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Evaluation of cordierite–ceria composite ceramics with oxygen storage capacity

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Abstract

Oxygen storage capacity (OSC) is an important parameter in three-way-catalysts (TWCs) for the purification of exhausts from gasoline engines of automobiles. Beciuse CeO_2 possesses the unique performance, it is added into catalytic coatings of converters to adjust the oxygen concentration of the exhausts. However, small amounts of CeO_2 existing in the coating is insufficient in this when air-fuel ratio fluctuates in a relatively wide range. In the present work, a kind of cordierite–CeO_2 ceramic was prepared through sol-gel method so as to append the OSC to the support on which the catalyst is coated. Advanced measurement techniques such as XRD, SEM and gas chromatograph were employed to evaluate the microstructure and properties of the composite ceramics. Results show that the composite ceramics consist both phases of cordierite and CeO_2. CeO_2 particles are uniformly and separately distributed in the cordierite matrix, their number and granularity dependent on the amount of Ce^{4+} addition. The cordierite and 10 wt.% CeO_2, possesses an apparent OSC, appropriate porosity, flexural strength and thermal expansion coefficient. It will be helpful to enhance the OSC of the catalytic converters and so improve the purification effects to the exhausts. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: CeO_2; Chemical properties; Composites; Cordierite; Silicates; Sol-gel processes

1. Introduction

Automobile exhausts have seriously been affecting the quality of the atmosphere, which has globally aroused great concerns. In the case of gasoline engine combustion, installing a catalytic converter is regarded as an effective method to reduce the emission of the harmful compounds such as N_xO, CO and C_xH_y. Generally, the converter consists of a ceramic monolith honeycomb support and a catalytic coating on it. Cordierite ceramic ($Mg_2A1_4Si_5O_{18}$) is a good candidate for the supports owing to its low thermal expansion coefficient (TEC).[1,2] With the aid of the converter, the undesirable compounds can be simultaneously removed to some extent, which is called "three way catalysts" (TWCs).[3,4] To ensure a relatively high conversion effect, the ratio of air to fuel (AIF) is expected to be kept about 14.7,[5] at which, there is a compromise oxygen concentration that is suitable for either reduction of N_xO or oxidation of CO and C_xH_y. However, under the present situation of combustion control and operation skill, it is difficult to keep the value stable.

OSC is decisive to the purification of the exhaust in the TWC process. Because CeO_2 possesses the unique oxygen storage capacity,[6,7] it has been adopted as an additive to the catalysts to adjust the oxygen concentration.[8–11] When a small fluctuation in the ratio (A/F) occurs, the CeO_2-contained catalytic coating can effectively adjust the balance of oxygen concentration; but when this ratio fluctuates in a relatively large range, the small amount of CeO_2, becomes insufficient for this action.

On the other hand, the cordierite ceramic support has no effect except "supporting the catalytic coating". It seems that, there is some work to be done on the cordierite

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ceramic, for example, appending the oxygen storage capacity to it by preparing cordierite–CeO_2 composites.

According to recent studies,[12,13] CeO_2 dissolves little into cordierite and hardly reacts with it. Consequently, there is a possibility for CeO_2 to exist as a secondary phase in the ceramic. Moreover, the catalytic coating and cordierite support possess a definite porosity.[14–17] If CeO_2 particles could be finely and uniformly distributed on the surface of the interconnected pores of the cordierite ceramics, it could be desireable that the OSC be appended to the cordierite support.

On the basis of above assumption, the sol-gel method was employed to prepare the cordierite–CeO_2 composite ceramics, which were then characterized for such aspects as microstructure, oxygen storage capacity and other properties in order to judge the possibility as catalytic supports with oxygen storage capacity.

2. Experimental procedures

2.1. Preparation of samples

The chemical reagents (AR) such as tetraethyl silicate (TEOS), aluminum isopropoxide ($A1(0C_3H_7^1)_3$), magnesium isopropoxide ($Mg(OC_2H_5)_2$) and cerium nitrate ($Ce(NO_3)_3$ 6HO) were used as precursor materials. Based on the stoichiometric composition of cordierite, the Ce^{4+} addition follows the formula of (1–x) $M_2A1_4Si_5O_{18}+$ x CeO_2 ($x=0$, 2, 4, 6, 8, 10, 20, 100 wt.%). The hydrolyzed alkoxides were mixed with the nitrate solution and strongly stirred at 60 °C for 3 h. Then catalysts HC1 and NH_4OH are successively added into the colloidal sols to adjust the pH value so as to obtain gelatins. The gels were then dried at 100 °C and calcined at 450 °C to remove the volatile, finally, they were ground into powders, through ball-milling, for use.

Plain CeO_2, which was used as a standard sample for testing OSC, was prepared through the precipitation from the cerium nitrate solution. The precipitated amorphous was calcined at 450 °C for use.

2.2. Measurement of oxygen storage capacity

According to the conventional method for measuring the oxygen storage of catalysts,[18–20] a gas chromatograph (model: HP6890) was employed, which is equipped with a normal pressure micro-reactor and a thermal conductivity cell detector (TCD). Helium gas and Ar–7% H_2 were used as the carrier and deoxidation gas, respectively. The samples were the powders (weighing 100 mg) sintered at 1200 °C and then coated with 1 wt.% of Pt coating by immersing them into $PtCl_3$ solution.

The samples were, respectively, heated from room temperature to 900 °C by temperature-programmed reduction (TPR) with a heating speed of 10 °C/min. After being deoxidized for 20 mm at 900 °C, they were cooled down to 420 °C (at which most reactions occur in actual situation), and swept by helium gas for 40 min. Ultimately, the samples were measured for oxygen storage by injecting impulse oxygen.

2.3. Examinations of microstructure. apparent porosity and other properties

The samples were molded by a compression of 50 MPa and then sintered at 1200 °C for 2 h in air. The phase in the samples was identified by an X-ray powder diffractimeter (XRD, Rigaku D/max-2400X), with copper K_α radiation (40 kv, 120 mA) and at a scanning speed of 4°/min. A scanning electronic microscope (SEM, model: CSM950) with energy dispersive spectrometer (EDS) was used to observe the surface morphology of the samples, which were polished and covered with carbon by an ion-sputtered method.

Apparent porosity of the ceramics was measured by water displacement techniques (Archimedes's principle). The porosity was calculated from the following formula.

$$P=(M_2-M_1)/(M_2-M_3)$$

Where, P is the apparent porosity; M_1 and M_2 are the masses measured in air for the dried and water-saturated samples respectively; M_3 is the one measured in water for the water-saturated samples.

The flexural strength was measured in a testing machine (model: AGS-10 KNG, Shimadzu), using three-point-bending samples (3×4×30 mm span, five samples per composition). The cross speed was controlled to be 0.5 mm/min in loading. The thermal expansion coefficient was inspected by a thermal dilatometer (model: Setaram/TMA92), at a heating speed of 10 °C/min. The samples were protected by Ar gas when heated.

3. Results and discussion

3.1. Microstructure of composites

Fig. 1 shows the XRD patterns of the samples with different amounts of ceria. It can be found that Ce^{4+}-containing samples are composed of cordierite and CeO_2. The variation in heights of the peak (111) of CeO_2 indicates the content of CeO_2 increases along with the increase of Ce^{4+} additions. This can be correlated to the little solid solubility of Ce^{4+} into cordierite crystalline, suggesting that Ce^{4*} mainly exists in the form of CeO_2.

As is shown in Fig. 2(a), in the cordierite matrix uniformly dispersed are a large amount of CeO, particles (white dots), which mainly distribute on the boundaries of cordierite grains [Fig. 2(b)]. So the granularity of the cordierite can be estimated to be several micrometers. From Fig. 2(c) and (d), it is obvious that even the large particles turn out to be an aggregation of small ones with about 100–200 nm

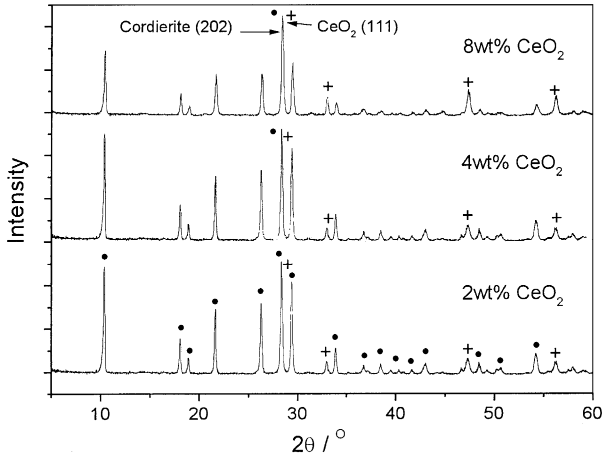
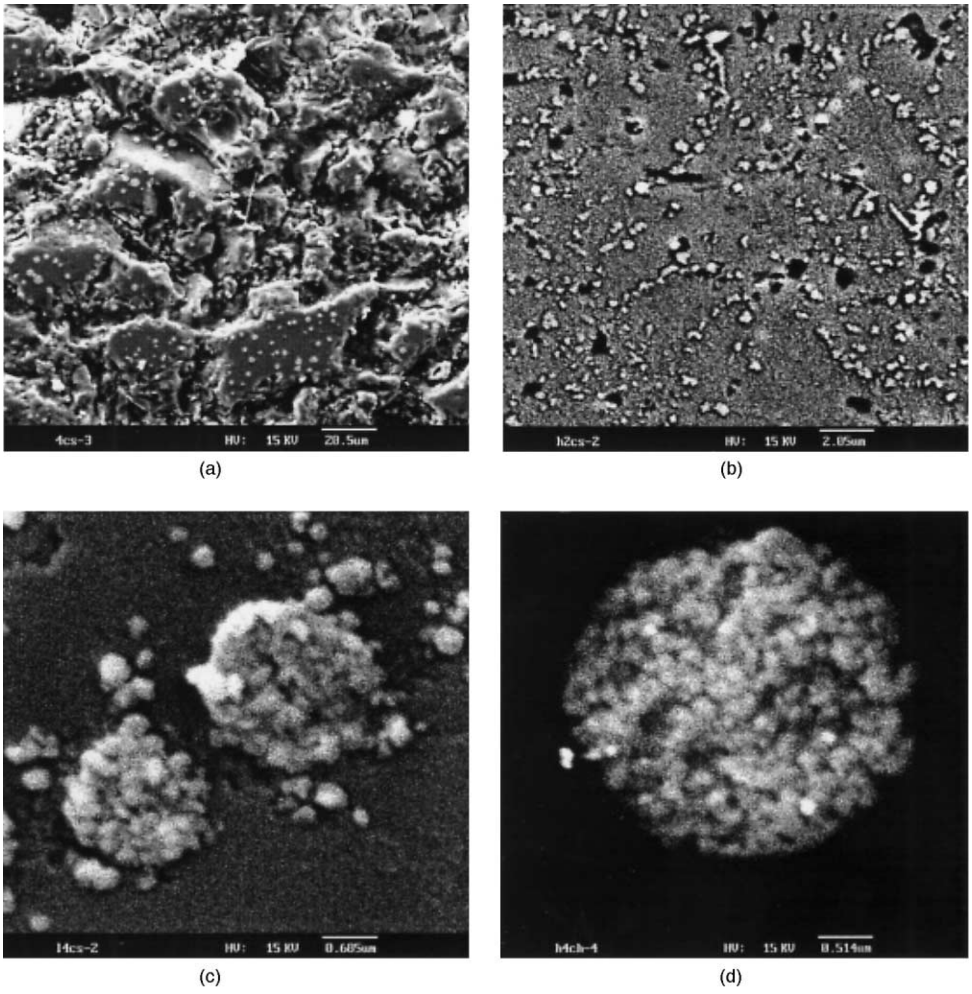


Fig. 1. XRD patterns of samples sintered at 1200 °C for 2 h. +: CeO_2, ●: α-cordierite.

3.2. Oxygen storage capacity of composites

The oxygen storage of the samples in the present work and other literatures[18–20] are shown in Table 1. It proves that these composites possess expected oxygen storage capacity, and the OSC increases with the increase of CeO_2 content. While comparing the OSC values of the samples containing 10 and 20 wt.% of CeO_2, the latter is little higher than the former.

This is because, in the process of sol→gel transformation, visible segregation of Ce^{4+} occurs only for the sample containing 20 wt.% of CeO_2. Accordingly, so long as the gel was calcined at 450 °C, the aggregations began to precipitate and grow up into large CeO_2 particles. Although the sample contains a relatively high amount of CeO_2, the total surface of CeO_2 particles has no more significant increase than that of the sample with l0 wt.% of CeO_2. Generally, the smaller the CeO_2 particles, the larger the surface of the particles, and so the stronger the oxygen storage. Consequently the oxygen storage does no longer present an obvious increase corresponding to the increase of CeO_2, content.



(a) (b) (c) (d)

Fig. 2. SEM photographs of samples; (a) 8 wt.% CeO_2,(b) 4 wt.% CeO_2, (c) 8 wt.% CeO_2, (d) 8 wt.% CeO_2.

Table 1
OSC values of the samples and reported in literatures[18–20]

Sample	Reduction temperature, °C	Measured temperature, °C	Oxygen storage,mmol/g	Reference
4 wt.% CeO_2-Cordierite	900	420	0.008	Present work
10 wt.% CeO_2-Cordierite			0.019	
20 wt.% CeO_2-Cordierite			0.023	
Plain CeO_2			0.56	
Pt/CeO_2	660–670	150	0.015–0.02	[18]
CeO_2 with high surface	1000	427	0.5–0.6	[19]
CeO_2 with low surface				
Pt/CeO_2/Al_2O_3 (fresh)	1000	500	0.3	[20]
Pt/CeO_2/Al_2O_3 (aged)			<0.125	

Moreover, the oxygen storage of the composites is less than that of Pt/CeO_2/Al_2O_3 and much smaller than that of pure CeO_2. The reason can be explained as follows. First, the content of CeO_2 in the composites is smaller than 20 wt.%, and only the parts distributed on the surface participate in the actions of adsorption–desorption. Second, since the smallest particle size of CeO_2 is about 100–200 nm, which is much larger than that of CeO_2 in the catalysts, this implies that the oxygen storage depends on the content, granularity of CeO_2 and the porosity of the composites.

From above analysis, the OSC of the composites are smaller than those of the catalysts. In fact, the catalytic coating contains a small amount of CeO_2 (usually less than 20 wt.%), and the mass of the ceramic support is much greater than that of the coating. As a whole, the total oxygen storage of the composite as a support is comparable with the one of CeO_2 in the catalytic coating. Therefore, we can say that, the OSC appended to the composite is satisfactory.

3.3. Porosity of composites

The variation of the porosity with CeO_2 content is shown in Fig. 3, it demonstrates that the sample with 4 wt.% of CeO_2 has the lowest porosity. While increasing the amount of CeO_2 up to 10 wt.%, the porosity increases to what the Ce^{4+}-free sample possesses. Compared with the surface morphologies of the samples shown in Figs. 2(a) and 4, the porosity corresponds to them very well. The reason affecting the porosity of the composites is proposed as follows.

Kim and Lee[21] reported that, proper addition of CeO_2 (2–4 wt.%) decreases the softening temperature of the cordierite glass phase, and strengthen its viscous flow, resulting in an increase in the density of the cordierite glass-ceramic, because the amorphous powders derived from the sol-gel method and the glass powders are identical in terms of the nature of the microstructure. In the present situation, the decrease of softening temperature of the amorphous phase containing 4 wt.% of CeO_2 can lead to an improvement on the density of the ceramic body as well. On the contrary, the amorphous phases containing higher amount of CeO_2 have higher softening temperatures, and prior to the viscous flow of the amorphous phases, a large amount of CeO_2 precipitate in the bodies. Consequently, the composites are prevented from high densification.

Fortunately, the composites with relatively high porosity are potentially suitable for catalytic supports, because large apparent porosity can make the CeO, particles locate on the surface as much as possible, enhancing the utility of the CeO_2 particles.

3.4. Mechanical and thermal properties of composites

3.4.1. Flexural strength

A moderate content of CeO_2 (4 wt.%) increases the flexural strength up to the highest as shown in Fig. 5. The flexural strength of the sample containing 10 wt.% of CeO_2 is slightly lower than that of the Ce^{4+}-free sample. The variation of flexural strength is just opposite to that of

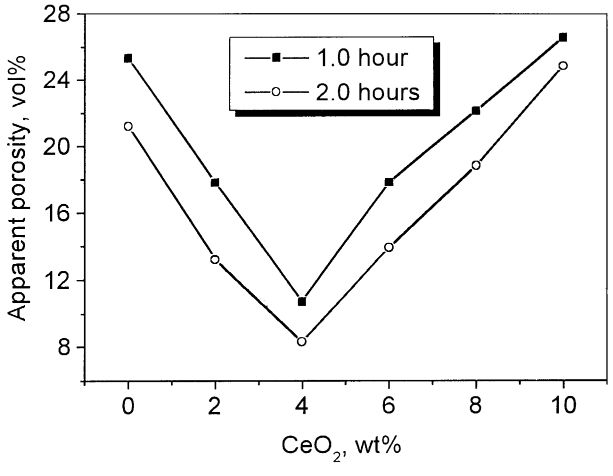
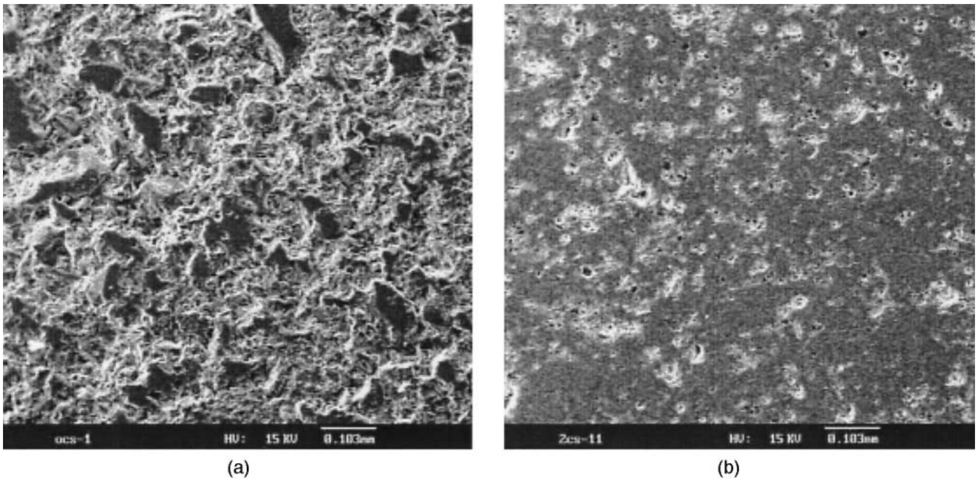


Fig. 3. Variation of apparent porosity of samples with CeO_2 contents.



(a) (b)

Fig. 4. Surface photographs of samples; (a) Ce^{4+} free, (b) 4 wt.% of CeO_2.

the apparent porosity. This indicates that the strength is mainly dependent on the porosity of the composites.

Actually, the strength of cordierite supports is not so high.[22] So, the porosity of the composites can further be increased to meet the demand for enhancing the utility of the CeO_2 particles.

3.4.2. Thermal expansion coefficient (TEC) of composites

The average TEC in the range of 20–800 °C are shown in Table 2. It is clear that CeO_2, increases the TEC of the composite. This is because CeO_2 has a higher TEC than that of cordierite.[23]

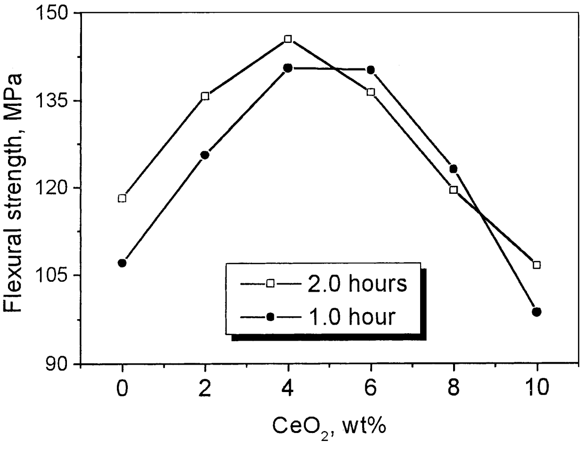


Fig. 5. Variation of flexural strength of composites with CeO_2 contents.

Table 2
TEC values of samples with different CeO_2 contents

CeO_2 content (wt.%)	Thermal expansion coefficient ($\times 10^{-6}$ / °C)
0	1.7
2	2.15
4	2.23
10	2.96

Even so, the TEC less than 3×10^6/°C is relatively low in the ceramic system.

4. Conclusions

The cordieirte–CeO_2 composite ceramics derived from the sol-gel route were characterized from the microstructure, oxygen storage capacity and other properties. Results show that, when sintered at 1200 °C, the composite ceramics consist of cordierite and CeO_2, whose amounts are dependent on the amount of Ce^{4+} added. Even the large CeO_2 particle is aggregated by small ones at about 100–200 nm. The particle size and content of CeO_2 affect the oxygen storage of the composites. With the increase of CeO_2, content, the TEC monotonously increases, and the flexural strength presents a variation of first an increase and then a decrease, while the apparent porosity presents an adverse variation to the former. Although the oxygen storage of the composite is smaller than those of CeO_2 in the catalysts, the total oxygen storage of the composite as the catalytic support will be comparable to the one of CeO_2 in the catalytic coating. The cordierite–ceria composite with 10 wt.% of CeO_2 possesses available OSC, suitable porosity, relatively high strength and low thermal expansion coefficients, accordingly it can be used as a catalytic support appended with oxygen storage capacity.

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