CO Oxidation Over Ceria-Based Catalysts: Comparison of Single and Binary Metal Oxides

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Abstract: A set of single metal oxides (CeO_2, ZrO_2, PrO_2, CuO and Fe_2O_3) and binary oxide catalysts (Ce80Zr20, Ce80Pr20, Ce80Cu20 and Ce80Fe20) prepared by the solution combustion synthesis was tested for the CO oxidation reaction. As a whole, the best catalytic activity was achieved for the Ce80Cu20 catalyst (binary oxide with Ce = 80 at.% and Cu = 20 at.%).This confirms that CeO_x and CuO_x phases may cooperate effectively for this oxidation process. The easier surface reducibility of this catalyst should promote the CO oxidation reaction. Likewise, it appears that the presence of metals, such as the Cu, Zr, Fe and Pr, into the ceria framework has a beneficial effect on the CO oxidation via cooperative phenomena among the redox active centres. All the prepared catalysts were characterized by the powder XRD, FE-SEM, N_2 physisorption at -196 °C and H_2-TPR analysis.

Keywords: CO oxidation, Ceria, Solution combustion synthesis, Cooperative phenomena, Oxidation catalysis.

1. INTRODUCTION

Every year, large amounts of CO are emitted in the world, mainly from transportation, power plants, industrial and domestic activities. Therefore, it is necessary to limit the CO emissions and develop new technologies to convert CO into valuable compounds. In this scenario, the growing petrochemical industry has resulted in the removal of CO from large gas streams and noble metals have been used to oxidize CO at low temperature. In fact, CO oxidation over noble metal based catalysts takes place in car exhaust after treatment systems, especially for gasoline engines since oxygen-deficient regions occur [1-3]. CO oxidation over solids represents the simplest heterogeneously catalyzed reaction and it can thus be considered as a prototypical reaction for heterogeneous processes. In other words, CO oxidation can be used as a suitable model reaction for more complex catalytic oxidation processes and for studying the nature of active sites [4, 5]. According to the literature, effective solid catalysts for the CO oxidation are found in the Group VIII metals. As a whole, noble metals are more active, but more expensive than base metals. Thus, several metal oxides (especially ceria-based materials) have been investigated and it has been observed that may exhibit interesting activity for the CO oxidation [4-7]. Moreover , it has been verified that the incorporation of metals (*e.g*. Fe, Cu, Zr, Pr) into the CeO_2 lattice may have a beneficial effect on the structural and electronic properties of the catalyst, thus improving their oxidation activity and thermal stability [7-9]. In heterogeneous catalysis, in fact, there are several characteristic examples in which the presence of multi-component catalysts influences the solid-state chemistry, since active phases (and promoters) may interact with each other [10-12]. In the present work, a set of single metal oxides (namely, CeO_2, ZrO_2, PrO_2, CuO and Fe_2O_3) and binary oxide catalysts (Ce80Zr20, Ce80Pr20, Ce80Cu20 and Ce80Fe20) was synthesized by the solution combustion synthesis (SCS) and their catalytic activity was tested for the CO oxidation. Then, the catalysts were characterized by complementary techniques, such as the powder XRD, FESEM, N_2 physisorption at -196 °C and H_2-TPR.

2. MATERIALS AND METHODS

2.1. Catalysts Preparation

A set of single metal oxides (CeO_2, ZrO_2, PrO_2, CuO and Fe_2O_3) and binary oxide catalysts (Ce80Zr20, Ce80Pr20, Ce80Cu20 and Ce80Fe20, where the numbers indicate the atomic %) was synthesized by means of solution combustion synthesis (SCS) [13, 14]. In short, for the preparation of binary oxide catalysts, 0.8 g of urea and 1.9 g of a stoichiometric mixture (80:20) of $Ce(NO_3)_3{\cdot}6H_2O$ and one of these following metal salt precursors: $ZrO(NO_3)_2$, $Pr(NO_3)_3$, $Cu(NO_3)_2$ and $Fe(NO_3)_3$, were dissolved in 50 m of deionized

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water and stirred at room temperature (r.t.) for 30 min. The homogeneous solution was then placed in oven at 600 °C for 20 min. Single metal oxide catalysts were prepared with the same procedure with the corresponding precursor (metal nitrate).

2.2. Catalyst Characterization

The X-ray diffraction patterns were collected on an X' Pert Philips PW3040 diffractometer using Cu K_α radiation (2θ range = 15°- 70°; step = 0.05° 2θ; time per step = 0.2 s). The XRD patterns were indexed according to the Powder Data File database (PDF 2000, International Centre of Diffraction Data, Pennsylvania). Sample morphology was observed through a field emission scanning electron microscope (FESEM Zeiss MERLIN, Gemini-II column). The specific surface area (SSA) and total pore volume (V_p) were measured by N_2 physisorption at -196 °C (Micrometrics ASAP 2020) on powders previously out gassed at 200 °C for 4 h to remove water and other atmospheric contaminants; SSA was determined according to the Brunauer-Emmett-Teller (BET) method. H_2-TPR analysis was performed to study the catalyst reducibility. Sample pretreatment was conducted prior to analysis by treating 50 mg of catalyst under air (40 ml min^{-1}) at 150 °C for 1 h, followed by cooling with Ar to r.t. H_2-TPR analysis was executed by increasing gradually sample temperature to 750 °C with the rate of 5°C min^{-1} under Ar (4.95 %-mol H_2 in Ar). The instrument was equipped with thermal conductivity detector (TCD) to recognize the H_2 signal.

2.3. Catalytic Activity Tests

Catalytic activity tests were performed in a quartz U-tube reactor with inner diameter = 4 mm, heated by an electric furnace; the temperature was measured by means of a thermocouple placed in the middle of the catalytic bed. In a typical run, 0.1 g of powdered catalyst was inserted in the reactor. Then, the catalytic bed was pre-treated in He (flow rate = 50 ml min^{-1}) for 1 h at 150 °C. The test started by flowing 50 ml min^{-1} gas containing 1000 ppm of CO and 10% O_2 in N_2 into the reactor (GHSV of 19100 h^{-1}). The temperature was then raised by 5 °C min^{-1} in the 50-450 °C temperature range. The CO and CO_2 concentrations at the outlet of the reactor were measured by NDIR analyzers (ABB Uras 14). Temperatures at which 10, 50, and 90 % of CO was converted were taken as indices of the catalytic activity ($T_{10\%}$, $T_{50\%}$ and $T_{90\%}$, respectively). The tests were conducted for 2 cycles to evaluate the stability of the catalysts.

3. RESULTS AND DISCUSSION

Figure **1** shows the X-ray diffractograms of the pure ceria and ceria-based materials. The binary oxide catalysts (Ce80Zr20, Ce80Pr20, Ce80Cu20 and Ce80Fe20) refer to a cubic fluorite structure of ceria, indicated by (111), (200), (220), (311), and (222) peaks [15, 16]. No additional peaks due to ZrO_2, PrO_2, CuO or Fe_2O_3 phases, respectively, were found in the diffractograms, thus confirming the presence of a single phase for these materials.

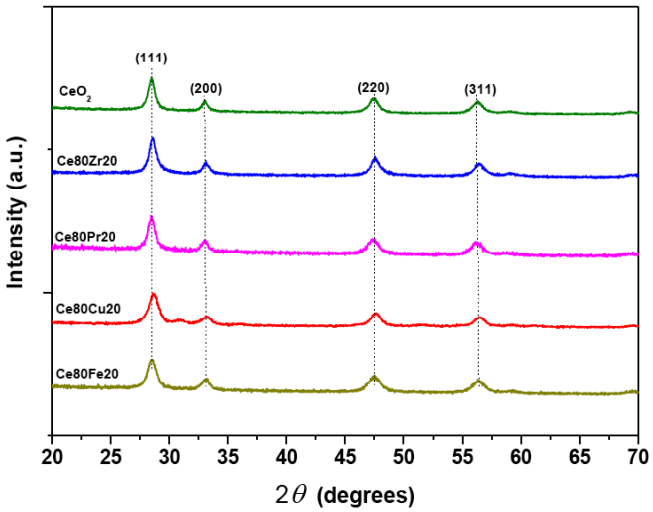

Figure 1: X-ray diffractograms of the ceria-based catalysts.

The BET specific surface area and total pore volume of the samples, derived from N_2 physisorption, are resumed in Table **1**. As a whole, the addition of foreign metals generally improves the textural

Table 1: Textural Properties of the Prepared Catalysts

Sample	SSA $m^2 g^{-1}$	V_p $cm^3 g^{-1}$
CeO_2	15	0.02
ZrO_2	1	0.01
PrO_2	9	0.03
CuO	1	0.01
Fe_2O_3	17	0.03
Ce80Zr20	23	0.04
Ce80Pr20	16	0.03
Ce80Cu20	18	0.03
Ce80Fe20	19	0.03

properties by increasing surface areas, as compared to pure ceria; however, the increment depends much on the nature of metals. Specifically, Zr, Fe and Cu species into the ceria enlarges the surface area in the 16-23 m^2g^{-1} range, as follows:

Ce100 ≈ Ce80Pr20 < Ce80Cu20 ≈ Ce80Fe20 < Ce80Zr20

On the other hand, embedding the Pr species into ceria does not significantly modify the textural features. This finding might be because both cerium and praseodymium ions are nearly identical in size.

Figure **2** shows the morphology for all the catalysts observed through the FESEM. As expected, different shapes can be observed for the CeO_2, ZrO_2, PrO_2, CuO and Fe_2O_3 samples. Briefly, spongy frameworks (agglomerated) occur for both the CeO_2 and Fe_2O_3, at variance of the PrO_2 and CuO samples, in which relatively large lamellar systems occur. On the other hand, small spherical particles (in the 10-20 nm range) can be observed for the ZrO_2 sample. All the binary oxides prepared by the solution combustion technique exhibit a spongy ceria-like framework (three-dimensional shapes) comprising of small nanoscale agglomerates. The presence of various foreign metals into the ceria lattice, indeed, does not significantly affect the ceria morphology.

Figure **3** shows the H_2-TPR curves for the prepared catalysts. Pure CeO_2 exhibits a wide peak centred at 475 °C due to the surface reduction of ceria [17, 18], while the reduction of bulk CeO_2 occurs above 900 °C. Indeed, the low-temperature reduction peak infers the role of surface oxygens, which are weakly attached to the solid surface; the final reduction is eventually triggered by the release of lattice oxygens at high temperature. A similar trend appears for the ZrO_2 sample. The PrO_2 sample has two reduction peaks centred at 407 and 495 °C, whereas the CuO and Fe_2O_3 samples exhibit the main reduction in the 380-420 °C temperature range. Among the binary oxide catalysts, the following increasing reducibility scale can be drawn:

Ce80Zr20 <Ce80Pr20< Ce80Fe20 < Ce80Cu20

The Ce80Cu20 sample appears the most reducible catalyst, having two peaks centred at 185 and 250 °C, corresponding to CuO_x clusters strongly interacting with CeO_2. In other words, the co-presence of CeO_x and CuO_x species may promote the surface reducibility and then the redox activity [18-21]. A similar trend, although with less extent, can be observed for theCe80Fe20 and Ce80Pr20 samples, showing reduction peaks centred at 375 °C and in the 405-490 °C range, respectively. Although the temperature for the main reduction peak of ceria-praseodymia sample is higher than that of pure ceria, the reduction of Ce80Pr20 commences at lower temperature. This finding suggests that praseodymium favors the weakening of Ce-O bonds, as observed in our previous work [22]. On the other hand, higher reduction temperatures appear for the Ce80Zr20 sample, thus confirming the role of Zr^{4+}cations on the reduction resistance of ceria [23].

Figure **4** shows the CO conversion to CO_2 (%) as a function of the temperature for the single metal oxides (dotted curves) and binary oxide catalysts (bold curves), along with the uncatalized reaction (black curve). As a whole, all the oxide catalysts improve

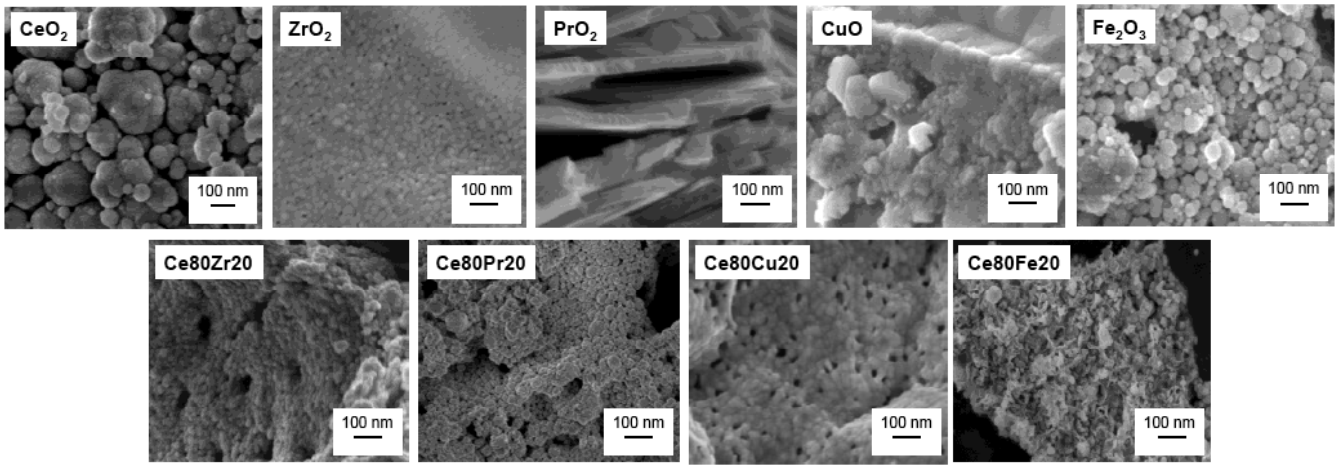

Figure 2: FESEM images of the prepared catalysts.

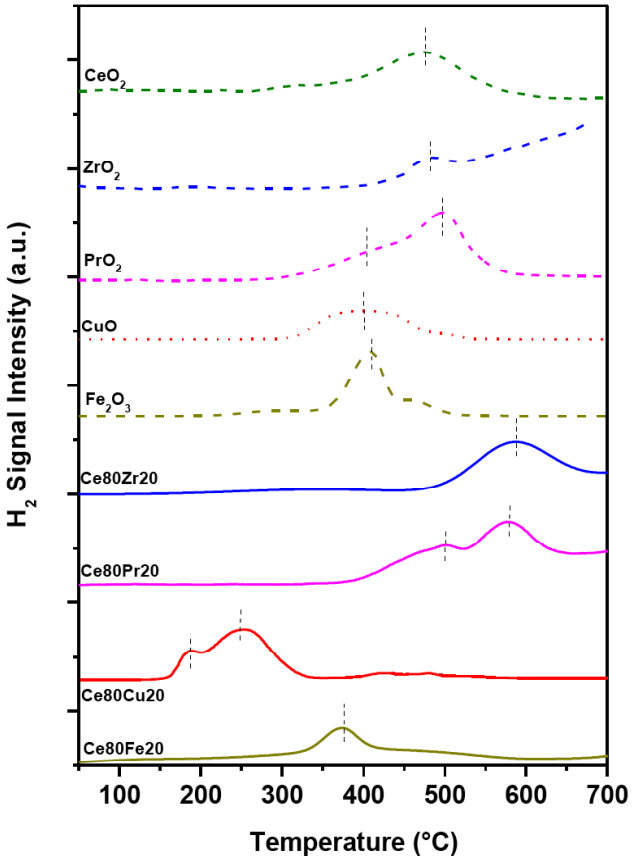

Figure 3: H_2-TPR profiles of the prepared samples.

greatly the CO conversion, where as ≈ 30% of CO converts thermally to CO_2 at 450 °C. For the single metal oxides, the following increasing oxidation activity order (measured in terms of $T_{10\%}$ and $T_{50\%}$) can be designed:

ZrO_2<PrO_2<CeO_2< Fe_2O_3< CuO

and for the binary oxide catalysts, the increasing order is:

Ce80Pr20 <Ce80Zr20< Ce80Fe20 <<Ce80Cu20

For both sets of catalysts, the activity trends are in fair agreement with the H_2-TPR data (*vide supra*), thus confirming that the catalyst reducibility has a beneficial effect on the CO oxidation. In fact, the more reducible the catalyst surface, the easier the release of surface oxygen accessible to CO molecules. On the other hand, high electronic conductivity and oxygen anion mobility are beneficial factors for the oxidation process [10, 24]. Figure **5** shows the catalyst activities (measured in terms of $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$) by means of the Venn diagrams. As a whole, it appears that the presence of metals such as the Cu, Zr, Fe and Pr in the ceria framework has a beneficial effect on the CO oxidation, as compared to pure ceria. However, the cooperation among the ceria and foreign metal oxides seems effective with transition metals rather than with praseodymium, since PrO_2 appears more active than CeO_2 and Ce80Pr20. The cooperation between ceria and foreign metal oxides is particularly marked for the Ce80Cu20 sample, thus rendering the latter material particularly interesting for oxidation applications.

CONCLUSIONS

In the present paper, we studied single metal oxides (CeO_2, ZrO_2, PrO_2, CuO and Fe_2O_3) and binary oxide catalysts (Ce80Zr20, Ce80Pr20, Ce80Cu20 and

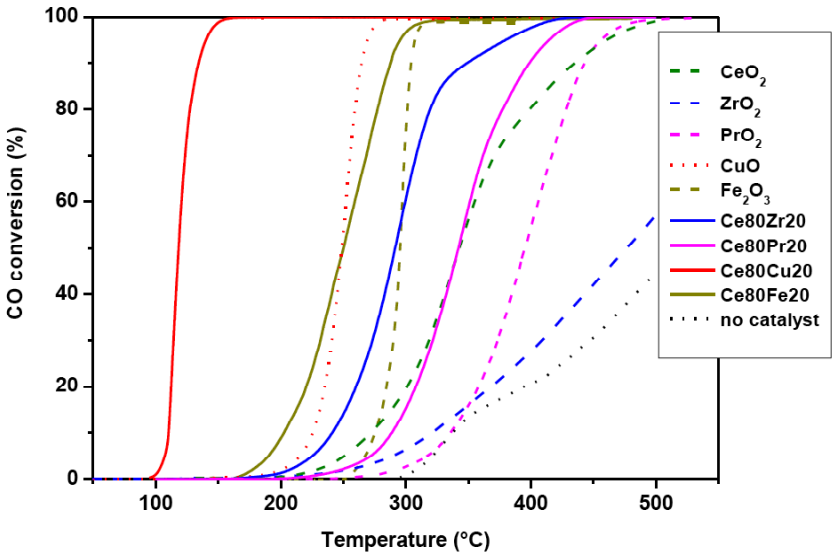

Figure 4: CO oxidation profiles as a function of temperature for the prepared catalysts (GHSV = 19100 h^{-1})

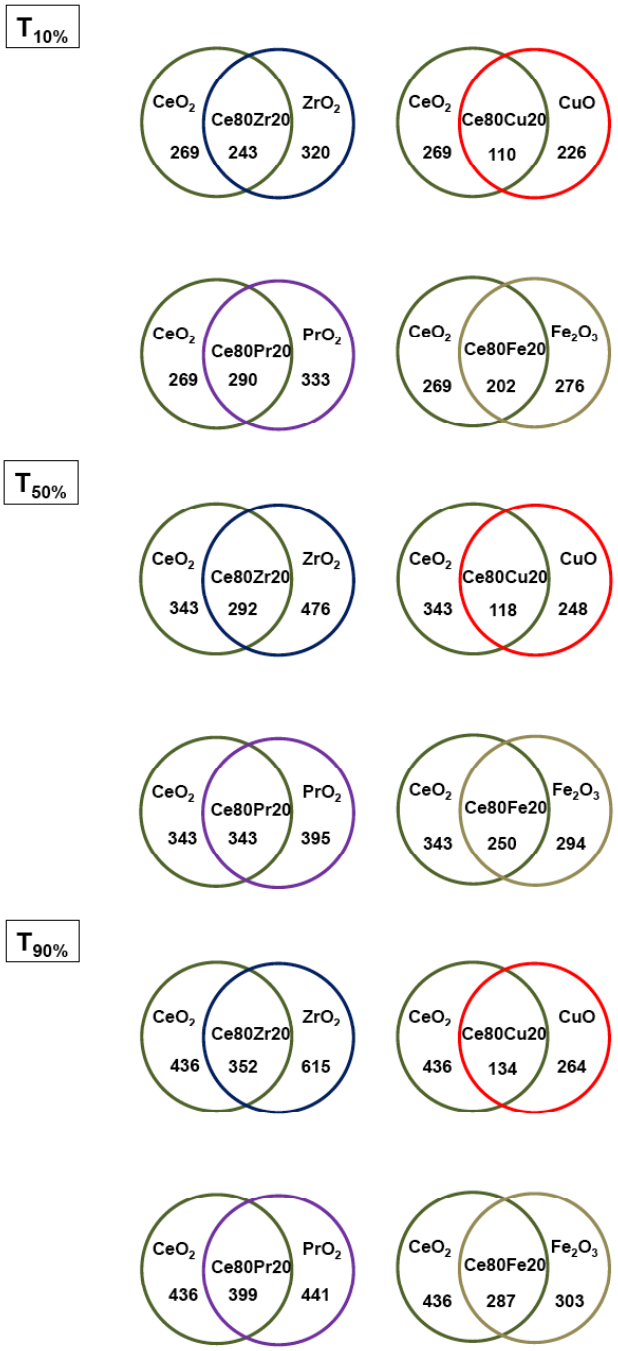

Figure 5: Venn diagrams of the catalytic performances (in terms of $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$) achieved for the prepared catalysts.

Ce80Fe20) prepared by the solution combustion synthesis, effective for the CO oxidation. For the single metal oxides, the increasing catalyst activity order (measured in terms of $T_{10\%}$and $T_{50\%}$) was:

$ZrO_2<PrO_2<CeO_2< Fe_2O_3< CuO$

where as for the binary oxide catalysts, the increasing activity order was:

Ce80Pr20 <Ce80Zr20 < Ce80Fe20 <<Ce80Cu20

For both sets of catalysts, the activity trends are in fair agreement with the H_2-TPR data, thus confirming that the catalyst reducibility has a beneficial effect towards the CO oxidation reaction. These results confirm that the presence of metals such as the Cu, Zr, Fe or Pr in the ceria framework may promotes the CO oxidation reaction via cooperative phenomena among the redox active centres. The cooperation between ceria and foreign metal oxides is particularly marked for the Ce80Cu20, thus rendering the latter catalytic material particularly interesting for future investigations in the field of oxidation catalysis.

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REFERENCES

[1] Ertl G, Knözinger H, Schüth F, Weitkamp J."Handbook of Heterogeneous Catalysis" (2nd ed.), Wiley-VCH, Weinheim, 2008. http://dx.doi.org/10.1002/9783527610044

[2] Hodnett BK."Heterogeneous Catalytic Oxidation", Wiley-VCH, New York, 2000.

[3] Freund HJ, Meijer G, Scheffler M, Schögl R, Wolf M. "CO Oxidation as a Prototypical Reaction for Heterogeneous Processes", Angew Chem Int Ed 2011; 50: 10064-10094. http://dx.doi.org/10.1002/anie.201101378

[4] Royer S, Duprez D. "Catalytic Oxidation of Carbon Monoxide over Transition Metal Oxides", Chem Cat Chem 2011; 3: 24-65. http://dx.doi.org/10.1002/cctc.201000378

[5] Wu ZL, Li MJ, Overbury SH."On the structure dependence of CO oxidation over CeO2 nanocrystals with well-defined surface planes", J Catal 2012; 285: 61-73. http://dx.doi.org/10.1016/j.jcat.2011.09.011

[6] Russo N, Fino D, Saracco G, Specchia V. "Supported gold catalysts for the CO oxidation", Catal Today 2006; 117; 214-219. http://dx.doi.org/10.1016/j.cattod.2006.05.027

[7] Piumetti M, Bensaid S, Fino D, Russo N. "Nanostructured ceria-zirconia catalysts for the CO oxidation: Study onsurface properties and reactivity", Appl Catal B 2016; 197: 35-46. http://dx.doi.org/10.1016/j.apcatb.2016.02.023

[8] Trovarelli A, Fornasiero P."Catalysis by Ceria and Related Materials" 2nd ed., Imperial College Press, London, 2013. http://dx.doi.org/10.1142/p870

[9] Bueno-López A."Diesel soot combustion ceria catalysts", Appl Catal B 2014; 146: 1-11. http://dx.doi.org/10.1016/j.apcatb.2013.02.033

[10] Vedrine JC, Appl. Catal. "A Revisiting active sites in heterogeneous catalysis: Their structure and their dynamic behaviour" 2014; 274, 40-50.

[11] Van Santen RA, Neurock M."Molecular Heterogeneous Catalysis", Wiley-VCH, Verlag 2006; 61-62

[12] Carson G, Coudurier JC, Védrine A, Laarif F, Theobald J. "Synergy effects in the catalytic properties of bismuth molybdates", J Chem Soc Faraday Trans I 1983; 79: 1921-1929. http://dx.doi.org/10.1039/f19837901921

[13] González-Cortés SL, Imbert FE."Fundamentals, properties and applications of solid catalysts prepared by solution combustion synthesis (SCS)", Appl Catal A 2013; 452: 117-131. http://dx.doi.org/10.1016/j.apcata.2012.11.024

[14] Civera A, Pavese M, Saracco G, Specchia V. "Combustion synthesis of perovskite-type catalysts for natural gas combustion", Catal Today 2003; 83: 199-211. http://dx.doi.org/10.1016/S0920-5861(03)00220-7

[15] Thrimurthulu G, Rao KN, Devaiah D, Reddy BM "Nanocrystalline ceriapraseodymia and ceria-zirconia solid solutions for soot oxidation" Res Chem Intermed 2012; 38:1847-1855 http://dx.doi.org/10.1007/s11164-012-0508-y

[16] Reddy BM, Thrimurthulu G, Katta L, Yamada Y, Park SE. "Structural characteristics and catalytic activity of nanocrystalline ceria-praseodymia solid solutions", J Phys Chem C 2009; 113: 15882-15890. http://dx.doi.org/10.1021/jp903644y

[17] Piumetti M, Bensaid S, Russo R, Fino D. "Nanostructured ceria-based catalysts for soot combustion:Investigations on the surface sensitivity", Appl Catal B 2015; 165: 742-751 http://dx.doi.org/10.1016/j.apcatb.2014.10.062

[18] Caputo T, Lisi L, Pirone R, Russo N. "On the role of redox properties of CuO/CeO_2 catalysts in the preferential oxidation of CO in H_2-rich gases", Appl Catal A 2008; 348: 42-53. http://dx.doi.org/10.1016/j.apcata.2008.06.025

[19] Avgouropoulos G, Ioannides T."Selective CO oxidation over $CuO\text{-}CeO_2$ catalysts prepared via the urea-nitrate combustion method", Appl Catal A 2003; 244: 155-167. http://dx.doi.org/10.1016/S0926-860X(02)00558-6

[20] Delimaris D, Ioannides T."VOC oxidation over $CuO–CeO_2$ catalysts prepared by a combustion method" Appl Catal B 2009; 89: 295-302. http://dx.doi.org/10.1016/j.apcatb.2009.02.003

[21] Heynderickx PM, Thybaut JW, Poelman H, Poelman D, Marin GB."The total oxidation of propane over supported Cu and Ce oxides: A comparison of single and binary metal oxides", J Catal 2010;272: 109-120. http://dx.doi.org/10.1016/j.jcat.2010.03.006

[22] Andana T, Piumetti M, Bensaid S, Russo N, Fino D, Pirone R. "Nanostructured ceria-praseodymia catalysts for diesel soot combustion", Appl Catal B2016; 197: 125-137. http://dx.doi.org/10.1016/j.apcatb.2015.12.030

[23] Piumetti M, Bensaid S, Russo N, Fino D. "Investigations into nanostructured ceria-zirconia catalysts for soot combustion", Appl Catal B 2016; 180: 271-282. http://dx.doi.org/10.1016/j.apcatb.2015.06.018

[24] Grasselli RK. "Genesis of site isolation and phase cooperation in selective oxidation catalysis" Top Catal 2001; 15: 93-101. http://dx.doi.org/10.1023/A:1016683117255

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