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Information on catalyst surface structure from crystallite morphologies observed by scanning electron microscopy (SEM)

S.C. Parker, P.J. Lawrence

School of Chemistry, University of Bath, UK

C.M. Freeman, S.M. Levine and J.M. Newsam

BIOSYM Technologies, Inc., 10065A Barnes Canyon Road, San Diego, CA 92121, USA

The shapes of small crystals grown under equilibrium conditions are governed by the stabilities of their exposed faces. Computer simulation methods can be used to calculate surface energies and hence crystallite morphologies, illustrated by results for Cr_2O_3. Such calculations can include the effects of surface impurity segregation. Comparison of the resulting calculated crystal morphologies with those directly observed in the SEM thus provides a direct link between atomistic simulation and experiment.

Keywords: Computer simulation; SEM; catalyst modelling; Cr_2O_3; crystal morphology; surface segregation; chromia

1. Introduction

Scanning electron microscopy (SEM) is used routinely to examine catalyst samples on a micron scale. The technique indicates particle sizes, the presence of impurities and the shapes or morphologies of the individual catalyst crystallites. For small crystals, grown under *equilibrium* conditions, the morphology of the crystallite can be directly related to the relative energetics of its component crystal faces. This is a consequence of the tendency of the growing crystal to minimize its total surface energy at a given volume. It was originally proposed by Wulff [1] that for a particular face, the surface normal from a given position within the crystal interior is proportional to its surface energy. Thus the most stable crystal faces will tend to dominate the crystal habit of the system.

Wulff's theorem can be exploited by comparing a predicted crystallite morphology based on crystal surface energies with that observed by SEM. In the equilibrium case, an observed morphology can then be interpreted in terms of the relative surface energies. Furthermore, for ionic systems surface energies can be computed to sufficient accuracy using computer simulation techniques, allowing the prediction of equilibrium morphologies. Computational techniques can thus help answer questions about surface segregation, or the effects of doping and catalyst aging. These phenomena are important in practical industrial catalyst applications.

In section 2 we introduce the simulation techniques which are needed to describe surface systems, illustrating their application to the Cr_2O_3 system, active in highly dispersed form as a polymerization catalyst. Previous theoretical studies have focussed on this material [2,3] and the isostructural Al_2O_3 [3–5].

2. Method

2.1. POTENTIAL MODEL

The simulations that are the basis for our predictions of crystal morphology are founded on the Born model of the solid [6]. Here the lattice energy, V, of the crystal is written as

$$V = \sum_{ij} \frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-r_{ij}/\rho_{ij}) - \frac{C_{ij}}{r_{ij}^6} \tag{1}$$

with appropriate potential parameters A_{ij}, ρ_{ij} and C_{ij} chosen for pairwise interatomic interactions. In the simulations described here we use formal charges, q_i, on ionic centers and, additionally the shell model of Dick and Overhauser [7] permits the incorporation of ionic polarizability. Parameterization of the model may be achieved by fitting to experimental properties readily calculated from the Born model [8] or, alternatively, by reference to non-empirical methods where interaction energies between ion pairs are calculated explicitly within the electron gas formalism [9,10]. In this study we have employed potentials of the latter variety [11].

It is a major assumption that a potential model which is derived from the equilibrium bulk properties of the solid is applicable at the surface of the crystal. The least squares fitting procedure will inevitably ensure that the quality of the potential is highest at the equilibrium interionic separations of the crystal structure. By contrast non-empirical potentials are obtained by sampling a range of interionic separations and therefore maximize the overall accuracy of the simulations. There is good evidence that simulations of ionic materials based on such potentials do indeed provide a realistic treatment of situations in which ions are far from the equilibrium coordination geometries observed in the bulk crystalline environment. For example, Mackrodt and Tasker [4] have successfully modelled impurity segregation in Al_2O_3 and Colbourn et al. [12] have described the simulation of impurities in MgO based on similar potential models.

2.2. SIMULATION TECHNIQUES

With a viable potential model for the solid, several different forms of simulation can be pursued based on energy minimization techniques [13]. Here we make use of the first derivative vector and second derivative matrix for the atomistic model and employ standard mathematical techniques to minimize the energy as a function of the structural variables of the system (see for example Norgett and Fletcher [14]). Bulk crystal simulations are achieved using the METAPOCS code of Parker et al. [15], whilst defects embedded in the bulk of the material are treated using the Mott–Littleton procedure [16], efficiently packaged in the CASCADE code [17]. Surface and defective surface calculations are performed using the MIDAS and CHAOS codes respectively, developed by Tasker and co-workers [18,19].

2.3. ISO-VALENT SURFACE SEGREGATION

Comparison of bulk and surface substitutional defect energetics permits the calculation of surface segregation energetics for the doped material [12]. The effects of varying surface coverage can also be obtained by performing simulations which implicitly include the effect of substituent ion interactions at the surface.

2.4. CRYSTAL MORPHOLOGY

Wulff's theorem may be written as

$$h_i = \lambda k_i, \tag{2}$$

where h_i is the surface normal energy for face i, λ is a constant depending on the absolute size of the crystal, and k_i a surface normal vector for a given crystal face to a point within the crystal [1]. Taking relative surface energetics from computer simulations yields an ensemble of relative surface normal lengths for a particular crystal's low index faces. Consideration of the known crystal symmetry and surface normal lengths is sufficient, therefore, under equilibrium conditions, to define the morphology of the crystallite. A computer graphics interface permits the visualization of the resulting crystal habits.

3. Results and discussion

Calculated relative energetics for low index faces for chromia are collected in table 1. Surface relaxation has a substantial effect on the absolute and relative surface energies as has previously been observed in the isostructural (i.e. corundum structured) Al_2O_3 [4]. These energetic relaxations are illustrated in fig. 1 which shows the effect of energy minimization on a three dimensional layered model of chromia. The effect of atomic relaxation can be clearly seen in this representation where cations have moved to a significant extent in order to maximize favorable electrostatic interactions at the surface. Surface reconstruction, of the type simulated here, may have important implications in heterogeneous catalysis and might significantly effect the interaction of reactant molecules

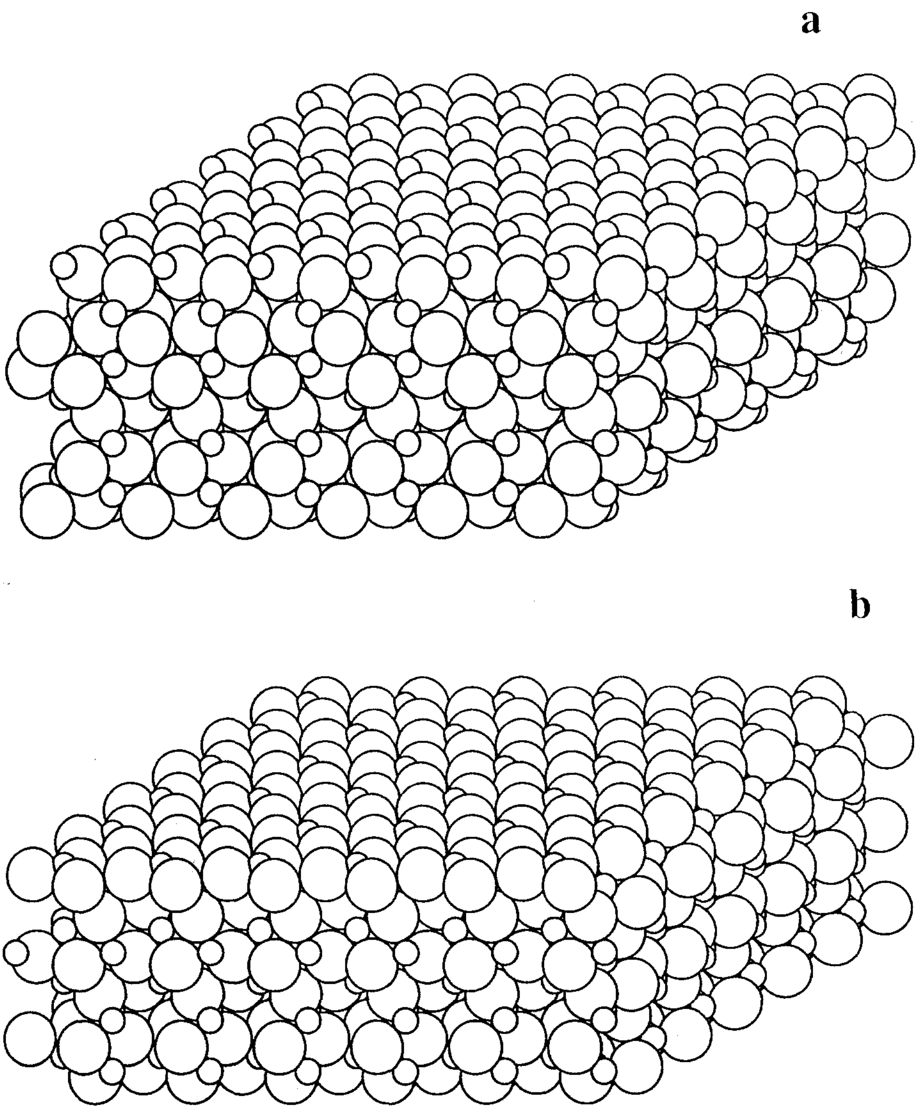

Fig. 1. The basal surface of Cr_2O_3 before (a) and after (b) energy minimization.

Table 1
Calculated surface energies (J m^{-2}) of the low-index planes of chromia before and after relaxation (energy minimization)

Surface	Unrelaxed	Relaxed
0001	4.77	2.21
1012	2.77	2.01
1010	4.99	2.27
1120	3.53	2.35
1011	5.18	2.76

with surface cations. The crystal morphologies predicted for Cr_2O_3 based on the energies of table 1 are illustrated in figs. 2a and 2b where we show respectively the morphology based on unrelaxed and relaxed surface energies. The pronounced effect of the reordering of plane stabilities on surface relaxation is clearly evident in these calculated crystal morphologies.

We have also investigated the effect of impurity segregation on the predicted crystal morphology. Calculated surface segregation energy curves for Y^{3+}, Al^{3+} and La^{3+} at the basal plane and the prism plane are presented in figs. 3 and 4.

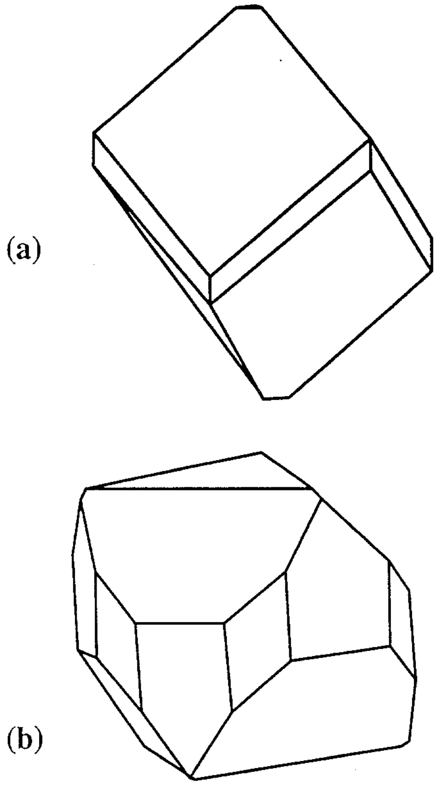

Fig. 2. The morphology of a pure Cr_2O_3 crystallite: from unrelaxed (a) and relaxed (b) surface energies.

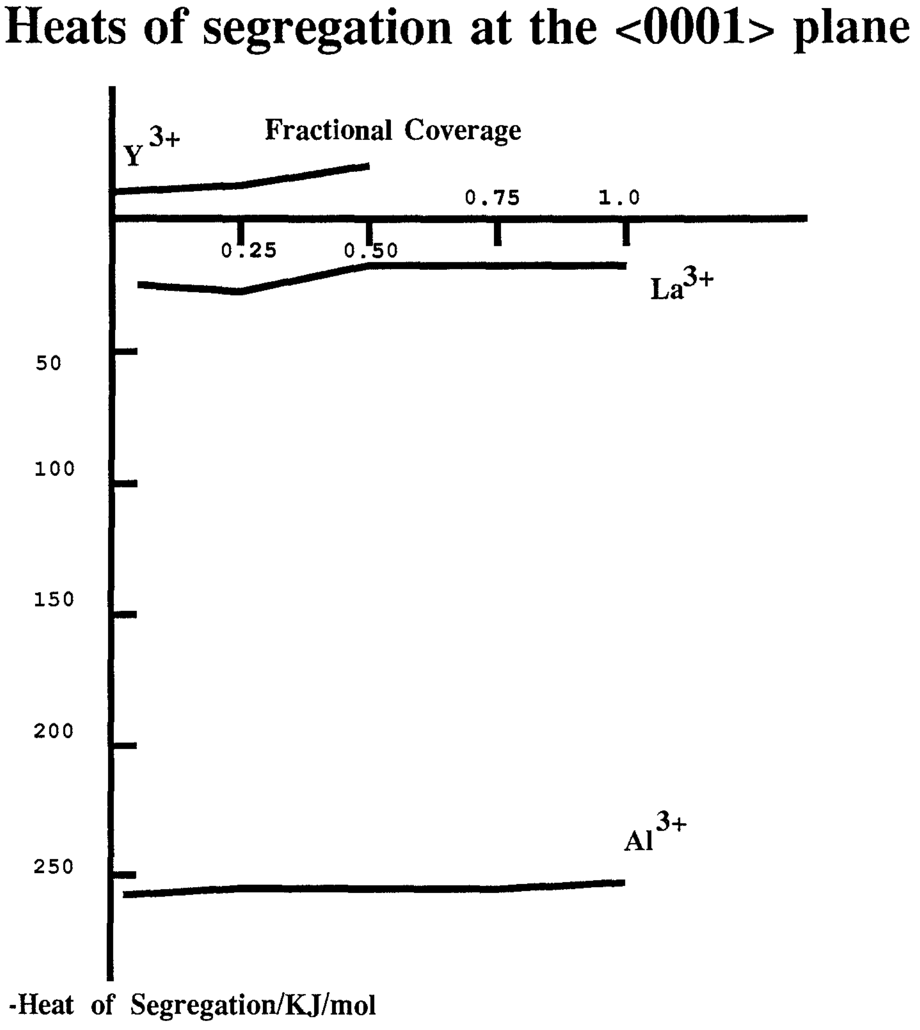

Fig. 3. Calculated heats of segregation at the Cr_2O_3 basal plane as a function of coverage.

Here we observe that for the basal plane both Al^{3+} and La^{3+} are predicted to preferentially segregate to the crystal surface, with negative heats of segregation, whereas the larger Y^{3+} ion will remain in bulk substitutional sites. The particularly favorable segregation of Al^{3+} may be attributed to this ion's ability to accommodate the non-octahedral surface environment (fig. 1) with greater ease than Cr^{3+}. Fig. 4 shows the calculated heats of segregation at the prism plane for Y^{3+}, Al^{3+} and La^{3+}. Here we see that all these ions are predicted to have favorable surface segregation energies at low fractional coverages with more complex behavior at higher coverages. With La^{3+}, for example, at high coverages steric factors begin to limit the degree of surface relaxation that can occur. Combining heats of segregation for various crystal faces with the pure face energetics, allows the effect of surface impurity ions on crystal morphology to be

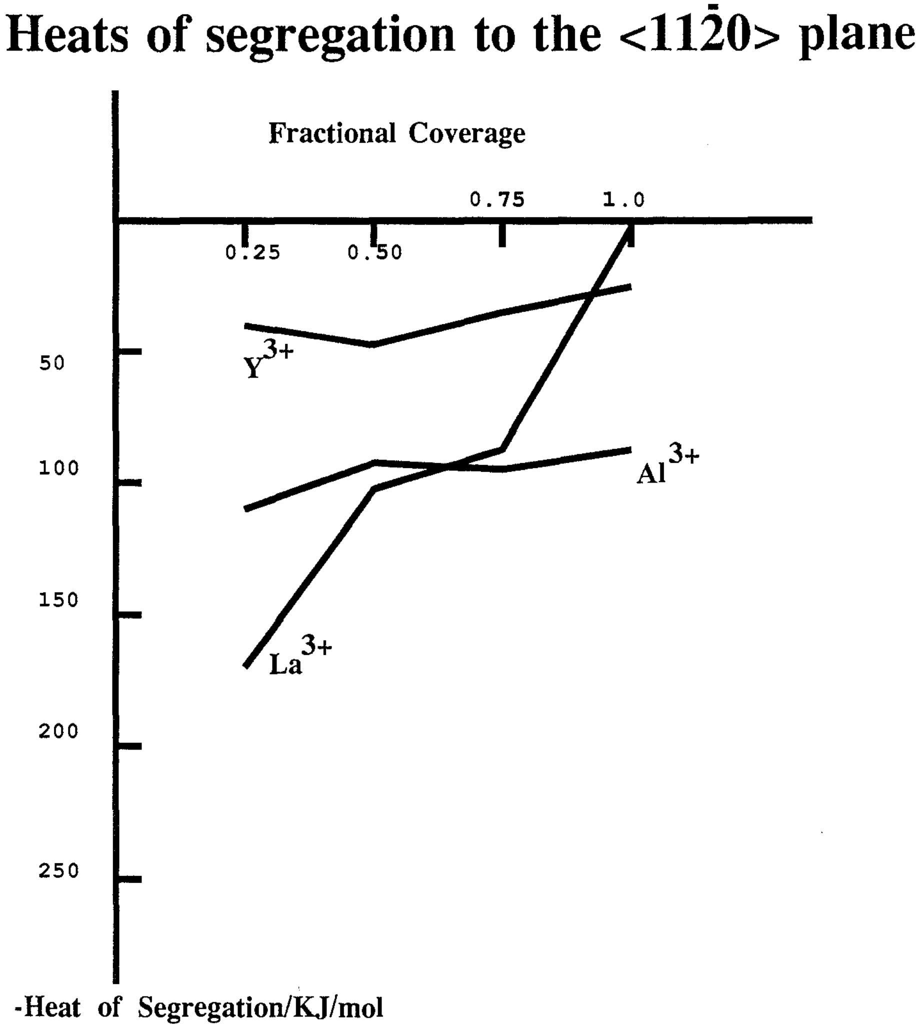

Fig. 4. Calculated heats of segregation at the Cr_2O_3 prism plane as a function of coverage.

determined. This is illustrated in fig. 5 for Al^{3+}, where increasing coverage increases the expression of the basal plane in the cystallite morphology. At full monolayer coverage the crystal is predicted to have a plate like form.

4. Conclusions

In this letter we have described how computer simulation methods may be used to model crystal surface structure and energetics at the atomic level. Using Wulff's theorem, and the resulting prediction of crystal morphology, this information can be compared with macroscopic observation of crystallite morphology, routinely obtained with the SEM technique. This marriage of atomistic

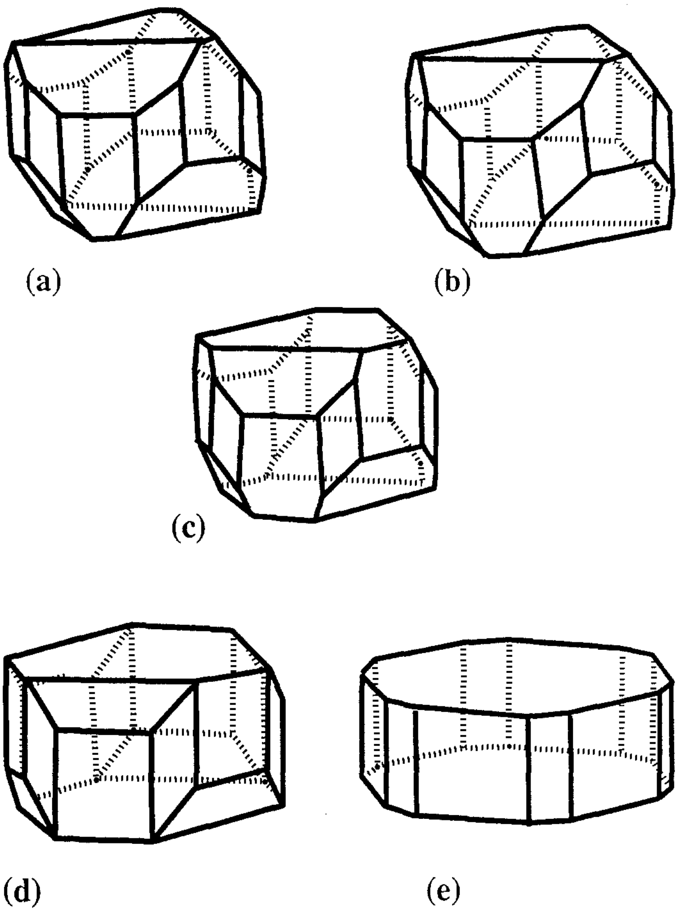

Fig. 5. The predicted equilibrium morphologies of Cr_2O_3 as a function of Al^{3+} surface coverage: (a) 0%, (b) 25%, (c) 50%, (d) 75%, (e) 100%.

modelling and its macroscopic consequences is further enhanced through the ability to model dopant ion segregation and its effects on crystal shape. Further work is required in the derivation of accurate, transferable potential models that will permit the simulation of a wide range of oxide and dopant systems. With continued progress in this area, the methods described here should prove extremely useful in allowing the extraction of information on catalyst surface structure contained in catalyst SEM micrographs. Extensions of the present approach to equilibrium morphology simulations to the more challenging regime of kinetically controlled morphology development are under consideration.

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