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## **Molecular Simulation**

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R. A. Van santen<sup>a</sup>; W. K. Offermans<sup>a</sup>; K. Malek<sup>a</sup>; E. A. Pidko<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering and Chemistry, Schuit Institute of Catalysis, Eindhoven University of Technology, Eindhoven, The Netherlands

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# Computational modeling of catalytic reactivity

R. A. VAN SANTEN\*, W. K. OFFERMANS†, K. MALEK‡ and E. A. PIDKO¶

Department of Chemical Engineering and Chemistry, Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

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Basic molecular concepts in heterogeneous catalysis are illustrated by recent results from periodic and cluster density functional theory (DFT) calculations. For reactions on platinum surfaces, differences in the activation barriers found for ammonia activation are analysed in terms of bond-order conservation principles. The notion of early and late transition-states is introduced and used to understand the difference between step edges versus terrace activation. Another important concept relates to the stereoselectivity of a catalytic reaction. For immobilized organo-metallic complexes, the ligand–reactant interaction dominates the selectivity. We analyse activation by immobilized salen complexes and show that attachment of the catalytically active complex to the wall of a microporous system can dramatically affect the conformation of the ligand and hence selectivity. In zeolites we find that the match of shape and size of pre-transition-state structures with the zeolite cavity dominates the stereochemistry of the reaction.

**Keywords:** Theoretical catalysis; Transition metals; Zeolites; Photocatalysis; Immobilized system

## 1. Introduction

The use of computational techniques in catalysis, homogeneous as well heterogeneous, has become widespread and extensive, mainly because of the sophistication of several density functional theory (DFT) software codes. They are useful not only to model molecular complexes and cluster models of catalytically reactive centres but also to study two-dimensional surfaces or cavities of zeolites using periodic versions of the DFT codes. Of great importance are the functionalities that allow for the optimisation of structures, not only in the ground state but also in the transition-states.

A significant drawback is the accuracy of predicted structures. Usually this accuracy is not better than 10 kJ/mol. This precludes an *ab-initio* prediction of overall kinetics except when there is a compensation of errors made in absorption energies and activation barriers [1].

Therefore, quantum-chemical studies are of use mainly to compare experimental and theoretical spectroscopic data of adsorption intermediates and to compare alternative reaction mechanistic schemes. The first is very useful, because errors in calculated spectroscopic

energies are relatively much less than in the calculated interaction energies. A comparison of reaction schemes for a particular overall reaction is useful if the energies of the elementary reactions differ more than 10 kJ/mol. This appears to be often the case. Results of such quantum-chemical studies can be considered useful input to subsequent kinetic simulations.

In heterogeneous catalysis we have a few important qualitative concepts that can be quantified with theory. They are very useful to understand trends in activation energies as a function of reaction centre topology and composition. A detailed overview is given in a recent book [2].

In this paper we will begin our analysis with an application of the concept of bond-order conservation [3]. We will analyse the relation between transition-state topology and transition-state energies. We will apply this to a study of the oxidation of ammonia by platinum. We are interested in elementary reaction steps of ammonia with coadsorbed O and OH [4].

A very important qualitative characterisation of transition-states is their degree of flexibility. Transition-states are called loose when they have a large entropy, but

\*Corresponding author. Tel.: +31-40-247-3082. Email: r.a.v.santen@tue.nl

†Tel.: +31-40-247-3781. Email: w.k.offermans@tue.nl

‡Tel.: +31-40-247-2124. Email: k.malek@tue.nl

¶Tel.: +31-40-247-2189. Email: e.a.pidko@tue.nl

tight when they are rigid and show less entropy. This of course affects the magnitude of the pre-exponent of the reaction rate constant. For the case of ammonia oxidation we will analyse the nature of transition-states using this characterisation. We will conclude the ammonia case with another characterization of transition-states that relates with their position along the reaction coordinate. The extreme situations are denoted as early and late transition-states and affect the height of the activation barrier.

Awareness of these concepts is important since they are the basis to the so-called Bronsted–Eyring–Polanyi relation that describes a linear relation between the activation energies and the corresponding reaction energies, provided that the nature of the transition-states does not vary.

Next we address another heterogeneous catalytic system: an immobilized catalytically active complex. We will discuss enantiomeric epoxidation using salen complexes [5]. Of specific interest is the comparison of the reactivity of immobilized and non-immobilized complexes.

Interestingly it appears that again the relation between transition-state and adsorbed product or reactant states is important.

Transition-state selectivity now competes with product adsorption and desorption. This particular case illustrates that in overall kinetics in addition to the activation of molecules, adsorption equilibria of reaction intermediates are also important.

Finally we will use an example from zeolite catalysis to illustrate the importance of adsorption effects to the selectivity of a reaction. We will introduce the concept of pre-transition-state stabilization [2, p. 177]. To the transition-state barrier there can be distinguished two essentially different energy contributions. One energy part is due to cleavage and formation of chemical bonds within the reacting molecules induced by contact with the catalyst, the other due to the need to prearrange reactants in the zeolite cavity. This is especially important when cavity size or shape affects the stereochemistry of the reaction. It is this part of the activation path of the reactants that is denoted as the pre-transition-state energy, a concept also used in enzyme catalysis.

We will illustrate this for two examples from zeolite catalysis. One case is alkylation of toluene by methanol. The other case is a photocatalytic oxidation reaction catalysed by zeolite Y.

## 2. Bond-order conservation analysis of transition-states

The principle of bond-order conservation has been introduced by Shustorovich [3] as a semi-empirical method to predict energies of interaction of adsorbates to metal surfaces. The method has been extended also to make predictions of reaction energetics [6]. The method is approximate and is useful as long as non-spherical

contributions to the bond energy and rehybridization effects can be neglected. The method can be quantified most easily by assuming a Morse type of potential between the atoms.

One assumes exponential dependence of bond-order on bond distance between two atoms:

$$x = e^{-r-r_0/a} \quad (1)$$

where  $x$  is the bond-order,  $r - r_0$  is the deviation from the equilibrium distance and  $a$  is a normalisation factor.

If the two-centre bond is described by a Morse potential, there exists a simple relation between potential  $Q$  and bond-order  $x$ :

$$Q_1(x) = -Q_0(2x - x^2) \quad (2)$$

with  $Q_0$  the strength of a single bond when the bond-order is 1.

The assumption of bond-order conservation implies the following relationships:

- (1) If an atom has  $n$  neighbours instead of one:

$$Q_n = \sum_i^n Q_i \quad (3)$$

the total bond energy can be written as a sum of two-body interactions, but the individual bond energy contributions become related.

- (2) Total bond-order is conserved:

$$x_n = \sum_i^n x_i = 1 \quad (4)$$

This is the key postulate, that is never rigorously true but, as we will see, very useful to estimate energy changes due to changes in surface reaction-path topologies.

Two important relations follow. If the bonds are equivalent, then:

$$x_i = 1/n \quad (5)$$

and:

$$1/nQ(n) = -1/nQ_0(2 - 1/n) \quad (6)$$

These expressions imply that the bond-order between two atoms is strongly dependent on the number of neighbours they share. For equivalent atoms the bond-order per bond decreases linearly with an increasing number of neighbours. As a consequence the equilibrium bond distance increases. This is also reflected in expression [6] that then shows that the energy per bond decreases.

Bond-order conservation can be understood to be due to the delocalization of electrons. The more bonds an atom has, the more the electrons will be distributed over the different bonds and the weaker the individual ones will be.

When applied to surfaces, these rules appear to be very useful to understand differences in the adsorption energies between adsorption configurations in which adatoms share bonding with a surface metal atom or not. On a metal surface for adsorbed atoms as C or O this energy difference is typically of the order of 10 kJ/atm.

We will illustrate these concepts with an analysis of the activation of ammonia by surfaces precovered with adsorbed oxygen (O<sub>ads</sub>) or hydroxyl (OH<sub>ads</sub>) [5]. In figure 1, we compare computed reaction energy diagrams of the subsequent dehydrogenation steps of NH<sub>3</sub> on a (111) surface of Pt for three situations: a surface covered only by ammonia, a surface covered by ammonia and coadsorbed oxygen atoms and a surface covered by ammonia and coadsorbed hydroxyl. The method used is a periodic DFT code, and the surfaces have been represented by slabs of a few metal atoms.

In figure 2, the corresponding surface structures are shown. For each elementary step, the vertical projections of initial, transition and final state are shown.

The question addressed is the influence of coadsorbates on the activation barrier of adsorbed NH<sub>3</sub>, NH<sub>2</sub> or NH. Comparison of the diagrams for the reaction of free ammonia and coadsorbed oxygen shows that for the reaction configurations studied, coadsorbed oxygen only activates the initial ammonia dissociation step. Consecutive reaction steps of NH<sub>2</sub> and NH are not promoted by coadsorbed oxygen. The explanation of this interesting observation is given by the bond-order principle. This can be deduced from a comparison of the corresponding reaction complex structures shown in figure 2(a)–(c).

Whereas in the transition-state between NH<sub>3</sub> and O<sub>ads</sub>, in the initial, transition or final state adatoms do not share

a bond with a surface metal atom, this is very different for the transition-states of NH<sub>2</sub> and NH (figure 2(a)). The high coordination of NH<sub>2</sub> and NH as well as of O<sub>ads</sub> now causes sharing of bonds between the adsorbates and surface metal atoms. According to the bond-order principle, this causes a repulsion. The resulting repulsion energy is not overcome by the more favourable interaction between the NH<sub>x</sub> hydrogenation and oxygen.

Inspection of figures 1 and 2(b) shows a completely different result for reaction of adsorbed ammonia with coadsorbed hydroxyl. Reaction with hydroxyl groups lowers the activation energies of all the reaction steps of NH<sub>3</sub>, NH<sub>2</sub> and NH towards adsorbed nitrogen. This is again understandable in terms of the bond-order principle. The OH group adsorbs preferentially atop of a surface atom. Therefore, in the consecutive transition states, there is no need to share bonding with the same surface metal atom. The more favourable interaction between NH<sub>2</sub> or NH hydrogen atom and hydroxyl dominates the transition-state energies.

### 3. Nature of transition-states, relation with BEP correlation

The studies on ammonia activation of the previous section can also be used to illustrate a few basic notions concerning transition states. First we will discuss this in relation to the determination of the pre-exponent of the transition-state rate expression:

$$r(\text{TST}) = \nu e^{-E_{\text{act}}/kT} \quad (7)$$

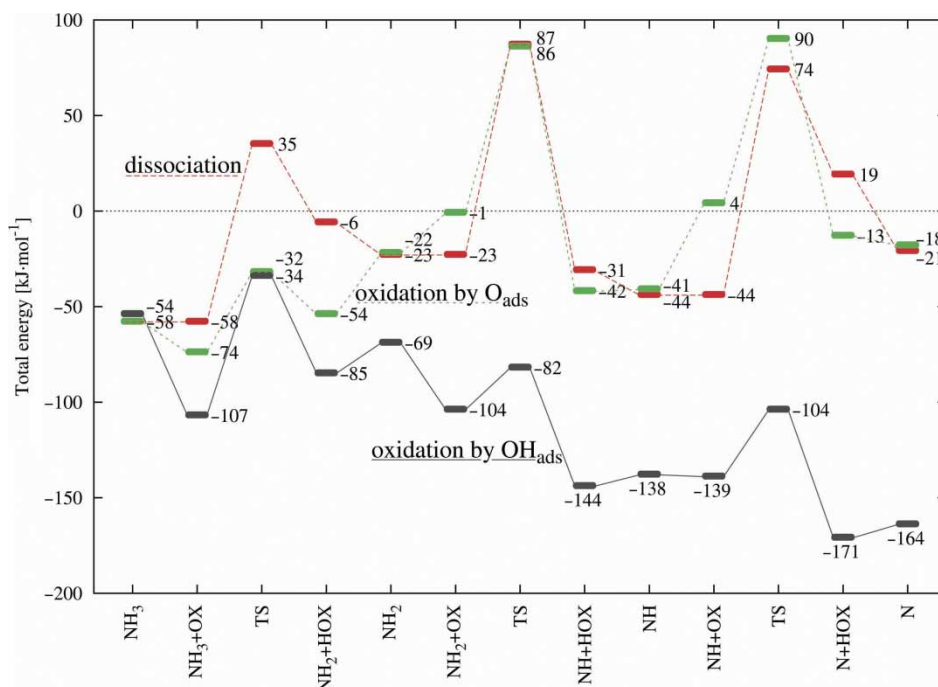


Figure 1. A comparison of activation barriers of NH<sub>3</sub> dehydrogenation by coadsorbed atomic oxygen and OH over Pt{111}. The energies are obtained from DFT calculations and are zero point energy corrected [4].

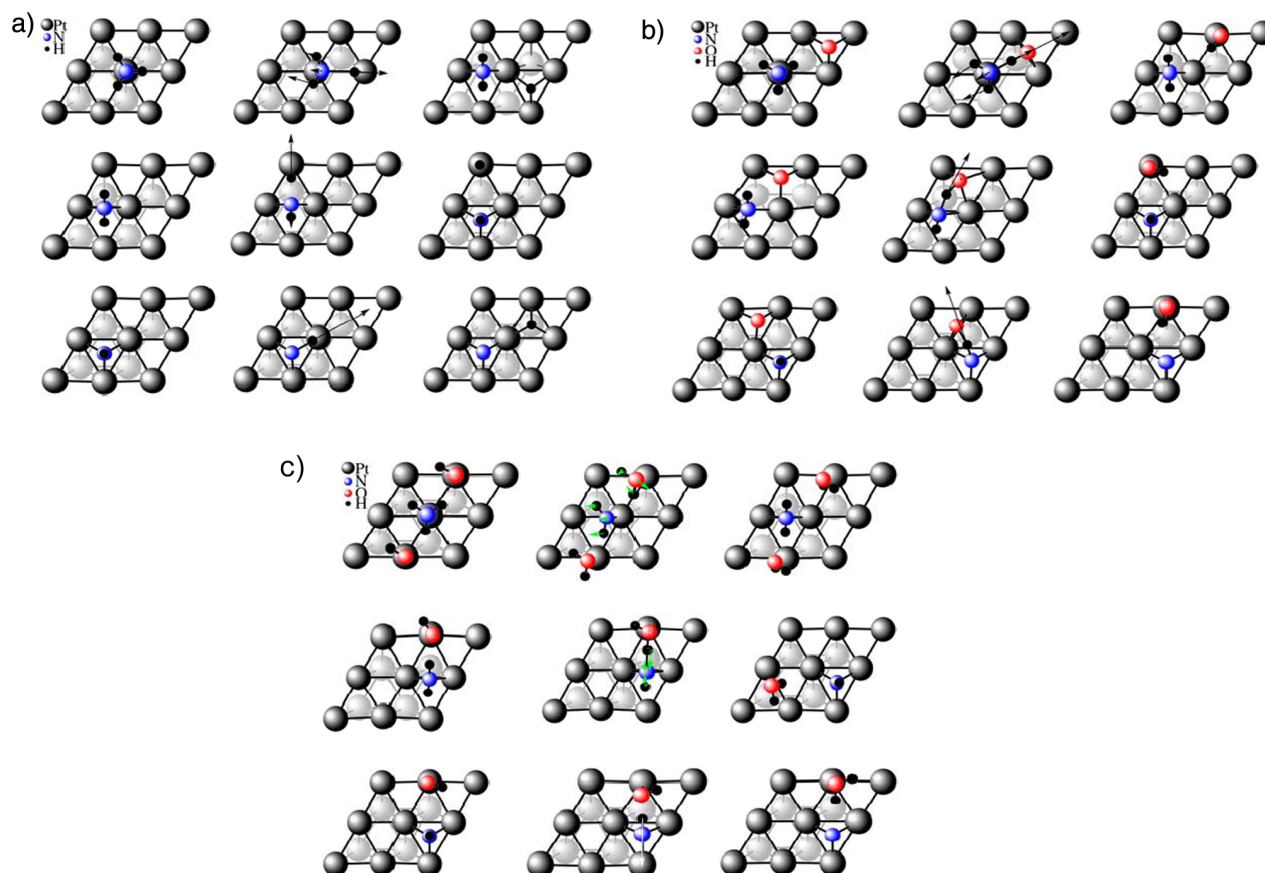


Figure 2. (a) The surface intermediates for  $\text{NH}_x$  dissociation. (b) The respective intermediates for  $\text{NH}_x$  dehydrogenation by  $\text{OH}_{\text{ads}}$ . (c) The respective intermediates for  $\text{NH}_x$  dehydrogenation by  $\text{OH}_{\text{ads}}$ .

$\nu$  is the pre-exponent of the rate expression, that according to elementary transition state reaction rate theory is given by equation (7):

$$\nu = \frac{kT}{h} e^{E_a/kT} \quad (8)$$

The pre-exponent of the reaction rate expression is determined by the difference in entropy of transition-state complex and reactant state, not including the reaction coordinate's degree of freedom from the transition state.

In table 1, calculated differences in entropy are presented for three elementary reaction steps. The entropies of the different intermediates have been computed from the

corresponding partition functions, for which computed normal mode frequencies have been used as input. The dissociation of adsorbed  $\text{NH}_3$  to adsorbed  $\text{NH}_2$  and the two consecutive steps are again considered. Whereas there is a substantial decrease in entropy for the transition-state in the first step, this is in the consecutive reaction steps. It results in a lowered pre-exponent for the first reaction step compared to the latter. Whereas ammonia loses rotational motion when it dissociates, in the other reaction steps the entropy of the initial states is close to zero.

The mobility of the transition-state intermediates is quite low. They represent so-called tight transition-states. To cleave the NH bond overlap between surface orbitals and orbitals in the bond-breaking fragment is a necessity. A low mobility of transition-states is quite general for surface reactions in which bonds are broken or formed catalysed by interaction with the metal surface. A loose transition state of high mobility is characteristic for

Table 1. (a) Computed activation entropies of ammonia activation on Pt(111) surface [4].

Reaction	$\Delta S^\ddagger (\text{J mol}^{-1} \text{K}^{-1})$ (300 K)	$\Delta S^\ddagger (\text{J mol}^{-1} \text{K}^{-1})$ (900 K)
$\text{NH}_{3(\text{vib})} \rightarrow \text{NH}_2 + \text{H}$	-24	-25
$\text{NH}_{3(\text{rot/vib})} \rightarrow \text{NH}_2 + \text{H}$	-17	-13
$\text{NH}_2 \rightarrow \text{NH} + \text{H}$	-3	-4
$\text{NH} \rightarrow \text{N} + \text{H}$	3	1
$\text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{OH}$	-25	-29
$\text{NH}_2 + \text{O} \rightarrow \text{NH} + \text{OH}$	-3	-9
$\text{NH} + \text{O} \rightarrow \text{N} + \text{OH}$	-9	-27
$\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}$	-16	-21
$\text{NH}_2 + \text{OH} \rightarrow \text{NH} + \text{H}_2\text{O}$	-12	-13
$\text{NH} + \text{OH} \rightarrow \text{N} + \text{H}_2\text{O}$	-7	-5

Table 1. (b) Computed pre exponents and activation barriers of ammonia activation on Pt(111) surface [4].

Reaction ( $T = 300 \text{ K}$ )	Pre-exponent (Hz)	$E_a (\text{kJ mol}^{-1})$
$\text{NH}_{3(\text{vib})} \rightarrow \text{NH}_2 + \text{H}$	$5.6 \times 10^{11}$	93
$\text{NH}_{3(\text{rot/vib})} \rightarrow \text{NH}_2 + \text{H}$	$8.6 \times 10^{11}$	93
$\text{NH}_2 \rightarrow \text{NH} + \text{H}$	$5.0 \times 10^{12}$	110
$\text{NH} \rightarrow \text{N} + \text{H}$	$7.2 \times 10^{12}$	118



Table 2. Comparison NH<sub>3</sub> activation energies on a Pt(111), Pt(100) and (100) surface step.

	Pt(111)[4]		Pt(211) <sub>edge</sub> [9]		Pt(100)[8]	
	<i>E<sub>ads</sub></i>	<i>E<sub>act</sub></i>	<i>E<sub>ads</sub></i>	<i>E<sub>act</sub></i>	<i>E<sub>ads</sub></i>	<i>E<sub>act</sub></i>
NH <sub>3</sub>	−69	112	−89	110	−90	120
NH <sub>2</sub> ( + H)	−18	131	−111	150	−105	180
NH(+2H)	−22	134	−17		−30	105

Energies in kJ/mol, non-zero point corrected.

transition states that lead to adsorption or desorption of molecules. The corresponding pre-exponents differ by several orders of magnitude.

A second important notion is that of early versus late transition-states. This characteristic is important because it defines alpha, the proportionality constant in the Bronsted–Eyring–Polanyi (BEP) expression [7, p. 199]:

$$\Delta E_{\text{act}} = \alpha \Delta E_{\text{reaction}} \quad (9)$$

In expression [9], *E<sub>act</sub>* is the activation energy of the reaction and *E<sub>reaction</sub>* is the reaction energy. The BEP relation is an empirical relation that makes the connection between activation energy change and reaction energy change through parameter alpha that relates to the nature of the transition-state. Elementary reaction steps occurring on different reaction centres can be compared when their reaction paths are similar.

Interesting is a comparison of the activation of NH<sub>3</sub> on a different terrace or step, see table 2.

Figure 3 shows the geometry and energies for dissociation of NH<sub>3</sub> along the 100 step edge. One of the most striking differences between binding to a step edge and terrace is the very strong stabilization of adsorbed NH<sub>2</sub>, that is twofold coordinated along the step edge of a (111) terrace, with the two hydrogen atoms perpendicular to the edge.

One can observe a similar stabilization of NH<sub>2</sub> on the (100) surface compared to its energy on the (111) surface. The increased reactivity of the (100) surface compared to the reactivity of (111) or (110) surfaces for reactions in which dissociation or recombination of fragments is rate limiting is a well-known observation [2, p. 124]. It relates to the interesting property of the square (100) surface to preferentially adsorb surface intermediates in two-fold coordination, as in our case the NH<sub>2</sub> fragment. Recombination of such fragments now proceeds through transition-states in which the recombining fragments

do not share bonding with the same surface metal atom. According to the bond-order principle, this results in transition-state barriers of low energy [2, p. 121]. The explanation for the unique reactivity of step edges is similar. Again transition-states are formed in which no bond to the same surface metal atom is shared.

Note that the activation energy for NH<sub>3</sub> dissociation has barely changed on the different surface sites. According to expression [9], this implies for this reaction step a value of alpha less than 0.1. If one inspects the corresponding transition state complexes, one will see that in that complex the nitrogen atom is still close to its original position. This position apparently controls the activation energy maximum. The transition state therefore is to be identified as early.

Late transition states are characterized by intermediates, in which the product fragment atom positions are close to those in the transition state. Well-known examples are the transition-states for dissociation of diatomic molecules as CO and NO [10]. In their tight transition-states parallel to the surface in the transition state, the metal atom carbon, oxygen or nitrogen are close to the final dissociated state. In this case alpha is close to 1.

#### 4. Immobilized enantiomeric metal–organic complex catalysts

Whereas in the previously discussed example of ammonia oxidation by a transition metal stereochemical considerations did only play a limited role, this is of course very different in enantiomeric catalysis. Now the weak van der Waals interactions between reactant and catalytic centre in essence controls the differences in observed selectivity. This can be considered an example of molecular recognition, where reaction is controlled by match of transition-state intermediate configuration and metal ligand.

On the other hand, when the interaction of product with catalytic centre is controlled by the same interaction principles as the transition-state intermediate (alpha close to 1), the product that is formed with preference will also strongly readsorb. In the heterogeneous immobilized system, this product poisoning may result in slow diffusion by the preferred product and, hence the overall selectivity will become biased towards the less preferred product. The overall kinetic result will be a decreased selectivity compared to catalysis by the non-immobilized system.

A second important feature of immobilized systems is the effect of a tether that links complex to solid and may have effects on the conformation of the organo-metallic complex. When the tether is coordinated to the metal centre, this can affect strongly ligand conformation.

Thirdly, when nanoporous systems are used to immobilize the transition metal complex, spatial constraints within the micropore may also induce additional selectivity effects.

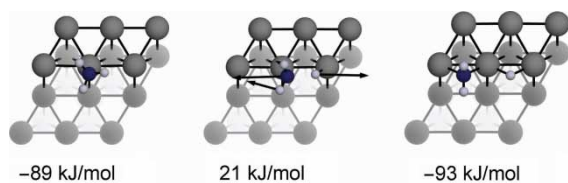


Figure 3. Dissociation of NH<sub>3</sub> along step edge [9].

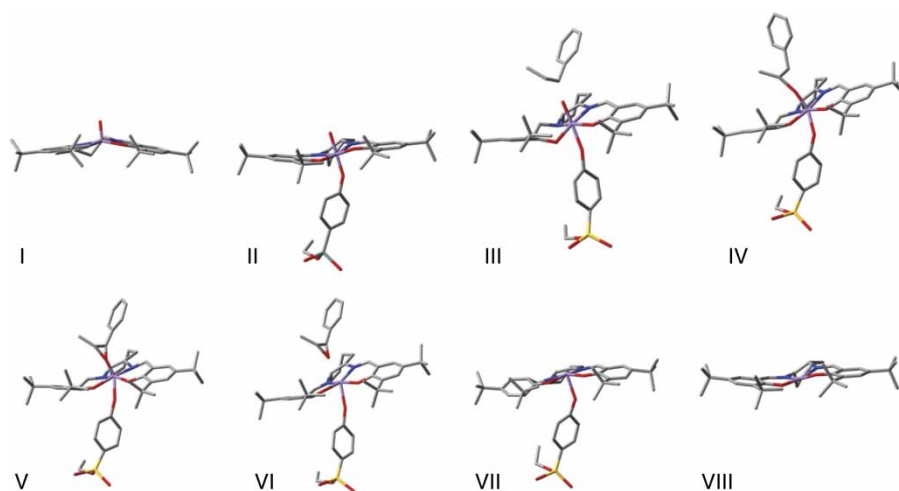


Figure 4. Optimized configuration of different steps along the reaction pathway for *cis*-methyl styrene substrate. The MCM-41 channel was removed for clarity. (I) Isolated oxo-Mn-salen; (II) the anchored complex; (III) docked olefin and encounter-complex of catalyst and substrate; (IV) radical intermediate complex of catalyst and substrate; (V) intermediate state; (VI) complex of reacted catalyst and product; (VII) de-oxygenated anchored catalyst; (VIII) isolated de-oxygenated catalyst [5].

We will present here a case study of the changes in enantioselectivity in the enantioselective epoxidation of methyl styrene by a Mn-salen complex. The analysis is based on the application of molecular mechanics docking simulations [5]. These simulations provide information on the conformation of the different reaction intermediates.

The enantiomeric character of the successive intermediates has been analysed using a method proposed by Avnir [11]. Avnir defined a normalized chirality content measure (CCM) that measures the geometrical deviation with respect to the most related non-enantiomeric structure. For the intermediates of figure 4, the corresponding CCM's are given in figure 5.

The different structures in figure 4 illustrate the changes in conformation that occur in the catalytically active salen complex upon tethering and when it interacts with the substrate. The sequence of structures starts with the free salen complex with an oxygen atom attached to Mn. Its structure is cup-like with a low CCM. *Cis*-methyl styrene fits best in the cavity created by this molecular conformation.

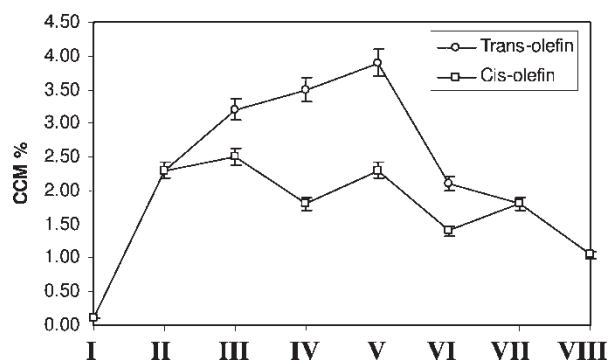


Figure 5. CCM of Mn-salen along the reaction pathway for *cis*- and *trans*-methyl styrene substrates [5].

The next structure 4(b) is obtained when the tether molecule is attached that links the complex to the MCM siliceous wall. Now the conformation of the salen complex changes and becomes step-like more suitable for interaction with *trans*-methyl styrene. Structures 4(c)–(f) illustrate intermediates with methyl styrene. As can be deduced from figure 5, interaction with the reactant enhances the CCM significantly. This is more significant for the *trans*-methyl styrene complex than its *cis* analogue. The intermediates of figure 4 can be related to reactant transition or product states by a comparison with quantum-chemical calculations of the epoxidation reaction [12]. Results of a study with ethylene indicate that in the transition state the C–O bond-distance is long compared to the M–C bonds, as in 4(c) or (d). The epoxides 4(e) and (f) represent adsorbed intermediates. In figure 6 the quantum chemical results for the epoxidation of ethylene of Cavallo and Jacobsen [12] are summarized.

The power of a combined molecular mechanics and CCM approach is that it provides an insight which products will be most selectively formed, as can be observed from figure 5. The prediction made is that in contrast to the homogeneous system, the heterogeneous system will show dominant enantioselectivity upon reaction with the *trans*-methyl styrene molecules. This also follows from the computed energy profile in figure 7.

In figure 7, energies of the groundstates as well as transition-states are shown for the epoxidation of *trans*- and *cis*-methyl styrene. The results are from DFT-based calculations and are shown for the triplet state. A comparison is made of the reaction energy profiles of catalysis for the free complex and the tethered complex.

One notes that for the tethered complex, the lowered barrier found for epoxidation of the olefin and also the relatively large energy of adsorption of the epoxide adsorbed to the immobilized complex leads to the earlier mentioned phenomenon of diffusion-desorption

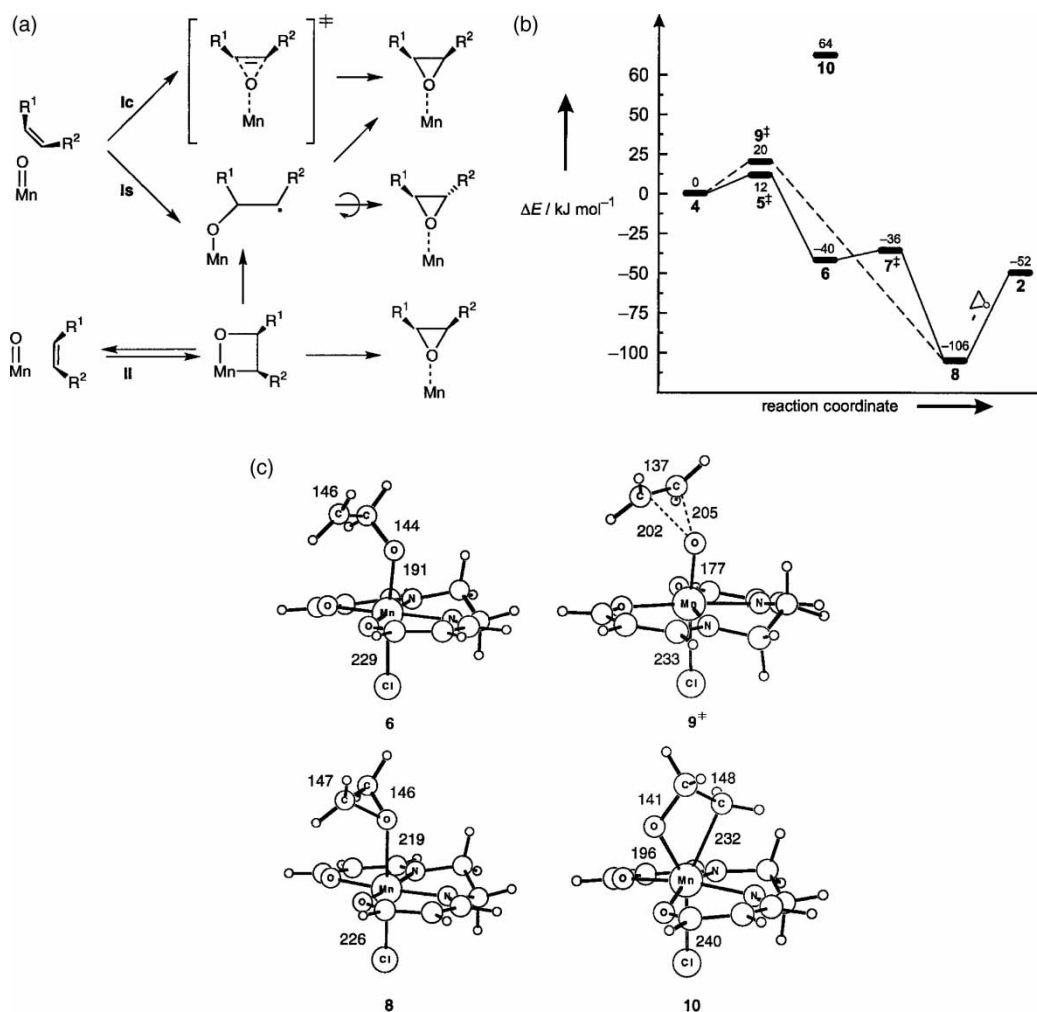


Figure 6. (a) Possible mechanisms for oxygen transfer in the Jacobsen-Katsuki epoxidation. For *Is*, rotational collapse leads to the *trans* epoxide, whereas direct collapse leads to the same *cis* product as pathway *Ic* [12]; (b) energy profile for the epoxidation reaction on the S2 [12]; (c) geometries for key structures in the S2 epoxidation reaction (Calculations on the BP86 level; all distances in pm) [12].

controlled product selectivity that competes with transition-state selectivity.

Obviously according to the calculations presented above, an important effect of immobilization in the micropore of the MCM material is the change in ligand structure due to the interaction of tether with the organo-metallic complex.

## 5. Zeolite catalysis; pretransition-states

In zeolites, with channels and cavities of a nanometre or less stereo-selective differences are dominated by the interaction of substrate with the zeolite wall. We will illustrate this for two catalytic systems. The first reaction that we will discuss is a reaction catalysed by zeolitic protons. We will analyse the alkylation of toluene by methanol to give ortho-, meta- or para-xylene [14]. The important concept illustrated by this reaction is pre-transition-state stabilization [2, p.177]. Since this is dominated by interaction with the zeolite wall and the forces are of the van der Waals type, similarly as in the

previous case we have to use a hybrid molecular mechanics and quantum-mechanical approach. DFT methods do not describe the van der Waals interactions well.

The other example is a photochemical reaction in cation-containing zeolites. Now the stabilization of the pre-transition-state is controlled by the strong interaction of reactants with the cations and hence dominated by strong electrostatic interactions [15].

### 5.1 Alkylation of toluene

The stereochemical issue is the question whether selectivity is controlled by differences in the rate of diffusion of the different products, the chemistry of the reaction and the nature of the respective transition-states or by selective adsorption effects of reaction intermediates.

A summary of the results of periodical DFT quantum-chemical studies corrected for van der Waals interactions is given in figure 8 [14].



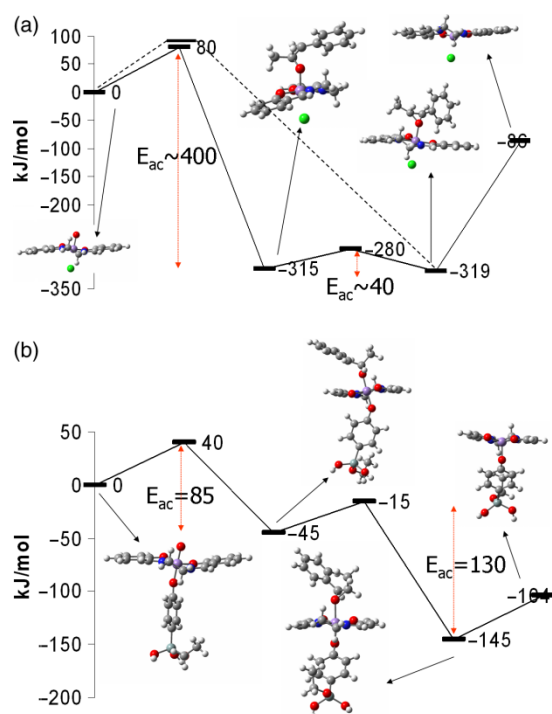


Figure 7. (a) Computed reaction energy profile for epoxidation of *cis*-methyl styrene by homogeneous *cl* complex. Complex in triplet state [13]; (b) corresponding computed reaction profile for tethered complex [13].

The zeolite structure selected is mordenite which has a one-dimensional 12 ring channel system. Each unit cell contains one Al atom that substitutes for a lattice Si atom that is compensated by a proton attached to a lattice oxygen atom.

Figure 8 is the reaction energy diagram of the alkylation reaction that shows the energies of reaction intermediates and transition-states formed in succession when a reaction progresses according to the particular mechanistic scheme we propose. The reactions leading to *ortho*-, *meta*- and *para*-xylene are compared. The first two steps correspond to the adsorption of methanol and toluene. Methanol adsorbs to the zeolitic proton through hydrogen bonds. Toluene has a dominant van der Waals energy controlled by the interaction with the zeolite wall to which it

preferentially adsorbs. Since DFT does not predict the latter interactions reliably, a force field type correction to the DFT computed energies has been added that describes the van der Waals interaction between molecular C and zeolite lattice O atoms.

Two most important features that can be deduced from figure 8. The differences in overall activation energies are determined mainly by differences in the rearrangement energy of reactants so that alkylation of methyl to toluene can occur to the proper toluene C atom by the pretransition-state energy. Secondly, chemical activation by the zeolite proton for alkylation by the methyl group to toluene has nearly the same activation energy for the three isomers. Different from liquid-phase organic chemistry within the zeolite in the alkylation reaction step, there is little preference for *ortho* versus *meta* or *para* addition.

In the overall reaction there is a large difference, but this is due to the differences in the reactant prearrangement energies. Due to the difference in the shapes of the intermediates and spatial restriction of the linear channel, the *para*-forming pretransition-state requires the lower energy.

One concludes that in this case transition-state control is realized through pretransition-state control determined by differences in the adsorption energy of the reaction intermediates. Hence one predicts that even when differences in selectivity due differences in diffusion rates can be excluded, there remains a preference for paraxylene formation. This can be verified experimentally by catalytic experiments using very small mordenite crystallites.

## 5.2 Photo-chemical oxidation

The concept of pretransition-state stabilization is quite general. It is a widely used concept in enzyme catalysis. Also in enzyme catalysis there is the question whether the transition-state or prearranged reactants are stabilized. Both of course enhance the reaction rate since the effective activation barrier for reaction with respect to the energy of reactants before contact with the catalyst is lowered.

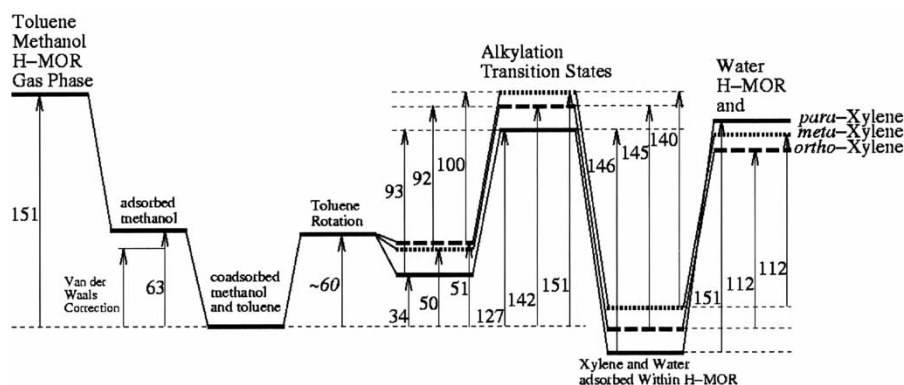


Figure 8. Reaction energy diagram for alkylation of toluene to xylene. Transition-state selectivity can be related to local intermediates prior to the transition-state for proton activation [14].

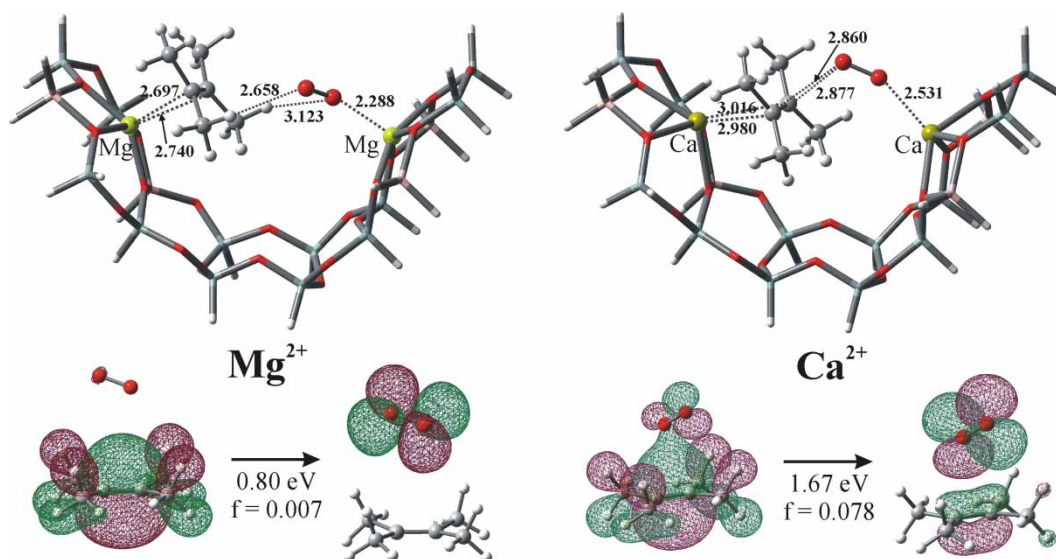


Figure 9. Dimethylbutene and oxygen co-adsorption on a cluster modeling a part of the Y-zeolite supercage [15].

In this subsection we will present a second example of pretransition-state stabilization in zeolite catalysis.

We will give a theoretical analysis of photochemical activation of dimethylbutene by oxygen using a cluster model of the supercage of cation exchanged zeolite Y [15]. In the experimental system alcohols and ketons are formed as the final product [16,17]. We are concerned here with the initial step in which the reaction is initiated by UV light-induced electron transfer between olefin and oxygen.

From a fundamental point of view, we are interested in the role of the large electrostatic field that is generated in the cavity of the zeolite due to the presence of cations. It has been suggested that stabilization of the cation–anion pair in the presence of this field is the dominant stabilizing factor. Our simulations show in contrast, the unique relative positions of adsorbed O<sub>2</sub> and dimethylbutene before reaction play a dominant role due to the location and size of cations in the zeolite cavity.

In figure 9 the structure of O<sub>2</sub> and dimethylbutene adsorbed to Ca<sup>2+</sup> located in the cavity of zeolite Y are shown. The molecules prefer to adsorb separately on different cations. When adsorbed to the same cation, there is a large repulsive interaction.

Key to the subsequent photochemical activation steps is the overlap of the  $\pi$  orbitals of the alkene and those of O<sub>2</sub>.

Figure 9 illustrates this overlap for the HOMOLUMO interaction of the dimethylbutene  $\pi$ –O<sub>2</sub> system. When there is significant overlap, the transition moment for charge transfer is significant and an electron is transferred from alkene to O<sub>2</sub> by absorption of UV radiation.

Comparable studies have been made for photochemical activation of the two molecules when adsorbed in Mg<sup>2+</sup> or Sr<sup>2+</sup>-exchanged zeolites. Results are summarized in table 3.

As can be seen, there is a substantial change in transition moments for these systems. The explanation is the poor overlap of the molecular complex  $\pi$  electron system in these materials. Due to unfavourable cation radii, overlap of  $\pi$  orbitals is very small.

Finally there is the important question to be answered on the role of the electrostatic field. In order to estimate this, in table 3 computed transition moments are reported for the system in the presence or absence of the zeolite cavity. For the latter studies the relative orientation and position of the molecules similar as computed for the adsorbed state in the zeolites have been chosen. Comparison shows convincingly that the role of the electrostatic field is only indirect. The electrostatics of the zeolite cavity affects the adsorption energies, however, the influence on the transition moments is minor. The main effect of the cations is to prearrange reactants in the zeolite cavity so that they can be activated in subsequent reaction steps.

Table 3. The optimized C...O distances ( $r$ ) and the estimated energies ( $E$ ) and oscillator strengths ( $f$ ) of the charge transfer in the DMB–O<sub>2</sub> complex.

	$r_{C...O}, \text{\AA}$	$E, \text{eV}$	$f$
[DMB–O <sub>2</sub> ]/MgZ	3.957/3.807	0.80	0.007
DMB–O <sub>2</sub> from MgZ <sup>†</sup>	3.957/3.807	1.25	0.005
[DMB–O <sub>2</sub> ]/CaZ	2.877/2.860	1.67	0.078
DMB–O <sub>2</sub> from CaZ <sup>†</sup>	2.877/2.860	1.90	0.057
[DMB–O <sub>2</sub> ]/SrZ	3.782/3.754	1.21	0.008
DMB–O <sub>2</sub> from SrZ <sup>†</sup>	3.782/3.754	1.41	0.007

<sup>†</sup>Data for the free DMB–O<sub>2</sub> complex with the geometry obtained from the optimization of the [DMB–O<sub>2</sub>]/MZ (M = Mg, Ca or Sr).

## 6. Summary

For three selected topics in heterogeneous catalysis, we have analysed transition-state intermediates using periodic and cluster DFT approaches. We have emphasized the importance of the relative positioning of the reactant molecules in the catalytically reactive complex. Computational studies allow the prediction of the detailed

structure of reaction intermediates. This provides indispensable mechanistic information on elementary reaction steps that reactants follow when they proceed through the catalytic reaction cycle.

On transition-metal surfaces, pretransition-state complexes are preferred that do not share chemical bonds with the same metal atom. When steric interactions between catalyst and reactants are important, the match between ligand shape and reactant configuration controls the stereochemistry of the reaction. This is also found for the role of the zeolite cavity in reactions that are stereochemically controlled.

## References

- [1] K. Honkale, A. Hellman, I.N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C.H. Christensen, J.K. Nørskov. Ammonia synthesis from first-principles calculations. *Science*, **307**, 555 (2005).
- [2] R.A. van Santen, M. Neurock. *Molecular Heterogeneous Catalysis*, Wiley-VCH, Weinheim (2006).
- [3] E.M. Shustorovich. Chemisorption phenomena: Analytic modeling based on perturbation theory and bond-order conservation. *Surf. Sci. Rep.*, **6**, 1 (1986).
- [4] W.K. Offermans, A.P.J. Jansen, R.A. van Santen. Ammonia activation on platinum {1 1 1}: A density functional theory study. *Surf. Sci.*, **600**, 1714 (2006).
- [5] K. Malek, A.P.J. Jansen, C. Li, R.A. van Santen. Enantioselectivity of immobilized Mn-salen complexes: A computational study. *J. Catal.*, **246**, 127 (2007).
- [6] A. Bell. *Metal-Surface Reaction Energetics*, E. Shustorovich (Ed.), 5, VCH, Weinheim (1991).
- [7] R.A. van Santen, J.W. Niemantsverdriet. *Chemical Kinetics and Catalysis*, Plenum, New York, NY (1995).
- [8] G. Novell-Leruth, A. Valcárcel, A. Clotet, J.M. Ricart, J. Pérez-Ramírez. DFT characterization of adsorbed  $\text{NH}_x$  species on Pt(100) and Pt(111) surfaces. *J. Phys. Chem. B*, **109**, 18061 (2005).
- [9] G. Novell-Leruth, J.M. Ricart, J. Pérez-Ramírez, W.K. Offermans, A.P.J. Jansen, R.A. van Santen. Ammonia dissociation on Pt{100}, Pt{111} and Pt{211}: A comparative density functional theory study, in preparation.
- [10] B. Hammer, J. Nørskov. Theoretical surface science and catalysis-calculations and concepts. *Adv. Catal.*, **45**, 71 (2000).
- [11] S. Alvarez, P. Alemany, D. Avnir. Continuous chirality measures in transition metal chemistry. *Chem. Soc. Rev.*, **34**, 313 (2005).
- [12] L. Cavallo, H. Jacobsen. Radical intermediates in the Jacobsen-Katsuki epoxidation. *Angew. Chem. Int. Ed.*, **39**, 589 (2000).
- [13] K. Malek, C. Li, R.A. van Santen. New theoretical insights into epoxidation of alkenes by immobilized Mn-salen complexes in mesopores: Effects of substrate, linker and confinement, in press. *J. Mol. Catal. A: Chemical* (2007).
- [14] A.M. Vos, X. Rozanska, R.A. Schoonheydt, R.A. van Santen, F. Hutschka, J. Hafner. A theoretical study of the alkylation reaction of toluene with methanol catalyzed by acidic mordenite. *J. Am. Chem. Soc.*, **123**, 2799 (2001).
- [15] E.A. Pidko, R.A. van Santen. Confined space-controlled olefin-oxygen charge transfer in zeolites. *J. Phys. Chem. B*, **110**, 2963 (2006).
- [16] F. Blatter, H. Sun, S. Vasenkov, H. Frei. Photocatalyzed oxidation in zeolite cages. *Catal. Today*, **41**, 297 (1998).
- [17] F. Blatter, H. Frei. Selective photooxidation of small alkenes by  $\text{O}_2$  with red light in zeolite. *J. Am. Chem. Soc.*, **116**, 1812 (1994).