

Chromium and Lanthanum on Transition Alumina Surfaces: The Role of Bulk Point-Defect Distributions on Catalytic Activity

S. N. Rashkeev,¹ K. Sohlberg,² M. V. Glazoff,³ J. Novak,³ S. J. Pennycook,^{1,4}
and S. T. Pantelides^{1,4}

¹Dept. Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, U.S.A.

²Dept. Chemistry, Drexel University, Philadelphia, PA 19104, U.S.A.

³Alcoa Technical Center, Alcoa Center, PA 15069, U.S.A.

⁴Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.

ABSTRACT

We are using a combination of scanning transmission electron microscopy (STEM) and first-principles density-functional calculations to investigate the interaction between metallic atoms and alumina catalytic supports. We show that there are two observed La sites at the porous γ -alumina surface, and single La atoms do not have tendency to cluster. Cr behaves very differently from La - it has a tendency to cover the alumina surface in ordered, periodic raft-like patches. The degradation of the chromia/alumina catalyst is related to the possibility for the chromium to move away from the surface into the bulk, and the activation barrier for such a process is higher in η -alumina than in γ -alumina, i.e., η -alumina is a more durable support for chromium catalyst.

INTRODUCTION

γ -alumina is one of many polytypes of Al_2O_3 that is used extensively as a catalytic support material because of its high porosity and large surface area [1]. However, at temperatures in the range 1000-1200°C, γ -alumina transforms rapidly into the thermodynamically stable α -alumina phase (corundum), the pores get closed thus suppressing the catalytic activity of the system [2]. The phase transformation can be slowed down by doping γ -alumina with one of many elements such as La, Ba, P, or Si. It was demonstrated that as little as 0.3-0.5% La can induce stabilization of γ -alumina [3]. Though the generic science of phase transformations is highly developed, the atomic-scale mechanisms and the role of dopants in specific systems remains wide open.

A second problem is related to the interactions of metal particles with different alumina substrates in catalytic systems. These interactions determine the size and shape of metallic particles, which in turn determine their catalytic activity. Direct Z-contrast atomic resolution imaging of individual dispersed catalyst atoms (Pt and Rh) on the insulating γ -alumina surface demonstrated that these atoms may exist on the surface as isolated atoms, in small clusters (dimers, trimers, etc.) or as more extended raft-like structures depending on the type of atoms [4].

In this paper we report the use of a combination of experimental and theoretical/computational tools to investigate the interaction between La and Cr atoms and alumina catalytic supports. This combination of tools has proven to be quite powerful in a range of other similar problems in materials science.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

On the experimental side, we use a scanning transmission electron microscope (STEM) equipped to produce atomic-resolution Z-contrast images and spatially resolved electron energy loss spectroscopy (EELS). The STEM at Oak Ridge National Laboratory exhibits resolution at 1.3 Å for Z-contrast imaging. Samples are fabricated at Alcoa Technical Center.

On the theoretical side we use first-principles density-functional calculations that have proven successful in our initial studies of bulk and surface structures of alumina polytypes and investigate stable atomic arrangements and dynamical rearrangements, including dopants, diffusion and phase transformations [5,6]. We are using the generalized gradient approximation (GGA) for exchange-correlation, and plane waves with ultrasoft pseudopotentials [7]. The VASP codes are used for electronic structure calculations [8]. The energy cutoff for the basis set was set at 24 Ry, and the integrations over the Brillouin zone were done using the Monkhorst-Pack scheme with four \mathbf{k} - points in the irreducible wedge. The alumina surfaces were modeled by infinitely repeating slabs with an interslab vacuum spacing of 10 Å. The structural relaxations were performed for supercells of slabs five atomic layers thick (70 atoms for γ - alumina and 72 atoms for α - alumina when the (110C) layer is exposed) described in detail earlier [9].

DISCUSSION

Chromium on transition alumina (γ - and α - polytypes) surfaces.

We have investigated the behavior of chromium on two different transition alumina (γ - and α - polytypes) surfaces. This problem is closely connected to the problem of the catalytic activity degradation of an industrially important chromia/alumina catalytic couple. γ - and α - alumina are both widely used as catalysts and catalytic supports. They have a high degree of porosity, i.e., a large specific surface area. When they are used as catalytic supports, they are coated with dispersed nanoparticles of transition and/or noble metals, e.g., Pt, Pd, Rh, Cr, etc.

Chromia/alumina catalysts are widely used for dehydrogenation of alkanes according to the reaction $C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2$ [10]. In this process different transition aluminas have been used as the catalytic support. At the present time, however, α - alumina is the preferred support in industrial processes because the Cr/ α -Al₂O₃ catalysts can last up to 2-3 years without significant degradation. At the same time, γ - alumina degrades within a few weeks [11]. The active chromium atoms disappear from the surface and have a tendency to six-fold coordination (i.e., form aluminum chromates). Considering the difference in degradation rate for catalysts using γ - versus α - alumina supports, it is quite puzzling because the two support materials have very similar crystalline bulk structures, differing essentially only in the distribution of cation vacancies and surface reconstructions [12].

Our first-principles calculations provided an opportunity to understand this difference in the behavior of Cr on different transition alumina surfaces. In particular, we found that this differ-

ence is related to the difference in the distributions of the bulk point-defects in these two alumina polytypes. On the *h*- alumina surface, chromium atoms always remain three-coordinated and re-

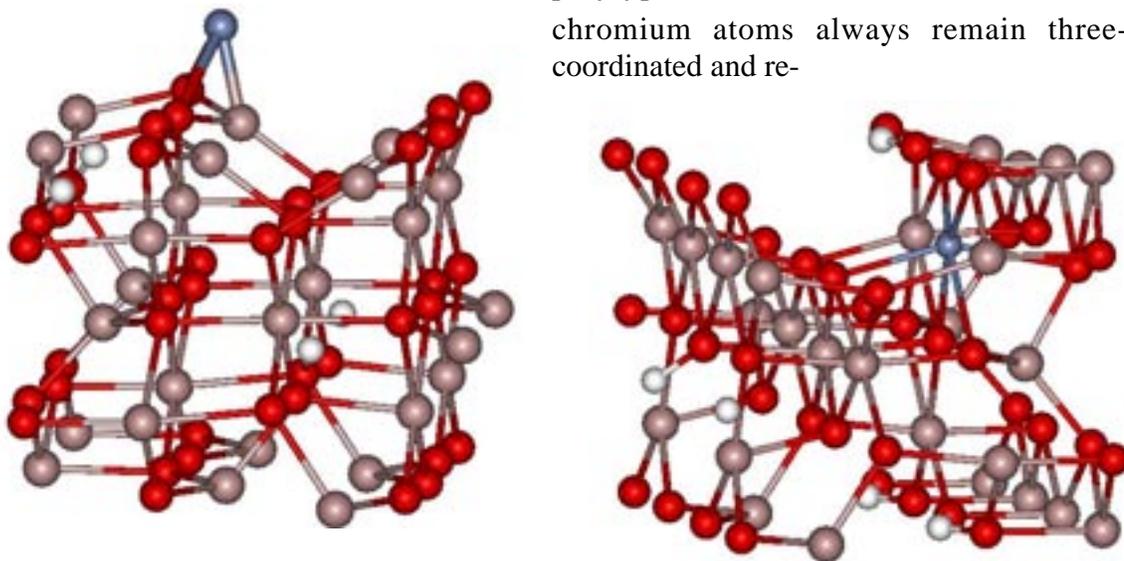


Figure 1. A chromium atom on the α - alumina (left) and γ - alumina (right) surfaces. Aluminum atoms are shown in gray, oxygen in red, hydrogen in white, chromium in blue.

active (Figure 1). They move laterally to the surface being attached to one Al and two O atoms at any moment. The activation barrier for Cr to enter into the bulk of the alumina (about 5 eV) is much higher than the activation energy to travel along the “groove” at the surface (2.5 eV). Therefore, Cr atom can stay for a very long time on the *h*- alumina surface.

The situation is completely different for γ - alumina surface. A chromium atom can travel along the “trench” of surface atoms (the activation energy being about 2.5 eV) where it remains reactive. However, it can also get trapped in the next-to-the surface layer in the octahedral interstitial position where it creates six bonds with the neighboring atoms, and this position is energetically very favorable (the energy gain is about 1.5 eV). The activation barrier to get into this position (2.2 eV) is quite comparable with the migration activation barrier along the “trench”, i.e., the trapping may occur quite often. When Cr is trapped in such a position, it cannot exhibit any chemical activity anymore, i.e., the catalytic activity of the whole system degrades. Such a simple analysis explains why the chromia/ γ - alumina catalytic system degrades much faster than the chromia/*h*- alumina catalyst.

The fact of such a disappearing of chromium from the γ - alumina surface is not trivial. The bulk γ - and *h*- alumina crystal structures are similar, and the *h*- alumina surface also octahedral interstitials similar to those at the γ - alumina surface. However, our calculations do not show any energy gain (in comparison with the surface position) when one puts Cr atom in one of such an interstitials in the next-to-surface layer in *h*- alumina. The analysis of atomic bonds and atomic forces shows that in *h*- alumina these octahedral interstitials are only metastable for the Cr atom. The bonds of Cr with nearest oxygen atoms are very different in length, and the longest bonds

can easily break when an external force is applied. This will generate an asymmetric force which will pop the Cr atom back to the surface. Therefore, the difference between the two alumina polytypes is related to different relaxation of their surfaces, not to difference in their bulk properties (that are very similar).

The position of Cr atom in the six-fold near surface interstitial seems to be stable. One could expect that isovalent species (e.g., Mo) should behave similarly to Cr. However, our first-principles calculations show that Mo is not stable in the subsurface vacancy but if placed in the vacancy, pops spontaneously to the surface. Furthermore, Mo does not occupy the same surface site as Cr

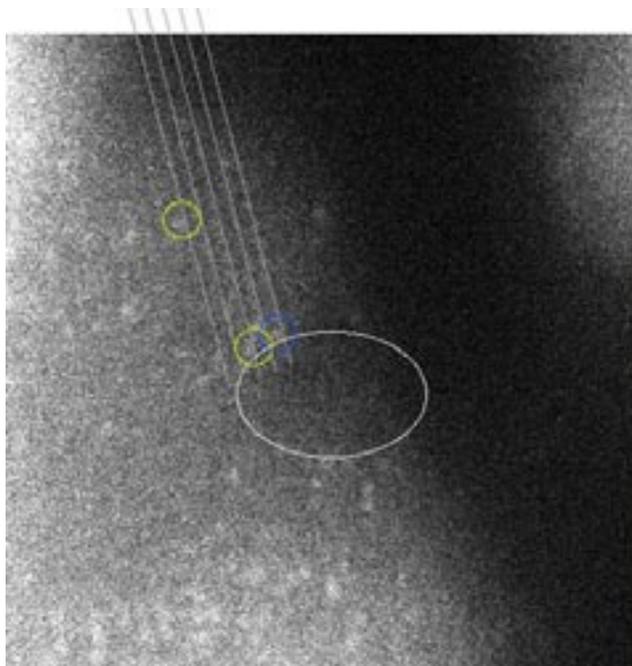


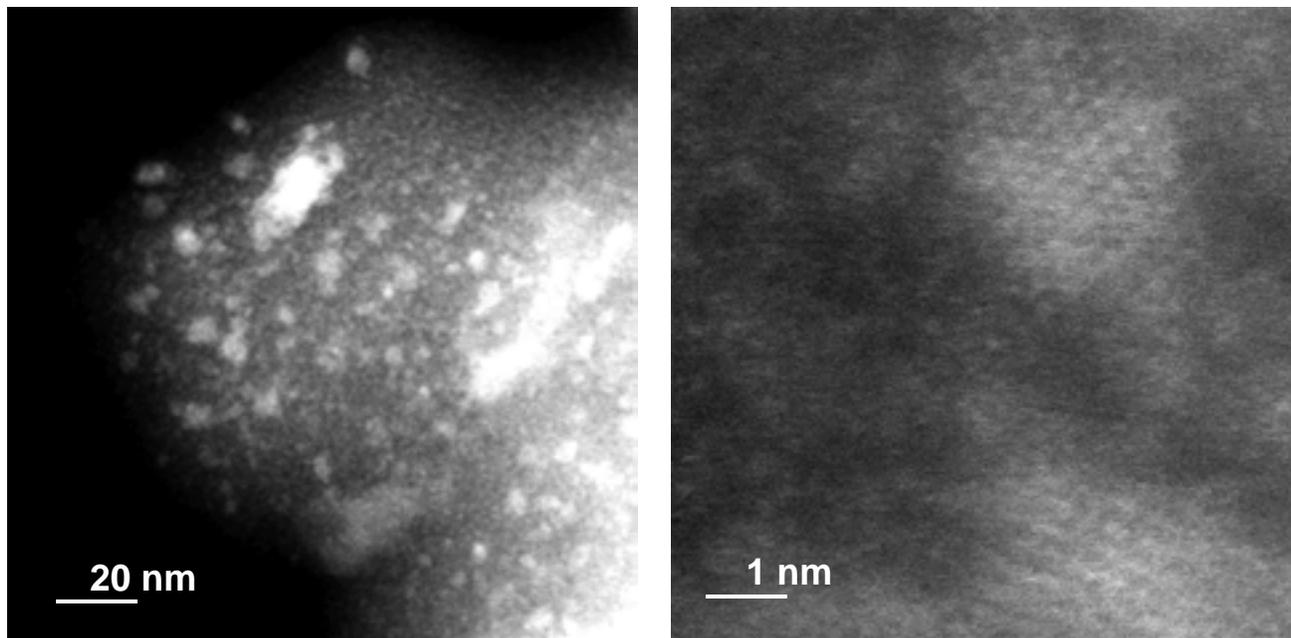
Figure 2. A typical Z-contrast image of a La doped γ - alumina sample. La atoms correspond to the bright spots (see the text).

(in the “groove”, attached to four oxygen atoms) either, preferring to coordinate to 2 Al and 2 O atoms, at the same time massively distorting the neighboring environment. At the same time, this effect cannot be explain by the larger atomic radius of Mo because it is only 0.08 Å larger that the atomic radius of Cr atom. Moreover, Mn atom, which is not isovalent with Cr (however, also six-valent in many chemical reactions) is indeed stable in the subsurface vacancy. There results show that the surface chemistry of cubic aluminas is based on very subtle effects requiring a detailed picture of the electronic structure.

Lanthanum atoms in γ - alumina

We have initiated systematic investigations of various La- doped samples of γ - alumina. Figure 2 provides a typical Z-contrast image for such a sample that describes the behavior of La atoms incorporated in γ - alumina. Z-contrast microscopy technique is a unique tool that provides *direct* images of materials at atomic resolution. Bright spots in Figure 2 correspond to the impu-

ities with the highest atomic number Z (in this case, La atoms with $Z=57$). In this image we are viewing layers of the bulk edge on. These layers are highlighted with gray lines. Several more layers can be identified to either side of the highlighted layers. This image provides information about the positions of the La in the two dimensions of the image but no information about the



position of the atom in the depth direction.

Some of the La atoms (white circles) appear to lie in the layers of the bulk edge on, but others (blue circle) lie in between the layers. It should also be noted that two of the La atoms seem to be on the edge of a larger structural feature, indicated with the large ellipse. (Note the dark patch in

Figure 3. Z-contrast images of Cr-doped γ -alumina (with two different magnifications) showing Cr segregated into patches.

the image.) It is natural to infer that La behaves similar to Cr- impurity on the γ - alumina surface (see above). Before adsorption into a subsurface layer, La resides in a “trench”. This position is between layers. After entering the empty site in the subsurface layer, the La atom becomes aligned with one of the layers. Therefore, we are seeing both types in the La images.

Segregation of chromium on the γ - alumina surface (Z-imaging)

When a significant amount of Cr is deposited on γ - alumina surface, it behaves very differently from La. Cr has a tendency to cover the surface in a rather uniform way (bright spots correspond to Cr). It looks like this pattern is mostly two-dimensional, i.e., Cr is staying near the surface. Another important observation is that Cr segregates on the alumina surface in “patches”. First-principles calculations show that Cr atoms on γ - alumina surface have a tendency to cluster. When two Cr atoms are placed in the nearest interstitials at the surface, they can form a

strong Cr-Cr bond. However, more calculations need to be performed in order to understand the periodic patterns of Cr atoms on γ -alumina surface.

CONCLUSIONS

We investigated the interaction between transition metal atoms (Cr, Mo, La) and the γ -alumina catalytic support using scanning transmission electron microscope (STEM) and first-principles density-functional calculations. It was demonstrated that La atoms on γ -alumina surface do not have tendency to cluster and found two different (in the layer and between the layers) sites for single La atoms. Cr atoms on γ -alumina surface behaves very differently from La. Cr atoms have a tendency to segregate into raft-like patches on the surface with a regular periodic structure. This conclusion may help to better understand the atomic mechanism of chromia/alumina catalysis. Our first-principles calculations show that the degradation of the chromia/alumina catalyst is related to the possibility for the chromium to move away from the surface into the bulk, and the activation barrier for such a process is higher in α -alumina than in γ -alumina.

ACKNOWLEDGMENTS

This work was supported in part by the NSF Grant DMR-0111841, DOE Grant at Drexel University DE-FC02-01CH11085, and by the William A. and Nancy F. McMinn Endowment at Vanderbilt University. Research at ORNL was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 managed by UT-Battelle, LLC.

REFERENCES

1. C. N. Satterfield, *Heterogeneous Catalysis in Practice* (McGraw Hill, New York, 1980).
2. K. Wefers, C. Misra, *Oxides and Hydroxides of Aluminum* (Alcoa Laboratories, Pittsburgh, 1987).
3. M.V.Glazov, L.G.Hector, and J. Novak, *Stabilization of Gamma-Alumina* (Alcoa Laboratories, Pittsburgh, 1999).
4. P. D. Nellist and S. J. Pennycook, *Science* 274, 413 (1996).
5. S.-H. Cai, S. N. Rashkeev, S. T. Pantelides, and K. Sohlberg. *Phys. Rev. Lett.* (submitted).
6. S. N. Rashkeev, K. Sohlberg, M. V. Glazov, J. Novak, S. J. Pennycook, and S. T. Pantelides. *Phys. Rev. Lett.* (submitted).
7. M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).
8. G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
9. K. Sohlberg, S. J. Pennycook, and S. T. Pantelides, *J. Am. Chem. Soc.* **121**, 10999 (1999).
10. S. De Rossi, G. Ferraris, S. Fremiotti, E. Garrone, G. Ghiotti, M. C. Campa, and V. Indovina, *J. Catalysis* **148**, 36 (1994).
11. S. Alerasool, Engelhard Corporation (private communication).
12. R.-S. Zhou and R. L. Snyder, *Acta Crystallogr.* **B47**, 617 (1991).