The Role of CeO$_2$-Doping of γ-Al$_2$O$_3$ on its Structural and Superficial Area

K. Aribi, M. Ghelamallah*, A. Bellifa and F. Bousehbab
Laboratoire de Matériaux, Applications et Environnement, Faculté des Sciences Exactes, Université Mustapha
Stambouli, BP 305, Route de Manoumia, Mascara 29000, Algeria

A series of samples, noted Al$_x$Ce$_{1-x}$ has been prepared by hydrolysis, from γ-Al$_2$O$_3$ and CeO$_2$. 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 H$_2$. 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 H$_2$ experiments showed that the samples are constituted of γ-Al$_2$O$_3$ and CeO$_2$. The global consumption of hydrogen increase with rate of CeO$_2$ added. At 1200°C, the sintering of the samples is very important and γ-Al$_2$O$_3$ is transformed into the α-phase. The decrease in specific surface area is more accentuated for Al$_1$Ce$_0$ sample, since sintering occurs due to the growth in crystallite size. Thermoreduction programmed under H$_2$ experiments show that reduction of CeO$_2$ much more accentuated for ceria samples or its decrease can reflect some alterations of the nature of interactions between Al$_2$O$_3$ and CeO$_2$.

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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-Al$_2$O$_3$ present problems at high temperatures due to phase transformations. The transition from γ-Al$_2$O$_3$ to α-Al$_2$O$_3$ 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-Al$_2$O$_3$ to α-Al$_2$O$_3$, 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 Al$_2$O$_3$ induced by CeO$_2$ addition, thermal treatment and reducing process has been studied.

2. Experimental
2.1. Preparation of samples
γ-Al$_2$O$_3$ and CeO$_2$ were used in this study, from Merck, purely 99.9% in mass, their surface areas are about 144.75 and 7.5 m$^2$ g$^{-1}$, respectively. Al$_2$O$_3$ was hydrolyzed in an excess of distilled, deionized water for 16 h at 80°C [8]. CeO$_2$ 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$_x$Ce$_{1-x}$ (x = at.%). Calcination was led under airflow of 3 l/h, in dynamic reactor: with heating rate of 10$^0$/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 anticaathode Cu $K_α$ ($λ_{Cu} = 1.5406$ Å). Temperature programmed reduction under H$_2$ (H$_2$-TPR) experiments were carried out in a fixed-bed reactor. 50 mg of sample were exposed to 5 vol.% H$_2$/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 1). Regarding changes on the specific surface area after calcination at 900°C, only a slight decrease is distinguishable for Al$_0$Ce$_1$ sample. The decrease in specific surface area is more accentuated for Al$_1$Ce$_0$ 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 surfaces areas do not exceed 10 m$^2$/g. The sintering induces important increase in the crystallinity of Al$_2$O$_3$ (5.0 nm to 36.7 nm).
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 $H_2$ consumption increases with the increase of the CeO$_2$ content in samples $A_l_1Ce_{1-x}$, indicating that the reduction of $Ce^{4+}$ to $Ce^{3+}$ becomes easier with the incorporation of Al$_2$O$_3$ (Table I).

**TABLE I**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area ($m^2g^{-1}$)</th>
<th>$H_2$ uptake [$\mu$mol/g]$^a$</th>
<th>Crystallites size [nm]$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_l_1Ce_0$</td>
<td>120.7</td>
<td>120.7</td>
<td>120.7</td>
</tr>
<tr>
<td>$A_0.85Ce_{0.15}$</td>
<td>88.3</td>
<td>77.3</td>
<td>8.1</td>
</tr>
<tr>
<td>$A_0.7Ce_{0.3}$</td>
<td>60.0</td>
<td>47.0</td>
<td>4.7</td>
</tr>
<tr>
<td>$A_0Ce_1$</td>
<td>5.8</td>
<td>5.4</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

$^a$On calcined catalysts from thermoreduction programmed under $H_2$ experiments.

$^b$Average crystallite size calculated from the characteristic reflections observed on XRD patterns.

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Fig. 1. XRD measurements on samples calcined in air at 450 °C; $A_l_1Ce_0$ (a), $A_0.85Ce_{0.15}$ (b), $A_0.7Ce_{0.3}$ (c), $A_0Ce_1$ (d); (○) $\gamma$-Al$_2$O$_3$, (♦) $\delta$-Al$_2$O$_3$, ( ObjectOutputStream) CeO$_2$.

Fig. 2. XRD measurements on samples calcined in air at 1200 °C; $A_l_1Ce_0$ (a), $A_0.7Ce_{0.3}$ (b), $A_0.5Ce_{0.5}$ (c), $A_0Ce_1$ (d); (●) $\alpha$-Al$_2$O$_3$, ( ObjectOutputStream) CeO$_2$.

Fig. 3. $H_2$ consumption profiles from $H_2$-TPR experiments recorded on calcined $A_l_1Ce_0$, $A_0.85Ce_{0.15}$, $A_0.7Ce_{0.3}$, $A_0Ce_1$ samples under air at 450°C.

Fig. 4. $H_2$ consumption profiles from $H_2$-TPR experiments recorded on calcined $A_l_1Ce_0$, $A_0.85Ce_{0.15}$, $A_0Ce_1$ samples under air at 900°C.
A broad signal appears at higher temperature, where a strong H$_2$ consumption was observed on Al$_{0.7}$Ce$_{0.3}$ and Al$_{0.85}$Ce$_{0.15}$ above 500°C corresponding to H$_2$ uptakes of 613, 283, and 164 µmol/g, respectively, indicating the reduction of CeO$_2$ calcined at 450°C (see Fig. 3). The results show a maximum shifting at the temperature of 825°C for Al$_{0.7}$Ce$_{0.3}$ and corresponding to H$_2$ uptake more than 600 µmol per gram, without significant H$_2$ consumption on Al$_{0.85}$Ce$_{0.15}$ calcined at 900°C (see Fig. 4) [13]. It is also worthwhile to notice that a lessening in H$_2$ consumption on Al$_{0.85}$Ce$_{0.15}$ would suggest that Al$_2$O$_3$ would likely interact with CeO$_2$ [14].

4. Conclusion

Structural and textural modifications of γ-Al$_2$O$_3$ induced by CeO$_2$ 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 Al$_{0.7}$Ce$_{0.3}$ sample after calcination at 900°C, which indicates its good thermal stability by decreasing the rate of the crystallite growth process. H$_2$-TPR experiments on alumina did not reveal the occurrence of significant reduction processes. Furthermore, the H$_2$ consumption increases with the increase of the CeO$_2$ content in samples Al$_{x}$Ce$_{1-x}$, indicating that the reduction of Ce$^{4+}$ to Ce$^{3+}$ becomes easier with the incorporation of Al$_2$O$_3$. Indeed, a significant lessening in H$_2$ consumption can reflect some alterations of the nature of interactions between Al$_2$O$_3$ and CeO$_2$.

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References