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Characterization of α-Al_2O_3 supports modified with CeO_2 and ZrO_2

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ABSTRACT

α-Al_2O_3 is a catalytic support adequate by its high stability, availability, and low cost, although it presents as principal disadvantage its limited surface area and reactivity. These disadvantages in the support lead to catalysts of low metallic dispersion and with weak interaction metal-support. According to characterization results obtained in this work, the addition of small amounts of Ce and Zr oxides to α-Al_2O_3 leads to $Ce_xZr_{1-x}O_2$ composites, thus conferring higher reactivity to the surface due to the presence of basic nature sites. This fact together with the well known oxygen storage capacity of these mixed oxides present in composites allow to obtain supports of optimal properties to prevent the sintering and the formation of superficial carbon present in the catalytic deactivation.

1. Introduction

In the development of supported metallic catalysts, the importance of the role that the support plays on the principal catalytic deactivation mechanisms is well known such as the sintering of metallic particles and the carbon deposition.

Among ceramic materials, aluminas are widely used in preparation of catalysts. Particularly, α-Al_2O_3 is characterized by its highly stable crystalline structure. It is adequate for industrial applications at high thermal levels (reforming for example), by its high availability and low cost as well as by its chemical and physical stability and mechanical strength. However, it presents the disadvantage of low superficial area and limited superficial reactivity, which originates catalysts scarcely dispersed with weak interaction with the active phase.

We have obtained well results in previous works with the addition of an aluminum oxide layer thus reducing sintering [1] or with the addition of alkaline metals such as Li or K decreasing carbon deposition [2]. On the other hand, several studies have demonstrated the advantages of the use of supports type CeO_2, La_2O_3 and/or ZrO_2 due to their oxygen storage capacities (Oxygen Storage Capacity, OSC) that favor carbon gasification [3]. The main disadvantage of these supports is its high cost, which makes them more restricted for technological applications.

The objective of this work is to try to develop supports based on α-Al_2O_3 modified by the addition of small amounts (1 and 5%) of CeO_2, ZrO_2 and CeO_2+ZrO_2 to use profitably properties of modifier oxides in the alumina matrix, evaluating morphological and structural changes of modified supports.

2. Experimental

α-Al_2O_3 (α), Rhone Poulenc (Spheralite 512), modified by dry impregnation with aqueous solutions of $ZrO(NO_3)_2x.H_2O$ and/or $Ce(NO_3)_36.H_2O$ was used to obtain the content of total oxides of 1 and 5 wt.%. The material was dried at 120 °C for 12 h and calcined in air for 4 h at 600 °C. Textural properties, specific surface Brunauer–Emmett–Teller (BET) and pore volume were determined in nitrogen adsorption equipment Micromeritics Accursorb 2100E. The characterization by X-ray diffraction (XRD) was carried out in an equipment Philips PW 1740, with CuKα radiation. X-ray photoelectron spectroscopy (XPS) was performed in sequential manner in an equipment Leybold Heraeus LHS10, with Al Kα radiation (1486.6 eV). Binding energy values (BE) were referenced to C1s at 285.0 eV. For Diffuse reflectance spectra (DRS), a spectrometer GBC Cintra 40/UV–Visible was used with 190–1000 nm wavelength range. The isopropanol decomposition reaction (ID) was tested in a continuous flow reactor of fixed bed between 150 and 400 °C at atmospheric pressure, feed of 4.5% IPA in Helium with a flow of 40 cm^3min^{-1}.

3. Results and discussion

The α-Al_2O_3 commercial support presents a specific surface area around 10 m^2g^{-1}. The content of modifier oxides did not exceed 5% wt/wt since it is intended to modify α-Al_2O_3 properties without generating a support in itself of oxides covering totally the alumina. The nomenclature used in the work for different materials is of the xCeyZrα type, where x and y indicate the percentage of CeO_2 and ZrO_2 respectively. Nitrogen adsorption results show a slight decrease in the specific surface at 7–8 m^2g^{-1} for modified supports, maintaining the mesoporous nature of α-Al_2O_3 (pore volume 0.2–0.4 cm^3g^{-1}).

The most intense peaks corresponding to cubic CeO_2 present at 2θ=28.54° (*) and 47.47° (JCPDS 81-0792) and to the tetragonal phase of ZrO_2 belonging to 2θ=30.27° (○) and 50.36° (JCPDS 88-1007) were identified by XRD analysis of Ceα and Zrα. In the diffractogram of Fig. 1, for the region 2θ=26°–34°, it is possible to distinguish for 5Zrα, besides the principal signal of the tetragonal phase of ZrO_2 (2θ=30.27° (○)), a small

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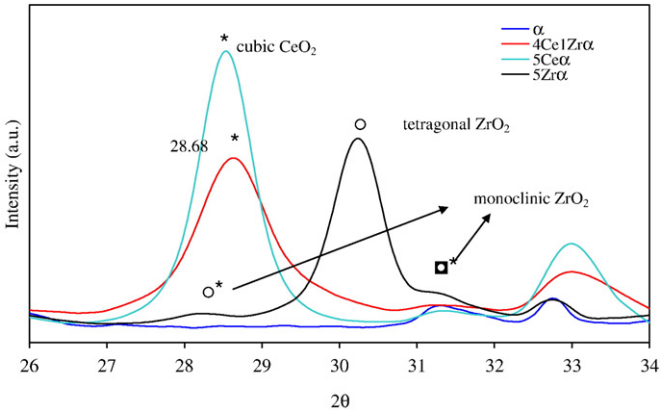

Fig. 1. XRD diffraction patterns.

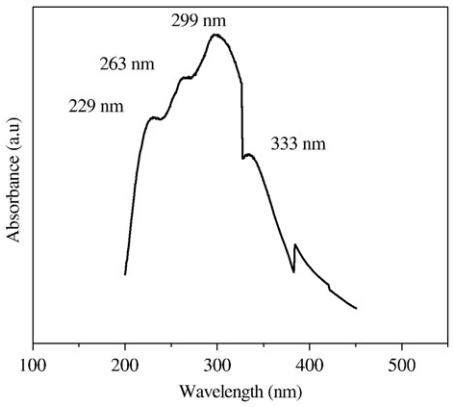

Fig. 2. UV diffuse reflectance spectra of 4Ce1Zrα composite.

contribution of monoclinic phase (2θ=28.4° (○*); 31.4° (*). In CeZrα composites, the Zr addition shifts diffraction peaks to higher 2θ angles (in Fig. 1, for 4Ce1Zrα, 2θ=28.68° (*) and 47.86°). This observation is attributed to the shrinkage of the lattice due to the replacement of Ce^{4+} with smaller cation radius Zr^{4+} [4]. ZrO_2 can be incorporated into the CeO_2 lattice to form a solid solution [4–6]. According to Koslov et al. correlation, when the peak position of plane diffraction (111) is between 2θ=28.55° and 29.25°, it would correspond to $Ce_xZr_{1-x}O_2$ of cubic phase, with x between 1 and 0.5 [7]. For 4Ce1Zrα composite, according to Koslov, would correspond the stoichiometry $Ce_{0.8}Zr_{0.2}O_2$.

Table 1 presents XPS results. The binding energy value of Al 2p has the same value of the corresponding to pure alumina 74.6±0.2 eV. In the 5Zrα system, the binding energy value for Zr $3d_{5/2}$ is in agreement with the value reported in the literature for Zr^{4+} in pure zirconia 182±0.2 eV, which indicates that there are no changes in the coordination number of zirconia [8].

The ratio of intensities determined for $(nZr/nAl)^S$ is higher than the bulk ratio, which indicates that Zrα systems are superficially enriched by ZrO_2 patches, and as it was determined by XRD they are fundamentally of tetragonal structure. With respect to the Ce spectroscopic behavior, the effect known as multiplet occurs due to coupling between the spin and the angular moment of decoupled electron f and the empty level 3d, known as spin-orbit coupling. In general, this effect is observed with a widening of bands. The binding energy value for Ce $3d_{5/2}$ present as pure cerium appears in the region 882.5, 887.8 and 898.5 eV [8]. The binding energy value for Ce $3d_{5/2}$ is in agreement with the value reported for Ce^{4+} in pure CeO_2 of 882±0.2 eV. Noticeable changes were not observed in BE values for Ce $3d_{5/2}$ in Ceα systems, which would indicate that there are no changes in the number of ceria coordination.

The ratio of intensities for $(nCe/nAl)^S$ in Ceα materials permits to interpret an enriched surface with CeO_2 patches better dispersed, this would be due to the presence of planar structures or 2D. These CeO_2 patches present a cubic structure considering results obtained by XRD.

Referring to CeZrα composites, the binding energy of Zr(IV) in the support matrix decreases from 182.3 eV (5Zrα) to 181.7 eV (4Ce1Zrα) since the Ce rich matrix is modified by the Zr presence (Table 1). This would indicate a strong interaction between Ce and Zr, probably by formation of a solid solution.

Fig. 2. shows the DRS diagram for the 4Ce1Zrα composite. According to DRS studies performed by Rao et. al., Ce_{1-x}–Zr_xO_2 solid solutions present 2 bands located at 263 nm and 299 nm corresponding respectively to $Ce^{3+} \leftarrow O^{2-}$ and $Ce^{4+} \leftarrow O^{2-}$ [9]. The band at 229 nm can be attributed to interband transitions when monoclinic ZrO_2 phase is present. Due to low contribution of the ZrO_2 monoclinic phase in the 4Ce1Zrα composite, the band at 229 nm could be due to the transition 4f–5d of Ce^{3+} ions that have Zr^{4+} as neighbors. The band at 333 nm on the higher wavelength side in the DRS may consist of interband and $Zr^{4+} \leftarrow O^{2-}$ transitions of the substituted fluorite lattice [9].

Table 1
Binding energies (eV) and surface atomic ratios as determined by XPS on the calcined supports

Support	O 1s	Zr $3d_{5/2}$	Ce 3 $d_{5/2}$	Al 2p	Surface atomic ratios (*)
	eV				
5Zrα	531.2	182.3		74.5	$(nZr/nAl)^b$=0.022
					$(nZr/nAl)^S$=0.059
5Ceα	530.8		882.4	74.5	$(nCe/nAl)^b$=0.016
	532.4		887.8		$(nCe/nAl)^S$=0.100
			898.4		
4Ce1Zrα	531.5	181.7	883.1	74.3	$(nCe/nZr)^b$=2.860
	533.4		887.8		$(nCe/nZr)^S$=3.200
			898.7		

(*) b: bulk ratio; S: $(I_A/S_A)/(I_B/S_B)$, S_A and S_B values from empirical answer factors.

These results and the ones of XRD and XPS induce to a similar conclusion and would confirm the presence of a solid solution in the CeZrα composite.

A superficial acidity characterization through an indirect method by catalytic decomposition reaction of isopropanol (ID) was carried out in order to determine acid-base properties of the support. As it has been demonstrated by Gervasini et al. [10], the isopropanol dehydration (that produces propylene and/or di-isopropylether) is catalyzed by acid sites. The dehydrogenation (that produces ketone), in absence of metals, is catalyzed by acid and basic sites through a concerted mechanism and serves as basicity measure of materials analyzed. Table 2 shows some isopropanol conversion results (X_{IPA} %) determined at 300 °C. All modified supports present higher global activity in the reaction, evidencing the increase of superficial active sites. The selectivity to ketone (S_{Ketone}) for modified supports was higher than the obtained for α-Al_2O_3. This indicates that the ID reaction is favored by the presence of strong basic sites. The selectivity to propylene ($S_{Propylene}$), on the contrary, decreases in modified supports indicating that there are less strong acid sites and there are no sites of the type strong base-weak Lewis acid.

In order to evaluate the effect of modified supports on the catalytic stability, catalysts with 2 wt.% Ni were prepared. Table 2 presents some results for methane dry reforming (DR) [11]. The stability was evaluated in terms of the activity coefficient a_{CH4}, which represents the ratio between the CH_4 consumption rate with 50 h in reaction and the initial rate. The NiCeZrα composites suffer lesser deactivation. Carbon content values on Ni4Ce1Zrα post-reaction samples were an order of magnitude lower than Niα (0.6% vs. 6.9 wt.% C). Table 2 also shows the increase percentage of the mean particle size of post-reaction samples. It is possible to note that the sintering of particles is lower for Ni4Ce1Zrα composites.

4. Conclusions

In a catalytic support, the reactivity and superficial area result to be very important in the preparation stage of a metallic catalyst due to the interaction with the metallic precursor. According to these characterization results, modified supports present larger number of superficial active sites at the expense of a slight decrease of α-Al_2O_3 surface area. The effect of the Ce/Zr ratio on formation of mixed oxides was demonstrated in CeZrα composites, finding that $Ce_{0.8}Zr_{0.2}O_2$ is formed for Ce/Zr=4. The known OSC capacity and the presence of strong basic sites of this mixed oxide result to give materials with optimal properties, that together with the ones of α-Al_2O_3 generate an effective support for both, sintering and superficial carbon deposition decrease in metallic catalysts.

Table 2
Activity results in isopropanol decomposition reaction (ID) and methane dry reforming reaction (DR)

Materials	ID reaction			Materials	DR reaction (*)		
	X_{IPA} (%)	S_{Ketone} (%)	$S_{Propylene}$ (%)		a_{CH4}	wt.% C (TPO/TGA)	% increase d_p (TEM)
α	21.3	3	97	Niα	0.24	6.9	60
5Ceα	30	12	88	Ni5Ceα	0.62	2.1	37
5Zrα	23	9	91	Ni5Zrα	0.44	1.8	47
4Ce1Zrα	47	14	86	Ni4Ce1Zrα	0.86	0.6	25

(*) at 1 atm, 700 °C and GHSV=3.10^5 $cm^3h^{-1}g^{-1}$ ($N_2/CH_4/CO_2$=6/1/1).

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