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# Stabilization of $\gamma$-$Al_2O_3$ surfaces by additives: insights from computer simulations

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Molecular dynamics simulations of the pure and doped surfaces of $\gamma$-$Al_2O_3$ were performed. Thermal behavior of both the D-layer of the (110) surface and the E-layer of the (001) surface was examined. An abrupt increase in mobility of surface ions was observed at high temperatures. An onset of diffusion occurs for the pure (110) surface at 1200 K. The instability is caused by the cation vacancies adjacent to the surface. Silicon and cerium ions deposited into the sub-surface vacancies reduce the mobility of the surface ions and prevent the onset of diffusion, cerium being more efficient in stabilization than silicon. This forms a microscopic picture of the role of additives in the stabilization of the $\gamma$-$Al_2O_3$ surfaces.

**Keywords:** $\gamma$-alumina; surface stabilization; molecular dynamics

## 1. Introduction

High surface area alumina is widely used as a metal catalyst support, e.g., in automotive catalytic converters used to reduce pollution from exhaust gases. The high surface area and an open porosity are the most important properties of the support, because they allow for high dispersion of the catalytic metal. The high dispersion guarantees efficient contact of the catalyst with flowing reactants. Supports made from $\gamma$-$Al_2O_3$ possess those crucial properties, but they lose them at high temperature. Two phenomena can account for the deterioration of the alumina support: sintering leads to pore closing and reduction in surface area, and phase transformation into corundum ($\alpha$-$Al_2O_3$) changes an active surface layer and promotes a low surface area structure. Preventing the alumina support from the thermal deterioration is an important task, because the high temperature can often occur in real working systems. A large number of additives to the $\gamma$-$Al_2O_3$ support have been shown to inhibit sintering and phase transformation. Such stabilizing

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additives include $SiO_2$, BaO, $CeO_2$, $La_2O_3$, etc. [1,2]. Although many experimental studies of the stabilization of the doped alumina have been performed over the last 30 years or more, the detailed atomistic mechanism of that process is still not fully understood. The role of the added cations is particularly unknown. Results of the molecular dynamics simulations presented in this paper provide new insights into the stabilization phenomenon.

Recently performed simulations of alumina crystals have shown that surfaces of $\gamma$-$Al_2O_3$ are significantly influenced by vacancies occurring in the crystals due to misfit between the stoichiometry of $Al_2O_3$ and the spinel structure [3]. Although the vacancies occur throughout the crystal, only those appearing near a surface directly affect the surface structure. Two surfaces are distinguished from all of the surfaces studied: the D-layer of the (110) surface and the E-layer of the (001) surface. While the bulk structure is generally preserved on those surfaces, some oxygens from the outermost layer are slightly rotated outside those surfaces. These are the oxygens that are located above the cation vacancies and thus have fewer bonds than the other oxygens on the surfaces. Regarding the surface stability, fewer bonds can imply an easier movement of the ions that can cause structural changes in the surface region. Therefore, thermal behavior of both these surfaces has been studied using molecular dynamics simulations. Pure surfaces, i.e., without any additives, as well as doped surfaces with additional cations deposited into the subsurface vacancies were examined and compared with each other to show the stabilizing effect and role of the additives. By the *sub-surface* positions we mean exactly the positions close to the surface, in the next deeper layer of atoms.

## 2. Computational procedure

Constant-pressure molecular dynamics simulations were performed with a fifth-order Nordsieck–Gear algorithm applied to integrate Newton's equations of motion with a time step of the integration of 0.2 fs. For the sake of pressure control, size of the simulation cell was weakly coupled to an imbalance between an internal stress tensor and the assumed external pressure of 1 atm. Only diagonal elements of the stress tensor were used, so each dimension of the sample was scaled independently every time step. Bulk samples were scaled in each of three directions. Surfaces were only scaled in the directions parallel to a surface. No scaling was imposed in the direction perpendicular to the surface. Temperature was controlled by scaling velocities every 20th time step.

Potential energy of the system is composed of contributions from two- and three-body interactions. The two-body part is a modified Born–Mayer–Huggins potential:

$$\Phi_{ij} = A_{ij}\exp(-r_{ij}/\rho_{ij}) + (q_i q_j e^2/r_{ij})\mathrm{erfc}(r_{ij}/\beta_{ij}),$$

where $q_i$ and $q_j$ are the ionic charges, $r_{ij}$ is the separation distance between ions $i$ and $j$, $e$ is the elementary charge, and erfc is the complementary error function. A repulsion between atomic cores is described by the first term. Coulomb interaction given by the second term is tempered by the error function due to screening of the ionic charges. The tempering reduces an effective range of the simulated electrostatic forces and allows for using of a short cut-off radius for the potential (5.5 Å). Masses and charges of the ions are shown in table 1. The softness parameter, $\rho_{ij}$, is equal to 0.29 Å for all pairs of the ions. The values of the adjustable parameters, $A_{ij}$ and $\beta_{ij}$, are summarized in table 2.

The three-body interactions imposed on all of the X–O–X and O–X–O triplets (where X is Al, Si, or Ce) have the following functional form:

$$\Psi_{jik} = \lambda_{jik} \exp[\gamma_{ij}/(r_{ij} - R_{ij}) + \gamma_{ik}/(r_{ik} - R_{ik})]\Omega_{jik}, \quad \text{if } r_{ij} < R_{ij} \text{ and } r_{ik} < R_{ik};$$

$$\Psi_{jik} = 0, \quad \text{if } r_{ij} \geqslant R_{ij} \text{ or } r_{ik} \geqslant R_{ik}$$

with the angular part, $\Omega_{jik}$, given by

$$\Omega_{jik} = (\cos\theta_{jik} + 1/3)^2, \quad \text{for X–O–X, and O–Si/Ce–O;}$$

$$\Omega_{jik} = [(\cos\theta_{jik} + 1/3)\sin\theta_{jik}\cos\theta_{jik}]^2, \quad \text{for O–Al–O}$$

where $\theta_{jik}$ is an angle formed by the ions $j$, $i$, and $k$ with the ion $i$ placed at the vertex. The values of the adjustable parameters, $\lambda_{jik}$, $\gamma_{ij}$ and $R_{ij}$, are listed in table 3. The same values of the two- and three-body parameters for the aluminum and oxygen atoms were used previously in the studies of bulk crystals and surfaces of aluminas [3]. The parameters for interactions with silicon were also already applied in the simulations of sodium aluminosilicate glasses [4]. The same parameters as for silicon are applied for cerium in this initial attempt. The main and only difference between the cations is in the atomic masses, but is has a visible effect on the dynamical properties of the doped surfaces, as discussed in the following sections.

Bulk samples of $\gamma$-$Al_2O_3$ with a desired orientation of the crystallographic planes were simulated at the beginning. A surface was created from the bulk sample by removing periodic boundaries in the vertical direction such that the desired plane became the surface exposed on the top of the sample. The periodic boundaries were kept in the other two directions. On average, the size of the surfaces was about 24 Å by 24 Å, while the height of the samples was about 50 Å. Atoms in the slab most apart from the surface were immobilized, so that they retained their

Table 1
Atom parameters

| Atom | Atomic mass | Charge |
|---|---|---|
| O | 16.000 | −2 |
| Al | 26.989 | +3 |
| Si | 28.090 | +4 |
| Ce | 140.120 | +4 |

Table 2
Two-body parameters

| Atom pair | $A_{ij}$ (fJ) | $\beta_{ij}$ (Å) |
|---|---|---|
| O–Al | 0.2490 | 2.34 |
| O–Si/Ce | 0.2962 | 2.34 |
| O–O | 0.0725 | 2.34 |
| Al–Al | 0.0500 | 2.35 |
| Al–Si/Ce | 0.2523 | 2.33 |
| Si/Ce–Si/Ce | 0.1877 | 2.30 |

original, bulk-like configuration. The thickness of the frozen slab was about 6 Å; that is more than the cut-off radius of the interactions. Above the surface, there was a thick slab of a free space terminated by a reflecting plane which redirected atoms reaching it back towards the surface.

The crystals of $\gamma$-$Al_2O_3$ have the structure of a defective spinel. There are two kinds of cation positions in the spinel: tetrahedral and octahedral. Some of them must be vacant as required by stoichiometry of $Al_2O_3$. In the simulated samples, the vacant positions were chosen randomly from tetrahedral sites of the bulk crystals [3]. The surfaces with different number and distribution of the vacancies in the surface or sub-surface layers were formed from such bulk samples. Therefore, the simulations were performed for several surfaces of each crystallographic orientation in order to obtain representative results.

After an initial relaxation of each surface for 10 ps at 300 K, Si or Ce ions were deposited one by one until all the vacancies present on the surface were filled. Some of the deposited cations were initially placed 5 Å above a surface after which they diffused until they were bonded by one of the surface oxygens and trapped into a vacant site. Such an event has shown that a diffusion-controlled process of cation deposition into vacancies can really occur. However, to speed up the deposition process, most of the deposited cations were placed close to vacant sites and then they moved quickly to the vacancies to find stable positions. The doped surfaces were also relaxed for 10 ps at 300 K. Both pure and doped surfaces were then used in the simulations at elevated temperatures up to 1500 K that also lasted for 10 ps each.

No attempt was made to compensate for a charge unbalance caused by the added cations. An electric field generated by them acts only on the ions located near the surface, because the electrostatic interactions have a short-range character in

Table 3
Three-body parameters

| Triplet [a] | $\lambda_{jik}$ (fJ) | $\gamma_{ij}$ (Å) | $R_{ij}$ (Å) |
|---|---|---|---|
| X–O–X | 0.001 | 2.0 | 2.6 |
| O–X–O | 0.024 | 2.8 | 3.0 |

[a] X = Al, Si, or Ce.

the present simulations. The total charge balance could be maintained by placing the compensating charges far away from the surface, e.g., at the bottom of the sample, but this could not influence the motion of the surface ions anyway.

## 3. Results

Two surfaces of $\gamma$-$Al_2O_3$ were studied in this work: the D-layer of the (110) surface and the E-layer of the (001) surface; the symbols taken from the commonly accepted notation [5]. Both surfaces are characterized by a significant influence of the sub-surface vacancies on the surface structure [3]. For each of the surfaces studied, the vacancies are not present in the outermost layer of atoms, because the cations only occupy octahedral positions there. However, in the next deeper layer, the sub-surface layer, the cations occupy sites of both kinds, so the vacancies occur just below the surface. Even being in the sub-surface layer, the vacancies are visible in pictures of the pure surfaces shown in fig. 1.

On the pure (110) surface, due to the presence of the cation vacancies in the sub-surface layer, some oxygens are bonded to only one aluminum ion each; these are the non-bridging oxygens (NBOs). Those anions are rotated above the surface and not only screen the cations to which they are bonded, but also expose the vacancies. After the deposition of the Si or Ce ions into the vacant sites, the NBOs return to the regular crystallographic positions as also shown in fig. 1. The former vacancies are then closed and the deposited cations do not appear on the surface. The oxygens are then bonded to two cations each: one Si (Ce) and one Al. On the pure (001) surface, there are two oxygens adjacent to each vacancy present in the sub-surface layer. Each of these oxygens is bonded to two, instead of three, Al ions. Although more strongly bonded than the respective oxygens on the (110) surface, those oxygens are also slightly rotated above the surface. When during the deposition the vacancies become filled with the cations, the anions go back to their regular crystallographic positions. For both of the (110) and (001) surfaces, although most of the vacancies in the bulk of the crystal remain empty while only those in the sub-surface layer are filled by the deposited cations, the doped surfaces accurately resemble those of the non-stoichiometric models of the $\gamma$-$Al_2O_3$ surfaces in which the vacancies are omitted [5].

Effect of temperature on behavior of the pure and doped surfaces is visible in the motion of the surface ions. Fig. 2 shows projections of the trajectories of the oxygen ions from the D-layers of the (110) surfaces at different temperatures. Trajectories of the aluminum ions and the deposited cations are not shown, but they follow the same pattern. On the pure surface, even at 300 K, the NBOs exhibit more extensive vibrational motion than the other oxygens. With temperature increasing up to 1200 K, vibration amplitudes increase for all the surface oxygens, but the trajectories remain localized. Diffusion of the ions appear at 1300 K. Trajectories of some oxygens, especially the NBOs, are no longer localized. The ions

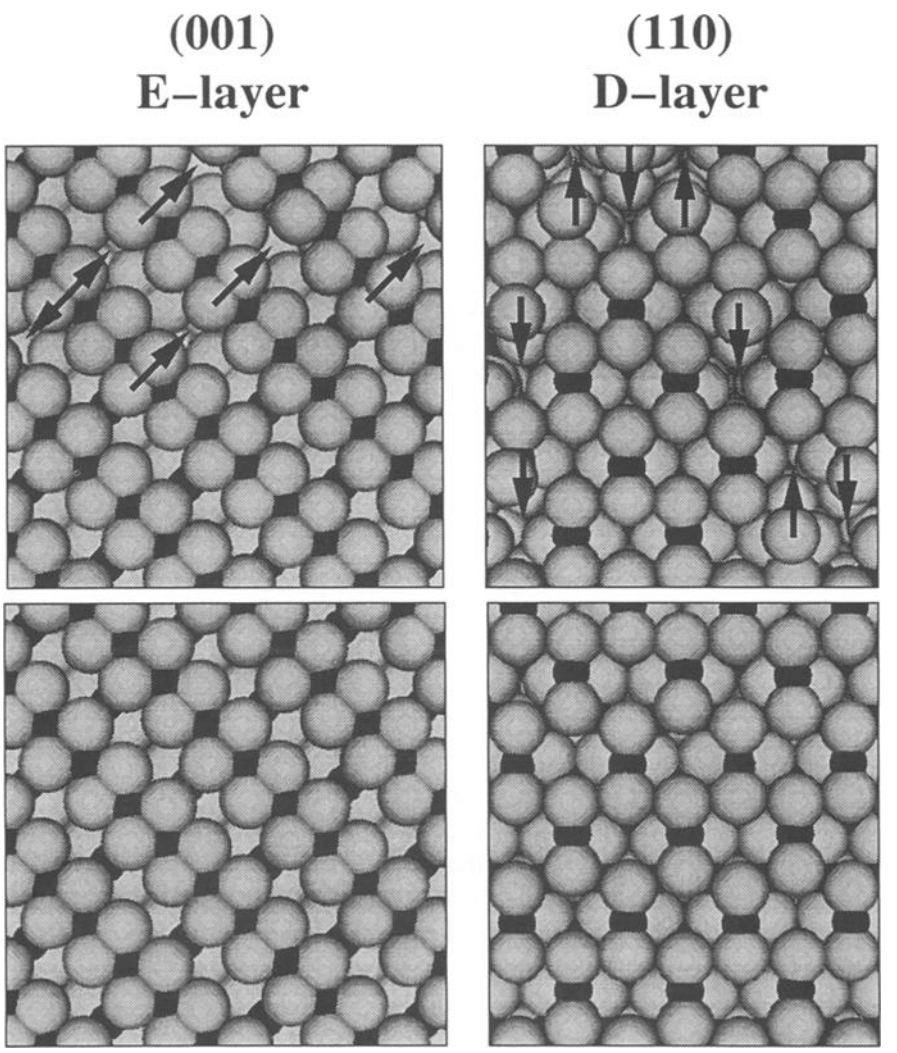


Fig. 1. Snapshots of the pure (top) and doped (bottom) surfaces of $\gamma$-$Al_2O_3$; O – large, gray circles, Al – small, black circles, Si/Ce – small, gray circles. Arrows indicate the sub-surface vacancies.

move across the surface. Behavior shown in fig. 2 is representative for all the surfaces studied. Three surfaces in four experience an onset of the diffusion at the temperature 1200–1300 K and one surface at 1100–1200 K.

Fig. 2 also shows that the surfaces doped with Si or Ce ions behave quite differently than the pure one. Not only are all of the oxygen ions located in the regular crystallographic positions, but also the vibrational motion of the ions is restrained even at 300 K. Vibrations on the surface ions have larger amplitudes at 1200 K than at 300 K, but nevertheless the amplitudes are smaller on the doped surfaces than on the pure one. Ion trajectories on the doped surfaces at 1300 K have a simi-

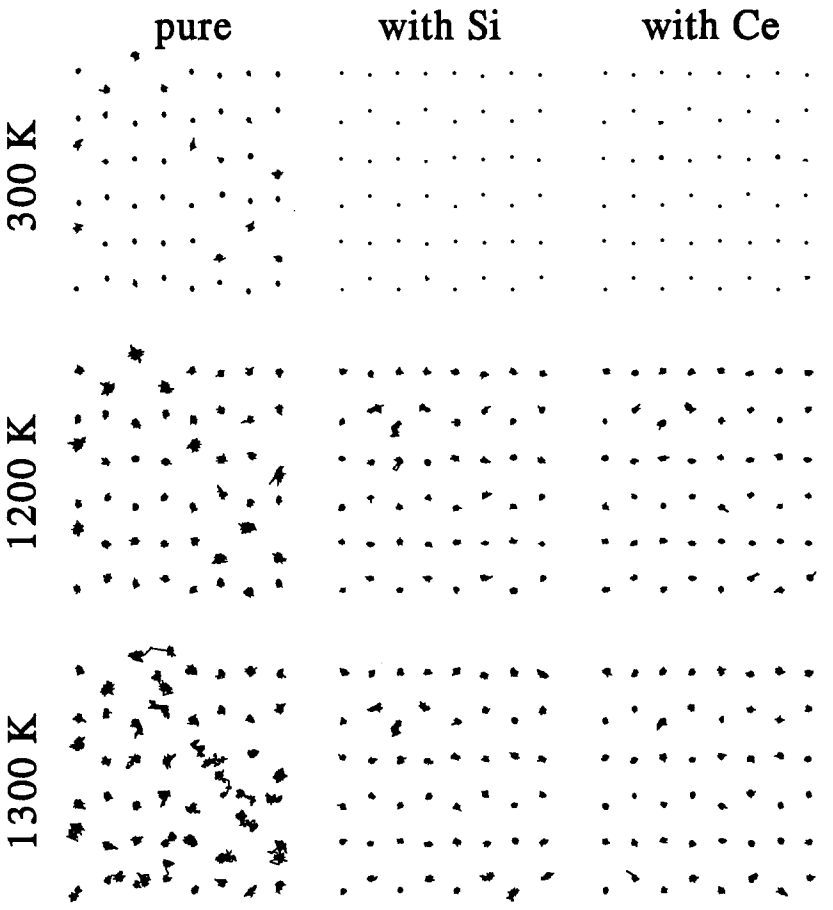


Fig. 2. Projections on the surface plane of the 10 ps trajectories of the oxygen ions on the pure and doped surfaces of the D-layer of $\gamma$-$Al_2O_3$ at 300, 1200, and 1300 K.

lar appearance to the ones at 1200 K. Motion of the ions is still localized. For the D-layer of the (110) surface, there is a dramatic difference between trajectories on the doped surfaces and on the pure one. At 1300 K, there is ion diffusion on the pure surface, but there is no such behavior on the doped surfaces. Moreover, surfaces doped with cerium, the heavier atom, are less affected by temperature than the surfaces doped with silicon. At higher temperatures (1200–1300 K), spots made by the projected trajectories of the ions on the surface with Ce are smaller than the ones with Si. It is also clearly visible in fig. 3, where the quantitative comparison of the movement of the surface ions at different temperatures is shown.

In fig. 3, profiles of the mean square displacements (MSD) of the oxygen ions are presented for the pure samples as well as the doped ones. The profiles were obtained by dividing a crystal into slabs parallel to a free surface and calculating an average MSD for atoms present in a slab at an initial moment. The slabs had a thickness of about 2 Å each, so every slab contained an entire layer of atoms. On

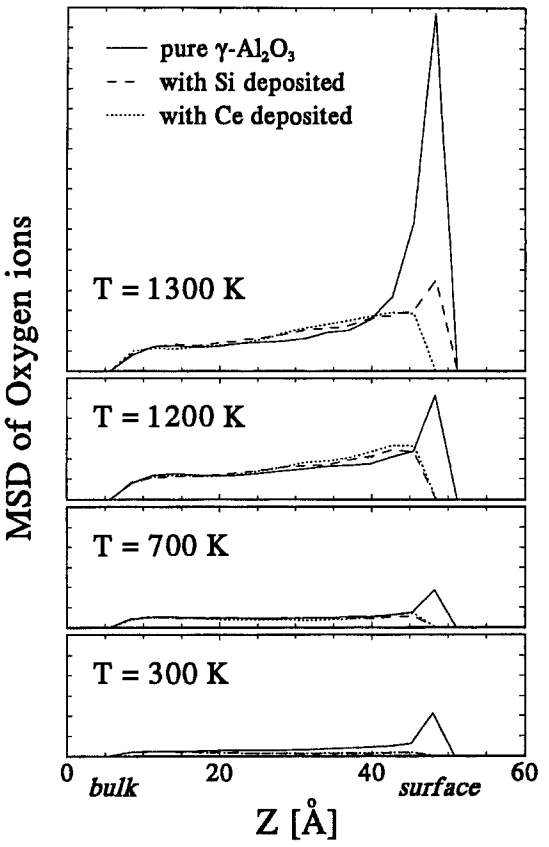


Fig. 3. Profiles of the mean square displacements (MSD) of the oxygen ions in the pure and doped samples of the D-layer of $\gamma$-$Al_2O_3$ at different temperatures shown versus distance perpendicular to the free surface. Although units are not shown on the MSD axes, all graphs are made in the same scale.

the pure (110) surface, for all the temperatures, the outermost layer formed by the NBOs has the MSD remarkably larger than other oxygens. There is no such apparent change across any of the profiles of the doped surfaces. The most abrupt change appears at 1300 K for the surface doped with Si, but not for the one doped with Ce. Moreover, the MSD of the ions in the outermost regions are significantly decreased on the doped surfaces compared to the pure one. The most distinct difference occurs again at 1300 K.

Projections of the trajectories of the oxygen ions on the E-layer of the (001) surface are shown in fig. 4. It is a little difficult to find out from the figure for the pure surface at 300 K which oxygens are located above the sub-surface vacancies. Their vibrations have the same amplitude as those of the other oxygens, but the less-bonded oxygens are displaced from the regular crystallographic positions and this can be seen as small distortions in the lines formed by atoms. However, the

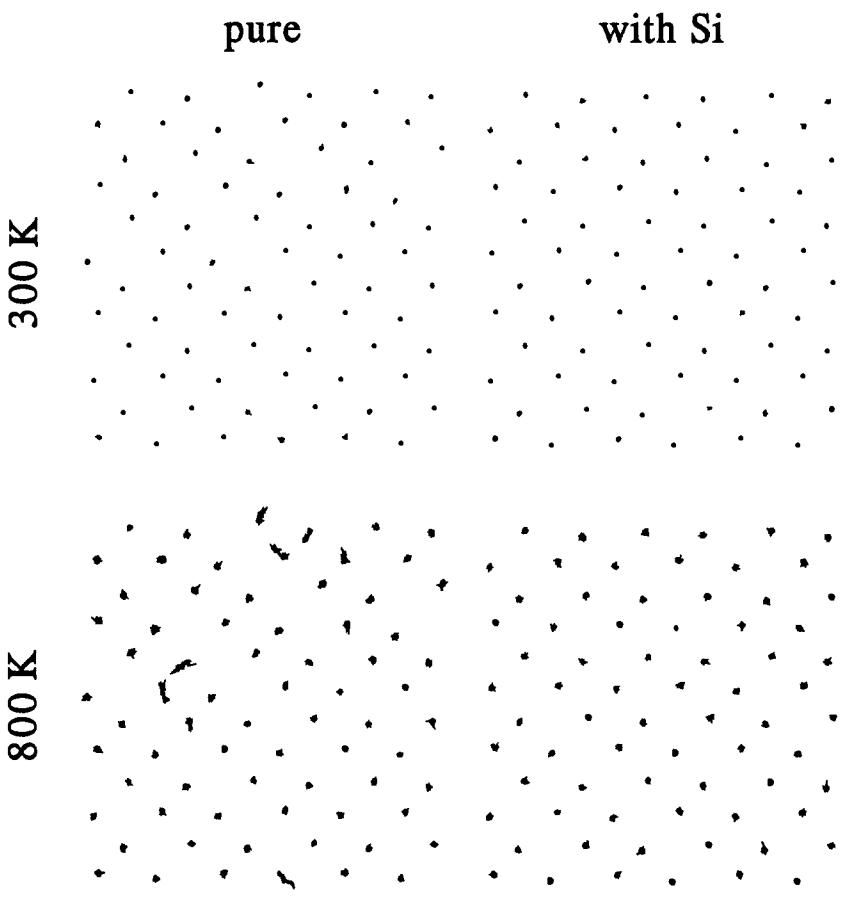


Fig. 4. Projections on the surface plane of the 10 ps trajectories of the oxygen ions on the pure and doped surfaces of the E-layer of $\gamma$-$Al_2O_3$ at 300 and 800 K.

lack of bonding cations is clearly revealed at 800 K. The oxygens bonded to only two cations each vibrate more strongly than the other oxygens and even try to change positions in a somewhat correlated way, but ion diffusion is not observed on the pure surface of the E-layer even at temperature as high as 1500 K. All the oxygen ions on the (001) surface doped with silicon vibrate in the regular positions with similar amplitude at 300 K. Amplitude of vibrations increases with temperature, but even at 800 K the picture of trajectories remains homogeneous. This is a clear difference in the behavior of the pure and doped surfaces of the E-layer at 800 K. The difference is even more visible in the plots of the MSD of the oxygen ions on the (001) surface shown in fig. 5. The oxygens are more mobile on the pure surface than on the doped ones at all temperatures, but the most striking difference occurs at 800 K. At this temperature the outermost layer of the pure surface has significantly larger MSD than the rest of the crystal. There is no such a change across the doped crystals.

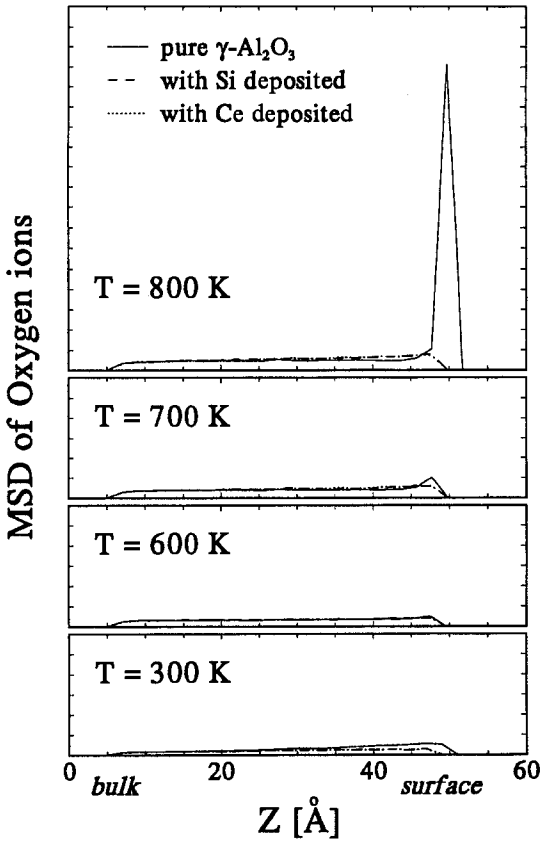


Fig. 5. Profiles of the mean square displacements (MSD) of the oxygen ions in the pure and doped samples of the E-layer of γ-$Al_2O_3$ at different temperatures shown versus distance perpendicular to the free surface. The curves for the doped samples coincide. Although units are not shown on the MSD axes, all graphs are made in the same scale.

## 4. Discussion

There are some similarities and some differences in the thermal behavior of the pure surfaces of the D- and E-layers of γ-$Al_2O_3$. For both surfaces, the vacancies occurring in the sub-surface layers induce motion of the surface ions at high temperatures because the oxygen ions that might be bonded to the vacant cations are instead more free to move. Such a movement can initiate sintering and phase transformation that lead to reduction in surface area of the alumina used as a catalyst support. While the motion starts at a lower temperature on the (001) surface than on the (110) one, the induced changes have limited range and can only lead to formation of local defects. However, on the (110) surface, there is an onset of diffusion at high temperature and it seems to be a key factor in the deterioration of the surface.

The destructive action is caused by a small fraction of all the vacancies present in the crystals of $\gamma$-$Al_2O_3$: the ones which are located close to the surfaces. When Si or Ce cations are deposited just into the sub-surface vacancies, they form additional bonds with the mobile oxygens and in this way stabilize the surface. Even at high temperatures, the movement of the ions on the doped surfaces is confined and the crystallographic structures of the surfaces are well preserved. This is a clear indication of the stabilizing action of the cations deposited into the sub-surface vacancies. Moreover, cerium ions stabilize the surfaces better than silicon ions. In the current simulations, this difference is only due to the difference in the atomic masses.

It is worthy to note that an agreement was found between results of the recent LEIS experiments [6] and the structures of the pure and doped surfaces of the D-layer obtained from the simulations. Screening of the aluminum ions by the non-bridging oxygens on the pure surface and return of those oxygens to the regular positions after deposition of additional cations may explain a sudden increase in the Al scattering signal observed after deposition of additives on the $\gamma$-$Al_2O_3$ surface [7].

Alvarez et al. have recently published results of their molecular dynamics simulations of $\gamma$-alumina doped with lanthanum ions [8]. It was shown in that paper that a perovskite-like phase is formed in such a system at 1500 K. A conclusion has been drawn that this might be responsible for the stabilization of the alumina surfaces by the additives. There exist important differences between those simulations and the present ones. Although surfaces were an object of interest of those studies, only bulk samples were simulated and the results were extrapolated for the surfaces. The simulations were performed at only one temperature, 1500 K, at which real $\gamma$-alumina is already expected to undergo sintering and the phase transformation. The role of the cation vacancies has not been discussed by the authors, although in the previous paper they have noticed presence of the vacancies [9]. Therefore, the work by Alvarez et al. is complimentary rather than contradictory to the present one, because it may describe behavior at later stages of the thermal process or at different conditions.

## 5. Conclusions

The simulations show that instability of the $\gamma$-$Al_2O_3$ surfaces is caused by the cation vacancies occurring near a surface. The surface oxygens which might be bonded to the vacant cations exhibit the strongest vibrational motion and some of them initiate diffusion that can cause deterioration of the surface. The surface Al ions follow the behavior of the oxygens. The vacancies cannot be avoided because they naturally exist due to the difference between stoichiometry of $Al_2O_3$ and the spinel structure. However, the destructive action of the vacancies can be limited by doping the surface with cations. Si or Ce ions deposited into the sub-surface vacan-

cies reduce mobility of the surface oxygens and prevent the onset of diffusion. Cerium having a larger atomic mass acts even more efficiently than silicon. In such a way the additives stabilize surfaces of $\gamma$-$Al_2O_3$ catalyst support against thermal deterioration.

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