CERIUM-ZIRCONIUM-PRASEODYMIUM OXIDE CATALYSTS FOR CO OXIDATION

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Abstract

Sets of Ceria, Ce-Zr (Ce 80 at.%, Zr 20 at.%), Ce-Pr (Ce 80 at.%, Pr 20 at.%) and Ce-Zr-Pr mixed oxide catalysts (Ce 80 at.%, Zr 10 at.% and Pr 10 at.%) have been synthesized by i) the solution combustion synthesis (SCS) ii) the multi-inlet vortex reactor (MIVR) and iii) the hydrothermal synthesis. The oxidation activity of the prepared catalysts has been tested towards CO oxidation. The prepared catalysts have been characterized by complementary techniques, including powder XRD, FE-SEM, N_2 physisorption at -196 °C, H2-TPR, O2-TPD and XPS to study the relationships between the structure and composition of materials and their performance. As a whole, the best catalytic results, in terms of CO oxidation, have been achieved for Ce-Zr-Pr mixed oxides, thus confirming the beneficial role of multicomponent catalysts (acting via collective redox properties) for this prototypical reaction.

Keywords

Oxidation catalysis; CO oxidation; soot oxidation; Ce-Cu-O catalysts

Introduction

During the last few decades, Ceria-based materials have received much attention in applied catalysis, thanks to their notable redox properties and OSC that allow quick intake and release of oxygen. Moreover, it has been observed that inserting aliovalent cations, like Zr^{4+} and Pr^{3+}/Pr^{4+} into Ceria framework gives more surface oxygen vacancies (structural defects) as well as redox active sites (Piumetti, 2015, 2016). As is known, nanostructured Ceria-based catalysts are of particular interest for catalysis and then several approaches have been exploited to synthesize small Ceria nanoparticles, including hydrothermal/solvothermal, sol-gel, microemulsion and precipitation.

In the present work, sets of Ceria, Ce-Zr (Ce 80 at.%, Zr 20 at.%), Ce-Pr (Ce 80 at.%, Pr 20 at.%) and Ce-Zr-Pr mixed oxide catalysts (Ce 80 at.%, Zr 10 at.% and Pr 10 at.%) have been prepared by the solution combustion synthesis (SCS), the multi-inlet vortex reactor (MIVR) and the hydrothermal synthesis. Their catalytic activity has been tested for CO oxidation, a prototypical reaction for probing the oxidation activity of Ceria-based materials. The catalysts have been characterized by complementary techniques, including powder XRD, FE-SEM, N_2 physisorption at -196 °C, H_2-TPR, O_2-TPD and XPS to investigate the relationships between the structure and composition of materials and their performance.

Experimental results

As shown in Figure 1, better results for CO oxidation have been obtained with mixed oxides prepared by SCS method (performance scale: Ce-Zr-Pr > Ce-Zr > Ce-Pr) rather than pure Ceria, thus confirming the beneficial role of multicomponent catalysts for this prototypical reaction. Since CO oxidation occurs via a Mars-van Krevelen (MvK) type mechanism over Ceria-based catalysts, it appears that the presence of both Zr and Pr species into the Ceria framework improves the oxidation activity, via collective properties, such as electrical conductivity, surface or bulk oxygen anion mobility (Vedrine, 2014).

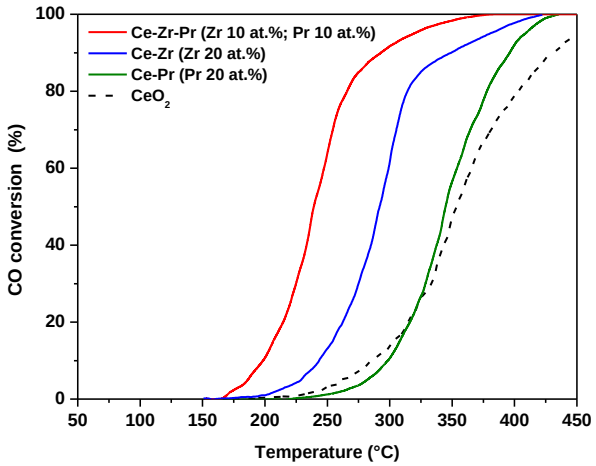

Figure 1. Conversion of CO to CO_2 as a function of temperature.

The Ce-Zr-Pr catalyst, indeed, exhibited easier reducibility and better redox properties, as revealed by H_2-TPR, O_2-TPD and XPS analysis.

In order to evaluate the possible role of the particle sizes on the catalytic activity, the multi-inlet vortex reactor (MIVR) has been used for application in flash nanoprecipitation (Bensaid, 2014). The latter technique allows to produce "spherical" nanoparticles of controlled size and unique physico-chemical properties (Figure 2).

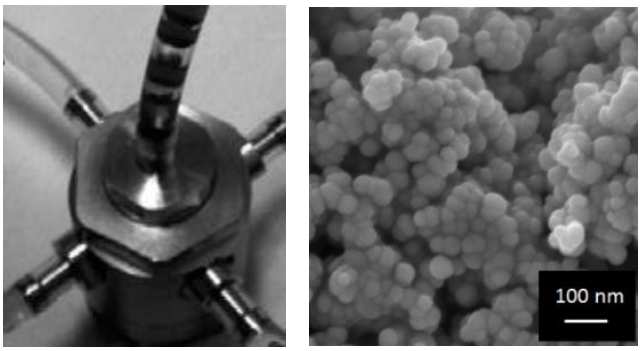

Figure 2. MIVR used for the synthesis of nanocatalysts (left) and FESEM image of the Ce-Pr-Zr sample (right).

Since the nanoprecipitation is highly dependent on the fluid dynamics within the reactor, feed volumetric flow rates were varied from 2 to 50 ml min^{-1} to observe changes in the particle size (in the range 5-50 nm). As expected, better results for CO oxidation have been obtained with mixed oxides than pure Ceria, thus confirming the role of collective properties for this oxidation reaction.

In particular, the oxidation of CO with Ce-Zr-Pr catalyst synthesized at 20 ml/min had a half-conversion at 167°C and total conversion one at 189°C (data not reported for brevity). However, the activity was not directly linked to the primary particle size. In order to better evaluate the structural properties of the nanoparticles for this reaction, a set of nanostructured Ceria-based catalysts, with well-defined crystalline planes, obtained via hydrothermal procedure (namely Ceria, Ce-Zr, Ce-Pr, Ce-Zr-Pr, Figure 3) has been tested. Surprisingly, the activity for CO oxidation followed the order of reactivity: Ceria > Ce-Zr > Ce-Pr > Ce-Zr-Pr. This trend is opposite with respect to that obtained for catalysts synthesized by either SCS or MIVR. This finding further confirms that collective properties of metal oxide catalysts (namely surface reducibility and redox properties) depend on both electronic and geometric factors.

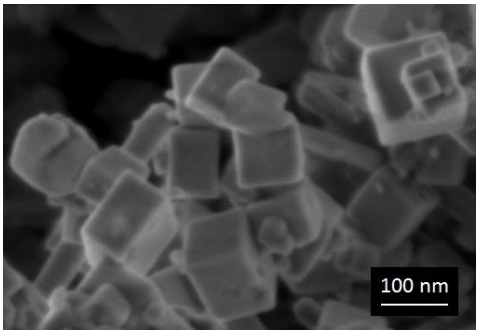

Figure 3. FESEM image of the Ce-Zr-Pr catalyst obtained by hydrothermal synthesis.

Conclusions

- Better performances for CO oxidation have been obtained with mixed oxides prepared by SCS method (performance scale: Ce-Zr-Pr > Ce-Zr > Ce-Pr) rather than pure Ceria. This finding confirms the beneficial role of multicomponent catalysts (acting via collective redox properties) for this reaction.
- The oxidation activity was not directly linked to the primary particle size (catalysts prepared by MIVR technique).
- A different catalytic trend has been observed for nanostructured materials. Indeed, the worst performance has been achieved for the Ce-Zr-Pr nanostructured catalyst.
- Collective properties of metal oxide catalysts (namely surface reducibility and redox properties) depend on both electronic and geometric factors.

References

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