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Onset of perovskite formation in the catalytic system La_2O_3/γ-Al_2O_3

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Molecular dynamics simulations of model systems for the surface interaction of lanthanum oxide supported on γ-alumina have been carried out at 1500 K. The onset of formation of perovskite-like phases has been analysed in samples containing four different concentrations of lanthanum oxide. A mechanism of the formation of perovskite-like polyhedra is proposed. This mechanism essentially involves a displacement of an oxide ion associated to an octahedral aluminum by a lanthanum ion and appears to be independent of La_2O_3 loadings.

Keywords: Alumina; perovskite; molecular dynamics

1. Introduction

It has been experimentally observed that when γ-Al_2O_3 is doped with lanthanide oxides there is a thermostabilisation effect of the alumina surface at high temperature [1]. The formation of perovskite-like phases has been claimed to be responsible for such an effect [2]. In industrial catalytic systems low lanthanum oxide loadings are usually employed [3], however experimental evidence of perovskite-like phases for these concentrations have not been reported to date because of the lack of techniques to follow the surface reconstruction process. Numerical simulation techni-

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ques constitute a valid alternative to study the mechanism of formation in systems with some degree of disorder [4]. In order to acquire an insight into the surface interaction between lanthanum oxide and alumina, molecular dynamics simulations of the structure of the γ-alumina lattice doped with lanthanum ions have been performed. In this work we report a possible mechanism of formation of perovskite-like phases as predicted by molecular dynamics simulations at high temperature based on the time evolution of the local structure around the lanthanum ions.

2. Method

Molecular dynamics simulations involve the solution of the classical equations of motion of a set of N particles which interact through a pairwise additive potential. In our simulations a Pauling type function was used, which includes a Coulombic term and a steric repulsion term given by

$$V(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} \left[1 + \text{sign}(q_i q_j) \left(\frac{\sigma_i + \sigma_j}{r_{ij}} \right)^n \right],$$

where r is the interatomic distance, q are the effective charges, and σ are the effective ionic radii. The exponent n was taken to be 9 following Adams and McDonald [5]. The values of charges and ionic radii used in the simulations are shown in table 1, and they are the same as previously used [6,7]. The long range Coulombic contributions of the potential were handled by the Ewald summation method, and the forces were calculated through numerical derivatives and spline interpolation. Energy fluctuations were at most 0.05% relative to the mean value with an integration time step $\Delta t = 10^{-5}$ s.

A set of molecular dynamics simulations in the microcanonical ensemble were performed on $La_2O_3/\gamma\text{-}Al_2O_3$ with 1.04, 5.03, 10.06 and 19.96 weight per cent of lanthanum oxide which cover the concentration range employed in experiments [6]. The initial configurations were taken from the equilibrated system at 300 K used in a previous work [8]. In all runs a period of 15 ps was allowed for equilibration before a production period of 25 ps. The formation of perovskite on lanthanum-doped γ-alumina surface has been detected by experimental techniques [6] at 1200 K, therefore the simulation temperature was chosen to be higher than the experimental one to promote ionic mobility and to shorten the simulation time.

Table 1
Potential parameters

	$q(e)$	σ(Å)
Al	1.65	0.62
O	−1.10	1.20
La	1.68	1.20

The environment of al lanthanum ions was then monitored as a function of time in order to observe any changes in either their position or coordination.

3. Results and discussion

On the left hand side of fig. 1 the typical environment of lanthanum embedded in the lanthanum-doped γ-alumina structure at 300 K is shown, and on the right hand side, the correspondent perovskite structure. In the first case the lanthanum ion can be described as located on the center of a face centered cubic structure, having octahedral coordination of oxygens. In the second case the oxygen ions are located in the middle of the edges of the cube, and therefore, the lanthanum coordination in this situation is twelve. After the formation of perovskite the situation depicted on the left hand side would be transformed into one of the type depicted on the right hand side.

The structural transformation illustrated by the snapshots of one lanthanum ion environment shown in fig. 2, can be described as follows, after monitoring the evolution of lanthanum ions environment through the molecular dynamics simulations. The increase of temperature from 300 to 1500 K promotes the mobility of all particles and hence the increase of collision probability. We can distinguish two kinds of collisions in which lanthanum ions are involved, as a function of the effectiveness in the formation of the new phase. They are related to the tetrahedrally and octahedrally coordinated aluminum cations found in γ-alumina. In general, after the collision a distortion of the lattice is created with a further reconstruction

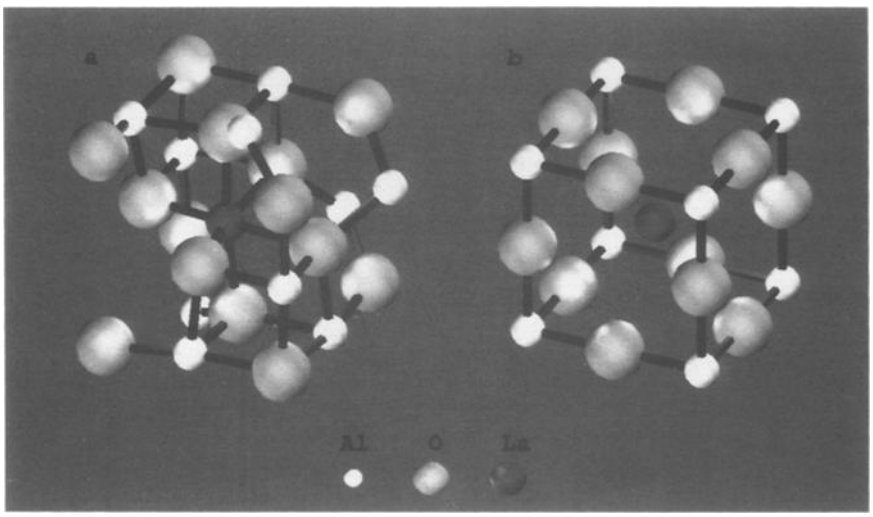

Fig. 1. (a) Typical environment of lanthanum in γ-alumina doped with 1.06 per cent of La_2O_3. (b) Environment of lanthanum in perovskite.

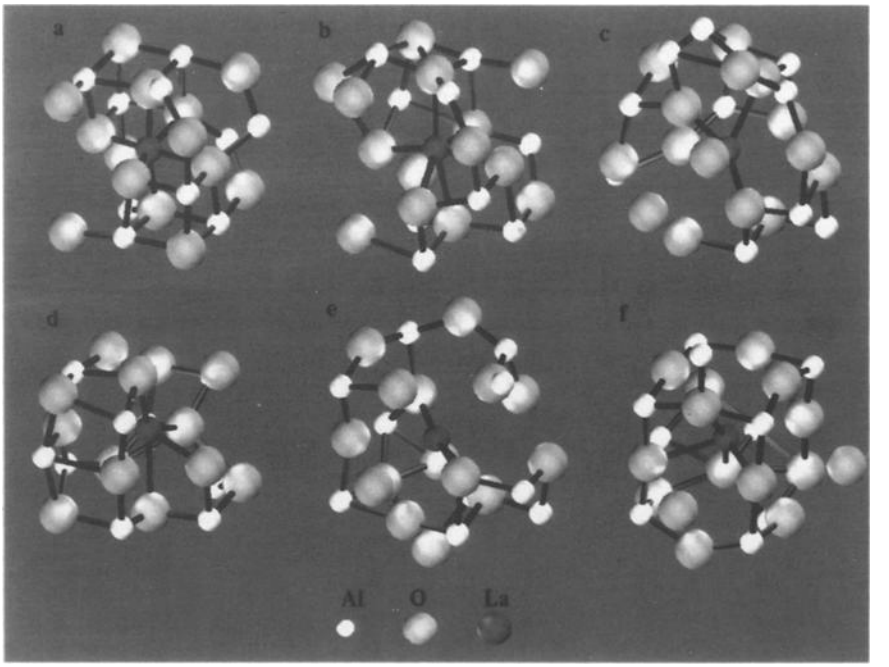

Fig. 2. Sequence of snapshots of the lanthanum environment in La_2O_3/γ-Al_2O_3. (a) Initial structure at 300 K; (b) displacement of lanthanum ion towards a neighbouring oxygen ion; (c) distortion of the structure after a collision; (d) relaxation of the structure after an unsuccessful collision; (e) collision of lanthanum against an oxygen ion likely to be removed and (f) relaxed structure after a successful collision.

of the structure (see figs. 2a–2d), but eventually a collision takes place with an oxygen susceptible to be removed from its relatively stable position (see figs. 2e–2f). When this event occurs the oxygen ion is displaced and the lanthanum occupies its lattice position. The vicinity of the new position of lanthanum is such that only small rearrangements are necessary to form a perovskite-like local structure, in which the central lanthanum is twelve coordinated in a cubic structural unit. The oxygen ions are located in the middle of the edges of the cube and aluminum ions approximately on the corners. The resulting structure (fig. 2f) is very similar to the ideal perovskite structure (fig. 1b). It has been found that within the simulation time limits, this migration and substitution process is not reversible, which reflects the higher stability of the new position of the lanthanum cation.

The lanthanum ion moves from its original location a distance equal to the La–O bond length of about 2.0 Å. The displaced oxygen occupies an interstitial position thus generating a nearby defect (see fig. 2f). The ease with which the perovskite structure is attained upon heating is due to the fact that some of the oxygens in γ-Al_2O_3 are in the same environment as lanthanums in perovskite. In fig. 3 the radial distributions of oxygen in γ-Al_2O_3 and lanthanum in perovskite are com-

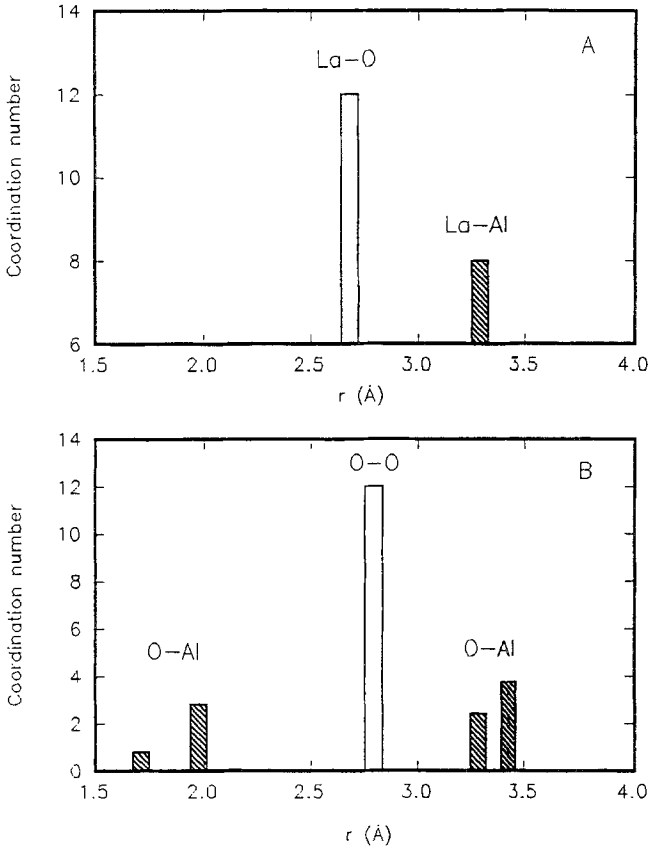

Fig. 3. Radial distribution of lanthanum (A) and oxygen (B) ions in the corresponding ideal structures of $AlLaO_3$ and γ-Al_2O_3, respectively.

pared. The only difference is the presence of neighboring aluminum ions. In the process of substitution, aluminum ions that were coordinating to oxygen undergo a displacement coupled to the motion of lanthanum in such a way that they tend to form new octahedral sites and the aluminum ions which were initially tetrahedrally coordinated must now occupy new positions with octahedral coordination. The resulting radial distribution of aluminum around lanthanum is in general agreement with the corresponding perovskite structure, as can be seen from fig. 4. The small differences observed, such as the peak shifts are due to the distortion of the lattice already mentioned. The origin of these distortions is the anomalous strains introduced by the relocalisation of aluminum ions. Those that preserve their tetrahedral coordination, when they should have octahedral coordination in the perovskite structure, are unstable because in the perovskite framework all the tetrahedral sites have a lanthanum cation in the first coordination sphere.

The local formation of perovskite structure around lanthanum is observed in all the lanthanum oxide concentrations used in the molecular dynamics simula-

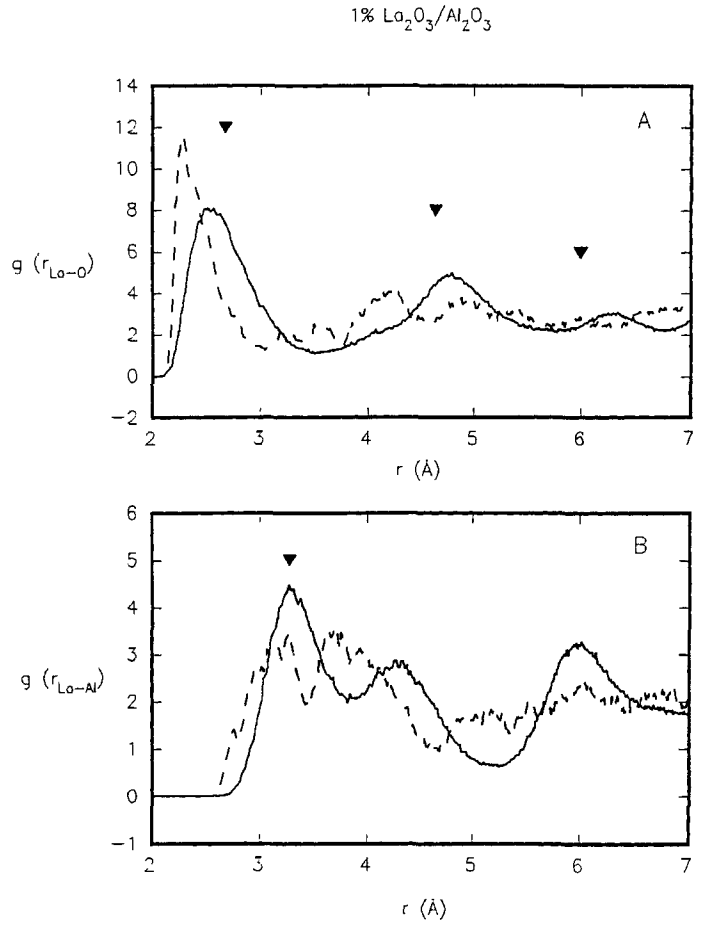

Fig. 4. Radial distribution La–O (A) and La–Al (B) obtained by molecular dynamics simulation of γ-alumina doped with 1 per cent of La_2O_3. Dashed line corresponds to 300 K and solid line to 1500 K. Peaks of ideal perovskite are indicated by bold triangles.

tions, although at high concentrations it is more difficult to form this new phase, and therefore long-range order is not present (see fig. 5). This result seems to disagree with the experimental findings where the crystalline perovskite phase is easily produced after calcination for a few hours. However, it is worth noting that in the present simulations, reconstructions owing to migrations of lanthanum ions induce noticeable strains in the bulk which necessarily have to be smaller on the surface. Even though simulated times are very short compared to calcination times the mechanism of formation is suggested by these results. These molecular dynamics findings can be used to explain the local disorder around the lanthanum ions and low coordination numbers observed by EXAFS [6] during the formation of perovskite-like phases on the surface of the system La_2O_3/Al_2O_3.

The collision of lanthanum with oxygen is likely to produce this structural

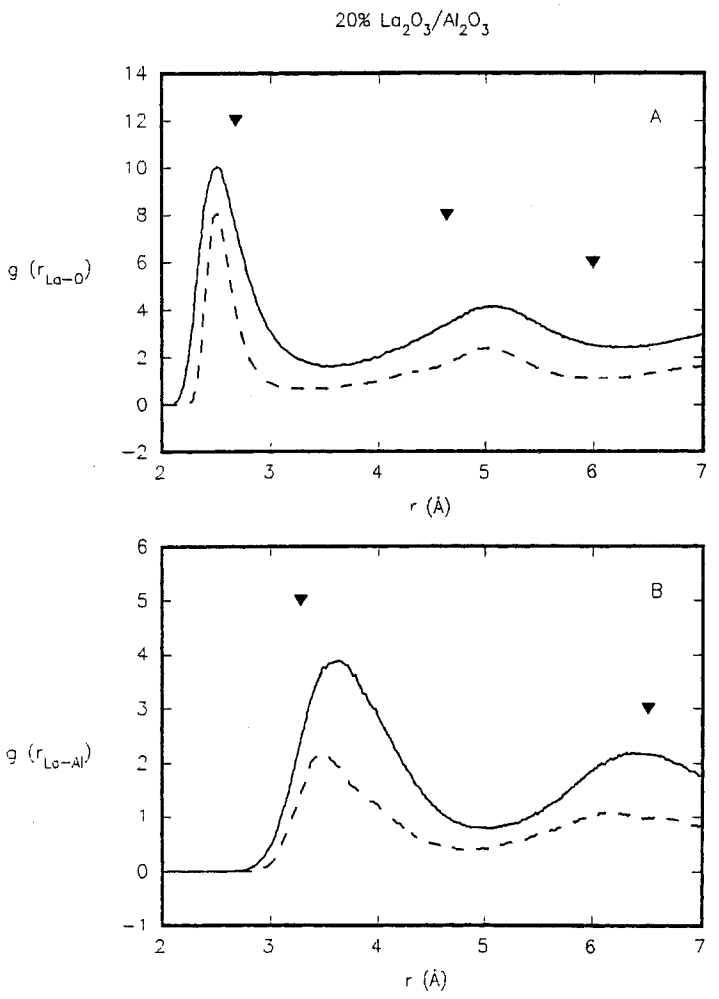

Fig. 5. Radial distribution La–O (A) and La–Al (B) obtained by molecular dynamics simulation of γ-alumina doped with 20 per cent of La_2O_3. Dashed line corresponds to 300 K and solid line to 1500 K. Peaks of ideal perovskite are indicated by bold triangles.

change when the latter is coordinated by octahedral aluminum, whereas when it is coordinated by tetrahedral ones the energy required to break the Al–O bond would be greater (see fig. 2). This behavior could explain the trends of the DRIFTS spectra of adsorbed hydroxyls on γ-alumina and La_2O_3/Al_2O_3 with different percentages of lanthanum shown in fig. 6. The γ-alumina spectrum has three main bands which are related to hydroxyls coordinated to two octahedral aluminums (peak at 3682 cm^{-1}), coordinated to one tetrahedral aluminum (3710 cm^{-1}), and coordinated to one octahedral aluminum (3764 cm^{-1}), according to Knözinger and Ratnasamy [9] and further reports [10,11]. Upon the increase of lanthanum oxide concentration the first band which disappears is that associated to one octahedral aluminum, and then that associated to two octahedral aluminums, whereas that

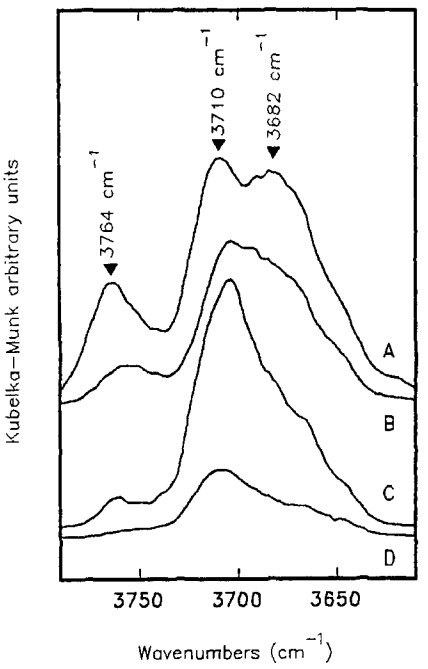

Fig. 6. DRIFTS spectra of γ-alumina (A), La_2O_3/γ-Al_2O_3 with 10% (B), 20% (C), and 40% (D) loadings.

associated to tetrahedral aluminum remains unchanged; a similar effect has been observed when the γ-Al_2O_3 is doped with Na^+ [11]. As stated above, the effective collisions of lanthanum ions in the formation of perovskite structures are favored when they take place against oxide ions coordinated to octahedral aluminums.

Finally, the degree of sinterization will be considered. Experimentally, it has been shown that the presence of lanthanum ions on the surface of γ-Al_2O_3 induces a thermostabilisation which inhibits the sinterization of the support. This higher stability of the surface has been generally related to an increase in the ratio of octahedral to tetrahedral aluminum. As we have shown, the addition of lanthanum ions to the support, can also lead to the modification of the coordination of the tetrahedral aluminum. This, in turn, prevents the reconstruction of the surface by inhibiting the mobility of the surface and hence the sinterization of the support.

4. Conclusions

The formation of a perovskite-like phase is associated with the substitution of an oxide ion by a lanthanum ion after a set of collisions, until a favourable one occurs. This event is when lanthanum ions collide against an oxide ion associated to an octahedrally coordinated aluminum. This mechanism of formation of the perovskite-like phase appears to be independent of the concentration of La_2O_3

in the γ-alumina. Numerical simulations have allowed us to propose a model for the onset of the formation of perovskite in γ-alumina and to give some physico-chemical insight into the formation of this phase on the surface of the support. Work is in progress to determine the minimum concentration of doping lanthanum oxide that would inhibit sinterization processes on the support.

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