

Effect of ceria–zirconia ratio on the interaction of CO with PdO/Al₂O₃–(Ce_x–Zr_{1–x})O₂ catalysts prepared by sol–gel method

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Abstract

The current work is devoted to study of CO interaction with PdO/Al₂O₃–(Ce_x–Zr_{1–x})O₂ catalysts. Ceria–zirconia–alumina supports with different Ce/Zr ratio were prepared by sol–gel technique. The FT-IR characterization of CO adsorbed at –120 and 25 °C on oxidized and reduced samples revealed that Ce/Zr ratio modifies the surface properties of support and oxidation state of palladium. The catalyst with Ce/Zr molar ratio 0.5/0.5 was characterized with the highest ability to stabilize palladium in oxide state and the highest activity to oxidize CO. Redox treatment of catalysts improves their catalytic activity.

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1. Introduction

The palladium-only three-way catalysts (Pd-only TWC) are used for automotive catalytic converters with closed-loop control systems [1–11], due to their lower cost, their ability to catalyze the hydrocarbon oxidation and their durability under high temperature conditions. In fact, the fourth generation of these catalytic converters has been available in the market since 1995 [12,13]. Pd-only catalysts can be effective as TWC for the simultaneous removal of NO, CO and hydrocarbons in automotive exhaust gases [7,14], but they typically show lower efficiency in NO conversion compared with TWC based on Rh [15,16]. Nevertheless, the catalytic activity of Pd-only TWC could be improved by doping with rare earth oxides. For instance, Trovarelli [17] reported that due to its properties, structure and capabilities of storing and releasing oxygen, CeO₂ is an important component in automotive emission-control (oxidation) catalysts. The role of oxygen vacancies and their

mobility on ceria surfaces, has been recently studied by Esch et al. [18]. The mechanism of oxygen vacancies appearance and their interaction upon further ceria reduction have been recently studied in detail by scanning tunneling microscopy and density functional calculations [18]. It was shown that on the slightly reduced surface single vacancies prevail and can be distinguished as two types. One type appears as depressions surrounded by three paired lobes and can be assigned to surface oxygen vacancies. A second type appears as triple protrusions centered about of the third layer oxygen sites. Upon further reduction almost all vacancies interact with each other with formation so-called linear surface oxygen vacancies with length of several nm. In addition the authors concluded that single vacancy formation around single Zr⁴⁺ dopants is facilitated.

The catalytic activity of the palladium catalysts depends as much on their method of preparation [19,20] as well as the composition of the support [21–25]. For Pd supported on Al₂O₃ catalysts modified with ceria and zirconia, the extent of the effect of this promotion on both the reduction of NO and the oxidation of CO depends on the interaction between the support and palladium, which determines the nature of the Pd species

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and its particle size. Thus, the physical and chemical characteristics of modifier play an important role in these reactions [26,27], which requires a strict control of the composition of the support to obtain the best thermal stability and optimal catalytic activity [28,29].

Incorporation of Ce–Zr by sol–gel into the alumina matrix can improve more efficient degree of Ce–Zr dispersion and thermal stability of alumina. The sol–gel method provides the capacity to mix several components in a single stage, and allows controlling the structure and composition of the final solid mixture at molecular level [30]. In addition, sol–gel methods give a homogeneous mixture of Al_2O_3 – MO_x binary oxides with enhanced efficiency for NO reduction. In the past, we have reported that palladium catalysts deposited on Al_2O_3 – La_2O_3 supports prepared by the sol–gel method show an enhancement in the reducibility properties, and that those changes influence the activity of reduction of NO by hydrogen [31]. It was suggested in that work that the higher selectivity towards the production of N_2 found on the catalysts of Pd/ Al_2O_3 – La_2O_3 , compared with the Pd/ Al_2O_3 catalysts at temperatures below 350 °C is due to the interaction of palladium particles and reduced species of lanthana.

The aim of this work was to determine the effect of ceria–zirconia ratio on the interaction of CO with PdO/ Al_2O_3 – $(\text{Ce}_x\text{–Zr}_{1-x})\text{O}_2$ catalysts in order to obtain further information about the catalyst structure and surface configuration by FT-IR spectroscopy, that is important in their efficiency in CO oxidation. The samples of alumina–ceria–zirconia mixed oxides were prepared by sol–gel method in order to get homogeneous support for catalysts and to promote the interaction between PdO and support.

2. Experimental

2.1. Preparation of catalysts

Alumina supports were prepared with different Ce/Zr ratios (Al_2O_3 – $(\text{Ce}_x\text{–Zr}_{1-x})\text{O}_2$ with $x = 0, 0.25, 0.33, 0.5, 0.66, 0.75$ and 1.0) by the sol–gel method from organic precursors following a procedure reported previously [32]. A solution of acetylacetonate of cerium (Aldrich) and/or acetylacetonate of zirconium (Alfa Aesar) in ethanol with moderate agitation was added to a mixture of aluminum sec-butoxide (Aesar Alpha) in

2-metil-2,4-pentenediol (Aesar Alpha), staying in reflux for 3 h, with moderate agitation at 94 °C. Hydrolysis was made by adding deionized water. The obtained gel was aged for 10 h. Samples were dried at vacuum (about 10^{-2} Torr) at 100 °C for 12 h and then calcined in N_2 atmosphere at 450 °C for 12 h, with a later treatment in air at 650 °C for 4 h.

The support impregnation was carried out using a palladium chloride solution of 0.12% (w/v), to give a concentration of 0.3 wt.% of palladium. After impregnation, the samples were calcined in air at 650 °C for 4 h.

Chemical analysis of prepared samples by inductive coupled plasma (ICP) technique was done using Optical Emission Spectrometer Optima 4300D. Before analysis samples were dissolved in sulphuric acid solution (1:1). The experimental composition of the prepared catalysts determined by ICP as well as the specific surface area determined by nitrogen adsorption and BET method are presented in the Table 1. According to the data presented in a previous paper [33] for most of the catalysts it could be concluded that $(\text{Ce}_{1-x}\text{Zr}_x)\text{O}_2$ mixed oxide is present like nano-crystallites which size is below the XRD detection limits. Only for the PdO/ Al_2O_3 – $(\text{Ce}_{0.75}\text{Zr}_{0.25})\text{O}_2$ catalyst it was observed formation of a $(\text{Ce}_{1-x}\text{Zr}_x)\text{O}_2$ mixed oxide solution. The particle size of PdO was about 6 nm for PdO/ Al_2O_3 – CeO_2 , it decreased to 3.3 nm for PdO/ Al_2O_3 – $(\text{Ce}_{0.25}\text{Zr}_{0.75})\text{O}_2$ and finally it increased a little for PdO/ Al_2O_3 – ZrO_2 (4.5 nm).

2.2. CO adsorption by FT-IR

The CO adsorption was performed as described in previous report [34]. Typical experiments were carried out step by step from low temperatures (LT, –120 °C) to room temperature (RT, 25 °C) and from 5 Torr of CO up to evacuation for 40 min at 10^{-2} Torr. Infrared spectra of CO adsorbed on the catalysts were registered with a resolution of 4 cm^{-1} , with a Bruker Equinox 55 Fourier-transformed infrared (FT-IR) spectrometer in transmittance mode with DTGS detector [35]. Experiments were carried out in a quartz laboratory-made cell with windows of NaCl able to work from –120 to 550 °C and pressures of 10^{-2} to 760 Torr. The catalyst powders were pressed into self-supporting discs of 13 mm of diameter and less than 20 mg of weight. Samples were exposed to 5 Torr of carbon monoxide (Matheson Research grade) purified using a trap cooled with

Table 1
BET surface area and experimental composition of catalysts

Catalysts	Surface area BET ($\text{m}^2\text{ g}^{-1}$)	Experimental composition ICP (wt.%)			Calculated value ^a (wt.%)
		Pd	Ce	Zr	
PdO/ Al_2O_3 – CeO_2	246	0.20	4.45	<0.007	95.34
PdO/ Al_2O_3 – $(\text{Ce}_{0.75}\text{Zr}_{0.25})\text{O}_2$	253	0.20	3.42	1.45	94.93
PdO/ Al_2O_3 – $(\text{Ce}_{0.67}\text{Zr}_{0.33})\text{O}_2$	260	0.24	3.09	2.03	94.64
PdO/ Al_2O_3 – $(\text{Ce}_{0.5}\text{Zr}_{0.5})\text{O}_2$	246	0.19	2.27	2.84	94.70
PdO/ Al_2O_3 – $(\text{Ce}_{0.33}\text{Zr}_{0.67})\text{O}_2$	253	0.20	1.37	3.68	94.75
PdO/ Al_2O_3 – $(\text{Ce}_{0.25}\text{Zr}_{0.75})\text{O}_2$	257	0.20	1.07	4.12	94.61
PdO/ Al_2O_3 – ZrO_2	249	0.18	<0.006	5.5	94.31
PdO/ Al_2O_3	214	0.29	<0.006	<0.006	99.70

^a Calculation was made by difference based on stoichiometry of Ce, Zr and Al oxides.

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