

Textural and Structural Changes in Transition Alumina Supports

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A γ_c alumina carrier is shown to be partly hydrated to bayerite or gibbsite in contact with an ammonia solution, or even water, at room temperature, and to boehmite when heated at 410 K and a pressure of 0.3 MPa in water.

Much attention has been devoted to the evolution of the precursors of the active species impregnated on transition alumina supports, a common type of carrier. Hitherto the modification of the alumina carrier during impregnation has been neglected. During work on platinum on alumina reforming catalysts, we have discovered that the shaped commercial carriers routinely used in catalytic research undergo significant morphological and structural modifications even under mild conditions. Although some limited indications of this have been given previously by Tertian and Papee,¹ no systematic work has been undertaken.

Treating a typical γ_c alumina carrier with water or aqueous ammonia gives rise to a noticeable structural and concomitant textural change which depends on the precise conditions (see

Table 1). The structural modification may be limited, being undetectable by *X*-ray diffraction, but can be detected by

Table 1. Treatment conditions.

	1	2	3
Solution	H ₂ O	NH ₄ OH	NH ₄ OH
pH	7	8.5	12
Temp./K	410	300	300
Pressure/MPa	0.3	0.1	0.1
Time/h	6	550	550
Phase	γ_c Alumina + boehmite	γ_c Alumina + bayerite	γ_c Alumina + gibbsite

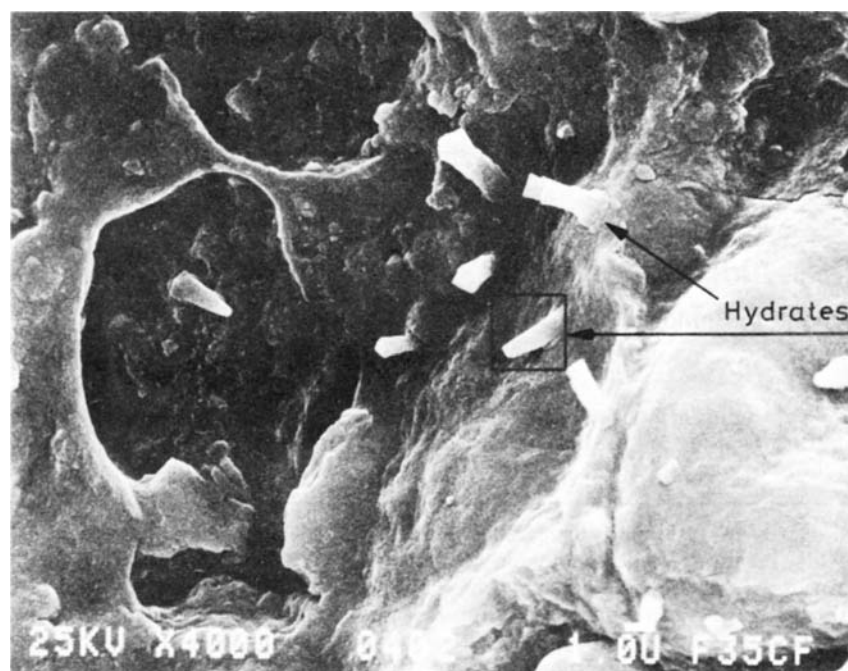


Figure 1. Stereopicture of the recrystallization of a γ_c alumina under the conditions of treatment 2 (*t* 8 h).

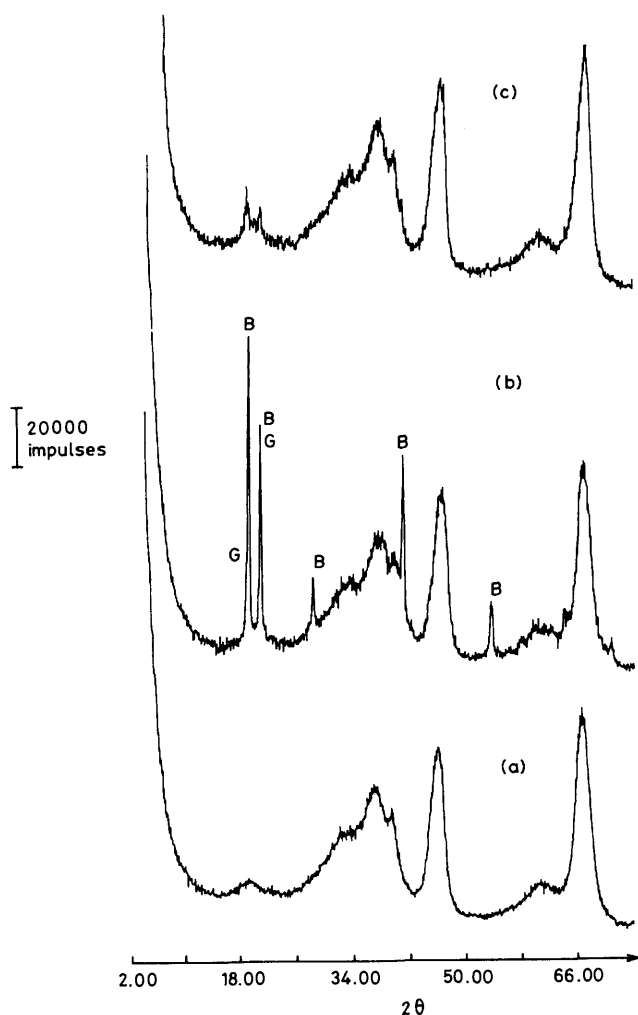


Figure 2. (a) X-Ray diffractogram of the γ_c alumina carrier; (b) X-ray diffractogram after treatment 2; (c) X-ray diffractogram obtained after the rehydration of a γ_c alumina carrier first hydrated then calcined. B = bayerite, G = gibbsite.

scanning electron microscopy (Figure 1). After a longer treatment period the structural modification can be extensive, as shown by the X-ray diffractograms in Figure 2, curves (a) and (b). The hydrated crystals may be very large, up to several microns in size. Careful examination of the diffractograms reveals no change in the γ_c alumina line intensities in the case of treatment under conditions 2 and 3. This indicates that the hydrates crystallize, not from the γ_c phase, but from a poorly crystalline phase present in the alumina carrier before treatment, and not detected by X-ray diffraction. The content of this amorphous phase may be roughly estimated as 10–20% by weight, according to the hydrate line intensities. Following treatment with NH_4OH , calcination at 640 K in air: (i) destroys the crystalline hydrates (at exactly 515 K); the X-ray diffractograms of the treated recalcined and the starting carrier are nearly identical; (ii) increases the specific area to $270 \text{ m}^2 \text{ g}^{-1}$ as compared to the initial value of $220 \text{ m}^2 \text{ g}^{-1}$ for the starting alumina; (iii) transforms the hydrates arising from the amorphous content of the material into a crystalline phase. This phase cannot be easily hydrated as shown in Figure 2, curve (c).

In conclusion, the transition alumina carrier cannot be considered as inert when in contact with aqueous solutions at high pH. This hydration phenomenon is related to the amorphous content of the alumina carrier. Ammonia treatment as described above is a sensitive method for determining this 'amorphous' content. We have further checked that similar effects are observed for other alumina carriers. A similar hydration phenomenon is likely to occur at low pH but will lead to an amorphous gel undetectable by X-ray diffraction. This phenomenon must be taken into account when examining and trying to interpret the deposition of active agents (such as platinum) in the course of the preparation of catalysts (such as naphtha-reforming catalysts) supported on alumina carriers.

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Reference

- 1 R. Tertian and D. Papee, *J. Chim. Phys.*, 1958, 341.