Structural stabilisation of $(CoO)_x$ clusters in ZSM5 zeolites

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The structure and stability of $(CoO)_x$ clusters in siliceous ZSM5 (silicalite) and on SiO_2 have been investigated using atomistic simulation techniques. The deconvolution of the energy into distortion and interaction contributions revealed that the improved stability of the supported clusters is due to the energy gained from the cluster–host interaction. $(CoO)_x$ clusters in ZSM5 of between 4 and 6 Co atoms showed an enhanced stability, while clusters larger than 18 Co atoms were sterically limited inside the zeolite lattice.

Keywords: $(CoO)_x$ /ZSM5; $(CoO)_x$ /SiO_2; clusters in zeolites; simulation

1. Introduction

Zeolites containing transition metal clusters are used as catalysts in many reactions, such as hydrocracking [1,2], hydroisomerisation [3,4], aromatisation [5,6] and selective hydrogenation [7]. In these bifunctional catalysts, the properties of metals and zeolites are synergetically linked with the shape selectivity, usually obtained on molecular sieve based catalysts [8]. If the catalytic sites are confined within the pore structure of the zeolite, the probability of forming product molecules is determined by the molecular dimensions and type of the catalytically active sites. Only molecules smaller than the pore diameter can enter the pores and have access to the reaction sites and only those molecules that can leave the pores will appear in the final product. Moreover, the regular, three-dimensional structure of a zeolite does not only constrain the environment for the reactants, it can also serve as a perfect host for small molecules or nano-crystal particles. By taking advantage of the dimensional constraints of pores and cages, small uniform arrays of clusters can be accommodated [9,10]. If the match between the particles and the zeolite host lattice is sufficiently strong, the particles can adopt geometries different from those exhibited at equilibrium in the gas phase or in the corresponding bulk material [11].

In this theoretical study we determined the structural properties of $(CoO)_x$ clusters in ZSM5 type zeolites. The total energy was deconvoluted into deformation and interaction contributions, in order to obtain the energy leading to an improved stability of the embedded clusters. The structural constraints of the pores of the zeolite upon the clusters were evaluated by comparing these results with $(CoO)_x$ clusters on a SiO_2 surface.

2. Methodology

The techniques for calculating the lattice energy used in this work have been described extensively elsewhere [12,13] and follow the methodology previously applied to determine the structural properties of $(CdO)_4$, $(CdS)_4$, $(ZnO)_4$ and $(ZnS)_4$ clusters in faujasite [14,15] and of metallic Ni clusters on SiO_2 [16].

For the calculations on $(CoO)_x$ clusters in ZSM5 an infinite lattice was generated by applying periodic boundary conditions to the unit cell of the zeolite. $(CoO)_x$ clusters between 1 and 24 Co atoms were placed inside the straight channels of ZSM5. For $(CoO)_x$ clusters on SiO_2 an infinite surface with (110) orientation was created using two-dimensional periodical boundary conditions [17]. Note that the (110) surface proved to be the most stable surface of SiO_2 [18]. On this surface $(CoO)_x$ clusters between 1 and 25 Co atoms were placed. The calculations of $(CoO)_x$ clusters in ZSM5 were carried out using the program GULP [19], the calculations of $(CoO)_x$ clusters on the SiO_2 surface were performed using the program MARVIN [20].

In both cases long-range Coulombic potentials were defined between ions and summed to infinity using the Ewald technique [21,22]. Short-range interactions between the ions were parameterised into a Buckingham potential form. The interaction between two ions, separated by a distance r_{ij}, was calculated from

$$E(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A\, e^{-r_{ij}/\rho} - \frac{C}{r_{ij}^6},$$

where q_i is the charge on the ion i; A, ρ and C are parameters of the Buckingham potential. The polarizability of the anions was treated by virtue of the shell model of Dick and Overhauser [23]. Further details about these

methods and derivation of potentials can be found in recent reviews [24,25].

Three sets of Buckingham potentials were needed in the simulation to describe the interactions (i) for the atoms of the support, (ii) for the atoms of the $(CoO)_x$ cluster and (iii) between the atoms of the cluster and the support.

For the first set of potentials, the values described by Jackson and Catlow were used [26]. These include harmonic three-body terms around the tetrahedral angle of the silicon atoms to describe the directional properties of the covalent framework bonds. The potential has been extended to include a hydrogen–oxygen potential for the hydroxyl termination of the silica surface [27,28].

The other sets of potentials were obtained by fitting the results of quantum mechanical cluster calculations. This technique was already applied for other transition metal oxide clusters, where a very satisfying agreement between the results of the calculations [14,15] and EXAFS experiments [29] was obtained. These calculations were based on the local density approximation (LDA) [30]. By using a double numeric basis set, including additional double numeric core and angular momentum number polarisation functions, negligible basis set superposition errors were assumed. The interparticle potentials were derived from the results of a quantum mechanical calculation on $(CoO)_4$ cubes. First, the geometry of the $(CoO)_4$ cube was optimised with respect to the energy and subsequently a grid of 10×10 points around the minimum geometry was defined, corresponding to a range of Co–Co and O–O distances. The energies of these geometries were determined quantum mechanically and the parameters of the Buckingham potentials were calculated by a least-squares fitting process of the energy hypersurface [14,19].

The potentials to describe the interaction between cluster and support were derived from quantum mechanical calculations on a cluster representing the support, i.e., $O(SiH_3)_2$ and a diatomic CoO particle. This particle was placed next to the O atom of the oxide fragment. The binding energies and the charges of the atoms were calculated as a function of the distance between the diatomic molecule and the oxide fragment.

Two calculations were carried out, one where the Co atom was pointing towards the O of the cluster and one where the diatomic cluster was reversed. The parameters of the Buckingham potentials were determined by a least-squares fitting procedure of the quantum mechanically determined energies of the different configurations [14]. These two orientations of the cluster were needed to determine the contributions of each of the cluster atoms (i.e., Co and O) to the cluster–host interaction. Essentially, the cluster atom closer to the zeolite fragment contributes to the changes in the energy described by the Buckingham potential, while the other atom, that is at a larger distance to the zeolite fragment, only contributes by Coulombic interactions (which were considered when fitting the potential). By using both orientations the parameters of the Buckingham potentials between the O atom of the zeolite fragment and each of the clusters atoms can be obtained, while the charges of the atoms, determining the Coulombic interaction, were obtained from the quantum mechanical calculations.

All potential parameters are summarised in table 1.

3. Results and discussion

$(CoO)_x$ clusters between 1 and 24 Co atoms were placed inside the straight channels of siliceous ZSM5 and on the (110) surface of SiO_2. The geometry was optimised with respect to the total energy. The energies per Co atom after subtracting the lattice energy of the support are compared to that of gas phase $(CoO)_x$ clusters in

Table 1
Potential parameters

Charges

Species	Charges
Si	4.00
O_{zeol} core	0.90
O_{zeol} shell	−2.90
$O_{hydroxyl}$	−1.43
H	0.43
Co	0.74
O_{clus} core	1.66
O_{clus} shell	−2.40

Buckingham potentials[a]

Species	A (eV)	ρ (Å^{-1})	C (eV Å^6)
Si–O_{zeol}	1284	0.321	10.66
O_{zeol}–O_{zeol}	22764	0.149	27.88
Co–O_{zeol}	22122	0.290	179.48
Co–O_{clus}	54678	0.159	26.18
O_{clus}–O_{clus}	203183	0.185	0.00
O_{zeol}–O_{clus}	13882	0.246	0.13
Si–O_{clus}	1284	0.321	10.66

Morse potential[b]

	D_e (eV)	α (Å^{-1})	r_0 (Å)
$O_{hydroxyl}$–H	7.0525	2.1986	0.9485

Three-body terms[c]

Species	K (eV rad^{-2})	θ_0
O–Si–O	2.09724	109.47

Shell model parameters

Species	Shell charge	k (eV A^{-2})
O_{zeol}	−2.87	74.9
O_{clus}	−2.40	74.9

[a] $E(r) = A\,e^{-r/\rho} - Cr^{-6}$.
[b] $E(r) = D_e(1 - e^{\alpha(r-r_0)})^2$.
[c] $E(\theta) = \frac{1}{2}K(\theta_0 - \theta)^2$ (for both O species).

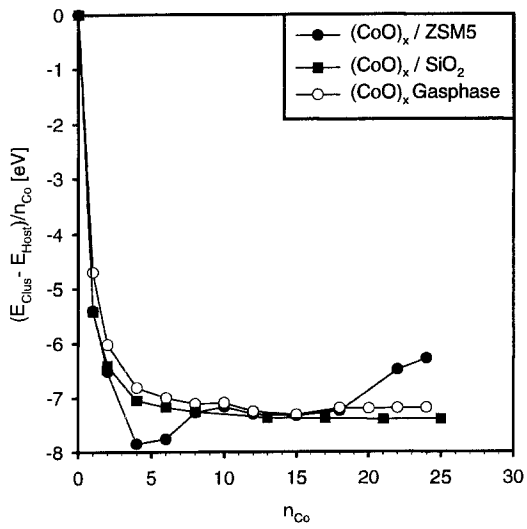

Fig. 1. Energies per Co atom after subtracting the lattice energy of the support.

fig. 1. The geometries of $(CoO)_4$ clusters in ZSM5 and $(CoO)_6$ clusters on SiO_2 are shown in figs. 2 and 3.

In ZSM5 clusters up to $(CoO)_{18}$ were energetically more stable than the corresponding clusters in the gas phase. For the $(CoO)_4$ and $(CoO)_6$ clusters a strong stabilisation, compared to the clusters in the gas phase, was observed. Clusters larger than $(CoO)_{18}$ were more stable outside the zeolite lattice. In contrast, for $(CoO)_x$ clusters on SiO_2 we observed a higher stability for all clusters sizes investigated in comparison with the gas phase clusters.

When $(CoO)_x$ clusters were in contact with ZSM5 and SiO_2, the lattice of the support and the clusters itself were distorted from their equilibrium shape. The total energy of the supported clusters, E_{ZC}, consists of the following energy contributions:

$$E_{ZC} = E_{UL} + E_{LD} + E_{GP} + E_{CD} + E_{CH} + E_{CC},$$

where E_{UL} is the energy of the unoccupied lattice in the optimised geometry, E_{LD} is the distortion energy of the lattice, E_{GP} is the energy of the isolated $(CoO)_x$ cluster equilibrated in the gas phase, E_{CD} is the distortion energy of the cluster, E_{CH} is the cluster–host interaction energy and E_{CC} is the cluster–cluster interaction energy. Note that the last term, E_{CC}, is a contribution resulting from the application of periodical boundary conditions. During the calculations not only an infinite lattice was generated, but also an infinite array of $(CoO)_x$ clusters and an interaction between the clusters via the periodical boundaries occurred. The extent of this interaction depends on the distance between the clusters, which was in our calculations determined by the size of the unit cell of the zeolite.

By adding $(E_{UL} + E_{LD})$ and $(E_{GP} + E_{CD})$, the lattice energies of the support and of the clusters (both constrained to the geometry when the clusters were embedded) can be obtained. This deconvolution into equilibrium energy and deformation contributions allows one to obtain the energy balance between distortion and interaction energies for the embedded clusters. Supported clusters are more stable if the energy of the clusters on the support is smaller than the sum of the energy of the clusters in the gas phase and the energy of the support itself, i.e., $E_{ZC} < E_{UL} + E_{GP}$. This was observed for $(CoO)_x$ clusters in ZSM5 up to 18 Co atoms and for all $(CoO)_x$ clusters on SiO_2 ($x = 1$–25). Energy was required to distort the support and the clusters, since this is a distortion from the equilibrium shape, i.e., $E_{LD} > 0$ and $E_{CD} > 0$. Therefore, the only possibility for the system to gain energy was the cluster–host and the cluster–cluster interaction, i.e. $E_{CH} < 0$ and/or $E_{CC} < 0$. As the distance between the clusters was much larger than the cluster–host distance, we expect E_{CC} to be a minor contribution to the interaction energy compared to E_{CH}. The contributions of distortion and inter-

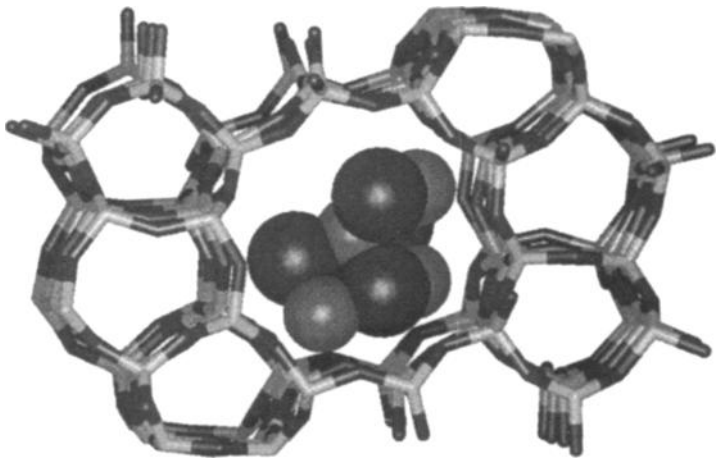

Fig. 2. Geometry of a $(CoO)_4$ cluster in ZSM5.

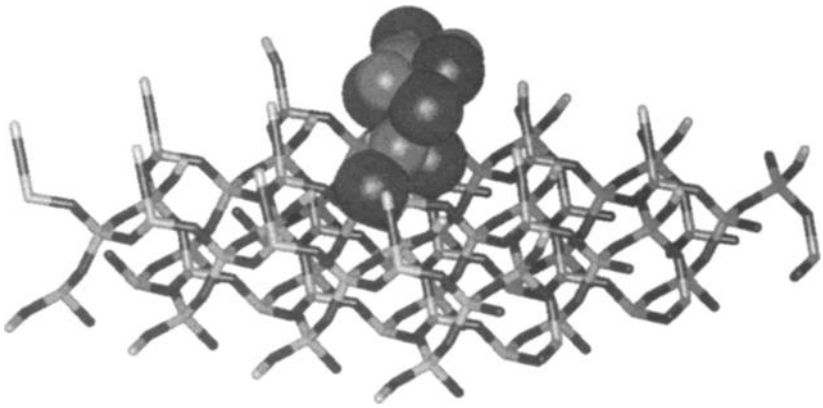

Fig. 3. Geometry of a $(CoO)_6$ cluster on SiO_2.

action to the total energies for $(CoO)_x$ clusters in ZSM5 are compiled in table 2.

As already outlined, energy was needed for the deformation of the zeolite lattice and of the clusters, while the system gained energy from the cluster–host and cluster–cluster interaction. This subtle balance between distortion and interaction energies led to an increased stability of $(CoO)_x$ clusters up to 18 Co atoms in ZSM5. Clusters containing between 4 and 6 atoms in ZSM5 showed the highest stability of all $(CoO)_x$ clusters. Due to the perfect match between the clusters and the zeolite lattice, a strong increase in the cluster–host interaction energy, but also in the deformation energy of the zeolite, was observed. For $(CoO)_x$ clusters larger than 18 Co atoms in ZSM5, the distortion of the lattice necessary to accommodate the clusters increased, giving a sharp rise to the lattice deformation energy (E_{LD}). For these clusters, the energy gained from the interaction was not sufficient to compensate the deformation energy and therefore clusters larger than $(CoO)_{18}$ resulted to be more stable outside the ZSM5 lattice.

The balance between deformation and distortion energies led to an upper limit for the size of $(CoO)_x$ clusters, which are energetically favoured inside the pores of ZSM5. For clusters below that critical limit, the gain in cluster–host interaction energy was larger than the energy required to distort the ZSM5 lattice and the clusters. For clusters above the limit, the distortion of the lattice would demand an amount of energy that could not be achieved from the interaction contributions and therefore embedding of these clusters in the zeolite is energetically not favoured. Such a limit should exist for all clusters embedded into molecular sieves, but will depend on the geometry of the pores and the size of the cluster atoms. For $(CoO)_x$ in ZSM5 we observed that the largest clusters, which could be incorporated into the zeolite (i.e. $(CoO)_{18}$), were not the most stable ones. Smaller clusters between 4 and 6 Co atoms showed a higher stability, because the ability of the zeolite lattice to accommodate $(CoO)_x$ clusters decreased with increasing occupation of the pores. Therefore the more favourable distortion of the zeolite lattice led to an increased cluster–host interaction. Note, this tendency was also observed for $(CdO)_4$ and $(ZnO)_4$ clusters in zeolite Y [15].

Table 2
Energy contributions in for $(CoO)_x$/ZSM5 (eV)

n_{Co}	E_{LD}	E_{CD}	E_{CC}	E_{CH}
1	0.15	0.24	−0.24	−0.84
2	0.11	0.28	−0.28	−0.55
3	0.36	0.24	−0.24	−0.49
4	2.03	0.81	−0.20	−2.16
6	3.33	0.91	−0.19	−2.04
8	0.48	0.36	−0.34	−0.24
10	0.81	0.43	−0.32	−0.27
12	0.40	0.62	−0.32	−0.39
15	0.64	0.59	−0.33	−0.32
18	1.80	0.38	−0.32	−0.21
20	18.23	0.29	−0.13	−0.25
22	18.36	0.34	−0.22	−0.25
24	14.87	0.45	−0.36	0.18

For $(CoO)_x$ clusters on SiO_2, the deformation energy E_{LD} of the SiO_2 surface was ~ 0.25 eV and independent of the cluster size. This energy contribution was smaller compared with $(CoO)_x$ clusters in ZSM5. The attractive cluster–host and cluster–cluster interaction energies led to a stabilisation of the $(CoO)_x$ clusters on the SiO_2 surface. An increasing size of the $(CoO)_x$ clusters did not induce an increased relaxation of the SiO_2 surface and therefore a structural limitation of the silica supported $(CoO)_x$ clusters was not observed up to $(CoO)_{25}$.

4. Conclusions

The cluster–host interaction energy led to an increased stability of supported metal oxide clusters. The incorporation of clusters into ZSM5 or onto SiO_2 resulted in a distortion of the support, which required energy. This energy was compensated for by the gain in energy from the cluster–host interaction.

For $(CoO)_x$ clusters up to 18 Co atoms in ZSM5 and

for all clusters on SiO_2 the interaction energy exceeded the deformation energy, leading to clusters with improved stability when in contact with the support. $(CoO)_x$ clusters in ZSM5 between 4 and 6 Co atoms were energetically most favoured. These clusters were highly stabilised by the strong interaction with the ZSM5 lattice. For $(CoO)_x$ clusters in ZSM5 the distortion of the lattice increased with the cluster size leading to a limit, above which the particles are energetically less stable inside the pores of the zeolite. We expect such a limit to exist for all molecular sieves, while on non-porous supports the structural limitation of the cluster size does not occur. This constraint on the particle size may lead to structurally stabilised clusters within the molecular sieves, which should have an improved stability and a higher dispersion than clusters on non-porous supports.

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