Short Communication

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

Rajasekhar Ch, Parag A. Deshpande, Giridhar Madras *

Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

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ABSTRACT

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.

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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

* Corresponding author. Tel.: +91 80 2293 2321; fax: +91 80 2360 0683.
E-mail address: giridhar@chemeng.iisc.ernet.in (G. Madras).

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
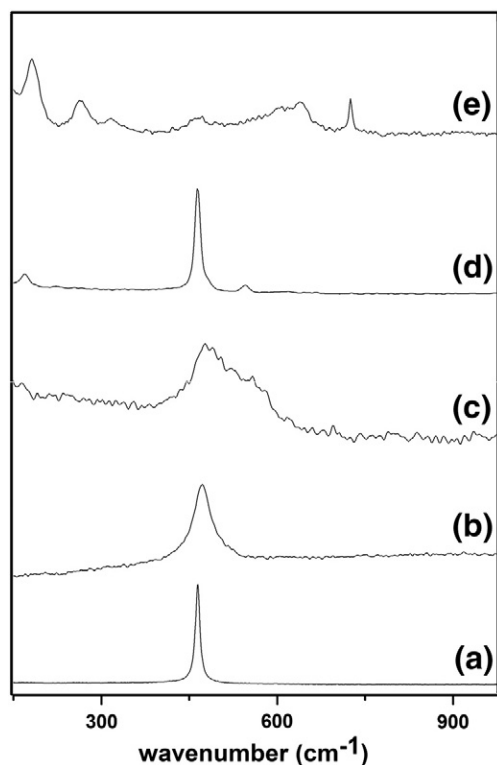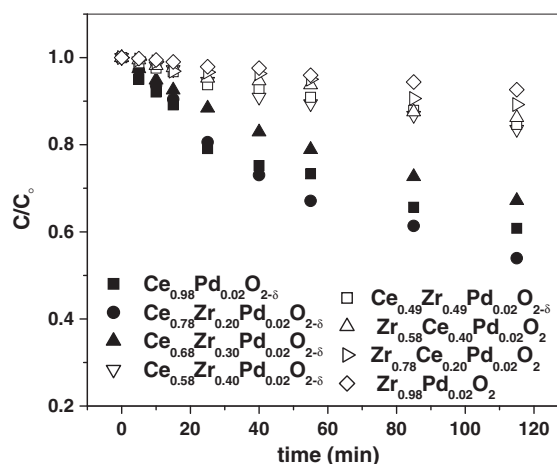

Fig. 2. Variation of normalized concentration of OG at 50 °C with time over different catalysts.

confirmed the crystal structure and substitution of Pd in ionic form in the crystal lattice.

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

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$_2$.

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

Zr^{4+} ions is 0.87 and 0.72 Å, respectively. Due to higher ionic radius of Ce^{4+} ions, complete substitution in Zr^{4+} sites may not be possible. The implications of the structure of the catalyst on the activity for the degradation of the dyes are discussed in detail later.

3.2. Catalytic Activity

We have previously reported a detailed investigation of OG degradation in the presence and absence of Pd ions over CeO_2 catalysts [8]. It was found that in the absence of Pd ions, degradation of OG was limited to 10% compared to more than 95% degradation in the presence of Pd ions. Further, the rates of reaction were found to be more than 25 times higher in the presence of Pd ions, as signified by the first order rate constants. Having established the effect of Pd ions on the activity of the catalyst, the effect of Zr^{4+}-ion substitution on the activity of the catalysts was investigated. In the results reported below the effect of catalyst composition on the activity of the catalyst is analyzed keeping Pd ion concentration same for all the cases.
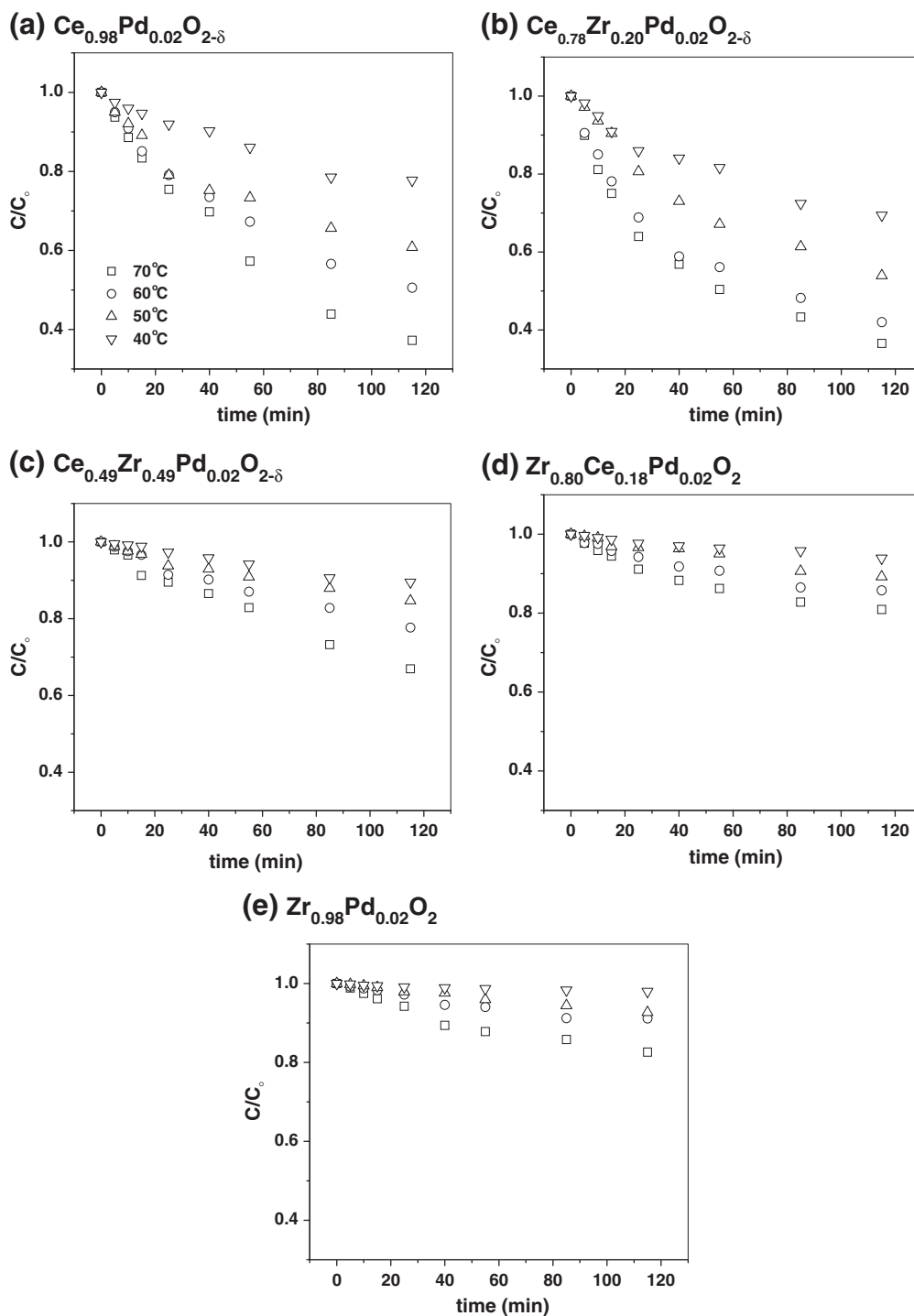

Fig. 3. Variation of normalized concentration of OG with time at different temperatures for (a) $Ce_{0.98}Pd_{0.02}O_{2-\delta}$, (b) $Ce_{0.78}Zr_{0.2}Pd_{0.02}O_{2-\delta}$, (c) $Ce_{0.49}Zr_{0.49}Pd_{0.02}O_{2-\delta}$, (d) $Zr_{0.80}Ce_{0.18}Pd_{0.02}O_2$, and (e) $Zr_{0.98}Pd_{0.02}O_2$.

The variation of normalized OG concentration at 50 °C with time over different catalysts is shown in Fig. 2. The activity of ZrO_2-based compounds was inferior compared to CeO_2-based compounds and $Zr_{0.80}Ce_{0.18}Pd_{0.02}O_2$ and $Zr_{0.98}Pd_{0.02}O_2$ showed 8–11% conversion in 2 h. The conversions obtained at the end of 2 h for various catalysts are listed in Table 2. In case of CeO_2-based compounds, the conversions were high and nearly 40% conversion was observed in 2 h over $Ce_{0.98}Pd_{0.02}O_{2-\delta}$. An increase in the activity of the compound was observed with Zr^{4+} substitution and nearly 47% conversion was observed in 2 h for $Ce_{0.78}Zr_{0.20}Pd_{0.02}O_{2-\delta}$. The first order rate constants in the present case are given in Table 2. From the magnitudes of the rate constants, the activity of the compounds followed the order $Ce_{0.78}Zr_{0.20}Pd_{0.02}O_{2-\delta} > Ce_{0.98}Pd_{0.02}O_{2-\delta} > Ce_{0.68}Zr_{0.30}Pd_{0.02}O_{2-\delta} > Ce_{0.58}Zr_{0.40}Pd_{0.02}O_{2-\delta} > Ce_{0.49}Zr_{0.49}Pd_{0.02}O_{2-\delta} \approx Zr_{0.58}Ce_{0.40}Pd_{0.02}O_{2-\delta} \approx Zr_{0.80}Ce_{0.18}Pd_{0.02}O_2 > Zr_{0.98}Pd_{0.02}O_2$. Therefore, it
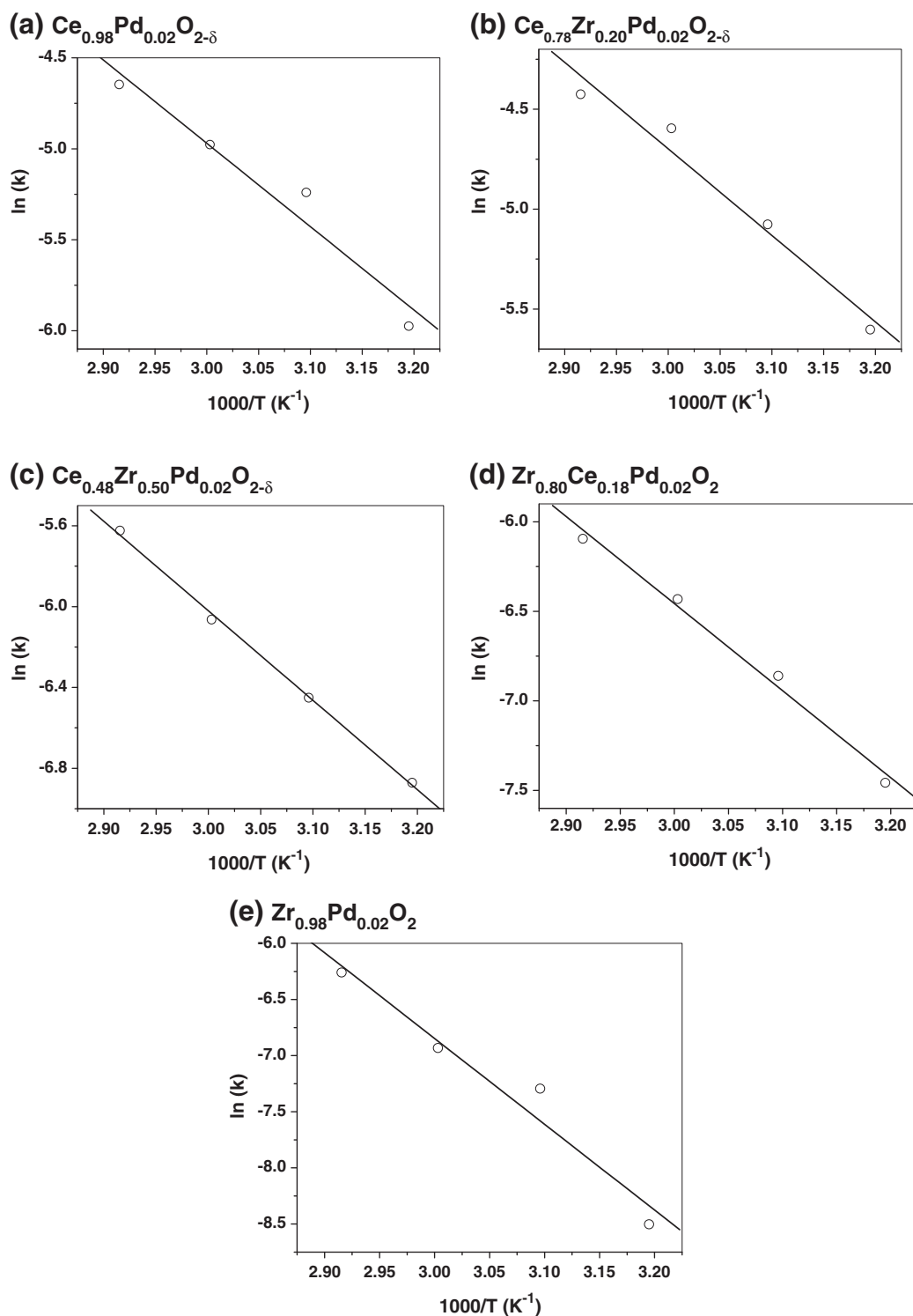

Fig. 4. Arrhenius plot showing the temperature dependence of the first order rate constant on temperature for (a) $Ce_{0.98}Pd_{0.02}O_{2-\delta}$, (b) $Ce_{0.78}Zr_{0.2}Pd_{0.02}O_{2-\delta}$, (c) $Ce_{0.49}Zr_{0.49}Pd_{0.02}O_{2-\delta}$, (d) $Zr_{0.80}Ce_{0.18}Pd_{0.02}O_2$, and (e) $Zr_{0.98}Pd_{0.02}O_2$.

Table 3
Rate constants and activation energies for the degradation of OG with different catalysts following first order degradation kinetics.

Catalyst	k (min^{-1})
$Ce_{0.98}Pd_{0.02}O_{2-\delta}$	$6.5 \times 10^3 \exp(-4583/T)$
$Ce_{0.78}Zr_{0.20}Pd_{0.02}O_{2-\delta}$	$4.0 \times 10^3 \exp(-4329/T)$
$Ce_{0.49}Zr_{0.49}Pd_{0.02}O_{2-\delta}$	$1.4 \times 10^3 \exp(-4429/T)$
$Zr_{0.78}Ce_{0.20}Pd_{0.02}O_2$	$3.4 \times 10^3 \exp(-4865/T)$
$Zr_{0.98}Pd_{0.02}O_2$	$9.6 \times 10^6 \exp(-7642/T)$

can be said that an initial increase in the activity of the catalyst took place on the substitution of Zr^{4+} ions. However, the increase was not monotonous and $Zr_{0.98}Pd_{0.02}O_2$ showed very less activity. Therefore, substitution of a small amount of Zr^{4+} ions is beneficial but higher amounts do not lead to higher activity. This will be discussed in detail later.

Conversions were found to increase with an increase in temperature of reaction and nearly 65% conversion was observed in 2 h at 70 °C for degradation in the presence of $Ce_{0.78}Zr_{0.20}Pd_{0.02}O_{2-\delta}$ (Fig. 3). However, even at 70 °C, the conversions were limited to 20% over $Zr_{0.80}Ce_{0.18-}Pd_{0.02}O_2$ and $Zr_{0.98}Pd_{0.02}O_2$. The first order rate constants at different temperatures were determined. The variation of first order rate constants with temperature was used to determine the activation energy of the reaction over the different catalysts. The corresponding Arrhenius plots are shown in Fig. 4 and the activation energies along with the expressions for the rate constants are given in Table 3. The trends in the variation of activation energy and first order rate constant with the catalyst composition are shown in Fig. 5. The effect of catalyst identity can clearly be seen from the values of activation energies. While the activation energy was found to be the lowest for the reaction over $Ce_{0.78}Zr_{0.2}Pd_{0.02}O_{2-\delta}$, it was found to be the highest over $Zr_{0.98}Pd_{0.02}O_2$. Using the first order rate constants given in Table 2, it is possible to determine the time requirement for a given conversion to be achieved. Therefore, although the results shown in Figs. 2 and 3 do not show complete conversion, the time required for almost complete conversion (95% or above) can be determined using the rate constants.

We account for the differences in the activity of the compounds on the basis of the structure of the compounds. We have previously discussed the catalytic activity of Pd-ion substituted CeO_2 for the degradation of OG, proposed the elementary steps, obtained the rate expression from the elementary steps and determined the associated rate parameters [8]. The mechanism of the reaction in the presence of Zr^{4+} ions remains the same. However, the relative rates of the different steps, especially the rate of lattice oxygen abstraction, change and therefore, the rates of the rea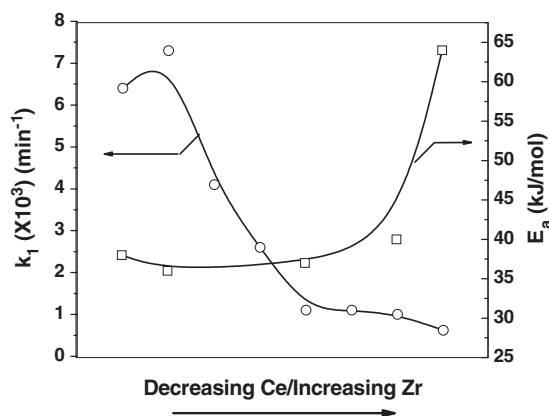ction observed over the two compounds differ. The various processes taking place over Pd ion-substituted CeO_2 during the degradation of OG [8] can be summarized as follows

1. Adsorption of the dye over Pd ions, electron transfers among the dye molecule, metal ion, and the support.
2. Dissociation of H_2O_2 over anionic vacancies resulting in oxidation of the support.
3. Dissociation of H_2O as hydroxyl radicals from electron capture.
4. Interaction of dye molecule with the different active species resulting in the degradation.

In the above mentioned sequence of processes, the reducibility of the compound governs the dissociation of H_2O_2 to release the reactive intermediates. Following this argument, an increase in the activity of the compound can be expected with an increase in the reducibility of the compound. The same was indeed observed in the present case also. Baidya et al. [7] have carried out H_2-TPR studies on Zr^{4+} substituted CeO_2. A large decrease in the temperature requirement for reduction was observed showing increased reducibility of the solid solutions. A large increase in oxygen storage was observed with an initial increase in substitution. Substitution of Zr^{4+} ions in the CeO_2 matrix resulted in the formation of differential bond lengths in the compound. The average Ce—O bond length differed from Zr—O bond length and a bond length distribution was observed in the DFT studies [11]. Thus in the present case, the weak oxygen was available during the reaction and, therefore, the activity of the compound increased the dye degradation. In spite of the oxidizing nature of H_2O_2 which was present in excess, an increase in the activity of the catalysts with Zr^{4+} ion substitution in CeO_2 showed the involvement of lattice oxygen in the reaction and is in support of our previous proposition.

The reaction over ZrO_2-based catalysts is expected to follow a different mechanism compared to the mechanism followed over CeO_2-based compounds in which lattice oxygen utilization is possible due to reducible nature. However, ZrO_2 have Lewis and Bronsted acid sites. These sites can act as centers for the dissociation of H_2O_2 releasing nascent oxygen for oxidation. Further, the electron transfers may also result in the dissociation of H_2O_2 to hydroxyl radicals. However, the mechanism differs from that over CeO_2 in lattice oxygen utilization and centers for dissociation of H_2O_2. While the defect sites in CeO_2 are responsible for the dissociation of H_2O_2, the acidic sites in ZrO_2 help in the dissociation of H_2O_2. The rate of reaction depends upon the relative rates of these steps over the two supports.

While a decrease in the activation energy was observed for CeO_2-based compounds on Zr substitution, the effect of substitution was found to be higher for Ce substitution in ZrO_2. Azzam et al. [12] have reported the possibility of lattice oxygen utilization during the water–gas shift reaction in metal-impregnated ZrO_2 systems. An enhancement in the reducibility of ZrO_2 with the introduction of Pt has been observed by Querino et al. [13]. The introduction of a metal in the ionic form in the lattice enhances the reducibility of the catalyst. Therefore, it can be expected that an enhanced reducibility of the compound resulted in an increase in the activity of the catalyst. This further proves the role of the reducibility of the support in enhancing the dye degradation rate.

4. Conclusions

Pd-metal ion-substituted CeO_2 and ZrO_2 solid solutions were found to be active for H_2O_2-assisted degradation of OG. FT-Raman studies confirmed the crystallization of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ and $Ce_{0.78}Zr_{0.2}Pd_{0.02}O_{2-\delta}$ in cubic phase, and $Zr_{0.98}Pd_{0.02}O_2$ and $Zr_{0.78}Ce_{0.20}Pd_{0.02}O_2$ in tetragonal phase. This showed the substitution of Zr^{4+} ions in CeO_2 and Ce^{4+} ions in ZrO_2. $Ce_{0.78}Zr_{0.2}Pd_{0.02}O_{2-\delta}$ was found to be the most active catalyst exhibiting the lowest activation energy of 36 kJ/mol for the degradation of the dye. The activity of $Zr_{0.98}Pd_{0.02}O_2$ was found to be very low and the activation energy for the degradation of the dye was found to be 64 kJ/mol. The study established the effect of reducibility of

Fig. 5. Variation of first order rate constant and activation energy with the composition of the catalysts.

the compound and the involvement of lattice oxygen during the degradation of the dye in the presence of H_2O_2.

Acknowledgments

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