The shape effect and its consequences for polar surfaces and for heterogeneous catalysis

Suplementary Information

Michael Springborg,[1*] Meijuan Zhou,[2] Bernard Kirtman[3]

[1] Laboratory of Theoretical Chemistry, Department of Chemistry,
Namur Institute of Structured Matter (NISM), University of Namur,
Rue de Bruxelles 61, 5000 Namur, Belgium,
[2] SDU-ANU Joint Science College, Shandong University,
Weihai 264209, People's Republic of China,
[3] Department of Chemistry and Biochemistry, University of California,
Santa Barbara, California 93106, USA

*To whom correspondence should be addressed; E-mail: michael.springborg@unamur.be.

Contents

S1. THE MODEL FOR THE ISOLATED, FINITE CRYSTAL

All calculations for the large, finite, crystalline samples were done using a home-made Fortran77 program.

A. Crystal structure

The crystal is defined through the three lattice vectors,

$$\begin{aligned} \vec{a} &= (3.0, 0.0, 0.0) \\ \vec{b} &= (0.0, 2.5, 0.0) \\ \vec{c} &= (0.0, 0.0, 3.0) \end{aligned} \tag{S1}$$

and the positions of the two atoms per unit cell,

$$\begin{aligned} \vec{r_1} &= (0.0, 0.0, 0.0) \\ \vec{r_2} &= (1.5, 0.0, 1.5). \end{aligned} \tag{S2}$$

B. Shapes of the finite systems

In Tables S1, S2, and S3 we collect the values of the parameters that define the different shapes of the finite systems. In Table S4 we list the number of atoms in the different shapes both before and after stoichiometry has been enforced.

In all cases, the reference surface is

$$n_0 = 1. \tag{S3}$$

C. Materials

The different materials have the same structure as given above but differ in the values of the model parameters. Larger values of $|\epsilon_{\rm X} - \epsilon_{\rm Y}|$ relative to the hopping integrals $t^0_{\rm X,Y}$ result in more ionic systems. On the other hand, larger values of U_k suppress charge transfers.

D. Results: PDOS

Some relevant information may be found by looking at the atom-resolved partial density of states (PDOS). For the kth atom of the large, finite, crystalline system, we define its PDOS as

$$\mathrm{PDOS}_k(\epsilon) = \sum_i |c_{ki}|^2 g(\epsilon - \epsilon_i). \tag{S4}$$

Here, c_{ki} is the orbital expansion coefficient for the contribution of the kth atom-centered basis function to the ith orbital, ϵ_i is the energy of that orbital, and $g(\epsilon - \epsilon_i)$ is a broadening function for which we use

$$g(\epsilon - \epsilon_i) = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(\epsilon-\epsilon_i)^2} \tag{S5}$$

where

$$\alpha = \frac{4 \ln 2}{(\mathrm{FWHM})^2} \tag{S6}$$

with the Full Width at Half Maximum (FWHM) being set equal to 0.06.

We present results for k being either the surface X atom at which the catalytic reaction takes place or an X atom in the center of the crystal (a bulk X atom). We also present the PDOS averaged over all atoms of the crystal, i.e., including atoms from all surfaces as well as the bulk. The results for the structures 1y – 8y, 21y – 28y, 12y, and 31y are shown in Figs. S1, S2, and S3. The structures 12y and 31y correspond to a non-polar surface. For such surfaces, no charge transfer is needed in order to stabilize the system and, accordingly, the X atoms tend to have a total charge similar to what is found in the inner part of the system. As the figures show, the PDOS for these surface atoms and for the bulk X atoms are very similar. The fact that the PDOS curves for the surface atoms of the different non-polar surfaces look quite similar can be understood as a consequence of the similar chemical surroundings for these atoms.

On the other hand, for the polar surfaces, i.e., the structures 1y – 8y and 21y – 28y, the PDOS for the corresponding surface and bulk atoms differ significantly. In 15 out of the 16 cases, the Fermi level passes through the PDOS curve for the polar surface X atom indicating that these atoms have a metallic behavior. Accordingly, for these atoms many orbitals are available for the catalytic reaction, suggesting that the model without Z is the more appropriate one.

A further observation can be made from the PDOS figures. Thus, the bulk atoms have a

vanishing PDOS at the Fermi level, indicating that the bulk part of the system is insulating / semiconducting. In contrast to this, with just a single exception most systems have a very small gap at the Fermi level, as can be seen in Table S6. This small gap is caused by orbitals localized to the surfaces.

Shape	Surface	a_i	b_i	c_i	d_i	Shape	Surface	a_i	b_i	c_i	d_i
1	1	0.0	0.0	-1.0	20.0	5	1	0.0	0.0	-1.0	20.0
	2	0.0	0.0	1.0	25.0		2	0.0	0.0	1.0	30.0
	3	0.0	-1.0	0.0	18.0		3	0.0	-1.0	0.0	18.0
	4	0.0	1.0	0.0	18.0		4	0.0	2.0	-1.0	18.0
	5	-1.0	0.0	0.0	23.0		5	-2.0	0.0	1.0	30.0
	6	1.0	0.0	0.0	21.0		6	2.0	0.0	-1.0	46.0
2	1	0.0	0.0	-1.0	20.0	6	1	0.0	0.0	-1.0	20.0
	2	0.0	1.0	1.0	25.0		2	0.0	0.0	1.0	30.0
	3	0.0	-1.0	0.0	18.0		3	0.0	-1.0	0.0	18.0
	4	0.0	1.0	0.0	18.0		4	0.0	2.0	-1.0	20.0
	5	-1.0	0.0	0.0	23.0		5	-1.0	0.0	0.0	23.0
	6	1.0	0.0	0.0	21.0		6	1.0	0.0	0.0	21.0
3	1	0.0	0.0	-1.0	20.0	7	1	0.0	0.0	-1.0	20.0
	2	0.0	0.0	1.0	24.0		2	0.0	0.0	1.0	30.0
	3	0.0	-1.0	0.0	18.0		3	0.0	-1.0	0.0	18.0
	4	0.0	1.0	0.0	18.0		4	0.0	1.0	1.0	24.0
	5	-2.0	0.0	1.0	25.0		5	-2.0	0.0	1.0	25.0
	6	1.0	0.0	0.0	23.0		6	1.0	0.0	0.0	21.0
4	1	0.0	0.0	-1.0	20.0	8	1	0.0	0.0	-1.0	20.0
	2	0.0	0.0	1.0	30.0		2	0.0	0.0	1.0	30.0
	3	0.0	-1.0	0.0	18.0		3	0.0	-1.0	0.0	18.0
	4	0.0	1.0	0.0	18.0		4	0.0	1.0	1.0	23.0
	5	-2.0	0.0	1.0	25.0		5	-1.0	0.0	0.0	25.0
	6	2.0	0.0	-1.0	56.0		6	2.0	0.0	-1.0	23.0

TABLE S1: The values defining the surfaces for the shapes 1 – 8 of the present study.

Shape	Surface	a_i	b_i	c_i	d_i	Shape	Surface	a_i	b_i	c_i	d_i
11	1	0.0	0.0	-1.0	18.0	15	1	0.0	0.0	-1.0	20.0
	2	0.0	0.0	1.0	18.0		2	0.0	0.0	1.0	30.0
	3	0.0	-1.0	0.0	20.0		3	0.0	-1.0	0.0	18.0
	4	0.0	1.0	0.0	20.0		4	0.0	2.0	-1.0	18.0
	5	-1.0	0.0	0.0	23.0		5	-2.0	0.0	1.0	30.0
	6	1.0	0.0	0.0	21.0		6	2.0	0.0	-1.0	46.0
12	1	0.0	0.0	-1.0	20.0	16	1	0.0	0.0	-1.0	20.0
	2	0.0	1.0	1.0	25.0		2	0.0	0.0	1.0	30.0
	3	0.0	-1.0	0.0	18.0		3	0.0	-1.0	0.0	18.0
	4	0.0	1.0	0.0	18.0		4	0.0	2.0	-1.0	20.0
	5	-1.0	0.0	0.0	23.0		5	-1.0	0.0	0.0	23.0
	6	1.0	0.0	0.0	21.0		6	1.0	0.0	0.0	21.0
13	1	0.0	0.0	-1.0	20.0	17	1	0.0	0.0	-1.0	20.0
	2	0.0	0.0	1.0	24.0		2	0.0	0.0	1.0	30.0
	3	0.0	-1.0	0.0	18.0		3	0.0	-1.0	0.0	18.0
	4	0.0	1.0	0.0	18.0		4	0.0	1.0	1.0	24.0
	5	-2.0	0.0	1.0	25.0		5	-2.0	0.0	1.0	25.0
	6	1.0	0.0	0.0	23.0		6	1.0	0.0	0.0	21.0
14	1	0.0	0.0	-1.0	18.0	18	1	0.0	0.0	-1.0	20.0
	2	0.0	0.0	1.0	18.0		2	0.0	0.0	1.0	30.0
	3	0.0	-1.0	0.0	20.0		3	0.0	-1.0	0.0	18.0
	4	0.0	1.0	0.0	20.0		4	0.0	1.0	1.0	23.0
	5	-2.0	0.0	1.0	25.0		5	-1.0	0.0	0.0	25.0
	6	2.0	0.0	-1.0	56.0		6	2.0	0.0	-1.0	23.0

TABLE S2: The values defining the surfaces for the shapes 11 – 18 of the present study.

Shape	Surface	a_i	b_i	c_i	d_i	Shape	Surface	a_i	b_i	c_i	d_i
21	1	-0.0	-0.0	-3808.0	121856.0	31	1	-0.0	-0.0	-4352.0	121856.0
	2	-3584.0	2176.0	952.0	34048.0		2	-3584.0	1904.0	1088.0	34048.0
	3	3584.0	2176.0	952.0	26880.0		3	3584.0	1904.0	1088.0	26880.0
	4	0.0	-4352.0	1904.0	60928.0		4	0.0	-3808.0	2176.0	60928.0
22	1	-0.0	-0.0	-3808.0	121856.0	32	1	-0.0	-0.0	-4352.0	121856.0
	2	-3584.0	2176.0	1904.0	3584.0		2	-3584.0	1904.0	2176.0	3584.0
	3	3584.0	2176.0	1904.0	-3584.0		3	3584.0	1904.0	2176.0	-3584.0
	4	0.0	-4352.0	-0.0	121856.0		4	0.0	-3808.0	-0.0	121856.0
23	1	-0.0	-0.0	-3808.0	121856.0	33	1	-0.0	-0.0	-4352.0	121856.0
	2	-3584.0	2176.0	-0.0	64512.0		2	-3584.0	1904.0	-0.0	64512.0
	3	3584.0	2176.0	0.0	57344.0		3	3584.0	1904.0	0.0	57344.0
	4	0.0	-4352.0	3808.0	0.0		4	0.0	-3808.0	4352.0	0.0
24	1	-0.0	-0.0	-3808.0	121856.0	34	1	-0.0	-0.0	-4352.0	121856.0
	2	-3584.0	2176.0	2244.0	-7296.0		2	-3584.0	1904.0	2176.0	3584.0
	3	3584.0	2176.0	2244.0	-14464.0		3	3584.0	1904.0	2176.0	-3584.0
	4	0.0	-4352.0	-680.0	143616.0		4	0.0	-3808.0	-0.0	121856.0
25	1	-0.0	-0.0	-3808.0	121856.0	35	1	-0.0	-0.0	-4352.0	121856.0
	2	-3584.0	2176.0	-340.0	75392.0		2	-3584.0	1904.0	-0.0	64512.0
	3	3584.0	2176.0	-340.0	68224.0		3	3584.0	1904.0	0.0	57344.0
	4	0.0	-4352.0	4488.0	-21760.0		4	0.0	-3808.0	4352.0	0.0
26	1	-0.0	-0.0	-3808.0	121856.0	36	1	-0.0	-0.0	-4352.0	121856.0
	2	-3584.0	2176.0	2856.0	-26880.0		2	-3584.0	1904.0	3264.0	-26880.0
	3	3584.0	2176.0	-952.0	87808.0		3	3584.0	1904.0	-1088.0	87808.0
	4	0.0	-4352.0	1904.0	60928.0		4	0.0	-3808.0	2176.0	60928.0
27	1	-0.0	-0.0	-3808.0	121856.0	37	1	-0.0	-0.0	-4352.0	121856.0
	2	-3584.0	2176.0	-952.0	94976.0		2	-3584.0	1904.0	-1088.0	94976.0
	3	3584.0	2176.0	2856.0	-34048.0		3	3584.0	1904.0	3264.0	-34048.0
	4	0.0	-4352.0	1904.0	60928.0		4	0.0	-3808.0	2176.0	60928.0
28	1	-0.0	-0.0	-3808.0	121856.0	38	1	-0.0	-0.0	-7052.0	197456.0
	2	-2128.0	1292.0	-952.0	68768.0		2	-2788.0	1462.0	-1763.0	112094.0
	3	2128.0	1292.0	2856.0	-57344.0		3	2788.0	1462.0	5289.0	-90938.0
	4	0.0	-2584.0	1904.0	11424.0		4	0.0	-2924.0	3526.0	21156.0

TABLE S3: The values defining the surfaces for the shapes 21 – 28 and 31 – 38 of the present study.

Shape	$N_{\mathrm{Y,initial}}$	$N_{\mathrm{X,initial}}$	$N_{\mathrm{Y,final}}$	$N_{\mathrm{X,final}}$	Shape	$N_{\mathrm{Y,initial}}$	$N_{\mathrm{X,initial}}$	$N_{\mathrm{Y,final}}$	$N_{\mathrm{X,final}}$
1	3375	3375	3375	3375	21	1165	1186	1165	1165
2	3360	3465	3360	3360	22	1828	1967	1828	1928
3	2535	2640	2535	2535	23	1752	1824	1752	1752
4	3450	3435	3435	3435	24	1761	1890	1761	1761
5	2743	2544	2544	2544	25	1770	1883	1770	1770
6	3270	3165	3165	3165	26	1761	1900	1761	1761
7	2946	2927	2927	2927	27	1763	1902	1763	1763
8	2997	3010	2997	2997	28	1814	1918	1814	1814
11	2925	3150	2925	2925	31	1884	1888	1884	1884
12	3630	3345	3345	3345	32	1828	1967	1828	1828
13	2691	2592	2592	2592	33	1880	1891	1880	1880
14	2652	2842	2652	2652	34	1828	1967	1828	1828
15	2781	2643	2643	2643	35	1880	1891	1880	1880
16	3375	3210	3210	3210	36	1881	1884	1881	1881
17	3220	2980	2980	2980	37	1886	1891	1886	1886
18	3214	2965	2965	2965	38	1165	1186	1165	1165

TABLE S4: The number of Y and X atoms both before and after stoichiometry has been enforced.

Parameter	w	x	y	z
ϵ_{X}	-2.0	-2.0	-2.0	-2.0
ϵ_{Y}	-3.5	-5.5	-6.5	-6.5
U_{X}	2.0	2.0	1.0	1.0
U_{Y}	2.0	2.0	1.0	1.0
t^0_{XX}	-0.6	-0.6	-0.6	-0.6
t^0_{XY}	-0.8	-0.8	-0.8	-0.8
t^0_{YY}	-0.5	-0.5	-0.5	-0.5
f_v	0.5	0.5	0.5	1.0
r_c	2.5	2.5	2.5	2.5
r_0	2.5	2.5	2.5	2.5

TABLE S5: The parameter values for the four different materials.

System	Gap	System	Gap	System	Gap	System	Gap
1y	0.0011	21y	0.0004	11y	0.0020	31y	1.3815
2y	0.0014	22y	0.0004	12y	0.0001	32y	0.0004
3y	0.0005	23y	0.0009	13y	0.0002	33y	0.0009
4y	0.0038	24y	0.0008	14y	0.0002	34y	0.0004
5y	0.0038	25y	0.0016	15y	0.0014	35y	0.0009
6y	0.0039	26y	0.0008	16y	0.0029	36y	1.5111
7y	0.0013	27y	0.0010	17y	0.0026	37y	0.6539
8y	0.0006	28y	0.0014	18y	0.0014	38y	0.0039
1w	0.0002	21w	0.0003	11w	0.0002	31w	0.0005
2w	0.0004	22w	0.0001	12w	0.0001	32w	0.0003
3w	0.0002	23w	0.0001	13w	0.0007	33w	0.0003
4w	0.0001	24w	0.0005	14w	0.0001	34w	0.0003
5w	0.0003	25w	0.0002	15w	0.0005	35w	0.0003
6w	0.0002	26w	0.0004	16w	0.0004	36w	0.0001
7w	0.0003	27w	0.0004	17w	0.0004	37w	0.0007
8w	0.0002	28w	0.0001	18w	0.0002	38w	0.0002
1z	0.0017	21z	0.0024	11z	0.0003	31z	0.9529
2z	0.0015	22z	0.0004	12z	0.0012	32z	0.0003
3z	0.0015	23z	0.0003	13z	0.0003	33z	0.0024
4z	0.0012	24z	0.0009	14z	0.0022	34z	0.0003
5z	0.0036	25z	0.0010	15z	0.0003	35z	0.0024
6z	0.0018	26z	0.0019	16z	0.0006	36z	1.1938
7z	0.0009	27z	0.0006	17z	0.0007	37z	0.0175
8z	0.0002	28z	0.0010	18z	0.0017	38z	0.0075
		21x	0.0008			31x	0.0053
		22x	0.0004			32x	0.0004
		23x	0.0026			33x	0.0005
		24x	0.0004			34x	0.0004
		25x	0.0003			35x	0.0005
		26x	0.0002			36x	0.0108
		27x	0.0005			37x	0.0031
		28x	0.0008			38x	0.0014

TABLE S6: The HOMO-LUMO gap for the large finite crystalline systems.

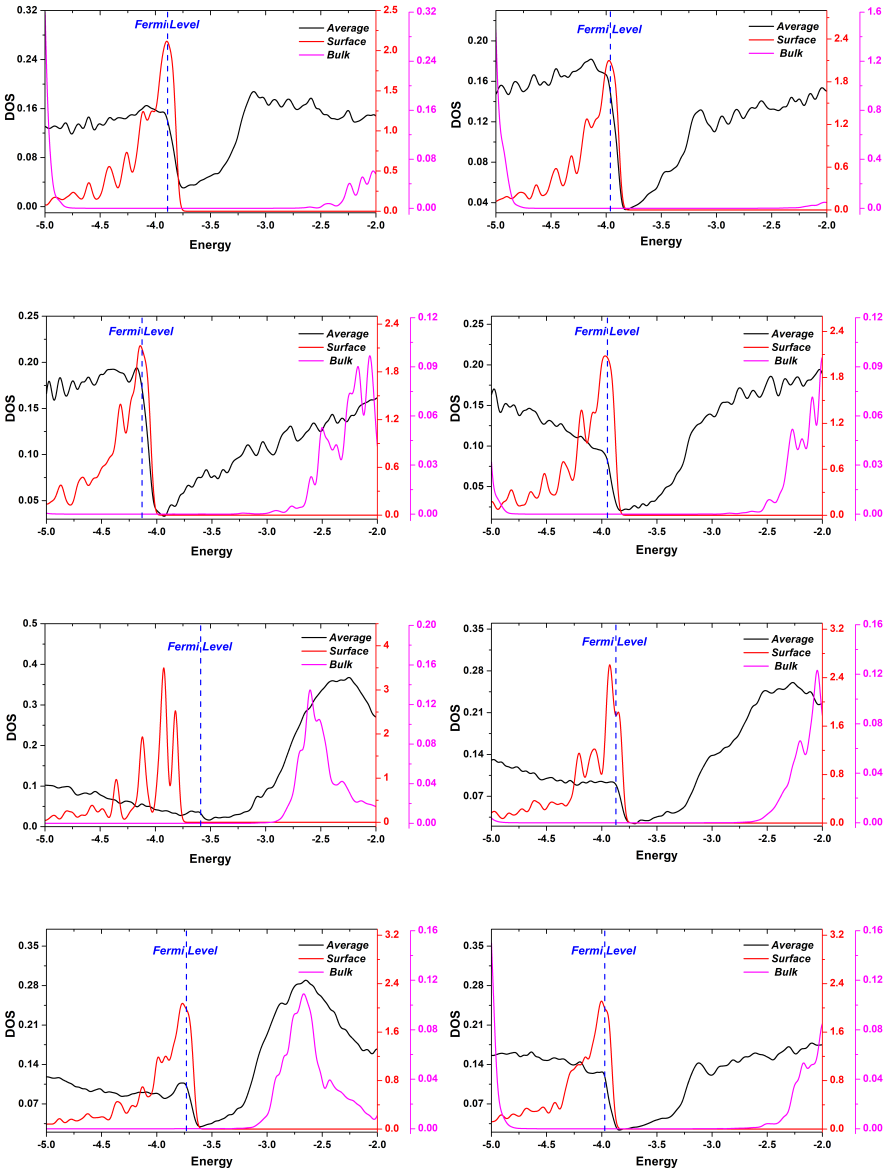

FIG. S1: PDOS curves for the structures 1y – 8y. The top left panel shows the PDOS for 1y, the top right one that for 2y, etc.

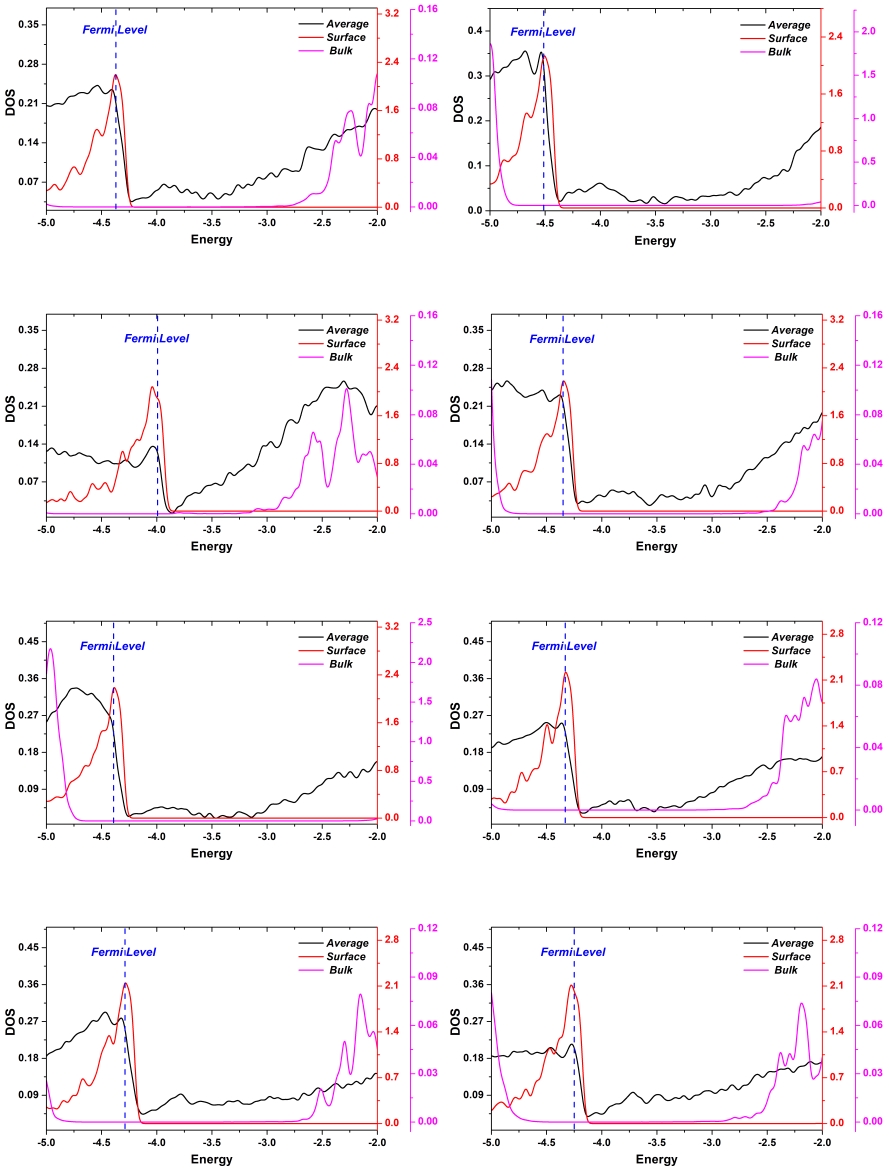

FIG. S2: As Fig. S1 but for the structures 21y – 28y.

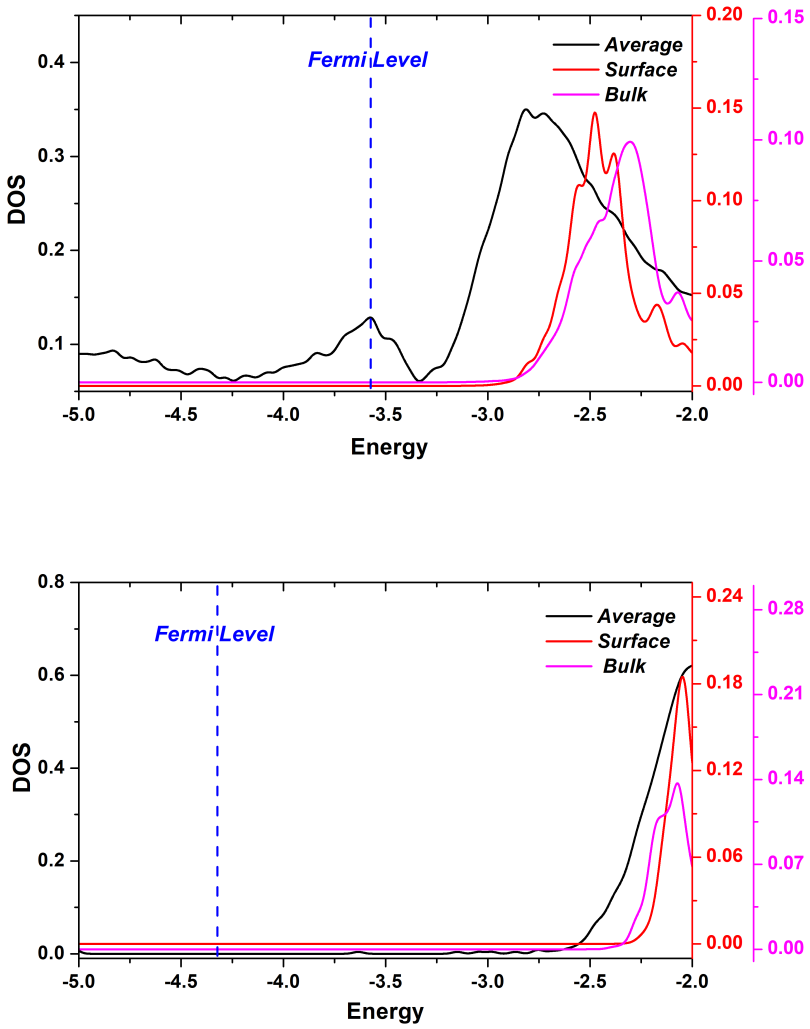

FIG. S3: PDOS curves for the structures (from top to bottom) 12y and 31y.

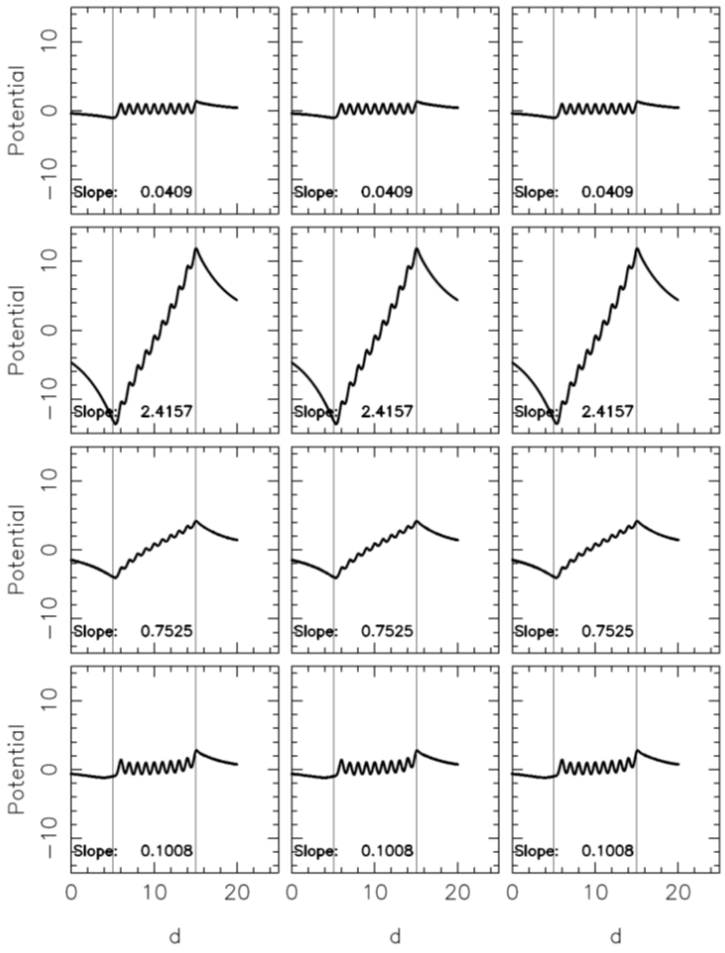

FIG. S4: The potential along three different lines passing through a small crystal. The vertical bars mark the boundaries of the crystal, and the three columns show the potential along the x, y, and z direction, respectively. The crystal has a CsCl-like structure with the lattice vectors along the x, y, and z directions. The four rows show the potential for different cases: Referring to Eq. (4) of the main text, in the top, $\hat{H}_{\rm lr}$ and $\hat{H}_{\rm sr}$ are both included; in the second row, none of those is included; in the third row, $\hat{H}_{\rm sr}$ is included; in the lowest row, $\hat{H}_{\rm lr}$ is included. Also given is the slope of a linear function fitting the curves. The oscillations are due to the atomic structure.

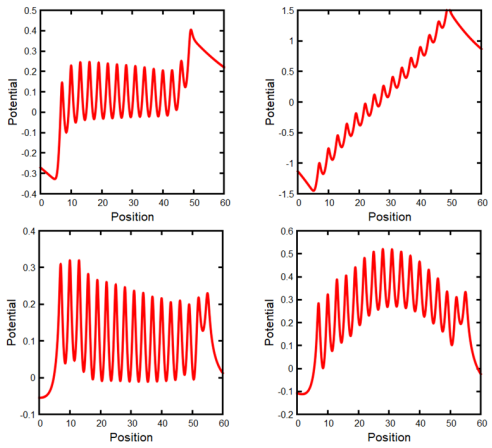

FIG. S5: The potential along one line passing through a small crystal from (at the left in each panel) slightly outside the common surface for all shapes and (at the right) to slightly outside the opposite surface. The results are for material w and for (top) shape 1 and (bottom) shape 5. In the right panels, all atomic charges have been set identical to the values of the central region. The oscillations are due to the atomic structure.

S2. HETEROGENEOUS CATALYSIS

Our goal in this section is to study the catalytic effect of shape on a representative heterogeneous reaction.

A. The parameters

All calculations related to heterogeneous catalysis were done using a home-made Fortran77 program. Fig. S6 contains an example of the relevant part of the input that was used, where the corresponding model system is given the name R1-y, meaning reaction 1 on catalyst y. The different reactions are defined through the values of the parameters of the Hamiltonian.

We now describe the input briefly. The three namelists, `inp3`, `inp4`, and `inp5`, contain parameter values which we split into those that describe solely the properties of the interacting species and those that specify the properties of the catalyst. We start with the parameters for the reacting species A,B,C:

- `epsa`, `epsb`, and `epsc`: on-site energies ϵ_A, ϵ_B, and ϵ_C.

- `tab0`, `tbc0`, `alab`, and `albc`: parameters for the nearest-neighbor hopping integrals t_{pq}, i.e., $t_{\mathrm{AB},0}$, $t_{\mathrm{BC},0}$, α_{AB}, and α_{BC}.

- `dab0` and `dbc0`: The equilibrium bond lengths, $d_{\mathrm{AB},0}$ and $d_{\mathrm{BC},0}$, for the isolated AB and BC molecules, respectively.

- `beab` and `bebc`: The parameters β_{AB} and β_{BC} for the repulsive potential.

- `nrepcase`: A parameter that describes whether an exponential (`nrepcase` = 1) or a power (`nrepcase` = 2) is used for the repulsive potential. Notice that the same type of dependence is used for all repulsive potentials as well as those describing the interactions with the catalyst.

- `vac` and `beac`: The parameters v_{AC} and β_{AC} for the next-nearest-neighbor repulsive potentials.

- Values for parameters v_{AB} and v_{BC} are calculated from the other parameter values.

Next, the parameters describing the properties of the catalyst are:

- `epsx`: The on-site energy ϵ_{X}.

- `txa0`, `alxa`, `bexa`, and `dxa0`: Parameters for the nearest-neighbor X-A interactions, i.e., $t_{\mathrm{XA},0}$, α_{XA}, and β_{XA}, as well as the equilibrium bond length for the isolated XA molecule. From these parameters v_{XA} is calculated.

- `vxb`, `vxc`, `bexb`, and `bexc`: Parameter values v_{XB}, v_{XC}, β_{XB}, and β_{XC} for the second- and third-nearest-neighbor repulsive potentials.

- `qx`: This is the atomic charge of the X atom that is employed when we do not use the charge of the selected surface atom for a given shape and surface within the no-Z model. Usually, we will set `qx` equal to the atomic charge of an X atom from the bulk of the crystal. By using this value for the atomic charge of X for all shapes, the effects of the variations in this charge on the catalytic properties can be studied.

For the repulsive potential, we also introduce

$$d_{\mathrm{AC},0} \;=\; d_{\mathrm{AB},0} + d_{\mathrm{BC},0}$$

$$
\begin{aligned}
d_{\mathrm{XB},0} &= d_{\mathrm{XA},0} + d_{\mathrm{AB},0} \\
d_{\mathrm{XC},0} &= d_{\mathrm{XA},0} + d_{\mathrm{AB},0} + d_{\mathrm{BC},0}.
\end{aligned} \tag{S7}
$$

B. Results

We report the following quantities:

- $E_{a,1}$: The activation energy for the reaction X-AB + C $\rightarrow$ X-A-B-C $\rightarrow$ X-A + BC, i.e., E_{tot}(X-A-B-C)$-E_{\mathrm{tot}}$(X-AB)$-E_{\mathrm{tot}}$(C).
- $E_{a,2}$: The activation energy for the reaction X-A + BC $\rightarrow$ X-A-B-C $\rightarrow$ X-AB + C, i.e., E_{tot}(X-A-B-C)$-E_{\mathrm{tot}}$(X-A)$-E_{\mathrm{tot}}$(BC).
- V_{X}: The long-range potential at the site of the X atom where the reaction takes place.
- $q_{0\mathrm{X}}$: The atomic charge of the X atom (no-Z model) where the reaction takes place before the reacting species have approached the surface.

Figs. S7 and S8 show the input files for the calculations using the catalyst y but for different shapes. In Tables S7 and S8 we list the resulting activation energies E_{a1} and E_{a2}.

As shown in Figs. S9 and S10, the activation energy shows a largely smooth dependence on the atomic charge of surface atom X prior to reaction.

Finally, we considered the other catalyst materials, i.e., the models x, z and w. For these materials only polar surface reaction 6 was examined. The input files are reproduced in Fig. S11 and the results summarized in Table S9. The activation energies as a function of the initial atomic charges of the surface X atom are shown in Fig. S12.

Fig. S13 shows how the charge on the X atom of one material varies with the charge on the X atom for another catalytic material when the shape is the same: different catalysts of different materials possess the same shape-dependence for the atomic charges on X and, consequently, the same shape-dependence for their catalytic performance.

```
&inp3 epsx=-5.5, epsa=-3.0, epsb=-3.2, epsc=-3.0,
txa0=3.0, tab0=5.0, tbc0=5.0, alxa=0.4, alab=0.5, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.1, bexa=4.5, beab=1.5, bebc=1.5,
nrepcase=2, &end
&inp4 qx=-0.86678, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
```

FIG. S6: The relevant part of the input file for the catalytic reaction of model R1-y.

```
&inp3 epsx=-5.5, epsa=-3.0, epsb=-3.2, epsc=-3.05,
txa0=3.0, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.5, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.05, bexa=4.5, beab=1.5, bebc=1.5,
nrepcase=2, &end
&inp4 qx=-0.86678, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
--------------------------------------------------------------------------------
&inp3 epsx=-5.5, epsa=-3.0, epsb=-3.2, epsc=-3.05,
txa0=3.0, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.5, albc=0.52,
dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.86678, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
--------------------------------------------------------------------------------
&inp3 epsx=-5.5, epsa=-3.0, epsb=-3.2, epsc=-3.05,
txa0=3.0, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.45, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.86678, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
--------------------------------------------------------------------------------
&inp3 epsx=-5.5, epsa=-2.8, epsb=-3.2, epsc=-2.90,
txa0=3.0, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.45, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.86678, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
--------------------------------------------------------------------------------
&inp3 epsx=-5.5, epsa=-2.8, epsb=-3.2, epsc=-2.60,
txa0=3.0, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.45, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.86678, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
```

FIG. S7: Input files for the catalytic reaction of the models (from top) R2-y, R3-y, R4-y, R5-y, and R6-y. The different models are separated by horizontal lines.

```
&inp3 epsx=-4.5, epsa=-2.8, epsb=-3.2, epsc=-2.60,
txa0=3.0, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.45, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.86678, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
--------------------------------------------------------------------------------
&inp3 epsx=-3.5, epsa=-2.8, epsb=-3.2, epsc=-2.60,
txa0=3.0, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.45, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.86678, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
--------------------------------------------------------------------------------
&inp3 epsx=-3.0, epsa=-2.8, epsb=-3.2, epsc=-2.60,
txa0=3.0, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.45, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.86678, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
--------------------------------------------------------------------------------
&inp3 epsx=-4.5, epsa=-2.8, epsb=-3.2, epsc=-2.60,
txa0=1.5, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.45, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.86678, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
--------------------------------------------------------------------------------
&inp3 epsx=-4.5, epsa=-2.8, epsb=-3.2, epsc=-2.60,
txa0=3.5, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.45, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.86678, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
```

FIG. S8: Input files for the catalytic reaction of the models (from top) R7-y, R8-y, R9-y, R10-y, and R11-y. The different models are separated by horizontal lines.

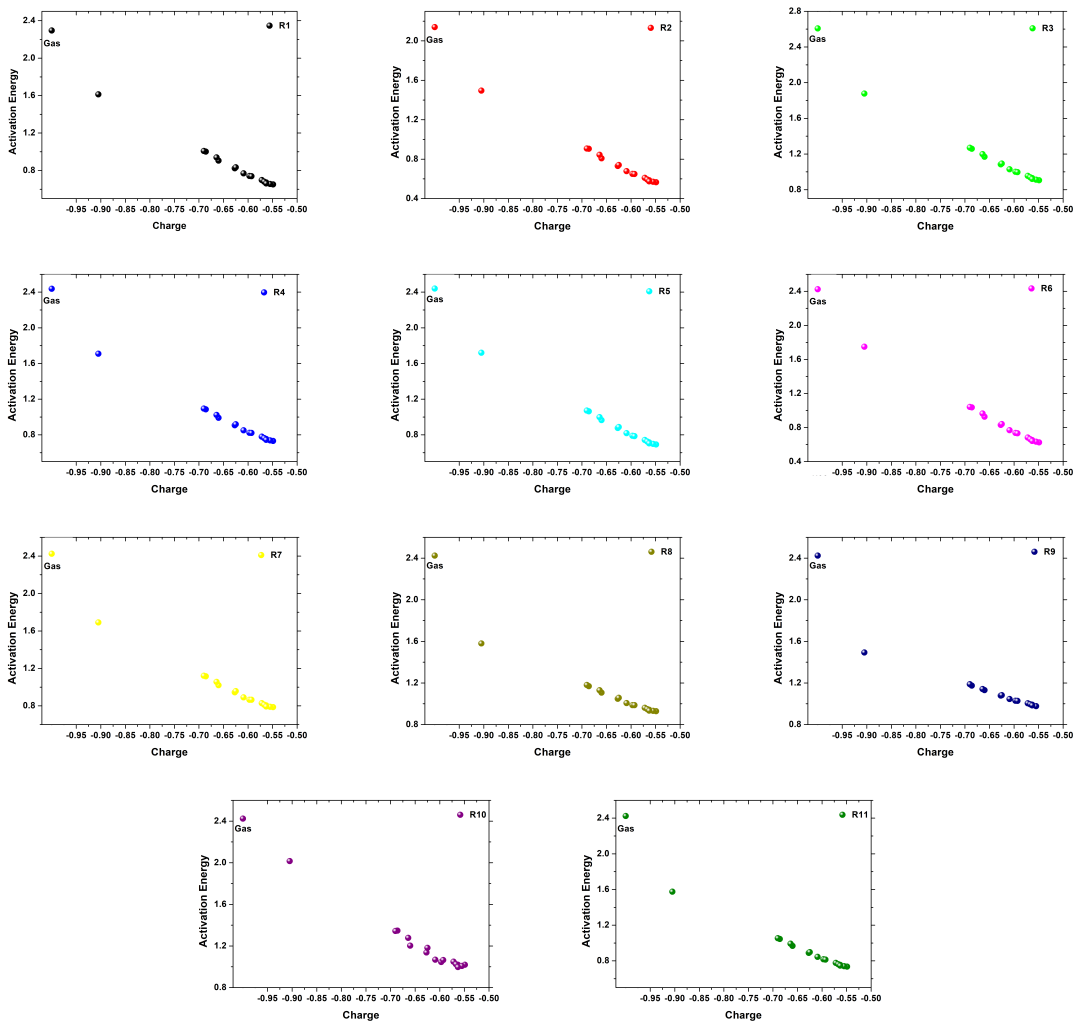

FIG. S9: Activation energy E_{a1} as a function of the initial atomic charge of the catalytic X atom for the reactions R1-y, R2-y, R3-y, R4-y, R5-y, R6-y, R7-y, R8-y, R9-y, R10-y, and R11-y from top left to bottom right. Only the polar surfaces are taken into account, i.e., the shapes 1y – 8y and 21y – 28y. The results marked 'Gas' are for the reaction in the gas phase without the catalyst.

R1-y																	
System:	1y	2y	3y	4y	5y	6y	7y	8y	21y	22y	23y	24y	25y	26y	27y	28y	Gas
E_{a1}	0.770	0.742	0.739	0.824	1.613	1.001	0.906	0.939	0.698	0.651	1.008	0.673	0.656	0.681	0.662	0.834	2.295
E_{a2}	2.882	2.903	2.917	2.862	2.474	2.789	2.801	2.818	2.958	3.003	2.780	2.970	2.987	2.961	2.962	2.878	2.295
System:	11y	12y	13y	14y	15y	16y	17y	18y	31y	32y	33y	34y	35y	36y	37y	38y	
E_{a1}	1.485	1.445	1.452	1.485	1.444	1.430	1.457	1.456	1.472	1.481	1.485	1.481	1.485	1.472	1.474	1.475	
E_{a2}	2.673	2.731	2.726	2.674	2.750	2.767	2.716	2.719	2.698	2.679	2.650	2.679	2.650	2.697	2.695	2.695	
R2-y																	
System:	1y	2y	3y	4y	5y	6y	7y	8y	21y	22y	23y	24y	25y	26y	27y	28y	Gas
E_{a1}	0.678	0.651	0.649	0.731	1.496	0.905	0.809	0.844	0.610	0.566	0.908	0.586	0.571	0.594	0.575	0.741	2.140
E_{a2}	3.019	3.041	3.056	2.997	2.585	2.921	2.932	2.952	3.099	3.146	2.909	3.112	3.130	3.102	3.104	3.014	2.368
System:	11y	12y	13y	14y	15y	16y	17y	18y	31y	32y	33y	34y	35y	36y	37y	38y	
E_{a1}	1.376	1.342	1.348	1.376	1.341	1.329	1.352	1.352	1.365	1.372	1.375	1.372	1.375	1.365	1.367	1.368	
E_{a2}	2.791	2.857	2.851	2.793	2.875	2.895	2.840	2.843	2.820	2.799	2.768	2.799	2.768	2.819	2.816	2.816	
R3-y																	
System:	1y	2y	3y	4y	5y	6y	7y	8y	21y	22y	23y	24y	25y	26y	27y	28y	Gas
E_{a1}	1.029	1.000	0.997	1.084	1.878	1.258	1.169	1.198	0.955	0.906	1.270	0.930	0.912	0.939	0.920	1.093	2.608
E_{a2}	2.838	2.858	2.872	2.818	2.435	2.742	2.760	2.773	2.911	2.954	2.738	2.923	2.939	2.914	2.916	2.834	2.304
System:	11y	12y	13y	14y	15y	16y	17y	18y	31y	32y	33y	34y	35y	36y	37y	38y	
E_{a1}	1.747	1.692	1.701	1.746	1.690	1.673	1.707	1.706	1.727	1.740	1.747	1.740	1.747	1.728	1.730	1.732	
E_{a2}	2.630	2.674	2.671	2.631	2.692	2.706	2.662	2.665	2.650	2.634	2.607	2.634	2.607	2.649	2.648	2.648	
R4-y																	
System:	1y	2y	3y	4y	5y	6y	7y	8y	21y	22y	23y	24y	25y	26y	27y	28y	Gas
E_{a1}	0.851	0.823	0.821	0.907	1.709	1.085	0.991	1.023	0.780	0.732	1.094	0.754	0.737	0.763	0.744	0.918	2.438
E_{a2}	2.260	2.281	2.295	2.239	1.858	2.165	2.179	2.196	2.337	2.381	2.158	2.348	2.365	2.339	2.341	2.257	1.723
System:	11y	12y	13y	14y	15y	16y	17y	18y	31y	32y	33y	34y	35y	36y	37y	38y	
E_{a1}	1.576	1.531	1.539	1.576	1.530	1.515	1.544	1.543	1.561	1.570	1.576	1.570	1.576	1.561	1.563	1.565	
E_{a2}	2.051	2.107	2.102	2.052	2.125	2.142	2.092	2.095	2.075	2.057	2.029	2.057	2.029	2.075	2.073	2.073	
R5-y																	
System:	1y	2y	3y	4y	5y	6y	7y	8y	21y	22y	23y	24y	25y	26y	27y	28y	Gas
E_{a1}	0.819	0.789	0.786	0.877	1.720	1.063	0.965	0.998	0.743	0.692	1.072	0.716	0.698	0.725	0.705	0.887	2.440
E_{a2}	2.230	2.251	2.264	2.210	1.829	2.135	2.151	2.166	2.304	2.347	2.128	2.316	2.333	2.307	2.309	2.225	1.720
System:	11y	12y	13y	14y	15y	16y	17y	18y	31y	32y	33y	34y	35y	36y	37y	38y	
E_{a1}	1.580	1.542	1.549	1.580	1.541	1.528	1.553	1.553	1.567	1.575	1.580	1.575	1.580	1.567	1.569	1.570	
E_{a2}	2.017	2.068	2.064	2.018	2.085	2.101	2.054	2.057	2.039	2.022	1.995	2.022	1.995	2.038	2.036	2.037	
R6-y																	
System:	1y	2y	3y	4y	5y	6y	7y	8y	21y	22y	23y	24y	25y	26y	27y	28y	Gas
V_X	-1.295	-1.233	-1.068	-1.215	-1.046	-1.221	-1.390	-1.148	-0.862	-0.747	-1.095	-0.895	-0.862	-0.910	-0.955	-0.917	
q_{0X}	-0.609	-0.597	-0.593	-0.627	-0.905	-0.686	-0.660	-0.664	-0.572	-0.549	-0.690	-0.563	-0.555	-0.567	-0.563	-0.625	
E_{a1}	0.769	0.736	0.732	0.831	1.749	1.036	0.927	0.964	0.683	0.626	1.042	0.653	0.634	0.663	0.642	0.841	2.424
E_{a2}	2.202	2.220	2.232	2.187	1.881	2.130	2.136	2.153	2.267	2.304	2.121	2.276	2.291	2.268	2.269	2.201	1.727
System:	11y	12y	13y	14y	15y	16y	17y	18y	31y	32y	33y	34y	35y	36y	37y	38y	
V_X	-0.064	0.779	0.687	-0.048	0.913	1.119	0.571	0.600	0.296	0.050	-0.278	0.050	-0.278	0.289	0.254	0.240	
q_{0X}	-0.853	-0.853	-0.852	-0.853	-0.852	-0.852	-0.853	-0.852	-0.853	-0.853	-0.853	-0.853	-0.853	-0.853	-0.853	-0.853	
E_{a1}	1.589	1.561	1.565	1.588	1.559	1.548	1.569	1.569	1.580	1.586	1.590	1.586	1.590	1.580	1.581	1.582	
E_{a2}	2.048	2.109	2.103	2.049	2.125	2.143	2.093	2.096	2.074	2.055	2.028	2.055	2.028	2.073	2.071	2.071	

TABLE S7: Calculated activation energies for models R1-y, R2-y, R3-y, R4-y, R5-y, and R6-y. Also shown, for R6-y, are the atomic charges of the catalyst X atom as well as the potential at the X site from the remaining part of the crystal. The results marked 'Gas' are for the reaction in the gas phase without the catalyst.

R7-y																	
System:	1y	2y	3y	4y	5y	6y	7y	8y	21y	22y	23y	24y	25y	26y	27y	28y	Gas
E_{a1}	0.891	0.865	0.865	0.944	1.691	1.115	1.021	1.056	0.829	0.787	1.121	0.805	0.790	0.812	0.793	0.957	2.424
E_{a2}	2.299	2.320	2.337	2.280	1.903	2.206	2.219	2.238	2.382	2.427	2.202	2.392	2.410	2.384	2.384	2.302	1.727
System:	11y	12y	13y	14y	15y	16y	17y	18y	31y	32y	33y	34y	35y	36y	37y	38y	
E_{a1}	1.553	1.485	1.495	1.552	1.481	1.458	1.504	1.503	1.529	1.545	1.556	1.545	1.556	1.529	1.532	1.535	
E_{a2}	2.110	2.162	2.159	2.111	2.182	2.197	2.149	2.152	2.134	2.116	2.084	2.116	2.084	2.133	2.131	2.132	
R8-y																	
System:	1y	2y	3y	4y	5y	6y	7y	8y	21y	22y	23y	24y	25y	26y	27y	28y	Gas
E_{a1}	1.007	0.987	0.987	1.048	1.580	1.169	1.107	1.130	0.961	0.929	1.181	0.943	0.932	0.949	0.934	1.057	2.424
E_{a2}	2.408	2.434	2.456	2.385	1.908	2.283	2.313	2.329	2.510	2.564	2.291	2.523	2.543	2.513	2.516	2.413	1.727
System:	11y	12y	13y	14y	15y	16y	17y	18y	31y	32y	33y	34y	35y	36y	37y	38y	
E_{a1}	1.457	1.321	1.321	1.455	1.315	1.277	1.357	1.355	1.406	1.439	1.463	1.439	1.463	1.407	1.413	1.418	
E_{a2}	2.153	2.166	2.149	2.154	2.188	2.190	2.163	2.167	2.164	2.153	2.123	2.153	2.123	2.164	2.163	2.166	
R9-y																	
System:	1y	2y	3y	4y	5y	6y	7y	8y	21y	22y	23y	24y	25y	26y	27y	28y	Gas
E_{a1}	1.046	1.029	1.028	1.078	1.493	1.174	1.131	1.142	1.005	17.699	1.188	0.991	0.977	0.995	0.985	1.083	2.424
E_{a2}	2.462	2.490	2.513	2.436	1.892	2.317	2.358	2.369	2.572	19.350	2.331	2.586	2.602	2.576	2.580	2.465	1.727
System:	11y	12y	13y	14y	15y	16y	17y	18y	31y	32y	33y	34y	35y	36y	37y	38y	
E_{a1}	1.374	1.194	1.220	1.371	1.188	1.140	1.240	1.236	1.305	1.349	1.382	1.349	1.382	1.295	1.301	1.321	
E_{a2}	2.153	2.127	2.138	2.153	2.149	2.140	2.135	2.136	2.150	2.148	2.122	2.148	2.122	2.139	2.139	2.156	
R10-y																	
System:	1y	2y	3y	4y	5y	6y	7y	8y	21y	22y	23y	24y	25y	26y	27y	28y	Gas
E_{a1}	1.068	1.046	1.065	1.138	2.016	1.347	1.203	1.278	1.049	1.019	1.344	1.019	1.008	1.025	0.997	1.182	2.424
E_{a2}	1.928	1.934	1.938	1.922	1.824	1.915	1.901	1.917	1.950	1.967	1.898	1.954	1.961	1.950	1.948	1.926	1.727
System:	11y	12y	13y	14y	15y	16y	17y	18y	31y	32y	33y	34y	35y	36y	37y	38y	
E_{a1}	1.895	1.894	1.897	1.896	1.889	1.878	1.900	1.899	1.901	1.899	1.895	1.899	1.895	1.901	1.901	1.900	
E_{a2}	1.910	1.998	1.987	1.912	2.013	2.043	1.973	1.976	1.944	1.921	1.898	1.921	1.898	1.943	1.940	1.938	
R11-y																	
System:	1y	2y	3y	4y	5y	6y	7y	8y	21y	22y	23y	24y	25y	26y	27y	28y	Gas
E_{a1}	0.844	0.817	0.814	0.889	1.575	1.045	0.967	0.992	0.777	0.735	1.054	0.755	0.740	0.762	0.746	0.898	2.424
E_{a2}	2.391	2.417	2.436	2.362	1.863	2.261	2.292	2.305	2.488	2.542	2.263	2.503	2.523	2.492	2.496	2.387	1.727
System:	11y	12y	13y	14y	15y	16y	17y	18y	31y	32y	33y	34y	35y	36y	37y	38y	
E_{a1}	1.446	1.368	1.380	1.446	1.365	1.343	1.388	1.387	1.417	1.436	1.449	1.436	1.449	1.418	1.421	1.424	
E_{a2}	2.095	2.114	2.116	2.097	2.133	2.138	2.109	2.112	2.107	2.097	2.070	2.097	2.070	2.106	2.105	2.108	

TABLE S8: Calculated activation energies for no-Z models R7-y, R8-y, R9-y, R10-y, and R11-y. The results marked 'Gas' are for the reaction in the gas phase without the catalyst.

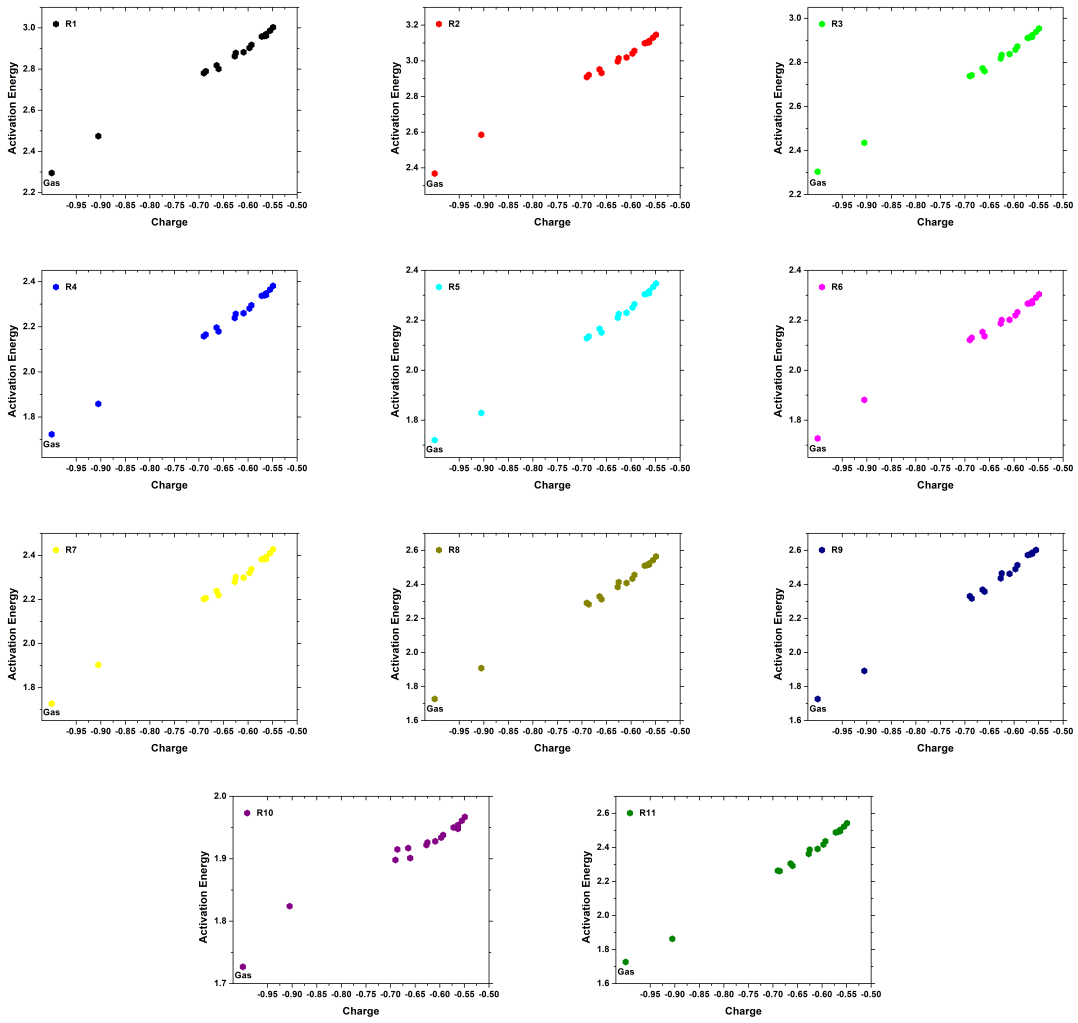

FIG. S10: As Fig. S9, but the activation energy E_{a2}. The results marked 'Gas' are for the reaction in the gas phase without the catalyst.

```
&inp3 epsx=-5.5, epsa=-2.8, epsb=-3.2, epsc=-2.60,
txa0=3.0, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.45, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.72058, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
-------------------------------------------------------------------------------
&inp3 epsx=-5.5, epsa=-2.8, epsb=-3.2, epsc=-2.60,
txa0=3.0, tab0=5.0, tbc0=5.1, alxa=0.4, alab=0.45, albc=0.5,
dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.86381, &end
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dxa0=2.0, dab0=2.1, dbc0=2.15, bexa=4.5, beab=1.5, bebc=1.52,
nrepcase=2, &end
&inp4 qx=-0.39991, &end
&inp5 vac=0.4, vxb=0.0, vxc=0.0, beac=3.0, bexb=1.0, bexc=1.0, &end
```

FIG. S11: Input files for the models (from top) R6-x, R6-z, and R6-w used for the catalytic reaction. The different models are separated by horizontal lines.

R6-x																	
System:	21x	22x	23x	24x	25x	26x	27x	28x	31x	32x	33x	34x	35x	36x	37x	38x	Gas
V_X	-0.421	-0.374	-0.526	-0.450	-0.466	-0.457	-0.458	-0.471	0.254	0.176	0.047	0.176	0.047	0.241	0.226	0.246	
q_{0X}	-0.507	-0.506	-0.534	-0.507	-0.509	-0.507	-0.504	-0.515	-0.699	-0.699	-0.699	-0.699	-0.699	-0.699	-0.699	-0.699	
E_{a1}	0.541	0.545	0.609	0.540	0.548	0.535	0.526	0.558	1.150	1.146	1.143	1.146	1.143	1.149	1.148	1.150	2.424
E_{a2}	2.382	2.390	2.345	2.381	2.380	2.378	2.380	2.367	2.233	2.225	2.214	2.225	2.214	2.232	2.230	2.231	1.727
R6-z																	
System:	1z	2z	3z	4z	5z	6z	7z	8z	21z	22z	23z	24z	25z	26z	27z	28z	Gas
V_X	-1.401	-1.305	-1.153	-1.301	-1.580	-1.313	-1.582	-1.243	-0.883	-0.686	-1.249	-0.926	-0.854	-0.958	-0.988	-1.022	
q_{0X}	-0.530	-0.525	-0.533	-0.552	-0.691	-0.570	-0.572	-0.562	-0.513	-0.484	-0.611	-0.498	-0.477	-0.504	-0.496	-0.563	
E_{a1}	0.475	0.468	0.504	0.555	1.030	0.643	0.591	0.605	0.464	0.402	0.743	0.416	0.364	0.428	0.397	0.599	2.424
E_{a2}	2.266	2.278	2.272	2.245	2.090	2.253	2.200	2.250	2.308	2.360	2.172	2.325	2.359	2.314	2.319	2.235	1.727
System:	11z	12z	13z	14z	15z	16z	17z	18z	31z	32z	33z	34z	35z	36z	37z	38z	
V_X	0.213	1.065	1.019	0.267	1.212	1.628	0.897	0.774	0.605	0.317	-0.111	0.317	-0.111	0.593	0.525	0.547	
q_{0X}	-0.872	-0.872	-0.872	-0.872	-0.872	-0.872	-0.872	-0.872	-0.872	-0.873	-0.873	-0.873	-0.873	-0.872	-0.872	-0.872	
E_{a1}	1.651	1.613	1.617	1.650	1.610	1.584	1.623	1.628	1.637	1.646	1.654	1.646	1.654	1.638	1.640	1.641	
E_{a2}	2.025	2.080	2.079	2.029	2.097	2.134	2.070	2.060	2.052	2.030	1.996	2.030	1.996	2.051	2.046	2.049	
R6-w																	
System:	1w	2w	3w	4w	5w	6w	7w	8w	21w	22w	23w	24w	25w	26w	27w	28w	Gas
V_X	-0.138	-0.117	-0.087	-0.115	-0.087	-0.069	-0.128	-0.126	-0.059	-0.065	-0.097	-0.079	-0.102	-0.062	-0.069	-0.092	
q_{0X}	-0.301	-0.300	-0.299	-0.300	-0.310	-0.305	-0.301	-0.302	-0.297	-0.298	-0.299	-0.298	-0.300	-0.297	-0.296	-0.298	
E_{a1}	0.046	0.049	0.048	0.047	0.051	0.044	0.040	0.042	0.045	0.046	0.048	0.050	0.103	0.080	0.045	0.057	2.424
E_{a2}	2.688	2.691	2.696	2.694	2.705	2.702	2.689	2.693	2.697	2.698	2.694	2.695	2.694	2.696	2.695	2.693	1.727
System:	11w	12w	13w	14w	15w	16w	17w	18w	31w	32w	33w	34w	35w	36w	37w	38w	
V_X	0.190	0.208	0.158	0.190	0.173	0.223	0.156	0.159	0.183	0.191	0.143	0.191	0.143	0.177	0.185	0.218	
q_{0X}	-0.396	-0.401	-0.400	-0.396	-0.400	-0.398	-0.399	-0.400	-0.396	-0.396	-0.398	-0.396	-0.398	-0.397	-0.396	-0.397	
E_{a1}	0.351	0.382	0.368	0.353	0.374	0.380	0.362	0.368	0.357	0.356	0.355	0.356	0.355	0.357	0.357	0.362	
E_{a2}	2.598	2.607	2.600	2.600	2.603	2.615	2.599	2.600	2.601	2.600	2.595	2.600	2.595	2.599	2.601	2.603	

TABLE S9: Calculated activation energies for the models R6-x, R6-z, and R6-w. Also shown are the initial atomic charge of the catalytic X atom as well as the potential at the same X site from the remainder of the crystal. The results marked 'Gas' are for the reaction in the gas phase without the catalyst.

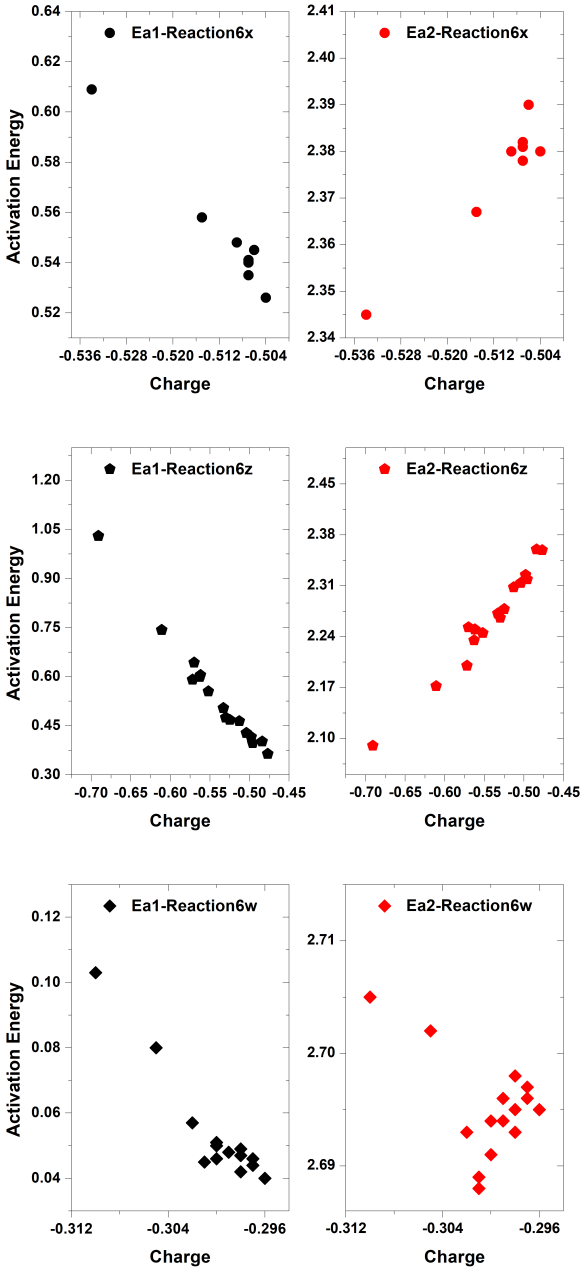

FIG. S12: Activation energies E_{a1} and E_{a2} as a function of the initial atomic charge of the catalytic X atom for the reactions (from top to bottom) R6-x, R6-z, and R6-w. Only the polar surfaces are taken into account, i.e., the shapes 1 – 8 and 21 – 28.

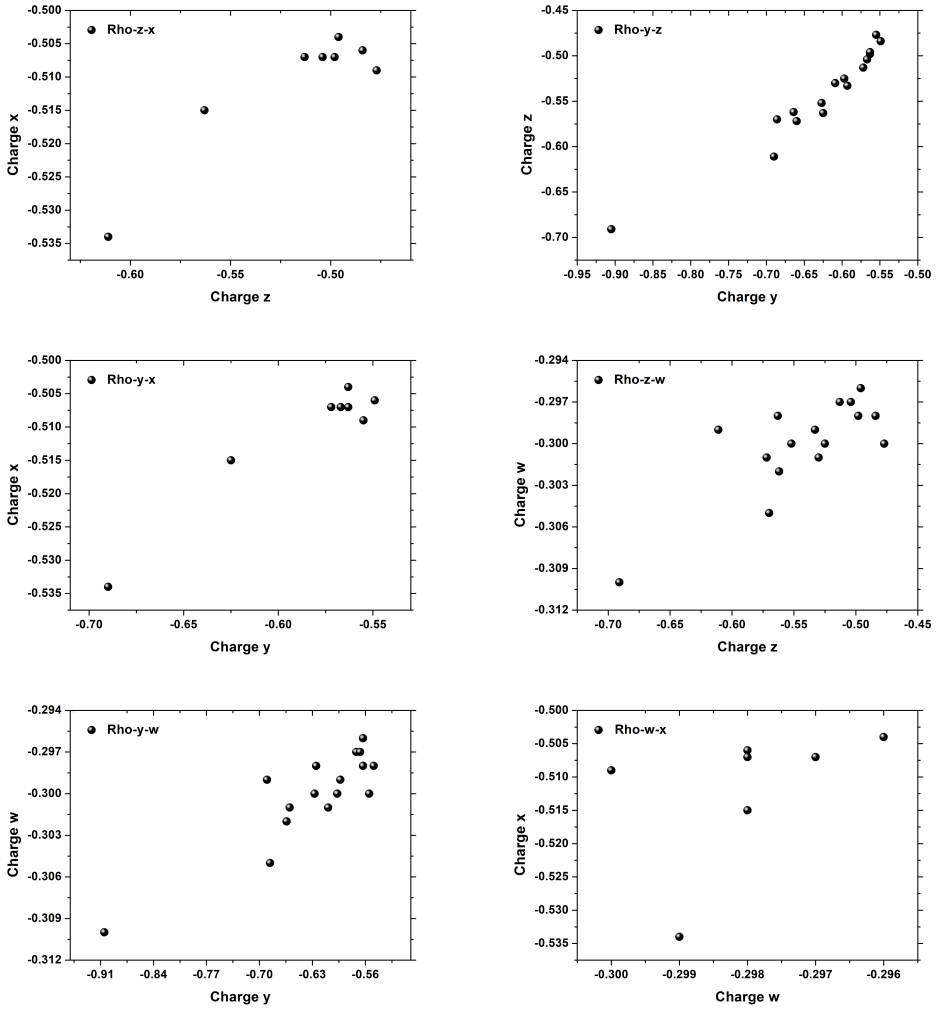

FIG. S13: Initial atomic charges for catalytic X atoms at the same position of the same surface and shape for different pairs of model catalysts. The panels are labelled Rho-z-x, Rho-y-z, etc. to denote the model pairs (z,x), (y-z), etc. Only the polar surfaces are taken into account, i.e., the shapes 1 – 8 and 21 – 28.