Alumina–Titania Nanofibers Synthesis Using Different Techniques of Ti Addition

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Introduction

The synthesis of materials with nano-scale dimensions and structure is of great interest and importance in materials science and nanotechnology[1]. Particularly, alumina nanofibers have great potential applications as adsorbents, catalysts support, composite materials, and ceramics, among others. In the last years, several studies on alumina nanofibers formation have been reported[2].

We have found that by implementation of a pH swing method, it is possible to obtain boehmite alumina with fibrillar morphology[3]. This pH swing method was first reported by Ono et al.[4], and consisted on swinging the pH value from acid to basic pH region which corresponded to the limits of the U-shaped solubility curve of alumina.

In this study, we aimed at obtaining alumina-titania by a pH swing method and combined with three different techniques to incorporate TiO_2 on Al_2O_3 (co-precipitation, deposition and stepwise deposition). The overall purpose was to disclose a method in which TiO_2 was highly dispersed.

Materials and Methods

These Alumina (A6S5) and TiO_2-Al_2O_3 mixed oxides were synthesized following a modified pH swing method[3]. A general preparation flow diagram is displayed in Figure 1. All preparations were carried out at constant 60 °C temperature. The first pH-swing cycle was as follows: In a glass vessel containing 200 ml of aqueous $Al_2(SO_4)_3$•NaO_2 (basic pH), an aqueous $Al_2(SO_4)_3$•$18H_2O$ solution (acid pH) was poured until reaching pH=2. Then the white precipitate was kept for 5 minutes and next aqueous Al_2O_3•NaO_2 solution was added until pH=8 stable in the reaction mixture, and aged for 5 minutes. This stage is the first pH swing cycle, and can be repeated a number of times to affect the textural properties. In this work, we carried out six pH swing cycles in all synthesis, maintaining all other conditions constant. For all alumina-titania portions we used $K_2[TiO(C_2O_4)_2]$•$2H_2O$ by Titania source. For all alumina-titania portions we calculated a theoretic 15 % weight in relation to alumina quantity in each portion.

Results and Discussion

Three different forms to incorporate titanium sulfate in pH swing process turn out in fibrillar aluminas-titanias, but with clear different titania dispersion and dependent to incorporation stage of Ti compound.

Deposit (Dx5) turn out in amount segregated anatasa formation in material surface and /or hided in inter-fibrillar porosity. Step deposit (Fx5) turns out in less formation of segregated anatase in material surface. Coprecipitation (Cx5) produces material with small anatase amounts on surface and TiO_2 formation very disperse in alumina fibrillar matrix. None of three alumina-titania systems to found other titania phases formation different to anatase phase (rutile or brokite). In the end to obtained Al_2O_3:TiO_2 nanofibrillar systems created in base of pH swing method, though were calcinated at 500 °C for 4 h, they conserve specific areas higher to 300 m^2/g, and pore volumes equal or higher to 1 cm^3/ g, besides they conserve its fibrillar morphology.
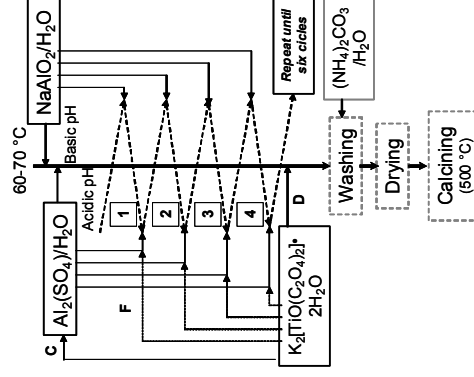

Figure 1. Preparation flow diagram of alumina and alumina-titania by a pH-swing method and the different incorporation techniques of titania. C: coprecipitation, D: deposit, F: stepwise deposit.

Significance

Use of alumina-titania as a catalyst support is a good alternative to improve hydrotreating catalysts performance, as long as high TiO_2 dispersions are achieved[5]. The importance of fibrillar alumina morphology lies on its inter-fibrillar pores, which favor the diffusion and eventual transformation of huge refractory asphaltene and Ni, V porfirinic molecules contained in oil residuals, which represent the most difficult hydrocarbons to transform in oil hydrotreatment reactions, and contribute enormously to deactivation of catalysts active sites[6].

References

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