The Generation of Catalytically Active Centres in the Surfaces of α-Al_2O_3 and α-Cr_2O_3–Al_2O_3 Solid Solutions

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Dedicated to Professor Walter Feitknecht

Summary

Model processes are described whereby the co-ordination numbers of cations and anions at the surface of the corundum (α-Al_2O_3) structure can be changed whilst still preserving electrical neutrality. A number of distinctive atom groupings can be generated in this way and speculations are made regarding their potential as active centres for heterogeneous catalysis. It is proposed that changes in surface co-ordination number can be induced by replacing Al^{3+} by Cr^{3+} ions, and that the catalytic characteristics will change non-uniformly as the chromium content of the phase α-$Cr_xAl_{2-x}O_3$ is progressively increased.

The understanding of many aspects of the reactivity of solids depends upon a precise knowledge of the positions of atoms within crystals, and structure determinations by the methods of X-ray and neutron diffraction have proved of enormous value in this field.[1] There is an incentive to extend the knowledge derived in this way to discuss not only reactions *in* solids but also reactions occurring on solid surfaces. The study of metal surfaces by field ion microscopy and low energy electron diffraction has confirmed that the atomic arrangements at surfaces are primarily determined by the same structural principles which define the arrangement in the bulk. However, a surface necessarily contains atoms (or ions) whose co-ordination is lower than in the bulk, and in accommodating the resulting valence unsaturation (or electrostatic inhomogeneity) crystals will adapt at the surface to give some roughness and local heterogeneity. This has consequences for surface reactions. Thus in chemisorption of gases and in corrosion, the surface of a solid usually behaves in a non-uniform way, with some areas showing greater reactivity than others. Equally in heterogeneous catalysis it is widely accepted that reactions often occur predominantly on a limited number of centres rather than equivalently on the crystal surface at large. In spite of a widespread awareness of the existence of surface heterogeneity, there have been rather few attempts to apply the principles of structural solid state chemistry to describe on an atomic scale the likely conformations for active centres on the surfaces of individual solids. One notable example, however, is the discussion by ARLMAN[2] of the active centre for propylene polymerisation at the surface of the Ziegler-Natta catalyst α-$TiCl_3$, and for metal crystals the treatment of face-centred cubic structures by VAN HARDEVELD, VAN MONTFOORT and HARTOG may be cited.[3] The present essay directs attention to the corundum (α-Al_2O_3) structure, and specifically to changes in surface arrangement which might accompany the incorporation of Cr^{3+} ions in solid solution in the phase α-$Cr_xAl_{2-x}O_3$ ($0 < x < 2$). Corundum-phase chromia-alumina has recently been investigated as a catalyst in various reactions.[4-7]

The corundum structure

Corundum can be regarded as a hexagonally close-packed assembly of oxygen ions ($r = 1.40$ Å) with cations occupying two-thirds of the octahedral holes.[8] Each cation is surrounded by six oxygen ions, and each O^{2-} ion by four cations. The radius ratio $r_{M^{3+}}/r_{O^{2-}}$ is 0.36 for Al^{3+}, below the value of 0.414 for anion–anion contact in an octahedron, so that no expansion of anion close-packing is necessary to accommodate Al^{3+} ions. Due to repulsion of cations across the common faces of adjacent occupied octahedra, the polyhedra are not regular, but exhibit a trigonal distortion.[9] This distortion, however, is not sufficient to destroy the usefulness of discussing the surface of corundum as the surface of a close-packed structure. The radius ratio $r_{Cr^{3+}}/r_{O^{2-}}$ is 0.46. In discussing α-$Cr_xAl_{2-x}O_3$ or α-Cr_2O_3, the excess of the radius ratio above 0.414 in CrO_6 octahedra is small enough to allow the consequences of loss of contact between anions to be neglected. The model of close-packed anions forming regular octahedra (and tetrahedra) is again a reasonable one for discussing the characteristics of the surface.

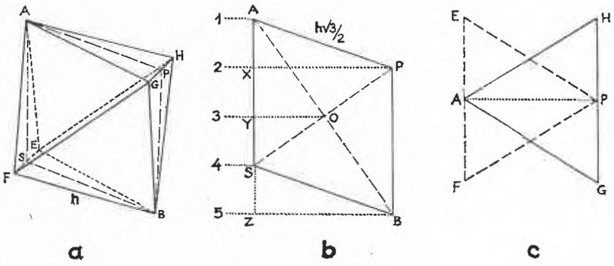

Fig. 1. (a) A regular octahedron $AHGBFE$ of side h, orientated with two opposite faces AEF and HGB vertical. (b) Section $APBS$ which bisects the octahedron shown in (a). (c) Projection of the octahedron shown in (a) on a plane at right angles to the parallel faces AEF and HGB. A, X and S are coincident in this projection, as also are P and B. $PX = h\sqrt{2}/\sqrt{3}$

Consider a regular octahedron $AHGBFE$ (Fig. 1a) of side h orientated so as to render the two opposite faces AEF and HGB vertical. In the plane section $APBS$ which bisects the octahedron (Fig. 1b), the distances AX, XY, YS and SZ in the orientation shown in Fig. 1b are all equal, and have the value $h/2\sqrt{3}$. The centre of the cation in the octahedral hole formed by anions with centres at A, H, G, B, E and F is at O, the centre of the rhombus $APBS$. We shall specify the points A, P, O, S and B in Fig. 1b as being at Levels 1, 2, 3, 4 and 5 respectively. A plan view of the octahedron $AHGBFE$ is illustrated in Fig. 1c. Fig. 2 shows a representation of hexagonal close-packing of spheres (anions) with small spheres (cations) in two-thirds of the octahedral holes. The close-packed layers are shown as I, II, I. A typical octahedron of the type $AHGBFE$ is formed by the centres of the spheres marked with these same letters in Fig. 2 on the right-hand side. On the left-hand side of

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[1] See, for example, W. FEITKNECHT, *Pure & Appl. Chem. 9* (1964) 423; W. FEITKNECHT, H. HÄNI and V. DVOŘÁK, *Proceedings of the 6th International Symposium on Reactivity of Solids (Schenectady, 1968)*, ed. J. W. MITCHELL, R. C. DEVRIES, R. W. ROBERTS and P. CANNON, p. 237, Wiley-Interscience, 1969.

[2] E. J. ARLMAN, *J. Catalysis 3* (1964) 89.

[3] R. VAN HARDEVELD and A. VAN MONTFOORT, *Surface Sci. 4* (1966) 396; R. VAN HARDEVELD and F. HARTOG, *Surface Sci. 15* (1969) 189.

[4] P. W. SELWOOD, *J. Amer. Chem. Soc. 88* (1966) 2676; P. W. SELWOOD, *Proceedings of the 4th International Congress on Catalysis (Moscow, 1968)*, Paper 66.

[5] H. SCHAEFER and E. BÜCHLER, *Z. Naturforsch. 22a* (1967) 2117, *23a* (1968) 1685.

[6] F. S. STONE and J. C. VICKERMAN, *Z. Naturforsch. 24a* (1969) 1415.

[7] F. PEPE and F. S. STONE, to be published.

[8] A. F. WELLS, *Structural Inorganic Chemistry*, 3rd Edition, Oxford University Press, 1962.

[9] R. E. NEWNHAM and Y. M. DE HAAN, *Z. Kristallogr. 117* (1962) 235.

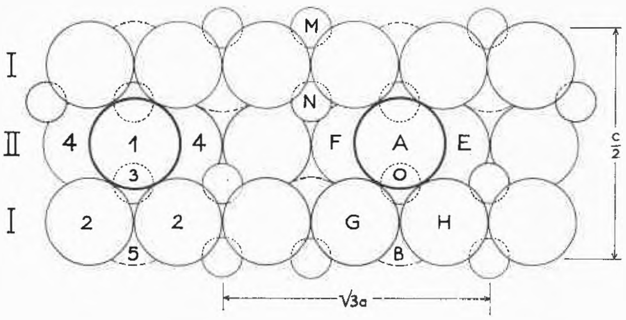

Fig. 2. A representation of the corundum structure as hexagonally close-packed spheres (oxygen ions) with small spheres (cations) occupying two-thirds of the octahedral holes. Elevation showing the close-packed layers I, II, I [(100) plane of hexagonal unit cell]. Arabic numerals represent levels in units of $h/2\sqrt{3}$ in a direction perpendicular to the paper (cf. Fig. 1), only two oxygen ions at Level 1 being shown. In the real structure of α-Al_2O_3, $a = 4.7589$ Å and $c = 12.991$ Å[9]

Fig. 2 a similar octahedron is marked with numerals showing the levels of the atoms. The small extent of the trigonal distortion in the real structure of α-Al_2O_3 can be seen by comparing Fig. 2 with Fig. 1 in the paper by Newnham and de Haan.[9]

Diagrams of the type of Fig. 2 will provide the basis for our discussion of the surface of corundum. The layers I, II, I are the basal planes in which the hexagonal a-axis lies and the c-axis is in the direction indicated. There are six anion layers in the unit cell of corundum, arranged in the stacking sequence I, II, I, II, I, II as demanded by hexagonal close-packing. Strictly speaking, the circles representing the anions in Type I Layers (Fig. 2) should intersect the circles representing the anions in Type II Layers (e.g. Circle *A* should slightly intersect Circles *G* and *H* instead of being tangent to them, as will be evident from close consideration of Fig. 1c), but this refinement has been eschewed as it would make our subsequent diagrams rather less clear.

Adaptations in surfaces parallel to the c-axis

Surfaces parallel to the c-axis are of special interest as they potentially expose the "cation pairs" which are a unique characteristic of the corundum structure. By cation pairs we imply cations in adjacent octahedra on opposite sides of an octahedral face common to the two polyhedra, i.e. on opposite sides of the close-packed layers (I or II). *M* and *N* in Fig. 2 are such a cation pair: their distance of separation in α-Al_2O_3 and α-Cr_2O_3 is only 2.65 Å.[9]

Fig. 3 shows a corundum surface obtained by cleaving parallel to the c-axis and exposing the cation pairs on opposite sides of the Type II Layers. This surface, which is charge-balanced, has "ridges" (formed by oxygen ions at Level 2) and "valleys" (formed by oxygen ions at Level 4). The cations of the surface are all at Level 3, and each one is 5-coordinated; two of the co-ordinating oxygens are at Level 2, two at Level 4, and one at Level 5. It is evidently a highly symmetrical and relatively smooth surface. The surface is nevertheless unstable to the extent that the cations in the exposed cation pairs can be expected to repel one another. With triply-charged cations at a nominal distance of separation of 2.65 Å, this is likely to be an important consideration. Let us consider, therefore, some of the ways in which this symmetrical surface can be adapted.

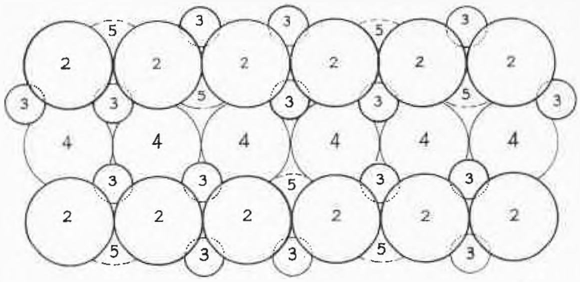

Fig. 3. Corundum surface formed by cleavage parallel to the c-axis. Numerals have the same significance as in Fig. 2

(i) First, let us suppose that the surface is exposed to a small amount of water vapour. Water molecules can be expected to chemisorb strongly at the exposed cation pairs, their oxygen atoms settling in Layer II at Level 1. The surface then has the appearance of Fig. 2. Such a chemisorption relieves the repulsion between the exposed cation pairs, and at the same time gives rise to full 6-coordination of those cations. Further chemisorption of water molecules can be expected in Layer II, their oxygen atoms again settling at Level 1 and in positions adjacent to the adsorbed atoms depicted in Fig. 2. Such chemisorption, however, completes the 6-coordination of only *one* cation per water molecule adsorbed; it will accordingly be a weaker adsorption. We may further note that the "strong" chemisorption (illustrated in Fig. 2) amounts to one-third of the total chemisorption. The chemisorption of water molecules on the surface of the corundum structure has also been discussed by Burwell and co-workers, with specific reference to α-Cr_2O_3.[10]

(ii) Secondly, let us consider an adaptation of the surface illustrated in Fig. 3 whereby oxygen atoms are displaced from Layer I (at Level 2) so as to occupy sites in Layer II (at Level 1) between the exposed cation pairs. The new surface, also charge-balanced, is illustrated in Fig. 4. The oxygen atoms displaced from Layer II are those which were not bonded to sub-surface cation pairs. In other words, we have displaced the oxygen ions which were 2-coordinated to cations and have left intact those which were 3-coordinated to cations. We may note that all the cations in this surface are again 5-coordinated, but we have removed the repulsion between exposed cation pairs which was characteristic of Fig. 3. The sur-

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[10] R. L. Burwell, G. L. Haller, K. C. Taylor and J. F. Read, *Advances in Catalysis 20* (1969) 1.

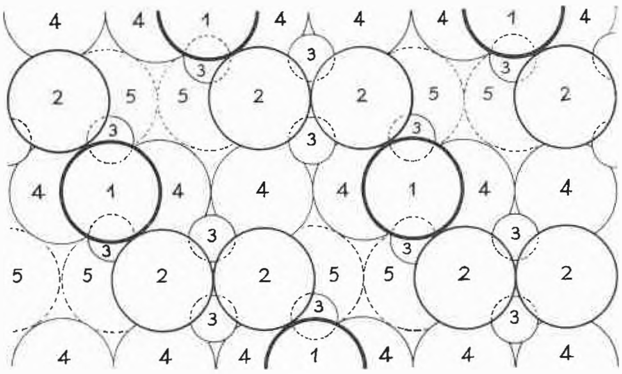

Fig. 4. Adaptation (ii) of Fig. 3

face has ridges and valleys which are rather more pronounced than those of Fig. 3. This surface can also be produced by removing adsorbed water from the surface shown in Fig. 2. It is merely necessary to postulate that the oxygen atoms removed as water are not those which were in the water molecules originally adsorbed; adsorption of water will effectively produce two OH^- ions by the reaction:

$$H_2O + O^{2-} \rightarrow OH^- + OH^-$$

We consider that the surface structure depicted in Fig. 4 should be a typical one for well outgassed α-alumina.

(iii) Let us next consider a re-organisation of the surface shown in Fig. 3 in which every third (weakly-bonded) oxygen atom from Layer I (Level 2) is again displaced, but in this case to a site where 6-coordination of 25% of the surface cations can be achieved. The new surface is shown in Fig. 5. It is a process in which 25% of the cations remain 5-coordinated, 25% become 6-coordinated, and 50% become 4-coordinated. We believe that the elements of such a surface would be favoured at low chromium contents in α-$Cr_xAl_{2-x}O_3$, the Cr^{3+} ions being those to assume 6-coordination. As is well known, octahedral coordination of Cr^{3+} (d^3) is strongly assisted by crystal field stabilisation. An important feature of this re-organisation is the production of sites near 4-coordinated cations where there is ample room for large molecules to be chemisorbed.

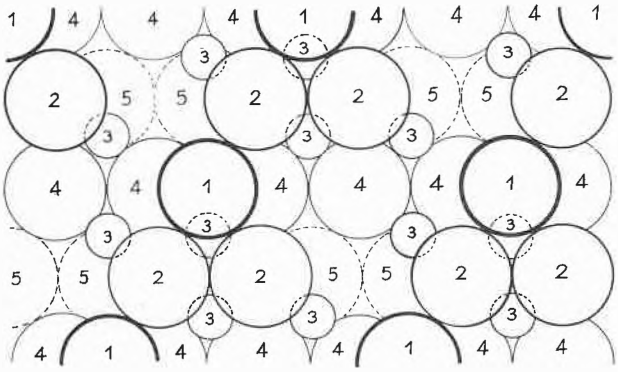

Fig. 5. Adaptation (iii) of Fig. 3

(iv) Finally, let us consider a re-organisation of the surface of Fig. 3 in which every third oxygen atom from Layer I (Level 2) is again displaced to Layer II (Level 1), but in such a way that we form "double-octahedra" (i. e. two MO_6 octahedra joined across a common face of 3 oxygens to form an M_2O_9 unit). The new surface is illustrated in Fig. 6. This structure also has 25% of the surface cations in 6-coordination, 25% in 5-coordination and 50% in 4-coordination, but it differs from the one depicted in Fig. 5 in having complete 6-coordination at one quarter of all cation-pair sites. It illustrates a surface element which we consider would become important as soon as the Cr content in α-$Cr_xAl_{2-x}O_3$ reaches a point where Cr–Cr pairs form in appreciable numbers.

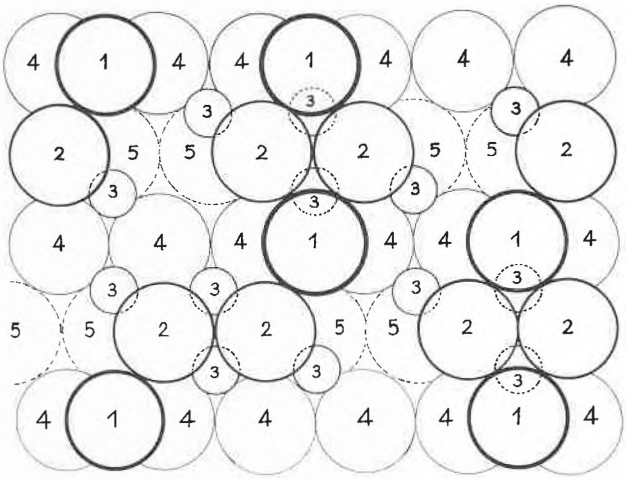

Fig. 6. Adaptation (iv) of Fig. 3

Potential catalytic centres

We now describe some of the possible consequences for catalysis of the surface re-organisations outlined above.

(a) A characteristic of the surfaces depicted in Fig. 5 and Fig. 6 is that Cr^{3+} ions in solid solution in α-alumina could act as promoters for generating catalytically-active low-coordinate Al^{3+} ions. The induced activity is not due directly to the chromium ions, but is brought about by their tendency to obtain crystal-field-stabilised 6-coordination at the expense of the oxygen ions which normally co-ordinate Al^{3+} ions. The 4-coordinate Al^{3+} ions produced in low-Cr solid solutions should act as Lewis acids. Such surfaces should show high activity in isomerisation and dehydration reactions.

(b) At high Cr contents, 4-coordinate chromium ions can be expected in Fig. 6, since not all chromium ions can be members of covered cation pairs. 4-coordination may presage a change of oxidation state from Cr^{3+} (d^3); for instance, adjacent exposed neighbours may exist as d^2–d^4 couples. In 4-coordination, both d^2 (Cr^{4+}) and d^4 (Cr^{2+}) probably enjoy greater crystal field stabilisation than d^3 (Cr^{3+}). Such d^2–d^4 couples could be useful centres in dehydrogenation or oxidation-reduction reactions.

(c) In the Cr_2O_9 double-octahedron of Fig. 6, the two "east-west" oxygens at Level 2 and the two "north-south" oxygens at Level 1 together form an exposed group of four anions. They are well placed for reductive attack by hydrogen and hydrocarbons. High-temperature hydrogen exchange reactions may proceed on such centres.

(d) A symmetrical four-atom group (Fig. 7a) of two oxygen ions at Level 2 and two cations at Level 3 occurs on each of the surfaces illustrated in Figs. 2–6. A similar four-atom group, but with the oxygen ions recessed (i.e. two oxygen ions at Level 4 and two cations at Level 3) occurs in the surfaces shown in Fig. 5 and Fig. 6. An especially accessible variety of this structure occurs in Fig. 6. These centres are likely to be important for low-temperature hydrogen-deuterium equilibration by a heterolytic mechanism. The symmetrical transition state shown in Fig. 7b superimposes on Fig. 7a.

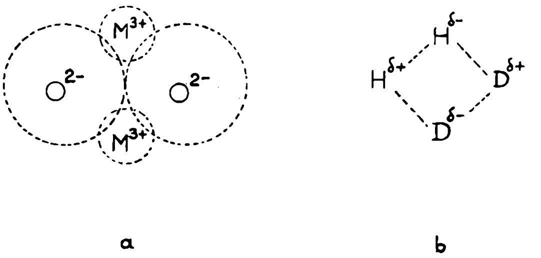

Fig. 7. (a) Arrangement of atoms in an element of the corundum surface. (b) Transition state for the heterolytic mechanism of H_2—D_2 exchange

These descriptions of potential catalytic centres are speculative. However, they serve to bring out the point that mere increase of the concentration of a solute ion without a change of the bulk phase can lead in principle to marked variations of catalytic activity. It has already been shown that, in H_2–D_2 equilibration, a progressive increase in chromium content in the solid solution α-$Cr_xAl_{2-x}O_3$ is not matched by a monotonic increase in catalytic activity. Special activity is associated with the concentration range in which Cr–Cr cation pairs form in appreciable numbers, demanding that the formation of particular kinds of active centre be considered.[6]

Conclusion

Attention has been focussed in this discussion on four prototype surfaces of the corundum structure parallel to the *c*-axis. Each preserves an electrically neutral condition, yet each shows unique characteristics. The surface formed by cleavage parallel to the basal plane can also adapt by adsorption or re-organisation, and it may be discussed using similar arguments to those already described. The cleaved surface of anions in that case is atomically flat, and is not likely to be electrostatically stable: however, the interesting features specific to accessible cation pairs will not develop in modifications of the virgin basal plane surface. The incorporation of foreign ions into solid solution in α-Al_2O_3 will affect the relative concentrations of the different surface features described. By taking the example of α-$Cr_xAl_{2-x}O_3$ it is shown that in general one would not expect the variations of catalytic activity with concentration of solute to be linear, and there is already experimental evidence in this direction. More experimental data are now required on the activity of such standard systems in a variety of catalytic reactions. One may then hope ultimately to use particular catalytic reactions as probes for different kinds of surface feature on corundum and other simple close-packed structures.

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