44 Å from the cationic complex. An extreme case of charge alternation is realized in Ga2O2/MOR-III SP. The positively charged Ga centres are separated by 5.31 and 8.36 Å from the lattice anionic sites. The substantial energy losses associated with the separation of charges are to a large extent compensated by the formation of a favourable tetrahedral coordination around the Ga centres, complemented by the energy gain owing to the formation of coordination bonds with the sufficiently basic framework oxygen atoms bridging lattice silicons. The oxygen-rich walls of zeolite channels act as a polydentate ligand providing numerous sites for coordinating the extraframework species.

Such a self-organization of intrazeolitic-oxygenated cations is expected to be a general phenomenon. To illustrate this, we considered the stabilization of [Zn−OH]+, [Al(OH2)]+ and [AlO]+ cations in mordenite. The first of these species have previously been considered as potential extraframework Zn sites active for the dehydrogenation of alkanes (Berndt et al. 1996; Aleksandrov et al. 2006). The last two complexes have been discussed as structural models for EFAl species in steam-activated acidic zeolites (Li et al. 2007; Rosenbach & Mota 2008).

Isolated [Zn−OH]+ cations in MOR-I and MOR-II models are characterized by a tridentate coordination of the zinc centres with two coordination sites occupied by framework oxygens from the [AlO2]− anionic lattice units (figure 3). The total energies of both models differ by not more than 5 kJ mol−1. Similar to the case of Ga considered above, the self-organization of [ZnOH]+ into binuclear [Zn(m−OH)2Zn]2+ cations is strongly favourable. These binuclear clusters are by −177 and −62 kJ mol−1 more stable than the two [ZnOH]+ species in the MOR-I and MOR-II models, respectively. The formation of a more favourable tetrahedral environment at the Zn centres achieved by locating the binuclear complex within the side-pocket of MOR-II allows further stabilization of the system by 15 kJ mol−1.

In the case of EFAl-containing MOR-I zeolite, a similar trend is observed (figure 4). The self-organization of tetrahedral [Al(OH)2]1+ cations into [HOAl(m−OH)2AlOH]+ within the mordenite side-pocket is favourable (ΔE =
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Figure 3. Self-organization of ZnOH\(^+\) cations in high-silica mordenite. The numbers above the errors are reaction energies (in kJ mol\(^{-1}\)) of the corresponding transformation. (Online version in colour.)

\[2\times[ZnOH/MOR, Si/Al = 23\]

\[\text{Figure 4. Self-organization of extraframework aluminium species in high-silica mordenite. The numbers above the errors are reaction energies (in kJ mol}\(^{-1}\)) of the corresponding transformation. (Online version in colour.)\]

\[-110 \text{kJ mol}\(^{-1}\).\] The EFAl species in the binuclear cluster show a distorted square–pyramidal coordination. Lattice oxygens of the zeolite and the two bridging extraframework OH groups are the equatorial ligands, while the terminal OH groups occupy the axial positions at each Al centre. The formation of the \([\text{Al(\mu-O)}_2\text{Al}]^{2+}\) cation from two isolated \(\text{AlO}^+\) species is less exothermic \((\Delta E = -68 \text{kJ mol}\(^{-1}\)).\) This is probably owing to the unfavourable confinement of the binuclear complex within the mordenite side-pocket that induces substantial distortions within the extraframework species.

The specific geometrical properties of the cation sites within the mordenite side-pockets and moderate framework Al concentration are not critical for promoting the self-organization of extraframework cations into binuclear clusters. This follows from the results of periodic DFT calculations on the stability of CuO\(^+\) and FeO\(^+\) cations in ZSM-5 zeolite with a Si/Al ratio of 47. These reducible complexes have previously been proposed as the active sites for deNO\(_x\) reactions.

Figure 5. Self-organization of CuO$^+$ cations in MFI zeolite (Si/Al = 47). The numbers above the errors are reaction energies (in kJ mol$^{-1}$) of the corresponding transformation. (Online version in colour.)

(Soscuţ et al. 2002; Pulido & Nachtigall 2009) and benzene to phenol oxidation (Fellah et al. 2010) in Cu- and Fe-modified ZSM-5 catalysts. To compensate for the charge of the extraframework cations, two of the 96 framework Si were substituted by Al. Two models, namely MFI-I and MFI-II, with different Al distribution were considered (figure 1b, c). In the MFI-I model, the Al ions were placed at the T7 and T12 crystallographic sites in a single eight-membered ring located within the sinusoidal channel of MFI (figure 1b). In the case of MFI-II, the Al atoms were introduced at the T2 and T12 sites as part of the six-membered rings at two distant intersections of the main and sinusoidal channel (figure 1c). The distance between framework Al atoms was 5.48 Å and 8.72 Å in MFI-I and MFI-II structures, respectively. In both models, lattice aluminium ions were separated by three silicons.

At all locations considered, CuO$^+$ species coordinate very similarly to the zeolite lattice (2 × CuO/MFI-I and 2 × CuO/MFI-II; figure 5). Tridentate copper complexes are characterized by a short Cu–O bond with a terminal oxygen ligand ($r$(Cu–O$_{ef}$) = 1.71 Å in all structures) and somewhat elongated coordination bonds with the framework oxygen sites ($r$(Cu–O$_{f}$) = 1.96–2.06 Å). For both MFI models, the self-organization of the mononuclear species into dimeric [Cu$_2$O$_2$]$^{2+}$ structures is strongly favoured: the associated energy gain equals $-188$ and $-165$ kJ mol$^{-1}$, respectively, for models MFI-I and MFI-II (figure 5). The structural details of the resulting binuclear species are substantially different. In the former case, a bis(μ-oxo)-dicopper complex is formed that is characterized by a substantial separation of the extraframework O ligands ($r$(O$_{ef}$–O$_{ef}$) = 2.22 Å). A uniform distorted square–planar coordination environment is realized for both Cu centres in Cu$_2$O$_2$/MFI-I ($r$(Cu–O$_{ef}$) =
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1.79–1.80 Å; \(r(\text{Cu}−\text{O}_f) = 1.92–1.97\) Å. An alternative \(\mu-(\eta^2 : \eta^2)\)-peroxo dicopper cation with \(r(O_{ef}−O_{ef}) = 1.47\) Å is formed via the dimerization of CuO\(^+\) species within MFI-II. The more distant location of framework Al ions necessitates substantial separation of the charge-compensating species. The associated geometrical constraints favour the formation of a binuclear complex with elongated Cu–O coordinations in Cu\(_2\)O\(_2\)/MFI-II (\(r(\text{Cu}−\text{O}_f) = 1.88–1.96\) Å; \(r(\text{Cu}−\text{O}_f) = 1.97–2.07\) Å). The formation of the isomeric bis(\(\mu\)-oxo) dicopper extraframework cation in the MFI-II configuration is less favourable by 20 kJ mol\(^{-1}\).

The overall trends observed in the case of iron-modified MFI models are very similar. Isolated FeO\(^+\) extraframework species are characterized by a tridentate coordination of the iron centres (2 \(\times\) FeO/MFI-I and 2 \(\times\) FeO/MFI-II; figure 6). When more lattice oxygens are available in the direct vicinity of Fe located within the zeolitic six-membered rings, additional longer Fe–O\(_f\) contacts (greater than 2.6 Å) can be formed. Nevertheless, for all structures, the mononuclear iron complexes are characterized by uniform Fe–O\(_{ef}\) bonds (1.67–1.68 Å) and main coordinations with the lattice (\(r(\text{Fe}−\text{O}_f) = 2.02–2.08\) Å). The assembly of these cations into oxygen-bridged dimers is highly exothermic. The calculated reaction energies for the self-organization process equal −267 and −211 kJ mol\(^{-1}\), respectively, for MFI-I and MFI-II. In both cases, bis(\(\mu\)-oxo)-di-iron extraframework complexes (\(r(O_{ef}−O_{ef}) = 2.34\) and 2.48, respectively, for Fe\(_2\)O\(_2\)/MFI-I and Fe\(_2\)O\(_2\)/MFI-II) are formed, while the formation of \(\mu-(\eta^2 : \eta^2)\)-peroxo-bridged clusters was not observed. The boat-shaped [Fe(\(\mu\)-O)\(_2\)Fe]\(^{2+}\) extraframework species in the latter case is, however, much more distorted than the cluster stabilized at the eight-membered ring cation site of MFI-I.
Whereas, in the latter structure, the iron coordination environment is quite uniform ($r(\text{Fe}–\text{O}_t) = 1.96–2.00\,\text{Å}$ and $r(\text{Fe}–\text{O}_{ef}) = 1.78\,\text{Å}$), substantial deviations of Fe–O distances are observed for Fe$_2$O$_2$/MFI-II ($r(\text{Fe}–\text{O}_t) = 2.01–2.12\,\text{Å}$ and $r(\text{Fe}–\text{O}_{ef}) = 1.75–1.91\,\text{Å}$).

These results convincingly demonstrate a general tendency of oxygenated extraframework cations in high-silica zeolite matrices to self-organize into binuclear structures. In low-silica zeolites with a high density of extraframework cations, such self-organization is spontaneous and results in larger multinuclear cationic complexes (Schüßler et al. 2011). The process is driven by the formation of a more favourable coordination environment at the cationic metal centres and the pronounced compensation of the high basicity of the terminal oxygen-containing ligands. In some cases, the associated energy gain dominates the necessity of the direct charge compensation of the extraframework cationic species by lattice anionic sites. The presence of multiple-charged binuclear oxygenated metal complexes in zeolites does not necessarily require the immediate proximity of an equivalent number of negative framework charges. Furthermore, the substantial flexibility and the increased size of the extraframework cation are also beneficial for the efficient charge compensation of randomly distributed framework anionic sites in high-silica zeolite matrices.

3. Catalytic reactivity of oxygenated extraframework cations

Binuclear oxygenated sites are found to be substantially more stable than their mononuclear counterparts. Often, an inverse correlation between the stability of a potential active site and its catalytic reactivity are observed. One may argue that, under reaction conditions, a small steady-state concentration of the isolated, less stable but more reactive mononuclear oxygenated complexes can explain the overall catalytic performance of a modified zeolite. To verify whether this is the case for the systems discussed in the previous section, we compared the energetics of elementary reaction steps involved in the relevant catalytic processes for the most stable binuclear clusters with those of the corresponding mononuclear extraframework oxygenated sites in Ga/MOR and Fe/MFI catalysts. We used ethane dehydrogenation to analyse the chemical reactivity of Ga/MOR zeolite (Pidko et al. 2008, 2009) and direct oxidation of benzene to phenol to probe the activity of the different candidate active sites in Fe-modified MFI catalysts (Li et al. 2011).

Alkane dehydrogenation by Ga-modified zeolites is catalysed by Lewis acid–base pairs associated with the extraframework Ga cations and adjacent basic oxygen ligands. The initial CH bond activation proceeds via its heterolytic dissociation ($\text{I_{Ga} + C}_2\text{H}_6 \rightarrow \text{II_{Ga}}$; figure 7). The reactivity of the zeolitic Ga complex at this step is directly correlated with the strength of the associated Lewis acid–base pair. During the heterolytic dissociation of an alkane over the isolated GaO$^+$ cations, Ga binds the anionic alkyl species and the terminal oxygen accepts a proton, resulting in an OH ligand. This results in a favourable tetrahedral coordination of the extraframework Ga species. The unfavourable coordination and high Lewis acidity of the Ga centre and the extreme basicity of the terminal O ligand in isolated GaO$^+$ result in a facile and highly exothermic ($\Delta E = -258\,\text{kJ}\,\text{mol}^{-1}$) initial alkane activation with a barrier ($\Delta E^\#$) of only
69 kJ mol$^{-1}$. The subsequent $\beta$-H elimination step resulting in ethylene desorption and the formation of the $[\text{Ga}(H)(\text{OH})]^+$ cation ($\Pi\text{Ga} \rightarrow \Pi\text{II}\text{Ga} + \text{C}_2\text{H}_6$; figure 7) does not depend on the local surroundings of the Ga$^{3+}$ ions (Pidko & van Santen 2009). At the next step, the catalytic cycle is closed and the initial GaO$^+$ site is regenerated via H$_2$ recombination ($\Pi\text{II}\text{Ga} \rightarrow \Pi\text{I}\text{Ga} + \text{H}_2$; figure 7). The high proton affinity of the initial basic site leads to prohibitively high barriers for the regeneration of the active site. In this case, the DFT-computed activation barrier for H$_2$ desorption exceeds 300 kJ mol$^{-1}$, suggesting that this step will not take place under the catalytic conditions.

The formation of a binuclear cluster with bridging oxygen atoms substantially reduces the basicity of the terminal O ligand and, at the same time, the positive charge on the Ga centre becomes more efficiently compensated. This leads to a decrease in the Lewis acidity of the extraframework site. These changes result in a slightly higher barrier and much lower exothermicity of the initial CH activation (figure 7). This modest loss in reactivity of the Ga-oxo cluster is compensated by a large decrease in the barrier for the regeneration of the initial active site. For this much more stable extraframework complex, the regeneration of the initial $[\text{Ga}(\mu\text{-O})_2\text{Ga}]^{2+}$ structure by H$_2$ desorption proceeds with a barrier of only 168 kJ mol$^{-1}$.

This case is a very good illustration of the Sabatier principle. For Ga-modified zeolites, there is an optimum strength of the Ga-containing Lewis acid–base pair which is strong enough, on the one hand, to promote initial C–H activation and, on the other, to bind the reaction intermediates moderately to allow the active site to regenerate (Pidko & van Santen 2009).

A somewhat similar behaviour is observed for the reactivity of mono- and binuclear iron-oxo species in the direct oxidation of benzene to phenol with N$_2$O as the oxidant. The reaction is initiated by the decomposition of N$_2$O over the extraframework iron complex, resulting in the formation of an additional reactive O ligand and the release of N$_2$. Although one would expect that the enhanced coordinative unsaturation of the Fe$^{3+}$ centres is beneficial for N$_2$O dissociation, the calculated activation barriers are very similar for isolated FeO$^+$ (\Delta E^\# = 94 kJ mol$^{-1}$; figure 8a) and binuclear $[\text{Fe}(\mu\text{-O})_2\text{Fe}]^{2+}$ ions (\Delta E^\# = 102 kJ mol$^{-1}$; figure 8b). In the former case, the resulting FeO$_4^{3-}$ species shows an almost perfect tetrahedral coordination of the iron centre. Subsequent benzene activation proceeds with an activation barrier of 25 kJ mol$^{-1}$ (figure 8a). The terminal O ligand introduced into the binuclear iron complex by N$_2$O dissociation is highly

![Figure 7](image-url)
mobile and reactive towards benzene oxidation. The reaction is associated with a stronger initial benzene adsorption and shows a barrier of only 15 kJ mol\(^{-1}\) (figure 8\(b\)). The resulting phenol product binds very strongly to these iron sites. The regeneration of the initial active complex via phenol desorption competes with an alternative path involving a heterolytic dissociation of the phenolic OH group over the Fe–O acid–base pair. In the case of the mononuclear FeO\(^+\) complex, phenol (PhOH) dissociates irreversibly because of the high basicity of the terminal O ligand. The DFT-computed reaction and activation energies for the formation of a \([\text{Fe(OH)(OPh)}]^+\) complex via the dissociation of PhOH over FeO\(^+\) equal \(-131\) and \(36\) kJ mol\(^{-1}\), respectively (figure 8\(a\)). The resulting iron complex is inactive towards further benzene oxidation. In the case of the binuclear cluster, this reaction is much less exothermic (\(\Delta E = -33\) kJ mol\(^{-1}\); figure 8\(b\)). This suggests that, in the latter case, desorption of phenol can, in principle, be achieved and the active site can be regenerated.

Nevertheless, it appears that the presence of oxygen ligands in the structure of extraframework iron complexes is not beneficial for their catalytic performance in the direct oxidation of benzene to phenol. The stable phenolate complexes formed with the assistance of these basic O sites are probably acting as the precursors for coke formation, leading to the long-term deactivation of the microporous catalyst. The active sites responsible for the enhanced benzene oxidation activity are bare exchangeable Fe\(^{2+}\) cations that are present in the Fe/ZSM-5 catalyst in very small concentrations at very specific cation sites (Li \textit{et al.} 2011).

4. Conclusions

Oxygenated and hydroxylated extraframework cations in high-silica zeolites demonstrate a tendency towards self-organization into binuclear multiple-charged cationic clusters. The isolated mononuclear oxygen-containing cations are usually unstable in high-silica zeolite matrices with a Si/Al ratio up to 47 independently of their topology. The energy benefit associated with the formation of oxygen-bridged complexes can reach values as high as 200–400 kJ mol\(^{-1}\). The

process of self-organization is driven by the stabilization of under-coordinated metal centres and excessively basic terminal O and OH ligands via the formation of oxygen-bridged complexes. In some cases, the associated energy gain dominates the additional stabilization energy owing to the direct charge compensation of the extraframework cationic species by framework anionic sites. This may lead to the formation of stable charge-alternating structures. The stability and the location of such cationic clusters are mainly controlled by the favourable geometric environment of metal ions. The enhanced flexibility and the size of the binuclear complexes are also beneficial for the efficient charge compensation of randomly distributed framework anionic sites in high-silica zeolite matrices.

Obviously, our study covered only a small fraction of possible structural configurations within a limited set of metal-containing zeolites. Nevertheless, the computational results obtained for these selected systems allow us to propose that the phenomenon of self-organization of oxygenated extraframework cations in zeolites is quite general. When constructing structural models for catalytic complexes in zeolites, one has to carefully consider the possibility of their agglomeration into multi-nuclear cationic aggregates. It is also important to note that, despite their much higher stability, the aggregated extraframework species can introduce a much higher catalytic reactivity than their less stable mononuclear counterparts. Because of the weaker binding of reaction intermediates, the regeneration of the binuclear extraframework cations in the course of a catalytic process can be substantially facilitated.

5. Computational details

The quantum chemical calculations were carried out using the Vienna Ab Initio Simulation Package (VASP) (Kresse & Furthmüller 1996a,b) within DFT with PW91 (Perdew et al. 1992) and PBE (Perdew et al. 1996) exchange–correlation functionals. The projected–augmented wave (PAW) method (Kresse & Joubert 1999) was used to describe electron–ion interactions and, for valence electrons, a plane wave basis set ($E_{\text{cut}} = 400\,\text{eV}$) was employed. To correctly describe the interactions between bulky phenolic species confined within the narrow MFI pores, the energetics calculated for benzene oxidation by Fe/MFI with DFT was further corrected for dispersion interactions by adding the contributions from van der Waals bonds between the confined hydrocarbon species and the zeolitic matrix. Further computational details and the excessive description of the zeolite models used can be found in Pidko et al. (2008, 2009) and Li et al. (2011).

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