

Hyperfine Interaction Measurements on Ni/Ce-ZrO₂ Catalysts

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Abstract: Hyperfine Interaction measurements were performed on several different compositions of Ni/Ce-ZrO₂, characterized by XRD, catalysts by Time-Differential Perturbed Angular Correlation spectroscopy.

Key words: Catalysis, Hyperfine Interactions, Angular Correlation

1) Introduction- Catalytic processes, largely employed in industrial production, are a basic tool for manufacture of a large set of materials essential for modern life: fuels derived from petroleum, pharmaceuticals, petrochemicals and basic chemicals etc. Such intensive applicability in industrial production stimulates constant search for new catalysts as well as to improve those that already exist, aiming to minimize environmental impacts and to improve their compatibility with sustainable development. As the catalysts are, presently, high-tech products, their study and development depend on multidisciplinary expertise in the fields of physics, chemistry, physical chemistry, chemical engineering besides using sophisticated tools for their characterization. In this context, it is suitable to find out structure-activity relationships in the catalyst/support system, which may influence their activity, selectivity, stability. To characterize the structures and consequent behaviors of such complex configurations many techniques, with bulk as well as with more localized site approaches, are needed and used.

In the present work, nickel catalysts supported on α -Al₂O₃, CeO₂ and CeO₂.ZrO₂ were prepared and characterized, among other techniques, by X-Ray Diffraction (XRD). In particular, the state of CeO₂.ZrO₂ and its modification by the presence of Ni were characterized by Time Differential Perturbed Angular Correlation (TDPAC), allowing furthering investigating these systems in an atomic scale.

In this work we are going to point out characterization results of investigations on Ni/Ce-ZrO₂ catalysts supported on α -Al₂O₃, forming a solid solution which presents a better oxygen storage capacity per unit of mass of Ce as compared to CeO₂. These catalysts are potential candidates for methane conversion processes, and there is an interest in investigating them.

2) Hyperfine Interactions - When the electromagnetic fields present in the interior of a crystalline net interact with the nuclear electric and/or magnetic moments of a suitable isotope-probe when in its intermediate state of a (γ_1 - γ_2)-radiations nuclear cascade, then, before emitting γ_2 -radiation, a “precession” (from a phenomenological point of view) of the nuclear “spin” occurs. This leads to a new and different “spin” orientation forcing the γ_2 -ray to be emitted in a new direction, in such a way changing the pattern of the registered coincidences between (γ_1 - γ_2)-radiations in the various measured angles. These are the result of the so called Hyperfine Interactions (HI)⁽¹⁾ which appear like wiggles in the measured TDPAC spectra, and may be described by a perturbation factor $G_{22}(t)$. The electromagnetic fields that contribute to the HI originate from charges and “spins” of atoms of the close neighborhood to the isotope-probe, leading to their characterization. In the case of nuclear electric quadrupole static interactions, in polycrystalline samples without texture or some other internal orientation (most current cases), $G_{22}(t)$ can be expressed as an overlapping of oscillatory components:

$$G_{22}(t) = \sigma_{20}(\eta, \omega_Q) + \sum \sigma_{2n}(\eta, \omega_Q) \cdot e^{-F(\delta, \omega_n, t)} \cdot e^{-\frac{1}{2} \tau_R^2 \omega_n^2} \cdot \cos(\omega_n t) \quad (1)$$

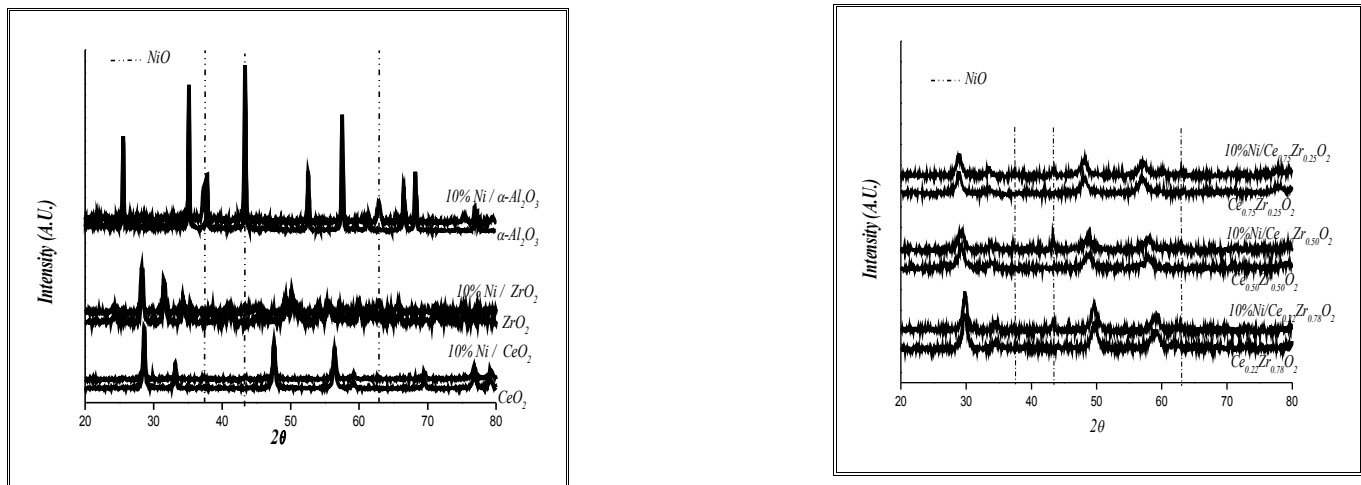
$\omega_n = f_n(\eta, \omega_Q)$: transition frequencies between the magnetic sub-levels related to the “spin” of the intermediate nuclear state of the probe-isotope; $F(\delta, \omega_n, t)$: lorentzian or gaussian distribution, which displays the fact that the “ensemble” of probe-isotope nucleae immersed in the sample is subject to a distribution rather than to a unique HI, and where δ represents the half width (generally normalized to 1.0) of it; τ_R : resolution time of the measuring setup (difference in the time registering of two events that would have to be, ideally, “simultaneous”); σ_{2n} : expansion coefficients;

Beside their static nature HI may also display a dynamical nature, mainly due to G_{22} fluctuations which occur in a time scale comparable to the life-time of the nuclear cascade intermediate level of the decaying isotope-probe. In such cases the spectra show a exponential characteristic.

3) Experimental Results-

a) X-ray Diffraction (XRD) Results - XRD experiments of calcined catalysts and supports were performed in a Miniflex model RIGAKU spectrometer using $\text{CuK}\alpha$ radiation. The diffractograms were obtained between $2\theta = 20^\circ$ and 80° using a 0.05° step (Figs. 1,2).

The diffractograms of the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ mixed oxides did not show the presence of separate phases of CeO_2 or ZrO_2 . Previous results concerning diffractograms of the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ mixed oxides always pointed out the formation of solid solutions as a result of reaction including CeO_2 and ZrO_2 ⁽⁴⁾. For the present studied Ni impregnated catalysts, beside the support diffraction lines mentioned above, also NiO diffraction lines were observed, as already reported for Ni/ α - Al_2O_3 catalysts⁽⁵⁾.



Figs. (1,2) – XRD Patterns of Ni catalysts and supports

b) TDPAC Results - TDPAC experiments included pure $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ (a-series) and Ni/ $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts (b-series) samples, in several experimental conditions: use of different gaseous atmospheres (H_2 or air) and sample temperature variations from room temperature (RT) until 800°C . Figures [3 ($x=0.75$), 4 ($x=0.50$), 5 ($x=0.22$)] and Table I present the TDPAC measured and adjusted spectra for the three concentrations, in both (a,b) series, where the b-series was prepared by Ni-impregnation of parts of the three irradiated supports not yet used; TDPAC measurements followed the same steps as in the non-impregnated samples. In general, in all cases, there are indications of slight neighborhood differences around isotope-probe's sites. The $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ measured TDPAC spectra, even for ratios $\text{Zr}/\text{Ce} > 3$, look different from those well-known measured TDPAC spectra for pure ZrO_2 ^(2,3), both prepared and thermal treated, in this way showing (and this also appears from the XRD's characterizations) the good integration of the probe-isotope in the final compounds. Starting with the a-series, as-irradiated samples, it's possible to advance that the decrease in Zr content favors the appearance of a low EFG value with unknown origin (Figure 3a/1). In between minimum and maximum Zr contents, there is an intermediate state where a $\eta = 1$ value predominates (Figure 4a/1), representative of local crystalline asymmetries. In order to better characterize these three supports let's to compare the (a,b) sets of Figs. (3,4,5),

where numbers-1 are related to the upper figures -starting measurements with as-irradiated samples, before any kind of treatment-, and where numbers-2 are related to the lower figures -last measurements, after treatment of the samples, here included the intermediate step measurements with under reductive atmosphere (H_2 flow at $800^\circ C$, experimental results displayed in Figs. (6)-: in the set-b (Ni-impregnated), mainly in both $x= 0.22$ and 0.75 rates, the spectra remain essentially the same when compared the final to initial conditions of treatment, even with changings at intermediate conditions (Figs. 6) with appearance of dynamical display in the measured spectra (Figs. 6), whereas in the set-a (absence of Ni) the spectra change remarkably after the same treatment. Finally, the reversibility shown by the b-series may be related to the increase in the redox properties of the support in the presence of the active metal.

The TDPAC experiments were carried out with the nuclear cascade of the probe-isotope $^{181}Hf/^{181}Ta$ (133 keV-482 keV), intermediate nuclear state level half life-time $\tau_{1/2}= 10.8ns$. Three samples -powder form- of $Ce_xZr_{(1-x)}O_2$ ($x= .22, .50, .75$), ≈ 100 mg weight each, were sealed in evacuated quartz ampoules and then irradiated for 25h at a flux of $\approx 2.0 \times 10^{13}$ n.cm $^{-2}$ s $^{-1}$ in the IPEN/CNEN Reactor, in order to activate the usually always present Hf impurity existent in Zr. In such way it guaranteed that the probe-isotopes are located in the Zr atoms sites in the catalyst. The 145 KeV γ -rays, contamination originated from the also activated ^{141}Ce (half-life isotope $\approx 33d$), was shown not “to blur” the measurements. TDPAC were carried out with a standard four-detector BaF_2 setup in the temperature range RT- $800^\circ C$.

4) Concluding Remarks - Taking into account the TDPAC patterns displayed in the spectra of the four sets concerning the different compositions (Figs. 3,4,5,6), it is possible to advance that a better defined lattice structure may be correlated to a higher Zr presence, in the sense that this atom may act like a counterbalance to the always present and intense vacancies dynamics in ceramics. Also the presence of Ni seems to improve the redox properties of the support, facilitating the oxygen storage capacity of the support. Finally, it would be interesting to perform modelling calculations to associate the suggested mechanisms to atomic/charge density dynamics.

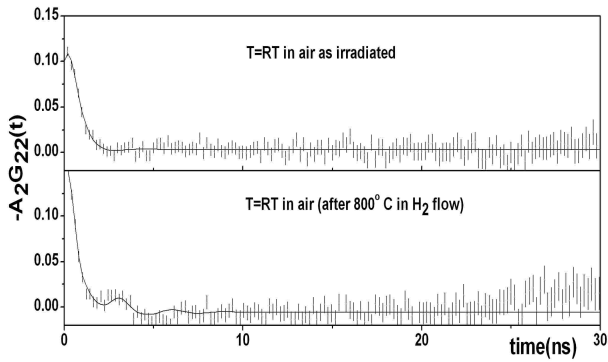
Table I: TDPAC Adjusted Parameters

$Ce_xZr_{(1-x)}O_2$ T = RT (in air)												
$X=0.75$	f_1	v_{Q1}	η_1	δ_1	f_2	v_{Q2}	η_2	Δ_2	f_3	v_{Q3}	η_3	δ_3
as irradiated	0.987	992(81)	0	1	0.013	80(42)	0	0				
after $800^\circ C/H_2$	0.647	549(28)	0	1	0.353	1470(67)	0.634	0.13				
$X=0.50$												
as irradiated	0.906	828(35)	1	0.5	0.094	100(17)	0	0.55				
after $800^\circ C/H_2$	0.842	911(66)	1	0.54	0.158	45(8)	0	1				
$X=0.22$												
as irradiated	0.589	1677(77)	0.52	0.26	0.315	1170(58)	0.46	0.14	0.096	60(6)	0	1
after $800^\circ C/H_2$	0.582	1549(65)	0.44	0.32	0.303	1171(46)	0.401	0.16	0.115	50(3)	0	1

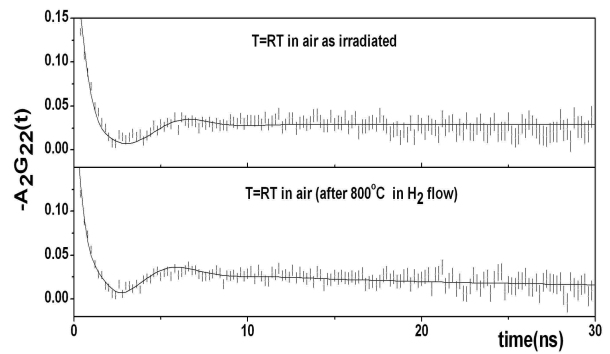
$Ni/Ce_xZr_{(1-x)}O_2$ T = RT (in air)												
$X=0.75$	f_1	v_{Q1}	η_1	δ_1	f_2	v_{Q2}	η_2	δ_2	f_3	v_{Q3}	η_3	δ_3
As irradiated	1	664(54)	0.386	0.58								
after $800^\circ C/H_2$	0.867	867	0.335	0.487	0.133	29	0	0				
$X=0.50$												
As irradiated	0.865	964(69)	0.48	0.31	0.135	47(8)	0	1				
after $800^\circ C/H_2$	0.874	990(73)	0.459	0.33	0.126	67(11)	0	1				
$X=0.22$												
As irradiated	0.77	1071(28)	0.474	0.18	0.115	939(39)	0	0.215	0.109	155(18)	0	1
after $800^\circ C/H_2$	0.935	1063(24)	0.454	0.71	0.065	64(6)	0	1				

f: site's proportion (generalized to 1); v_Q : nuclear electric quadrupole frequency (MHz); other parameters defined in Eq. 1.

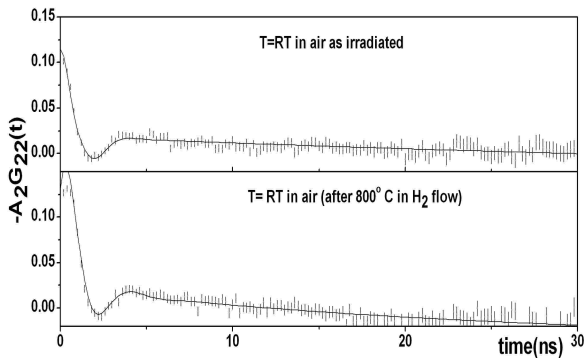
Figs. 3a(1,2) – TDPAC spectra of $Ce_{0.75}Zr_{0.25}O_2$



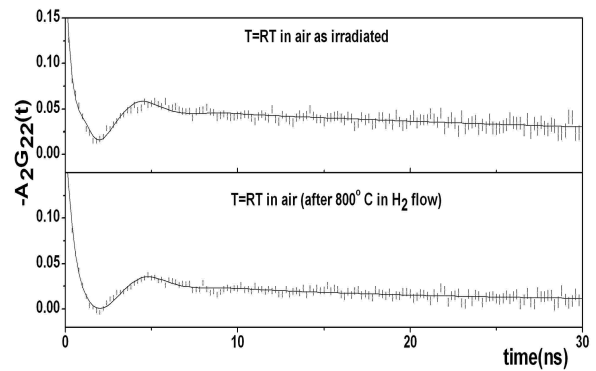
Figs. 3b(1,2) – TDPAC spectra of $Ni/Ce_{0.75}Zr_{0.25}O_2$



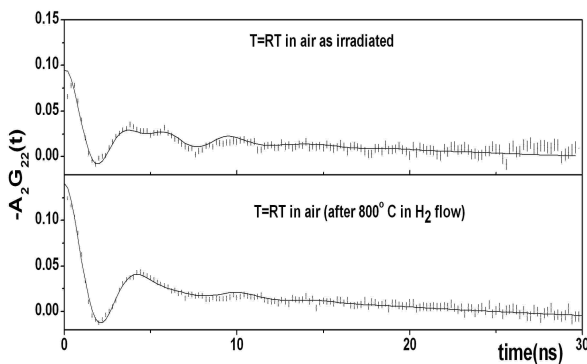
Figs. 4a(1,2) – TDPAC spectra of $Ce_{0.50}Zr_{0.50}O_2$



Figs. 4b(1,2) – TDPAC spectra of $Ni/Ce_{0.50}Zr_{0.50}O_2$



Figs. 5a(1,2) – TDPAC spectra of $Ce_{0.22}Zr_{0.78}O_2$



Figs. 5b(1,2) – TDPAC spectra of $Ni/Ce_{0.22}Zr_{0.78}O_2$

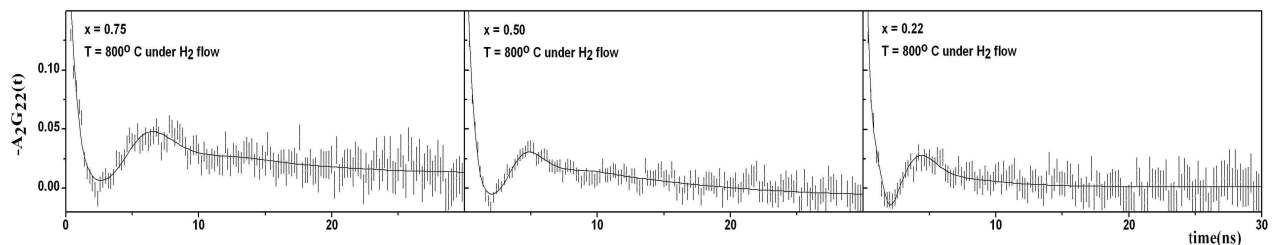
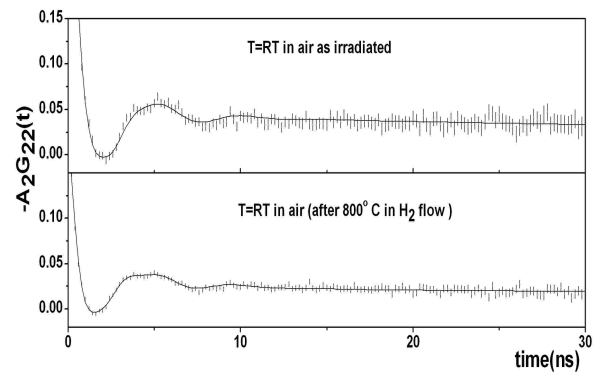


Fig 6 – TDPAC spectra of $Ni/CexZr(1-x)O_2$

References -

- 1) H. Saitovitch et al. - Química Nova 28/3(2005)529
- 2) M. Forker et al. - Phys. Rev. B 57/9(1998)5177
- 3) M.C. Caracoche et al. - Hyperfine Interactions 120/121(1999)469; J. American Ceramic Soc. 78/5(1995)1329; J. Sol-Gel Science&Technology 3(1994)241.
- 4) P. Fornasiero et al. - Appl. Cat. B:Env 22(1999)L11; S. Pengpanich et al. - Appl. Cat. A:Gen234(2002)221; H.S Roh et al. - J. Mol. Catal. A:Chem.181(2002)137; P. Pantu et al. - Appl. Cat. A:Gen193(2000)203; C.E. Hori et al. - Appl. Cat. B:Env.16(1998)205.
- 5) S. Wang, G.Q.M. Lu - Appl. Catal. B: Env 16(1998)269.

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