

The Role of CeO₂-Doping of γ -Al₂O₃ on its Structural and Superficial Area

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A series of samples, noted Al_xCe_{1-x} has been prepared by hydrolysis, from γ -Al₂O₃ and CeO₂. These samples were calcined under air at 450, 900 and 1200 °C, and then characterized by specific surface area, X-ray diffraction and thermoreduction programmed under H₂. Obtained results show that after calcination at 450 and 900 °C, the cerium decreases the surface of alumina. Results of X-ray diffraction and thermoreduction programmed under H₂ experiments showed that the samples are constituted of: γ -Al₂O₃ and CeO₂. The global consumption of hydrogen increase with rate of CeO₂ added. At 1200 °C, the sintering of the samples is very important and γ -Al₂O₃ is transformed into the α -phase. The decrease in specific surface area is more accentuated for Al₁Ce₀ sample, since sintering occurs due to the growth in crystallite size. Thermoreduction programmed under H₂ experiments show that reduction of CeO₂ much more accentuated for ceria samples or its decrease can reflect some alterations of the nature of interactions between Al₂O₃ and CeO₂.

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1. Introduction

The alumina is an attractive material extensively used in chemical applications due to its high specific surface and much cleared pore structure [1, 2]. However, the most catalytically active phases, such as γ - and η -Al₂O₃ present problems at high temperatures due to phase transformations. The transition from γ -Al₂O₃ to α -Al₂O₃ leads to a considerable reduction of the surface area, causing a degeneration of the catalytic activity [3]. Thermal stability can be enhanced by retarding or delaying phase transitions and it has been shown that rare earth element, such as Ce, will not only retard the phase transformation from γ -Al₂O₃ to α -Al₂O₃, but will also stabilizes the pore structure of alumina [4–6]. The oxygen storage properties of ceria play a key role in all catalytic applications [7]. In this work a structural and superficial area modification of Al₂O₃ induced by CeO₂ addition, thermal treatment and reducing process has been studied.

2. Experimental

2.1. Preparation of samples

γ -Al₂O₃ and CeO₂ were used in this study, from Merck, purely 99.9% in mass, their surface areas are about 144.75 and 7.5 m² g⁻¹, respectively. Al₂O₃ was hydrolyzed in an excess of distilled, deionized water for 16 h at 80 °C [8]. CeO₂ was added to these solutions, the mixture was homogenized at the same temperature during 5 h. The products obtained were filtered and dried overnight in air at 120 °C, there are noted Al_xCe_{1-x} ($x =$

at.%). Calcination was led under airflow of 3 l/h, in dynamic reactor: with heating rate of 10°/min and isothermal at 450 and 900 and 1200 °C during 3 h.

2.2. Characterization

Nitrogen physisorption measurements were performed in a Micrometrics ASAP 2010 apparatus at –196 °C. Helium was used as the carrier gas. The samples were degassed in vacuum for at least 2 h at 120 °C before analysis. The crystal phase and crystal size of samples were determined by X-ray diffraction (XRD) patterns using a Philips PW1800 diffractometer fitted with an anticathode Cu K α ($\lambda_{Cu} = 1.5406 \text{ \AA}$). Temperature programmed reduction under H₂ (H₂-TPR) experiments were carried out in a fixed-bed reactor. 50 mg of sample were exposed to 5 vol.% H₂/Ar with a continuous flow rate of 50 ml/min from room temperature to 950 °C with a heating rate of 10 °C/min.

3. Results and discussion

The averaged values of the Brunauer–Emmett–Teller (BET) surface area of the mixed oxides calcined at 450 °C decrease with an increase in Ce loading and may be caused due to the formation of agglomerates during the synthesis (Table I). Regarding changes on the specific surface area after calcination at 900 °C, only a slight decrease is distinguishable for Al₀Ce₁ sample. The decrease in specific surface area is more accentuated for Al₁Ce₀ sample. Since sintering occurs due to the crystallite growth, alumina loses 27% of their surface area [9, 10].

By way illustration, XRD patterns recorded of Al_{0.85}Ce_{0.15} and Al_{0.7}Ce_{0.3} samples are dominated by characteristic X-ray lines of γ and δ -alumina coexistence for samples calcined at 450 °C (see Fig. 1). After calcination at 1200 °C (see Fig. 1), the specific surface areas do not exceed 10 m²/g. The sintering induces important increase in the crystallinity of Al₂O₃ (5.0 nm to 36.7 nm).

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The average particle size of sample shows the fact that crystallites are often agglomerated to form larger particles [11, 12].

The quantitative analysis of the reduction peaks shown

that H₂ consumption increases with the increase of the CeO₂ content in samples Al_xCe_{1-x}, indicating that the reduction of Ce⁴⁺ to Ce³⁺ becomes easier with the incorporation of Al₂O₃ (Table I).

TABLE I

Reducibility textural and structural properties of Al_xCe_{1-x} samples calcined at 450, 900 and 1200 °C.

| Sample | Specific surface area (m ² g ⁻¹) | | | H ₂ uptake [μmol/g] ^a | | Crystallites size [nm] ^b | | |
|---------------------------------------|---|--------|---------|---|--------|-------------------------------------|--------|---------|
| | 450 °C | 900 °C | 1200 °C | 450 °C | 900 °C | 450 °C | 900 °C | 1200 °C |
| Al ₁ Ce ₀ | 120.7 | 106.0 | 8.1 | 1 | <1 | 5.0 | 5.6 | 36.7 |
| Al _{0.85} Ce _{0.15} | 88.3 | 77.3 | – | 164 | 139 | 9.5 | 28.8 | – |
| Al _{0.7} Ce _{0.3} | 60.0 | – | 4.7 | 283 | – | 30.5 | – | 39.3 |
| Al ₀ Ce ₁ | 5.8 | 5.4 | <1 | 613 | 611 | 37.5 | 38.5 | 43.0 |

^aOn calcined catalysts from thermoreduction programmed under H₂ experiments.

^bAverage crystallite size calculated from the characteristic reflections observed on XRD patterns.

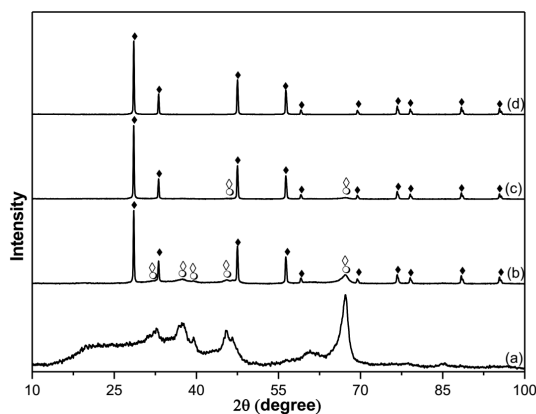


Fig. 1. XRD measurements on samples calcined in air at 450 °C; Al₁Ce₀ (a), Al_{0.85}Ce_{0.15} (b), Al_{0.7}Ce_{0.3} (c), Al₀Ce₁ (d); (○) γ-Al₂O₃, (◇) δ-Al₂O₃, (◆) CeO₂.

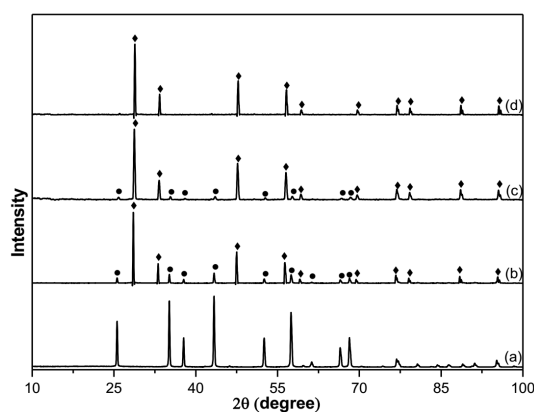


Fig. 2. XRD measurements on samples calcined in air at 1200 °C; Al₁Ce₀ (a), Al_{0.7}Ce_{0.3} (b), Al_{0.5}Ce_{0.5} (c), Al₀Ce₁ (d); (●) α-Al₂O₃, (◆) CeO₂.

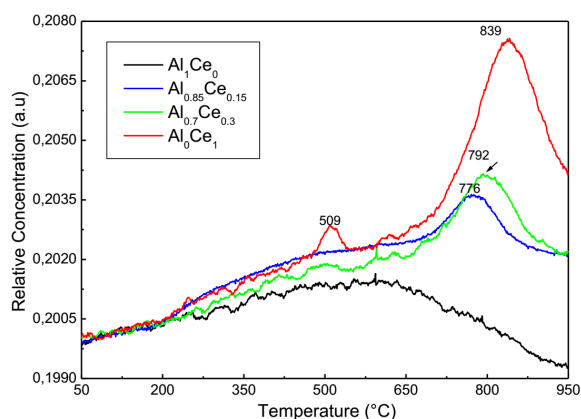


Fig. 3. H₂ consumption profiles from H₂-TPR experiments recorded on calcined Al₁Ce₀, Al_{0.85}Ce_{0.15}, Al_{0.7}Ce_{0.3}, Al₀Ce₁ samples under air at 450 °C.

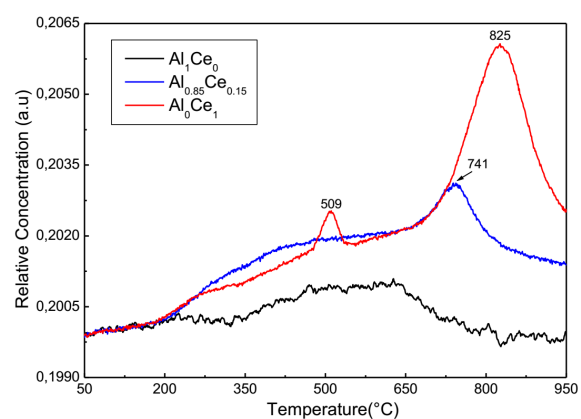


Fig. 4. H₂ consumption profiles from H₂-TPR experiments recorded on calcined Al₁Ce₀, Al_{0.85}Ce_{0.15}, Al₀Ce₁ samples under air at 900 °C.

A broad signal appears at higher temperature, where a strong H₂ consumption was observed on Al₀Ce₁, Al_{0.7}Ce_{0.3} and Al_{0.85}Ce_{0.15} above 500 °C corresponding to H₂ uptakes of 613, 283, and 164 μ mol/g, respectively, indicating the reduction of CeO₂ calcined at 450 °C (see Fig. 3). The results show a maximum shifting at the temperature of 825 °C for Al₀Ce₁, and corresponding to H₂ uptake more than 600 μ mol per gram, without significant H₂ consumption on Al₁Ce₀ calcined at 900 °C (see Fig. 4) [13]. It is also worthwhile to notice that a lessening in H₂ consumption on Al_{0.85}Ce_{0.15} would suggest that Al₂O₃ would likely interact with CeO₂ [14].

4. Conclusion

Structural and textural modifications of γ -Al₂O₃ induced by CeO₂ addition, thermal treatment and reducing process have been investigated. At low temperature, the addition of cerium decreases the surface area of alumina. Specific surface area and crystallite size measurements remained unchanged on Al₀Ce₁ sample after calcination at 900 °C, which indicates its good thermal stability by decreasing the rate of the crystallite growth process. H₂-TPR experiments on alumina did not reveal the occurrence of significant reduction processes. Furthermore, the H₂ consumption increases with the increase of the CeO₂ content in samples Al_xCe_{1-x}, indicating that the reduction of Ce⁴⁺ to Ce³⁺ becomes easier with the incorporation of Al₂O₃. Indeed, a significant lessening in H₂ consumption can reflect some alterations of the nature of interactions between Al₂O₃ and CeO₂.

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