

Editorial

Catalytic Applications of CeO₂-Based Materials

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Among the metal-oxides, ceria represents one of the most promising materials for chemical transformations mainly for environmental applications and energy conversion systems. The fundamental interest in, and commercial applications of, cerium oxide as a catalytic material is due to its high abundance in the Earth's crust; Cerium is the most abundant of the so-called rare-earth elements, and is more abundant than copper or nickel [1]. Relatively low cost and unique properties, such as high oxygen storage capacity and mobility, acid–base properties and the ability to form solid solutions with a large variety of metals, are other key features in its successful application [2]. The great scientific interest is also due to the possibility to control the final morphology and size of the ceria materials through improved synthetic methods. As an example, reducing the ceria particles to the nanoscale has a profound impact on the catalytic behavior [3], opening new possibilities in terms of catalytic potential for different applications. Since the 1980s, the unique and irreplaceable role of ceria materials have been confirmed in advanced car converters removing hydrocarbons/CO/NO_x for exhaust gas pollution control [4]. Parallel to this well-established use in three-way catalysts (TWCs), ceria is emerging as a catalyst component in many new sectors, for a wide range of catalytic applications, including hydrogen production and fuel cell [5,6]; CO₂ conversion to fuels and chemicals [7], soot oxidation [8] CO oxidation to CO₂ [9], oxygen sensors [10] and complex organic reactions [11]. This Special Issue reports some examples on the potential role of ceria based catalysts as a critical material for the development of alternative and sustainable technologies in an era in which the environmental issues and the depletion of conventional sources of energy strongly demand on this. Thus, in the following, a brief description of the papers included in this issue is provided to serve as an outline to encourage further reading.

Air pollution has received much attention because of the adverse effects on health and the environment. To better understand the contribution of ceria to develop advanced materials for environmental applications, Su et al. prepared three kinds of CeO₂ catalysts from different Ce-Metal Organic Frameworks (Ce-MOFs) with specific topological structures and coordinate environments [12]. The CeO₂ samples, derived from Ce-MOF-808, Ce-BTC, and Ce-UiO-66, have been synthesized by Pyrolysis Processes and successfully applied in the catalytic combustion of toluene as a representative model compound of VOC (Volatile Organic Compounds). The results evidenced how the preparation method, mainly the calcination process, affected the structures and surface morphologies of the catalysts. Small particle size, stacking mode, and structural defects play a crucial role in the catalytic combustion of toluene. Coordinate environments of MOFs are critical for the particle formation process, and ceria catalysts with more defective sites can be formed by the protection of the carbon skeleton in Ce-MOF-808 and Ce-BTC. Among the catalysts prepared, CeO₂-MOF-808 showed the best catalytic performance due to it having the smallest particle size, largest specific surface area, abundant active surface oxygen species, and the greatest reductive properties.

Inside the same application field, Ai et al. explored the possibility to use a series of Ce/Zr catalysts (K/Zr_{0.84}Ce_{0.16}O₂, Zr/Zr_{0.84}Ce_{0.16}O₂, Co/Zr_{0.84}Ce_{0.16}O₂, Zr_{0.84}Ce_{0.16}O₂, Co/Ce_{0.75}Zr_{0.25}O₂ and Ce_{0.75}Zr_{0.25}O₂), prepared by sol-gel method, in diesel emission control [13]. This investigation reveals the ability of ceria to form solid solution with other metals, resulting in a material characterized by

unique properties that are fundamental to obtain remarkable catalytic performance for soot oxidation. In the Ce-Zr solid solution system, Zr increases the oxygen storage capacity of Ce and prevents cerium oxide from sintering at high temperatures. The incorporation of isovalent non-reducible elements, Zr⁴⁺ ions, into a ceria lattice has a beneficial influence on the physicochemical and catalytic properties of Ce, improving its reducibility, thermal stability, oxygen vacancies, and thus can significantly improve the catalytic activity. The catalytic results revealed that some soot particles could react with adsorbed oxygen, and other parts of diesel soot reacted with lattice oxygen. The activity of these catalysts was attributed to the synergistic effect arising from the combination of K/Co/Zr and Ce-Zr solid solution, which led to the decrease in the soot ignition temperature from 497 °C to 294 °C. The authors proposed a reaction pathway to explain the catalytic combustion process of soot, i.e., the combination of K/Co/Zr with Ce-Zr solid solution reduced the binding energy of Ce-Zr solid solution, which was conducive to provide more active sites to release the active oxygen (O²⁻) or lattice oxygen (O²⁻).

The excellent redox properties of the Ce³⁺/Ce⁴⁺ couple make possible the utilization of CeO₂ as catalysts, especially in the field of pollutant removal applications. In this regard, Feng et al. evaluated ceria with different morphologies as catalysts for CO oxidation [14]. The results confirmed that the Ce⁴⁺/Ce³⁺ redox cycle confers the ability to absorb gaseous O₂, thus forming active oxygen at the catalyst surface, which can be transferred to the catalyst interface by superficial diffusion promoting the oxidation reaction. In other words, CeO₂ acts as an oxygen buffer through the fast Ce³⁺/Ce⁴⁺ cycle involving the participation of lattice oxygen. This work also evidenced the important role of the preparation method to determine the morphology of the catalyst and in turn, its catalytic activity. CeO₂ in nanoscale with different morphologies of rod, tube and cube were prepared through a hydrothermal process. The results exhibited that the rod-like CeO₂ showed a far superior activity to the other two catalysts for CO oxidation (T₉₀ = 228 °C at space velocity of 12,000 mL·gcat⁻¹·h⁻¹). The highly reducible oxygen species on the surface of CeO₂ nanorods is considered to be the main reason. In addition, the rod-like CeO₂ sample possessed a large specific surface area (51.4 m²/g), that could be another reason for its superior activity.

Zhao et al. synthesized a series of Ce and/or Zr modified WO₃-TiO₂ catalysts by the impregnation method, that were employed for selective catalytic reduction of NO_x by NH₃ [15]. The performance of the prepared catalysts was evaluated in a simulated real engine exhaust (Composed of NH₃, NO_x, CO, CO₂, C₃H₆, H₂O, O₂ and N₂). The Ce₂₀Zr_{12.5}WTi catalyst exhibited high catalytic activity and thermal stability due to the formation of Ce-Zr solid solution. The introduction of Zr to CeWTi catalyst facilitated the redox of Ce⁴⁺/Ce³⁺ and the formation of more acid sites, more Ce³⁺ ions, more oxygen vacancies, larger quantities of surface adsorbed oxygen species and NH₃, which were beneficial for the excellent selective catalytic reduction (SCR) performance.

Hydrogen, which has been identified as a good “energy carrier” to support sustainable energy development, can be obtained from a number of sources, both renewable and non renewable by various processes. Furthermore, ceria-based materials play a key role in promoting innovative technologies.

The present Special Issue includes a work of Landi and Di Benedetto focused on the development of ceria supported nickel catalysts washcoated onto silicon carbide (SiC) honeycomb monoliths [16]. The performances of these structured catalysts have been evaluated under steam reforming to produce hydrogen from real spent solvent streams, coming from the distillation plant of the packaging industry company Icimendue. The effect of the Ni content (5–15 wt%) and the type of ceria were studied. The best performances were obtained at low Ni content and by using micrometric rather than nanometric ceria as support. In this case the presence of ceria promotes the dispersion of nickel as well as strong interaction between the metal and the ceria support. In addition, yield to coke is always lower than 1%, suggesting a high coking resistance of the catalytic layer. These results suggest that the proposed structured catalysts could be successfully applied in the solar reforming of spent solvents.

Fischer–Tropsch (FT) synthesis is a classical heterogeneous reaction whereby syngas (CO + H₂) molecules react on the surface of the metal sites (Co, Fe, Ru, etc.) to produce heavier hydrocarbons (gasoline, diesel fuel and jet fuel) olefins, wax and an aqueous stream containing light oxygenates as

a major by-product [17]. The low carbon concentration of the organics makes its thermal recovery unprofitable. Thus, novel processes are needed to utilize this waste carbon content to make this stream less harmful for the environment. Aqueous-Phase Reforming (APR) is a promising strategy for the valorization of aqueous side-streams. Coronado et al. developed a kinetic model for the APR of FT water to convert the organic hydrocarbons into hydrogen [18]. The model is based on experimental data obtained by a real FT water in a continuous packed-bed reactor at different operating conditions of temperature (210–240 °C), pressure (3.2–4.5 MPa) and weight hourly space velocity (WHSV) (40–200 h⁻¹) over a nickel-copper catalyst supported on ceria-zirconia. The experimental results proved that it is possible to upgrade the oxygenated compounds in the FT water to valuable compounds such as hydrogen. Moreover, the experimental results revealed that the desired full reforming of alcohols and WGS reaction, as well as the unwanted dehydration—AWS of ethanol to form AcOH, were favoured with the increase in temperature and with the decrease in pressure and WHSV. According to the product distribution obtained in the APR of FT water, these reactions were predominantly compared to other commonly reported reactions in APR such as methanation and dehydrogenation. This study demonstrates, once again, the surprising ability of ceria-based materials to enhance complex catalytic processes, such as the APR of FT water wastes that is a three-phase system with several competitive and consecutive reactions. As guest editors, I would like to thank all the authors who contributed to this issue. Their contributions represent excellent examples of the current research trends in the field of ceria catalysis. I also wish to thank the editorial staff of *Catalysts* for their help to organize this issue. I hope that the topics presented in this issue will inspire the readers to explore the exciting science of ceria catalysis further.

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