



The surface of transitional aluminas: A critical review



Guido Busca*

University of Genova, Department of Civil, Chemical and Environmental Engineering, p. J.F. Kennedy 1, 16129 Genova, Italy

ARTICLE INFO

Article history:

Received 11 May 2013

Received in revised form 29 July 2013

Accepted 3 August 2013

Available online 5 September 2013

ABSTRACT

The data reported in the literature concerning the structure, the morphology and porosity, the physico-chemical properties and the surface properties of transitional aluminas are reviewed critically. Original experimental data are reported to discuss the nature and assignment of the OH stretching bands associated to surface hydroxyl groups and the nature of the surface acidity and basicity. Suggestions are made for further investigations.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Medium and high surface area transition aluminas have wide applications in catalysis and adsorption technologies. Among the most prominent catalytic applications, they are used in the catalytic steps of the Claus process, the production of sulphur from H₂S in the refineries [1,2]. They are very active in the dehydration of alcohols to olefins and to ethers [3], being practically used to produce dimethylether from methanol [4], e.g. as a first step in the methanol to propylene [5] and methanol to olefins (MTO) [6] processes.

Aluminas are or have been used in the refining of Fischer Tropsch syncrude [7]. In particular, they are used to increase octane number through position isomerization of terminal to internal olefins, for the skeletal isomerization of n-pentene to isopentene as well as to dehydrate higher alcohols to olefins. They are also used as commercial acid catalysts of the alkylations of phenol with alcohols, such as the synthesis of o-cresol and 2,6-xyleneol using methanol at 300–400 °C [8]. Aluminas are reported to be used in the production of chloromethane from methanol and hydrogen chloride [9] and for the dehydrofluorination of alkylfluorides which are byproducts of the HF catalyzed isobutane/butylene alkylation process [10]. In all these cases, the Lewis acidity or the acido-basicity of the alumina surfaces are considered to be their key features.

Indeed, the main interest for aluminas in the catalysis field is likely as supports of catalysts. In particular, they are the standard supports for many metal and sulphide catalysts. When applications requiring relatively low reaction temperature (<500 °C) are considered, such as for hydrotreating with supported sulphides [11] or hydrogenation using platinum, palladium or nickel metals [12] as the active phases, high surface area γ -, δ - or η -Al₂O₃, can be used. These transitional aluminas are also used as supports of copper

chloride for the oxychlorination of ethylene to ethylene dichloride in the process to produce vinyl chloride monomer [13].

These supports, however, are characterized by high acidity and reactivity, thus not applicable when very reactive compounds are present in the reactant mixture. They are also unstable at temperatures >500 °C. For these reasons, less reactive and more stable lower surface area aluminas are used in several applications. θ -Al₂O₃ is a common support for total oxidation catalysts [14,15], such as those based again on Pt and Pd, as well as for some dehydrogenation [16] and hydrogenation catalysts [17]. Low surface area α -Al₂O₃ or α -Al₂O₃/ θ -Al₂O₃ mixed phases are largely used when high inertness and/or high thermal stability are needed, such as in the case of Pd/Al₂O₃ 1,3-butadiene hydrogenation catalysts [18] as well as Ag/Al₂O₃ catalysts used for ethylene oxidation to ethylene oxide [19].

In the applications of transitional aluminas as catalyst supports, the unique acidity or acido-basicity is its crucial property because implies good dispersion of the supported active species. Much experimental work was done to define the main properties of transitional aluminas: among the most relevant contributions we would like to cite the work of Peri [20], of Tsyganenko and Filimonov [21], of Morterra [22] and of Knözinger [23,24]. In particular, the model proposed by Knözinger and Ratnasamy [24] has been, and still is, a reference for any further work on the surface properties of aluminas as well as of any metal oxide. In spite of the new experimental and theoretical techniques developed today, still a comprehensive picture of this subject is far from obtained. In this review we will attempt a summary of the state of art on this topic.

2. Solid state chemistry of alumina polymorphs

A schematics of the most relevant paths in alumina polymorphic transformations is reported in Fig. 1 [25]. As it is well known, at the end of the thermal transformation of aluminas always α -Al₂O₃ (corundum, S.G. R $\bar{3}c$, Z=6) is formed. This phase

* Tel.: +39 0103536024; fax: +39 0103536028.

E-mail address: Guido.Busca@unige.it

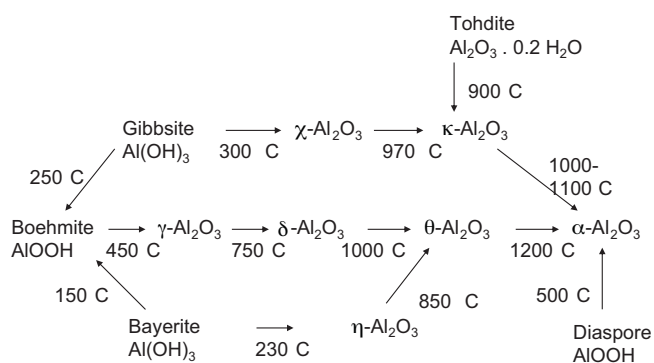


Fig. 1. Schematics of the main solid state transformations of aluminas [25].

is the thermodynamically stable polymorph if the free energy of the bulk is considered. In this polymorph the oxide ions have an hexagonal close packing (hcp) array and all Al cations are octahedrally coordinated. This polymorph can be produced by thermal decomposition of the oxy-hydroxide diaspore (usually denoted as α -AlOOH) or by calcination of any other aluminum oxide or hydroxide at sufficiently high temperature.

The most common “transitional” alumina polymorphs which are applied in the catalysis field are those that may be prepared by thermal decomposition of the oxy-hydroxide boehmite (γ -AlOOH) or of the hydroxide bayerite (α -Al(OH)₃). Differently from corundum, these alumina polymorphs are all based on cubic close packing array of oxide anions. The product of boehmite calcination is denoted as γ -Al₂O₃ while the product of bayerite calcination is denoted as η -Al₂O₃. Both these phases, whose structure has still not been completely defined, convert at higher temperatures into θ -Al₂O₃, whose structure is, instead, well defined (β -Ga₂O₃ – type). However, while η -Al₂O₃ converts directly into θ -Al₂O₃, intermediate phases are usually (but not always) observed upon the conversion of γ -Al₂O₃ into θ -Al₂O₃.

3. On the crystal structure of γ -Al₂O₃

As said, γ -Al₂O₃ is, by definition, the product of decomposition of boehmite, the oxy-hydroxide denoted as γ -AlOOH. It has been described by Lippens and de Boer [26] to be a cubic defective (or non-stoichiometric) spinel. The cubic spinel structure concerns compounds with the AB₂O₄ stoichiometry (space group Fd $\bar{3}$ m with Z=8); it is constituted by a ccp sublattice of oxide anions, with A²⁺ and B³⁺ cations occupying tetrahedral (T_d) and octahedral (O_h) interstices, with Wyckoff positions 8a and 16d, respectively. In the case of normal spinels A²⁺ cations occupy the T_d (8a) positions and B³⁺ cations occupy the O_h (16d) positions. In the case of inverted spinels A²⁺ cations occupy half of the O_h (16d) positions and B³⁺ cations occupy the T_d (8a) positions and the other half O_h (16d) positions. In the case of random spinels the two positions are occupied random. Actually, some extent of disorder always exists in the occupancy of these positions also in normal and inverted spinels.

In the case of γ -Al₂O₃ it has been supposed that, according to the presence of Al³⁺ ions only (and the consequent cation deficiency with respect to the spinel stoichiometry), these cations would partially occupy the same T_d (8a) and O_h (16d) interstices, leaving vacancies in the remaining positions. Thus, the percentages of T_d and O_h cations can theoretically range from 25% T_d and 75% O_h if all vacancies are on T_d sites to 37.5% T_d and 62.5% O_h if all vacancies are on O_h sites. The position of Al cations can be investigated by ²⁷Al NMR spectra as well as by the Rietveld analysis of the X-ray and neutron scattering patterns [27], and indicate that in γ -Al₂O₃ tetrahedral Al is 25–33% of all Al ions the rest being almost exclusively octahedral.

However, the results of several studies, including Rietveld refinement of XRD patterns, suggested that part of Al cations may occupy non-spinel sites [28], i.e. interstices of the ccp oxide lattice which are unoccupied in the case of stoichiometric spinels. These “non-spinel sites” are other T_d (8b and 48f) and O_h (16c) interstices. Additionally, ²⁷Al NMR spectra of γ -Al₂O₃ show a small fraction of Al ions in coordination five [29,30], or highly distorted tetrahedral. Some authors have also interpreted the structure as tetragonal, due to the contraction of the cubic lattice along one of the cubic crystallographic directions, with space group, *I*4₁/*amd* and the occupancy of non-spinel sites [31,32], 32.8% tetrahedral and 67.2% octahedral sites. Digne et al. [33,34] and Krokidis et al. [35] proposed a structure based on a orthorhombically distorted ccp oxide lattice and non-spinel cationic positions (space group P2₁/m, Z=8), with 25% of Al ions in tetrahedral interstices and no structural vacancies. According to the calculations of these authors, this non spinel model is more stable than alternative spinel type structures.

In contrast, Ferreira et al. [36] considered by DFT calculations a spinel type model with 37.5% tetrahedrally coordinated Al cations and 62% octahedrally coordinated cations against the non-spinel type model of Krokidis et al. [35], and concluded that the best match with experimental data was obtained for the spinel-type model. Ab initio calculations performed by the same authors [37] of the ²⁷Al MAS NMR spectra for different structural models of γ -Al₂O₃ allowed to conclude that the best fit is obtained with a model of a spinel-type structure with space group Fd $\bar{3}$ m and Z=32, where 64% Al ions are octahedral, 34.4% tetrahedral and 1.6% pentacoordinated.

4. The structure of other transitional aluminas and their thermal evolution

As said, while some authors report the direct conversion of γ -Al₂O₃ into θ -Al₂O₃ by calcination near 650 °C, most studies find the formation of intermediate phases [25]. According to Lippens and de Boer [26] and Wilson et al. [38], a phase closely related to that of spinel and of γ -Al₂O₃, denoted as δ -Al₂O₃, is formed continuously in the range 500–650 °C. δ -Al₂O₃ has been determined as a tetragonal spinel superstructure whose unit cell is constituted by three spinel unit blocks with tetragonal deformation, likely with a partial ordering of Al ions into octahedral sites. However, data on location of Al ions for pure δ -Al₂O₃ are still incomplete [39]. According to Paglia et al. [31] a slightly different spinel superstructure is formed, denoted as δ' -Al₂O₃ (SG P4m2, Z=16, 66(3)% octahedral and 34(3)% tetrahedral Al cation coordination).

By decomposing Bayerite (α -Al(OH)₃) at 200–300 °C, another phase, denoted as η -Al₂O₃, is obtained, which is also considered to be a spinel-derived structure very similar to γ -Al₂O₃ but (according to Rietveld analysis of X-ray and neutron diffraction patterns and ²⁷Al NMR) with more tetrahedrally coordinated (35%) and less octahedrally coordinated Al ions [40,41]. Calcination of η -Al₂O₃ at increasing temperatures gives rise directly to θ -Al₂O₃ [38] at temperatures lower than those needed to convert γ -Al₂O₃ to θ -Al₂O₃. Much less efforts have been devoted to the clarification of the structure of η -Al₂O₃, with respect to those devoted to γ -Al₂O₃. In particular, it can be noted that the “non-spinel” model of γ -Al₂O₃ [35] does not account, to our understanding, for the possible reasons for the slight differences between the two closely related polymorphs η -Al₂O₃ and γ -Al₂O₃, as well as the slight differences between γ -Al₂O₃ and δ -Al₂O₃.

5. On the limits of bulk theoretical calculations

As cited above, a number of theoretical calculations concerning the stabilities of the possible bulk structures of γ -Al₂O₃ have been

Download English Version:

<https://daneshyari.com/en/article/54503>

Download Persian Version:

<https://daneshyari.com/article/54503>

[Daneshyari.com](https://daneshyari.com)