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Short Communication

Effect of Zr^{4+}-ion substitution in CeO_2 on H_2O_2-assisted degradation of orange G

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A B S T R A C T

A series of Pd ion-substituted CeO_2–ZrO_2 solid solutions were synthesized using the solution combustion technique. H_2O_2-assisted degradation of orange G was carried out in the presence of the catalysts. The activity of the catalysts was found to increase with the introduction of the second component in the solid solution, as signified by an increase in the rate constants and lowering of activation energy. The study showed the involvement of lattice oxygen and the importance of reducibility of the compound for the reaction.

1. Introduction

Oxygen storage materials form an important category of catalytic materials with an ability to catalyze oxidation reactions by lattice oxygen exchange. CeO_2 is one of such materials used widely for catalyzing a large number of oxidation reactions. A large enhancement in the activity of the compound is observed with the introduction of a noble metal in the compound. Several reactions including CO oxidation [1], water–gas shift reaction [2], steam reforming [3], and oxidative dehydrogenation reactions [4] have been reported over noble metal dispersed CeO_2 compounds. The activity of the compound depends upon the reducibility of the material and several efforts have been directed towards achieving enhanced lattice oxygen exchange.

CeO_2-based materials have been extensively used for exhaust catalytic applications [5]. For such applications, the thermal stability of the compound is important and CeO_2–ZrO_2 systems show improved properties compared to CeO_2 [6]. However, solid solutions of CeO_2 and ZrO_2 offer an additional advantage of enhanced reducibility. It has been proved experimentally as well as by density functional theory calculations that substitution of Zr^{4+} ions in CeO_2 matrix results in increased oxygen storage capacity and, thus, enhanced CO oxidation can be observed [7]. Solution combustion is a novel technique for the synthesis of nanocrystalline solid solutions. We have synthesized a series of Pd ion-substituted solid solutions of CeO_2 and ZrO_2 and tested the activity of the compounds for the degradation of orange G (OG).

The degradation of dyes involves oxidation of the dye molecule and the formation of CO_2 and H_2O can be expected on complete degradation. We have previously established high activity of Pd^{2+} ions in CeO_2 matrix for H_2O_2-assisted degradation of OG [8]. The mechanism of degradation of the dye was proposed to take place via the utilization of lattice oxygen. Replenishment of the lattice oxygen in the reduced catalyst was proposed to take place by the dissociation of H_2O_2 over anionic vacancies in the reduced compound. In this study, we have rationalized the proposition of lattice oxygen exchange for the degradation of the dye by carrying out the reaction over CeO_2–ZrO_2 solid solutions. The reducibility of CeO_2 increases with substitution of Zr^{4+} in the matrix. On the other hand, ZrO_2 is not reducible. Therefore, the high activity of the compound can be expected at intermediate compositions. We discuss in detail the effect of solid solution composition on the activity of the compounds and present the kinetics of dye degradation over the different compounds.

2. Experimental

The catalysts were synthesized by the solution combustion technique using oxalyl dihydrazide (ODH) as the fuel. The precursor solution was heated in a muffle furnace at 350 °C and the catalysts were obtained after combustion. Table 1 gives the stoichiometry of the different precursors used for the synthesis of different compounds. The details of the synthesis can be found elsewhere [9]. The catalysts were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, FT-Raman spectroscopy and transmission electron microscopy. The details can be found elsewhere [9,10].

Degradation of OG was carried out in 100 ml round bottom flask. Dye solution of a known concentration was made and heated in a mantle heater to the desired temperature. The temperature of the reaction mixture was controlled using a PID controller with the temperature sensor placed in the reaction mixture. In all experiments, 5 M H_2O_2

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Table 1
Different catalysts synthesized and the precursors used.

S.no	Catalyst	CAN[a]	ZN[a]	$PdCl_2$	ODH
1	$Ce_{0.98}Pd_{0.02}O_{2-\delta}$	0.98	0	0.02	2.34
2	$Ce_{0.78}Zr_{0.20}Pd_{0.02}O_{2-\delta}$	0.78	0.20	0.02	2.25
3	$Ce_{0.68}Zr_{0.30}Pd_{0.02}O_{2-\delta}$	0.68	0.30	0.02	2.25
4	$Ce_{0.58}Zr_{0.40}Pd_{0.02}O_{2-\delta}$	0.58	0.40	0.02	2.16
5	$Ce_{0.49}Zr_{0.49}Pd_{0.02}O_{2-\delta}$	0.49	0.49	0.02	2.16
6	$Zr_{0.58}Ce_{0.40}Pd_{0.02}O_{2-\delta}$	0.40	0.58	0.02	2.16
7	$Zr_{0.80}Ce_{0.18}Pd_{0.02}O_2$	0.18	0.80	0.02	2.07
8	$Zr_{0.98}Pd_{0.02}O_2$	0	0.98	0.02	1.98

CAN — ceric ammonium nitrate; ZN — zirconium nitrate.
[a] Amount in mole.

solution and 75 mg of catalyst were added to the solution and samples were taken at regular intervals. The catalyst was separated by centrifugation and the samples were analyzed using a UV–vis spectrophotometer. Further details can be found elsewhere [8].

3. Results and Discussion

3.1. Structural Characterization

We have reported a thorough XRD analysis of Pd-ion substituted CeO_2, ZrO_2 and CeO_2–ZrO_2 solid solution in our previous studies [9,10]. In brief, all the CeO_2-based compounds were found to crystallize in cubic fluorite structure while ZrO_2-based compounds crystallized in tetragonal structure. Complete substitution of Pd^{2+} ions in the matrix was confirmed by Rietveld refinement of the patterns, which showed changes in the lattice parameters on substitution. No peak corresponding to the Pd metal was observed in any of the cases.

The ionic nature of the metal in the compounds was further confirmed using XPS in which Pd was found to be in a +2 state. High resolution TEM images and electron diffraction patterns further confirmed the crystal structure and substitution of Pd in ionic form in the crystal lattice.

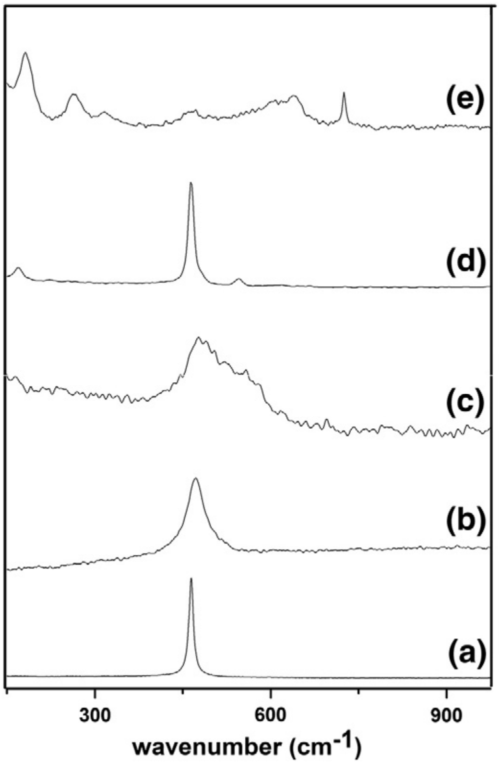

Fig. 1. FT-Raman spectra of (a) $Ce_{0.98}Pd_{0.02}O_{2-\delta}$, (b) $Ce_{0.78}Zr_{0.2}Pd_{0.02}O_{2-\delta}$, (c) $Ce_{0.49}Zr_{0.49}Pd_{0.02}O_{2-\delta}$, (d) $Zr_{0.80}Ce_{0.18}Pd_{0.02}O_2$, and (e) $Zr_{0.98}Pd_{0.02}O_2$.

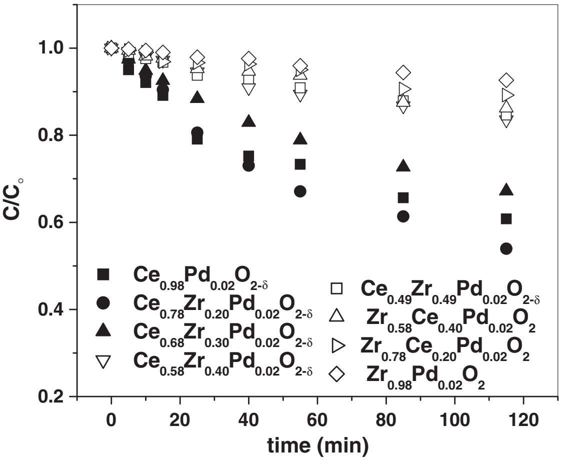

Fig. 2. Variation of normalized concentration of OG at 50 °C with time over different catalysts.

Although XRD is a standard technique for the determination of the crystal structure, we discuss in detail the observations from FT-Raman spectroscopy only. Solution combustion technique results in the formation of nanocrystalline compounds, which show broad XRD peaks due to which the distinction between cubic and tetragonal structure becomes difficult. Therefore, FT-Raman spectroscopy becomes a reliable technique for structure determination. Fig. 1 shows the spectra of different compounds in a range of 100 to 1000 cm^{-1} where the characteristic peaks appear. It can be seen from Fig. 1(a) that Pd ion-substituted CeO_2 was crystallized in the cubic structure. The characteristic intense peak of cubic structure at 470 cm^{-1} can be observed. Similarly, the peak in $Ce_{0.78}Zr_{0.20}Pd_{0.02}O_{2-\delta}$ corresponded to the formation of cubic structure showing the substitution of Zr^{4+} ions in Ce^{4+} sites. The formation of solid solution, therefore, was confirmed using FT-Raman analysis.

The spectra of $Zr_{0.98}Pd_{0.02}O_2$ showed peaks characteristic of tetragonal phase of ZrO_2. We have previously observed the same phase for unsubstituted and Pd/Pt-ion substituted ZrO_2 by solution combustion [9]. However, it is interesting to note that the spectra of $Zr_{0.80}Ce_{0.18}Pd_{0.02}O_2$ showed both cubic as well as the tetragonal phase. This can be either due to the crystallization of ZrO_2 in cubic phase or incomplete substitution of Ce in ZrO_2. Since cubic is the high temperature stable phase of ZrO_2, crystallization of ZrO_2 in cubic phase by solution combustion technique is very unlikely. Therefore, it can be hypothesized that complete substitution of Ce^{4+} ions in Zr^{4+} sites was not possible and the compound can be considered to be a mixed oxide. $Ce_{0.49}Zr_{0.49}Pd_{0.02}O_{2-\delta}$ was found in the cubic structure and, therefore, this indicates that the substitution of Zr^{4+} ions in Ce^{4+} sites is possible even in larger amounts. The ionic radius of Ce^{4+} and

Table 2
First order rate constants at 50 °C and % OG degradation in 2 h over the different catalysts.

Catalyst	First order rate constant ($\times 10^3$) (min^{-1})	% degradation after 2 h
$Ce_{0.98}Pd_{0.02}O_{2-\delta}$	6.4	40
$Ce_{0.78}Zr_{0.20}Pd_{0.02}O_{2-\delta}$	7.3	47
$Ce_{0.68}Zr_{0.30}Pd_{0.02}O_{2-\delta}$	4.1	33
$Ce_{0.58}Zr_{0.40}Pd_{0.02}O_{2-\delta}$	2.6	17
$Ce_{0.49}Zr_{0.49}Pd_{0.02}O_{2-\delta}$	1.1	15
$Zr_{0.58}Ce_{0.40}Pd_{0.02}O_{2-\delta}$	1.1	14
$Zr_{0.80}Ce_{0.18}Pd_{0.02}O_2$	1.0	11
$Zr_{0.98}Pd_{0.02}O_2$	0.62	8