



Simultaneous catalytic oxidation of carbon monoxide, hydrocarbons and soot with Ce–Zr–Nd mixed oxides in simulated diesel exhaust conditions



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ABSTRACT

Ce_{0.73–x}Zr_{0.27}Nd_xO₂ mixed oxides ($x \leq 0.3$) were prepared, characterized by XRD, Raman spectroscopy, N₂ adsorption isotherms and H₂-TPR, and tested for simultaneous CO, propylene, benzene and soot oxidation in a gas mixture containing O₂, NO_x, H₂O, CO₂, CO, propylene (model aliphatic hydrocarbon) and benzene (model aromatic hydrocarbon) that simulates a diesel exhaust. Ce–Zr mixed oxide doping with a low atomic fraction of neodymium ($0.01 \leq x \leq 0.09$) promotes the creation of oxygen vacancies, has a minor effect in the BET specific surface areas of the oxides, increases the surface ceria reducibility and has a positive effect in the catalytic activity. On the contrary, higher neodymium atomic fractions ($x = 0.2$ and 0.3) promote sintering, with a drastic decrease of the BET specific surface area, surface reducibility and catalytic activity. The Ce_{0.73–x}Zr_{0.27}Nd_xO₂ catalysts with $x \leq 0.09$ are able to accelerate simultaneously soot, propylene and benzene combustion, and as a general trend, the catalytic behavior of Ce_{0.73}Zr_{0.27}O₂ is improved by low atomic fraction neodymium doping ($0.01 \leq x \leq 0.09$). These Ce_{0.73–x}Zr_{0.27}Nd_xO₂ mixed oxides with $0.01 \leq x \leq 0.09$ are also able to accelerate CO oxidation in a certain extent, but there is a net production of CO during soot combustion because the oxidation capacity of these oxides is not high enough to oxidize all CO released as soot combustion product.

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1. Introduction

Cerium-based oxides are part of the active phases used in three way catalysts (TWC) for gas pollution control in gasoline vehicles [1–4]. Cerium oxides improve noble metals dispersion and stabilization, store and release oxygen buffering the fluctuations of the O₂ concentration in the gas mixture and catalyze (together with noble metals) some reactions like CO and hydrocarbons oxidation.

Cerium oxide-based catalysts have been also proposed for soot combustion in diesel vehicles, where the gas exhaust is highly oxidizing [5–9]. Diesel engines also emit CO and hydrocarbons, but in much lower concentration than gasoline engines [10–13]. Usually, a platinum-containing diesel oxidation catalyst (DOC) is used in diesel vehicles for simultaneous CO, hydrocarbons and NO oxidation. The NO₂ produced, which is much more oxidizing than NO and O₂, starts the combustion of soot collected downstream in a diesel particulate filter (DPF).

Noble metal-free catalysts are being investigated for soot combustion in diesel exhausts in order to lower the cost of the after-treatment devices. Ceria-based oxides are promising candidates, and the role of O₂ and NO_x in the ceria-catalyzed combustion of soot is well understood. One of the ceria-catalyzed soot-combustion mechanisms consists of the oxidation of NO to NO₂ (as described for platinum-containing DOC), and other consists of the production of active oxygen by oxygen exchange between the ceria-based catalyst and the oxygen-containing gas molecules, mainly O₂. Depending on the ceria catalyst features and on the reaction conditions (temperature, gas composition, etc.) either both mechanisms progress synergically together or one of them prevails.

Platinum catalysts are much more active for NO oxidation to NO₂ than ceria catalysts, but the latter are able to approach the activity of platinum for soot combustion if the active oxygen mechanism gets involved. The main handicap of the active oxygen mechanism is that the contact between soot and ceria catalyst particles must allow the active oxygen species to be transferred from catalyst to soot, otherwise they recombine to each other and yield O₂ [14]. Therefore, ceria catalysts must be impregnated into the DPF instead

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of being loaded in a DOC located upstream the DPF, as usually done with platinum.

The substitution of the Pt-DOC+DPF soot removal device by a ceria-DPF configuration seems promising, but it must be analyzed whether ceria-catalysts are able to remove simultaneously soot, hydrocarbons and CO, as platinum catalyst does, or if further improvements are required.

We have recently analyzed the effect of H₂O, CO₂ and SO₂ in the catalytic activity for soot combustion of Ce_{0.73}Zr_{0.27}O₂ and Ce_{0.64}Zr_{0.27}Nd_{0.09}O₂ in simulated diesel exhaust conditions, concluding that all these three gases lower the activity of both catalysts and that the inhibiting effect follows the trend SO₂ ≫ H₂O > CO₂ [15]. The poisoning effect of SO₂ was already reported by other authors [16–19], but less attention was paid in the literature to the effect of H₂O and CO₂. In situ DRIFTS experiments showed that CO₂, H₂O and SO₂ compete with NO_x for the adsorption sites on the catalysts' surface [15]. CO₂ and H₂O partially hinder the catalytic oxidation of NO to NO₂ while SO₂ chemisorption inhibits almost all the activity due to sulfate formation. The catalytic activity for soot combustion of Ce_{0.64}Zr_{0.27}Nd_{0.09}O₂ was equal or higher to that of Ce_{0.73}Zr_{0.27}O₂ in the presence of NO_x, O₂, H₂O and/or CO₂, because Nd³⁺ doping promotes the participation of the active oxygen mechanism, which seems to resist the presence of H₂O and CO₂ better than the NO₂-assisted soot combustion mechanism [15]. For this reason, the Ce_{0.64}Zr_{0.27}Nd_{0.09}O₂ mixed oxide was identified as a potential catalyst with practical relevance for diesel vehicles running with sulfur-free fuel, since it maintained significant activity for soot combustion even in the presence of H₂O and CO₂.

As far as we know, the simultaneous ceria-catalyzed combustion of soot, CO, and hydrocarbons has not been studied and reported in the literature, and this is one of the goals of the current study. In addition, the positive effect of Nd³⁺ doping in the catalytic activity the Ce–Zr mixed oxide for soot combustion, which was first reported in [20], has lead us to focus the current study to ternary Ce–Zr–Nd mixed oxides. A series of Ce_{0.73–x}Zr_{0.27}Nd_xO₂ mixed oxides were prepared with different neodymium content, and were characterized and tested for the simultaneous oxidation of CO and hydrocarbons, both in the absence and presence of soot. A complex gas mixture that mimics a diesel engine exhaust containing NO_x, O₂, H₂O, CO₂, CO, propylene and benzene was used. Propylene and benzene were selected as model aliphatic and aromatic hydrocarbons, respectively.

2. Experimental details

2.1. Catalysts preparation

Six Ce_{0.73–x}Zr_{0.27}Nd_xO₂ mixed oxides were prepared, with $x = 0, 0.01, 0.05, 0.09, 0.2$ and 0.3 . Formally, the stoichiometric coefficient of oxygen in the neodymium-containing catalysts should be lower than 2, since the tetravalent cation “Ce⁴⁺” is replaced by a trivalent one (Nd³⁺). However, the subscript 2 has been maintained in the nomenclature for the sake of simplicity.

The required amounts of Ce(NO₃)₃·6H₂O (Sigma Aldrich, 99%), Nd(NO₃)₃·6H₂O (Aldrich, 99.9%) and/or ZrO(NO₃)₂·xH₂O (Fluka, $x \approx 6$) were dissolved in water and an ammonia solution was dropped to keep the pH at about 9, leading to the precipitation of the cations. After filtering, the precipitates were firstly dried at 110 °C in air overnight and then calcined in air at 800 °C for 90 min to ensure thermal stability and practical meaning.

The synthesis method and the amount of zirconium on the mixed oxides were selected based on our previous studies on soot combustion, where catalysts with different Ce–Zr ratios were prepared by different methods [21,22].

2.2. Catalysts characterization

X-ray diffractograms of the catalysts were recorded in a Rigaku Miniflex II diffractometer, using CuK_α radiation ($\lambda = 0.15418$ nm). The diffractograms were recorded between 10° and 80° (2 θ) with a step of 0.025°.

Raman spectra were recorded in a Bruker RFS 100/S Fourier Transform Raman Spectrometer with a variable power Nd–YAG laser source (1064 nm). The laser beam was focused on the sample in a 180° backscattering configuration and 128 scans at 100 mW laser power were recorded.

The BET specific surface area of the oxides was determined by physical adsorption of N₂ at –196 °C in an automatic volumetric system (Autosorb-6, Quantachrome). The samples were outgassed at 150 °C for 4 h before the N₂ adsorption measurements.

Temperature programmed reduction (H₂-TPR) experiments were carried out with 15 mg of fresh mixed oxide, which were pre-treated in situ at 500 °C for 1 h in a 35 mL/min flow of 5 vol.% O₂ in He. Once cold, the flow gas was switched to 35 mL/min of 5 vol.% H₂ in Ar and the temperature was increased at 10 °C/min up to 1050 °C.

2.3. Catalytic tests

Catalytic tests were performed at atmospheric pressure in a cylindrical reactor coupled simultaneously to a HP 6890 gas chromatograph equipped with a TCD and two columns (Porapak Q, for CO₂ and Molecular Sieve 13 \times , for O₂, N₂ and CO) and a Pfeiffer Vacuum mass spectrometer (model OmniStar) to monitor NO, propylene, NO₂ and benzene concentrations following the $m/z = 30, 39, 46$ and 78 signals, respectively. The total flow rate was 100 mL/min (GHSV = 42,000 h^{–1}) and the gas composition was 300 ppm CO/120 ppm propylene/3% CO₂/180 ppm benzene/1000 ppm NO_x (~0 ppm NO₂)/5%O₂/2%H₂O and He as balance gas. Gas flow controllers were used to feed the required amount of each individual gas, and the O₂ flow was bubbled in water at 72 °C before mixing with the remaining flows to add steam into the gas mixture. This complex composition simulates a real diesel engine exhaust and allows evaluating the simultaneous catalytic oxidation of CO, propylene, benzene and soot in quite realistic conditions.

Catalytic tests were performed with and without soot. Experiments performed without soot consisted of the simultaneous CO, propylene and benzene catalytic oxidation studied at selected temperatures from room temperature up to 550 °C. 100 mg of each mixed oxide catalyst was used for these experiments, which were diluted with 300 mg of SiC to avoid pressure drop and favor heat transfer. The experiments were extended until steady-state at each temperature, typically for 30 min.

Experiments were also performed with 100 mg of catalyst mixed with 25 mg of soot and 300 mg of SiC. Soot and catalyst were mixed with a spatula in the so-called loose contact conditions to simulate the contact in a real DPF filter [23]. The model soot used was a carbon black supplied by Evonik–Degussa GmbH (Printex U). The soot-catalyst-SiC mixture was heated at 530 °C in 13 mL/min He. Then, the inert gas was replaced by the reactive gas mixture and the gas composition was monitored as a function of time.

Propylene and benzene conversions were determined following the m/z 39 and 78 signals, respectively, by mass spectrometry and CO conversions were determined from gas chromatography measurements. The conversions of CO, propylene and benzene were calculated as follows:

$$\text{Conversion (\%)} = 100 \times \left(\frac{[\text{pollutant}]_{\text{in}} - [\text{pollutant}]_{\text{out}}}{[\text{pollutant}]_{\text{in}}} \right)$$

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