Das Ergebnis ist insofern erstaunlich, da diese Messungen nur möglich sind, wenn die Schichten genügend fehlstellenfrei sind, da — ebenfalls nach MURRAY und MEYER [6] — eine Fehlstellendichte von 10^{15} cm^{-3} die mittlere Exzitonenreichweite schon um eine Größenordnung vermindern würde.

Wir danken der Deutschen Forschungsgemeinschaft und der Fraunhofer-Gesellschaft für Unterstützung.

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The Catalysis of H_2-D_2 Equilibration by Solid Solutions of α-chromia-alumina

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(Z. Naturforsch. **24 a**, 1415—1417 [1969]; received 14 July 1969)

In studying the catalytic activity of transition metal ions present in dilute solid solution in diamagnetic oxides such as α-Al_2O_3 or MgO [1–5], it is of interest to know not only how active the transition metal ions are in isolation, but also the way in which the activity per dissolved ion changes with increasing concentration [2]. SCHAEFER and BÜCHLER [5] have recently reported an interesting comparison of the activity of Ti^{3+}, V^{3+} and Cr^{3+} ions, present at 0.1 atom per cent concentration in corundum, for the catalysis of H_2-D_2 equilibration. The effect of concentration was not reported. We describe here some results from our laboratory on the activity of α-$Cr_xAl_{2-x}O_3$ in this reaction. The two studies are complementary, since we have varied the Cr concentration from 0.01 to 10 atom per cent.

Cations are grouped in pairs along the *c*-axis of the corundum structure, and it has been suggested that at the surface they may act co-operatively in catalysis [6, 7]. This possibility may be examined by studying the activity of the α-$Cr_xAl_{2-x}O_3$ phase in the range from 0 to 10% Cr content. Below 1% Cr, the transition metal ions are mostly isolated; between 1% and 10% Cr, statistical considerations imply that the number of Cr-Cr pairs increases rapidly, whilst multiple groups (more than two Cr together) will still be few by comparison. Thus activity measurements below 1% Cr (such as those of SCHAEFER and BÜCHLER [4, 5]) serve to establish mainly the properties of isolated Cr ions, and those between 1% and 10% Cr will reflect to an increasing extent any special properties of pairs. α-$Cr_xAl_{2-x}O_3$ was selected for this work since e.p.r. studies [8] confirm that spin coupling develops in this oxide with increasing Cr^{3+} content in much the way expected for statistical (random) distribution of Cr^{3+} ions, in contrast to α-$Ti_xAl_{2-x}O_3$ and α-$V_xAl_{2-x}O_3$ where pairs appear to form preferentially [9].

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α-$Cr_xAl_{2-x}O_3$ solid solutions with surface areas of approximately 2 m^{2}g^{-1} were prepared by impregnating boehmite with CrO_3 solution, compressing to pellets and heating in air at 1350°C for 30 hours with an intermediate cooling and regrinding. Oxides were designated as AC *N*, where *N* is the number of Cr atoms per 100 Al atoms. AC 0.01, AC 0.1, AC 1, AC 3, AC 7 and AC 10 were prepared, and also α-Al_2O_3 as control. H_2-D_2 equilibration was studied at a pressure of 5 torr in a circulating system with a capillary leak to a mass spectrometer. Catalysts were outgassed at 850°C and activities, measured from — 120° to 500°C, were expressed as specific first-order velocity constants *k* (min^{-1} m^{-2}).

All the solid solutions exhibited two temperature zones of activity, illustrated for AC 3 in Fig. 1. α-Al_2O_3 was sig-

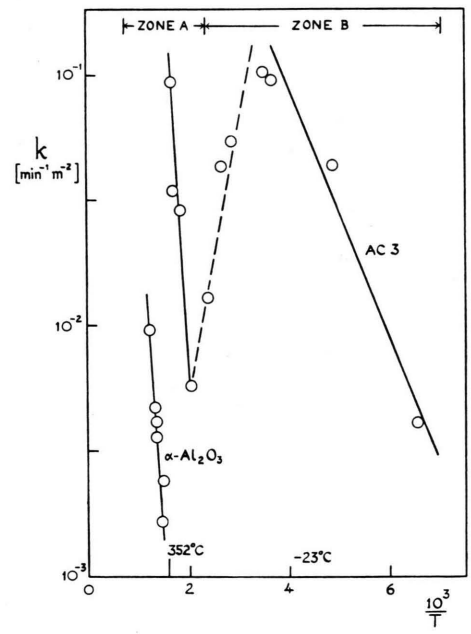

Fig. 1. H_2-D_2 equilibration on α-Al_2O_3 and on α-chromia-alumina solid solution AC 3 (approximately $Cr_{0.06}Al_{1.94}O_3$).

[1] P. W. SELWOOD, J. Am. Chem. Soc. **87**, 1804 [1965]; **88**, 2676 [1966]; Fourth Internat. Congr. on Catalysis, Moscow 1968, preprint 66.

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nificantly active only at high temperatures (Zone A). Thus the large low-temperature activity (Zone B) is specific to the presence of chromium ions. (Zone B activity due to Cr was also reported by, SCHAEFER, BÜCHLER[5]: our Arrhenius plot for AC 0.1 is quite similar to their curve for a crushed ruby with 0.1% Cr.) Fig. 2b illustrates the variation of activity with Cr content in Zone B. The filled circles show the activity *per chromium ion* (k/[Cr]). It is seen that (a) k/[Cr] decreases between AC 0.01 and AC 1, where Cr ions are isolated from one another, and (b) k/[Cr] increases (AC 1 to AC 10) when the concentration of Cr-Cr pairs begins to increase significantly. For Zone A, the weak activity of α-Al_2O_3 is greatly enhanced when Cr ions are introduced (Fig. 1). Activity again shows an increase when the range AC 1 to AC 10 is reached (Fig. 2a). Activity in Zone B (but not

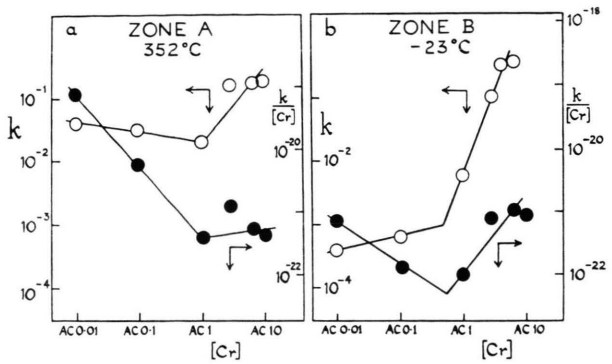

Fig. 2. H_2-D_2 equilibration as a function of chromium content at (a) 352 °C and (b) −23 °C. Units of k are $min^{-1}m^{-2}$; [Cr] is expressed as the number of chromium ions in the mass of catalyst having a surface area of 1 m^2.

in Zone A) depends upon previous outgassing at 850°C and is destroyed by exposure to water vapour. Pre-treatment of outgassed specimes (AC 1 to AC 10) in hydrogen at 550°C and below led to a diminished activity in Zone B (cf. SCHAEFER and BÜCHLER[5]), but did not eliminate it. It is possible that SELWOOD[1] did not observe H_2-D_2 equilibration for crushed ruby below 100°C because of an OH-poisoned surface.

Fig. 2 establishes that there is a *co-operative* effect of Cr ions in H_2-D_2 equilibration at Cr concentrations above AC 1. This implies that the presence of two *adjacent* Cr ions in some way favours the catalysis. Now two Cr ions and two oxygen ions together form a good 4-atom centre for H_2-D_2 exchange by a heterolytic mechanism. However, several different conformations of 4-atom centre can be expected on the surface of a corundum structure, depending on whether the two metal atoms are in octahedra joined by a common corner, a common edge or a common face, and on whether all the oxygen atoms of the octahedra are present at the surface. We shall discuss here only the surface centre produced by two MO_6 octahedra joined by a common face (Fig. 3). This is an important case as it is the one for which adjacent metal atoms have the closest separation (the case of c-axis pairs). The three oxygen ions (O_2, O_3 and O_7 in Fig. 3a) of the octahedral face which intersects the axis of the cation pair (Cr_A and Cr_B) are likely to be retained at

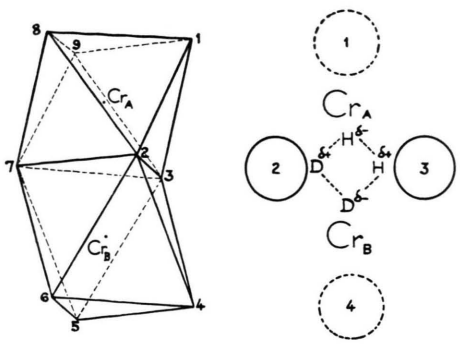

Fig. 3. (a) A Cr_2O_9 double-octahedron (two octahedra joined across a common face) in the corundum structure. Oxygen positions are labelled by numbers; chromium positions (Cr_A and Cr_B) are near the centres of the octahedra. (b) Plan view of an exposed surface of the Cr_2O_9 unit, with schematic heterolytic adsorption of $H_2 + D_2$ superimposed. The indicated positions of the H and D atoms are not meant to be precise, and are shown as a square array inside the Cr and O atoms only for the sake of clarity.

the surface, since they help to minimise the repulsion between the near-sited cations. Two of these ions (say O_2 and O_3) will commonly be exposed to the gas phase. These negative ions, and the two (slightly recessed) positive Cr ions, form together a compact 4-atom centre for heterolytic dissociation of two hydrogen molecules, and hence for low-temperature H_2-D_2 exchange without surface diffusion of H atoms (Fig. 3b). Adsorption in this form will be weak, and the complex may not be stable at higher temperatures, thereby accounting for the decline of catalytic activity above 0°C (Fig. 1). In Zone A, at higher temperatures, we consider that there is a second, different mode of adsorption, more activated and involving strong chemical combination with the oxygen ions of the surface. This type of hydrogen adsorption, as OH^- (or OD^-), is in fact rather general on oxides, and presages reduction. A special function of c-axis Cr-Cr pairs in the Zone A reaction may be to provide some places where *all* of the possible exposed oxygen positions of the M_2O_9 double-octahedron are intact at the surface, at the expense of other surface cations whose oxygen co-ordination is decreased. For the Cr^{3+} (d^3) ion, the crystal field effect provides a strong driving force for complete six-fold co-ordination of the metal ion at the surface.

Chromium oxide has long been known as a very active catalyst for H_2-D_2 equilibration. The ability of Cr^{3+} to change its valency or to re-distribute its electronic charge no doubt assists catalysis, and is actually implicit in our models for both Zone A and Zone B catalysis, but this is a general feature of transition metal ions. We attribute the special features of chromium first to the high tendency of Cr to form octahedral co-ordination with O or OH, and secondly to Cr-Cr pairs contributing to provide favoured reactive configurations for the activated complex. Some of the principles invoked here are very similar to those recently described by BURWELL and co-workers[10]. The stimulation

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of H_2-D_2 equilibration activity at the surface of the alumina matrix by trace quantities of chromium ions (AC 0.01) is also of interest, and will be discussed in more detail elsewhere. We believe it may also be related to the acquisition by surface Cr^{3+} ions of a full anion octahedron, thereby rendering the neighbouring surface AlO_n polyhedra more co-ordinatively unsaturated[10] and accordingly catalytically active.

Gitterschwingungsspektren. III. Mitteilung *, [1, 2]

Die Symmetriekoordinaten und die Schwingungsformen der Gitterschwingungen in Spinellen

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(Z. Naturforsch. **24 a**, 1417—1419 [1969]; eingegangen am 12. Mai 1969)

Zur Klärung der Frage, inwieweit die Gitterschwingungen der Spinelle bestimmten Koordinationspolyedern oder der gesamten Elementarzelle zuzuordnen sind, wurden die Zahl, der Schwingungstyp und die Symmetriekoordinaten der Schwingungen aus der Faktorgruppe des idealisierten Spinellgitters (Raumgruppe $F4_1/d\bar{3}2/m$) abgeleitet. Die aus den Symmetriekoordinaten sich ergebenden Schwingungsformen der Gitterschwingungen werden mitgeteilt.

Bei ihren Untersuchungen über die IR-Spektren von Oxospinellen haben sowohl Waldron [3] als auch Hafner [4] weitgehend unabhängige Schwingungen der Atome in tetraedrischer Koordination und der Atome in oktaedrischer Koordination angenommen und das kurzwellige Maximum der Spektren, das in der Reihe der Aluminium-, Chrom- und Eisenspinelle im Bereich von $600-700\ cm^{-1}$ liegt, der Valenzschwingung von MeO_4-Tetraedern und das Maximum bei etwa $500\ cm^{-1}$ der Schwingung von MeO_6-Oktaedern zugeordnet.

Im Rahmen unserer Arbeiten über Schwermetallthiospinelle [5] beabsichtigten wir, die Gitterschwingungen dieser Verbindungen im langwelligen Infrarot zu untersuchen und zur Charakterisierung der Bindungskräfte und der Kationenverteilung in den Thiospinellen heranzuziehen. Die Zuordnung der erhaltenen Spektren, die im Bereich von $50-500\ cm^{-1}$ vier charakteristische Absorptionsmaxima zeigen, zu Schwingungen der verschiedenen Koordinationspolyeder war jedoch nicht widerspruchsfrei möglich. Es war vielmehr anzunehmen, daß an jeder dieser 4 Schwingungen alle Atome der Elementarzelle beteiligt sind (vgl. auch Tarte und Mitarbeiter [6]).

In der vorliegenden Arbeit werden deshalb zunächst die Symmetriekoordinaten und die Schwingungsformen der Gitterschwingungen, die wir aus der Faktorgruppe der idealisierten Spinellstruktur abgeleitet haben, mitgeteilt. Über die Spektren der Thiospinelle und ihre Zuordnung wird an anderer Stelle berichtet.

* Sonderdruckanforderungen erbeten an Priv.-Doz. Dr. H. D. Lutz, Institut für Anorganische Chemie der Universität zu Köln, *D-5000 Köln*, Zülpicher Straße 47.

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[2] H. D. Lutz u. R. Heider, Z. Naturforsch. **24 a**, 476 [1969].

1. Zahl und Schwingungstyp der Gitterschwingungen des Spinellgitters

Die Elementarzelle des Spinellgitters enthält 8 Einheiten der allgemeinen Formel AB_2X_4, wobei A Metallatome in tetraedrischer Koordination, B Atome in oktaedrischer Koordination und X Nichtmetallatome in kubisch dichtester Kugelpackung darstellen (Normalspinell). Die der Abzählung der Gitterschwingungen mit dem Wellenvektor $k=0$ zugrunde liegende Basiszelle (primitive unit cell) enthält 2 Formeleinheiten (vgl. Abb. 1). Die zur Raumgruppe des Spinellgitters ($F4_1/d\bar{3}2/m$) bzw. der zugehörigen Basiszellengruppe isomorphe Punktgruppe ist O_h.

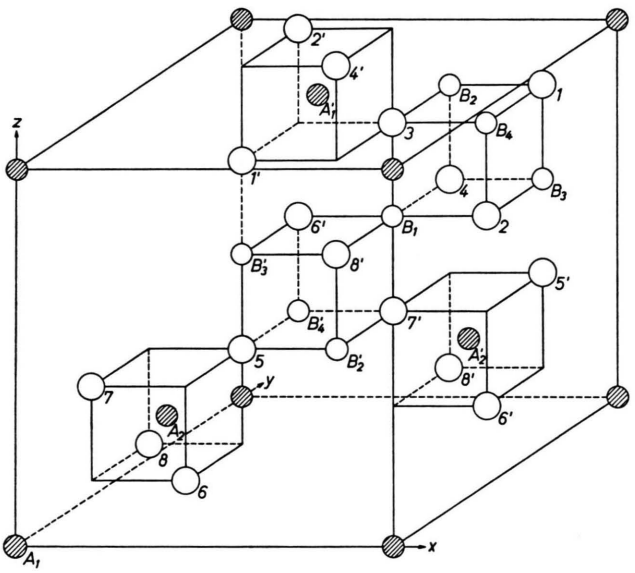

Abb. 1. Das Spinellgitter (Normalspinell). Eingezeichnet sind die der Abzählung der Gitterschwingungen zugrunde liegende Basiszelle (numerierte Atome) sowie die in Abb. 2 zur Darstellung der Schwingungsformen verwendeten Teilwürfel der Elementarzelle.

In Tab. 1 sind die Zahl und der aus der Faktorgruppe folgende Schwingungstyp der Gitterschwingungen des idealisierten Spinellgitters zusammengestellt. IR-aktiv sind nur die 4 dreifach entarteten Schwingungen der Symmetrieklasse F_{1u}. Die Schwingungen vom Typ A_{1g}, E_g und F_{2g} sind Raman-aktiv.

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