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HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPIC (HRTEM) DETERMINATION OF THE PREFERENTIALLY EXPOSED FACES ON γ-Al_2O_3 AND η-Al_2O_3

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High resolution transmission electron microscopy has been used to examine the crystallites in γ-Al_2O_3 and η-Al_2O_3. γ-Al_2O_3 has been found to be nearly hexagonally shaped crystallites whose identity distances and angles of fringe patterns indicate that (110) planes are preferentially exposed. η-Al_2O_3 showed preferentially exposed surfaces of (100), (110) and super imposed (111)/(211). This information is valuable to the catalyst researcher trying to model the surfaces of these two supports.

The transition aluminas γ-Al_2O_3 and η-Al_2O_3 are frequently used as catalysts and catalyst supports [1]. The catalytic activity and interactions with materials to be supported depend on the nature of the exposed crystal planes. Thus the orientation of the exposed planes on transition aluminas has been subject of much discussion [2–9]. Several models for the dehydration and catalytic site geometry have been presented: Peri [2] used the (100) face of γ-Al_2O_3 for his dehydroxylation models. Butt and associates [3,4] also used the (100) face for Monte Carlo simulation of a catalytic alumina surface and Hombeck et al. [5] assumed the presence of this face when discussing alkali ions on γ-Al_2O_3. Lippens [6,7] has projected that the (111) face will be preferentially exposed on η-Al_2O_3 and the (110) or (100) faces will be preferentially exposed on γ-Al_2O_3. Knozinger and Ratnasamy [8] state that in practice the (111) and (110) faces are considered to form the surface layers of η-Al_2O_3 and γ-Al_2O_3 respectively. Certainly the relative abundances of these exposed faces will vary between different aluminas and within a crystallographic type depending on the preparation conditions [9]. For the commonly used aluminas, however, more realistic models can be discussed, if experimental evidence is at hand with respect to the preferentially exposed crystallographic planes present. Iijima [10] has observed (111) facetting on specially grown "spherical" γ-alumina particles. A correlation

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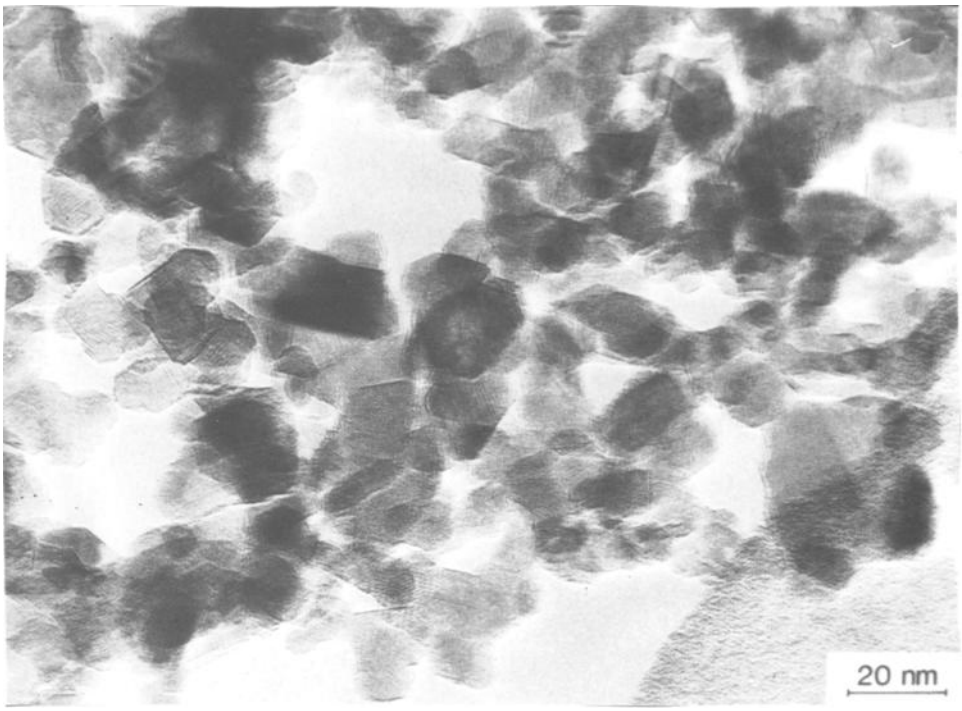

Fig. 1a. Electron micrograph of agglomerated γ-Al_2O_3 crystallites (Aluminum Oxide C, Degussa AG).

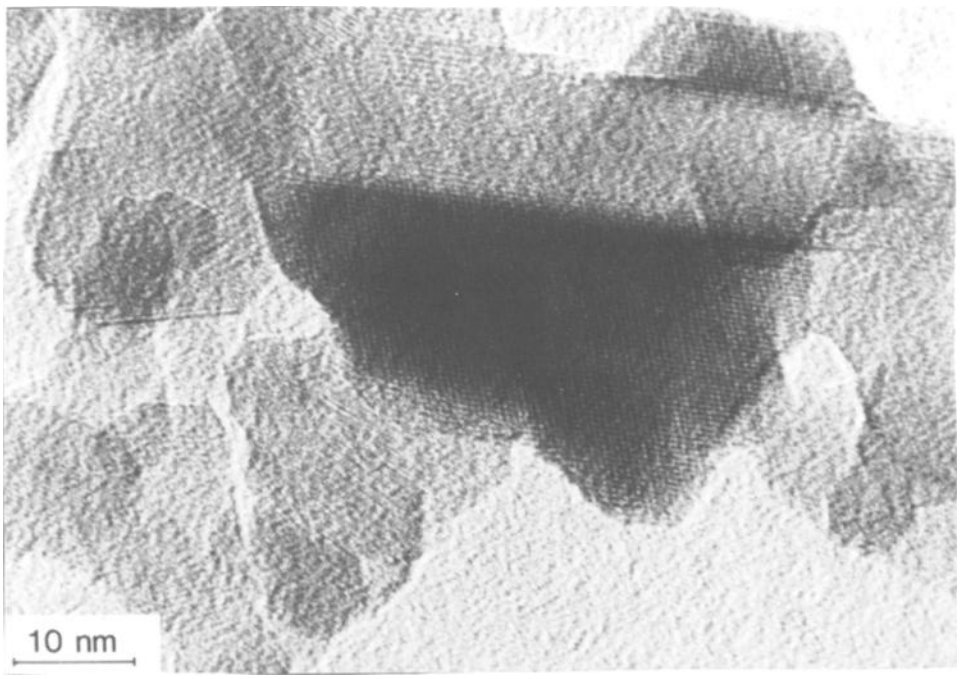

Fig. 1b. High resolution electron micrograph showing an isolated γ-Al_2O_3 crystallite (Aluminum Oxide C, Degussa AG) with the (110) plane exposed.

is yet to be established between these findings and those expected for the more commonly used types of alumina.

In a program to determine the preferential orientation of transition aluminas by HRTEM we have examined γ-Al_2O_3 (Aluminum Oxide C, Degussa AG) and η-Al_2O_3 prepared in our laboratory by the method of Yoldas [11] using aluminum isopropoxide as a precursor material.

As is shown in fig. 1a the γ-Al_2O_3 is made up of very small, nearly hexagonally shaped crystallites with diameters of 10 to 20 nm and a thickness of less than 5 nm. The fact that these crystallites are so small, prevents a direct determination of the orientation of the predominant surface planes by selected area electron diffraction (SAED). Moreover, the observation of Moiré fringes indicates that these platelets, are agglomerated, which hinders a respective orientation determination by means of optical diffraction of the electron micrographs. A

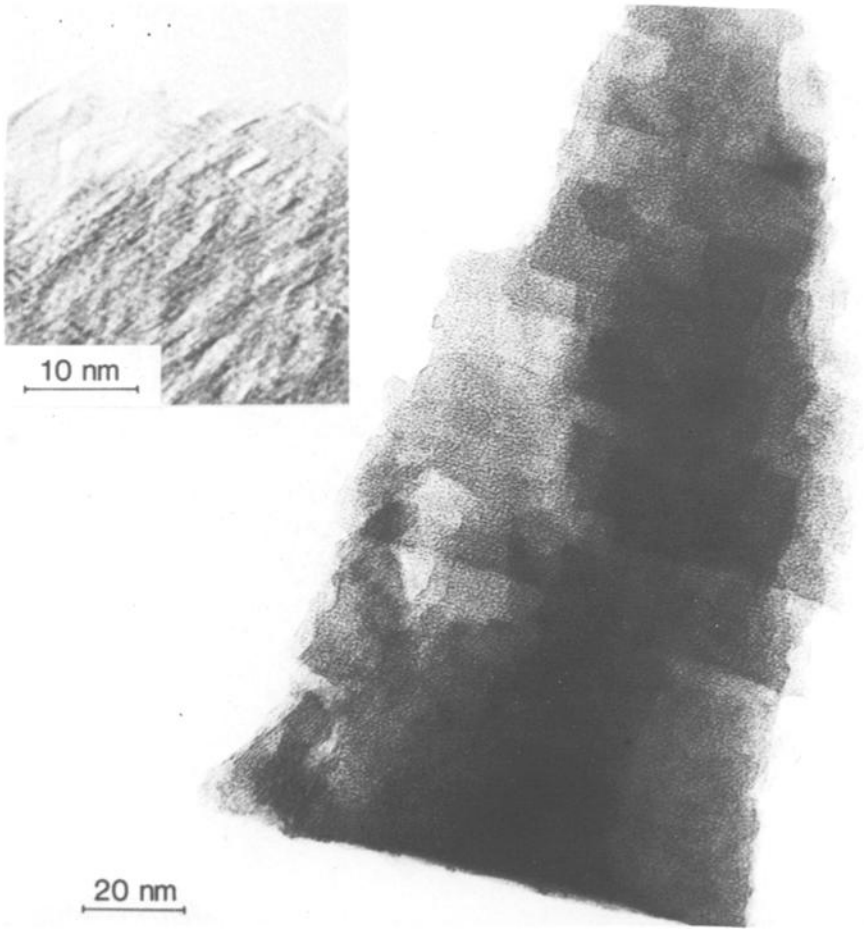

Fig. 2a. Electron micrograph of a η-Al_2O_3 particle prepared from aluminum isopropoxide. The inset (upper left) shows a magnified section of the parent particle.

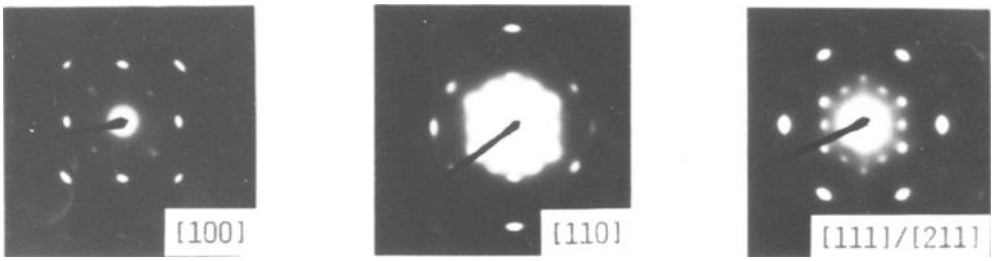

Fig. 2b. Electron diffraction patterns of different η-Al_2O_3 particles prepared from aluminum isopropoxide.

thorough examination of the enlarged electron micrographs, however, allowed the measurement of the parent identity distances and the angles of the fringe patterns ($d \cong 0.46$ nm, $\alpha \cong 110°$) as is shown in fig. 1b. These observations lead to the conclusion that the preferential orientation of the surface planes of these γ-Al_2O_3 platelets correspond to the crystallographic (110) planes. In addition, the high resolution electron micrographs prove that, in spite of the small size, the platelets are perfectly crystalline, i.e. the material investigated is made up of extremely small γ-Al_2O_3 single crystals with preferentially exposed (110) faces.

η-Al_2O_3 has been prepared by hydrolysis of aluminum isopropoxide and subsequent, thermogravimetrically monitored dehydroxylation. Electron micrographs of the product obtained revealed that relatively large particles were formed. A typically shaped particle is shown in fig. 2a. Respective electron diffraction patterns taken of several different particles proved that the preferentially exposed surfaces correspond to the crystallographic planes of the type (100), (110) and superimposed (111)/(211) (see fig. 2b). The broad reflections of all patterns obtained, however, indicated that these particles are made up of many small, but highly oriented crystalline domains of η-Al_2O_3. This was confirmed by high resolution electron micrographs, which gave evidence that these η-Al_2O_3 particles are made up of poorly crystalline but highly oriented domains. This fact not only indicates that the dehydroxylation process is topo-

tactical, but also leads to a reasonable explanation of the higher catalytic activity of η-Al_2O_3 in comparison to γ-Al_2O_3.

In conclusion, we have found, using HRTEM that γ-Al_2O_3 (Aluminum Oxide C, Degussa AG) to be oriented with the (110) planes preferentially exposed and the η-Al_2O_3 prepared from aluminum isopropoxide precursor to be oriented with a number of different planes, i.e. (100), (110), (111), and (211) exposed. In addition, there are distinct differences with respect to the crystallinity of the respective phases, γ-Al_2O_3 being made up of micro-single-crystals and η-Al_2O_3 being made up of poorly crystalline, highly oriented domains. This information should be quite useful to those modelling the transition aluminas for catalytic purposes. A more general investigation on the preferentially exposed crystallographic planes of different aluminas including catalytically less relevant phases as well as the changes occurring during respective transitions is in progress.

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