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Dynamic oxygen mobility and a new insight into the role of Zr atoms in three-way catalysts of Pt/CeO₂-ZrO₂

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The dynamic oxygen mobility and oxygen storage capacity (OSC) on three-model three-way catalysts of Pt/CeO₂-ZrO₂ (CZ-O, CZ-D and CZ-R) was characterized by the ¹⁸O/¹⁶O isotopic exchange (IE) reaction combined with CO oxidation. The measured oxygen surface and bulk diffusion coefficients, OSC, and oxygen release rates were correlated with XRD spectra, surface areas, metal dispersions and the other physical parameters. We found that the oxygen mobility was parallel to the structural homogeneity of Zr introduction into the CeO₂ framework, decreasing as CZ-R > CZ-D > CZ-O. The oxygen diffusion coefficients over CeO₂-ZrO₂ oxides hinted us that oxygen species are mobile in the oxide support. In addition to the contribution to the space effect, we proposed a new insight to the role of zirconium atoms as carriers for the oxygen transfer, although further investigation is necessary. These results showed that the combined IE reaction could be counted as a reliable technique for qualifying the oxygen mobility, the OSC and oxygen release rates, and is expected to be a direct probe into the nature of CeO₂-ZrO₂ oxygen storage materials and further development of more efficient oxygen storage materials.

Keywords: Oxygen mobility; Isotopic exchange (IE); Oxygen storage capacity; CO oxidation; Pt/CeO₂-ZrO₂ catalysts

1. Introduction

Automotive exhaust is regarded as a major source to the atmospheric pollution. Along with the more stringent environmental regulations imposed on the automobile industry, more efficient catalysts are necessary to detoxify the harmful exhaust, and increasing efforts are being investigated to optimize the efficiency of three-way catalysts. Oxygen storage materials used in three-way catalysts regulate the oxygen storage property through oxygen storage and release, which is regarded as the most important and remarkable feature of the three-way catalyst. A buffer between the lean-rich swings in exhaust gas composition during vehicle operation is achieved in order to keep a stoichiometric atmosphere, so that HC, CO and NO_x are efficiently converted [1,2]. Meanwhile, oxygen storage material can suppress the sintering of

supported noble metals and enhance the hydrogen formation under a reductive atmosphere. Therefore, work with oxygen storage material is an important approach to enhance the performance of an automotive catalyst.

Oxygen storage and release materials containing ceria in the automotive exhaust catalysts is a typical example of a workable concept for oxygen spillover in the creation of the storage system [3]. Oxygen storage capacity (OSC) is currently used as the key parameter for evaluating the performance of a certain oxygen storage material, and regarded as the most important indicator for the development of an oxygen storage material. Instead of the static or theoretical oxygen storage capacity, the dynamic oxygen mobility or oxygen diffusivity relates more closely with the efficient oxygen storage capacity and the oxygen storage/release rate, or the amount of the oxygen that could be actually stored and released during the transient period involved in the practical catalytic process. The oxygen mobility and oxygen storage capacity are both very critical parameters for the formulation of a real catalysts or making a new catalyst recipe. As a

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matter of fact, most published papers are concerned with the static oxygen storage capacity, while the dynamic oxygen mobility, especially the oxygen diffusivities on the surface and in the bulk of the oxides, has been scarcely investigated or discussed, more rarely on an in situ and dynamic base.

For studying the spillover of chemisorbed species, isotopic exchange reaction has been taken as a very useful technique. Hall and Lutinski [4] and Carter et al. [5] have studied the exchange of D₂ with the OH groups of Pt/Al₂O₃. A similar study over Rh/Al₂O₃ was reported by Cavanagh and Yates, who followed the H/D exchange by IR spectroscopy [6]. Quantitative measurements of surface diffusivities were carried out by Conner et al. [7,8] by means of a spatially resolved FTIR apparatus. In 1987, Duprez and coworkers developed a method of isotopic exchange for the study of surface mobility, and systematically studied the supported metal catalysts and some mixed oxides [9–13]. In our research, in order to establish a characterization method to quantify the oxygen mobility or spillover rates from the metal to the surface of the support and from the surface to the bulk, we applied ¹⁸O/¹⁶O isotopic exchange (IE) reaction technique onto three catalysts of Pt/CeO₂-ZrO₂, which have the same Ce/Zr ratio of 1:1 but different structures. One important modification we made was to combine CO oxidation reaction after the IE reaction, thus upgrading the previous IE reaction into a dynamic and in situ measurement of the oxygen spillover rates as well as the oxygen storage capacity and oxygen release rate. Through correlating the results obtained from this combined IE reaction with XRD and other physical parameters, we tried to reveal the relationship between the structure and the actual oxygen mobility, to gain deeper insight and understanding to the oxygen storage materials. The obtained results hopefully give us some hints for the actual catalyst formulation and maximize the efficient oxygen storage capacity of some certain oxygen storage material to the theoretical limit, thus to develop more efficient automotive three-way catalysts.

2. Experimental

2.1. Catalyst preparation

Three different types of CeO₂-ZrO₂ (CZ-O, CZ-D, and CZ-R) with the same Ce/Zr molar ratio of 1 were synthesized [14] and studied respectively. CZ-O was prepared by precipitation of Zr(OH)₄ on a fine ceria powder (ANA KASEI Co., Ltd., 99.9% purity, specific surface area of 120 m²/g) using hydrolysis of ZrO(NO₃)₂ with aqueous NH₃. The solid was dried at 90 °C and calcined at 500 °C for 5 h in air. CZ-R was prepared via the same procedure as the CZ-O, except that the oxide was first reduced at 1200 °C for 4 h by CO and then re-oxidized by at 500 °C for 3 h in air. CZ-D was prepared by the mechano-chemical reaction of CeO₂ and

ZrO₂ powder with high energy ball milling. Thereafter, Pt (1.0 wt.%) was supported by conventional impregnation using Pt (NH₃)₂(NO₂)₂ as platinum precursor and then calcinations at 500 °C for 3 h in air.

2.2. Characterization

The specific surface areas were measured by N₂ adsorption, one-point BET method on Micro Sorb 4232 II (Micro Data Co., Ltd.). Pt dispersion was analyzed by CO chemical adsorption in a flow-type adsorption apparatus using CO pulse gas (OHKURA RIKE R6015-S). Pt particle sizes and the grain sizes of CeO₂-ZrO₂ oxides were determined by Sherrer equation from XRD spectra (RINT2200, Rigaku Co., Ltd., with Cu Kα radiation).

2.3. Isotopic exchange reaction

The isotopic exchange reaction experiments were carried out in our recycle reactor (ca. 100 cm³) coupled to a mass spectrometer (ULVAC QMS), as shown in Fig. 1. The masses 32, 34, 36 (oxygen isotomers, ¹⁶O₂, ¹⁸O¹⁶O and ¹⁸O₂) plus mass 28 (to detect a possible leak) were continuously monitored. The vacuum connection to the mass spectrometer was thermo-regulated so as to maintain a constant pressure of 10⁻⁶ Torr, while the pressure in the reaction loop was 50 Torr. Under these conditions, the vacuum connection creates a negligible decrease of the total micro-reactor pressure (2 Torr for 4.0 h for an initial pressure of 50 Torr). Moreover, no gas-phase limiting diffusion was observed. The catalyst samples (ca. 30 mg) were put into a quartz reactor, and then submitted to an “in situ” pre-treatment. After a reduction under hydrogen during 15 min at 500 °C, an oxidation by normal oxygen for 60 min at 500 °C, and an evacuation at 500 °C for 1 h. The sample was cooled down to room temperature. A 50 Torr dose of pure ¹⁸O₂ (99.2% of ¹⁸O, ICON) was then introduced at the reaction temperature. The pressure variation of the oxygen

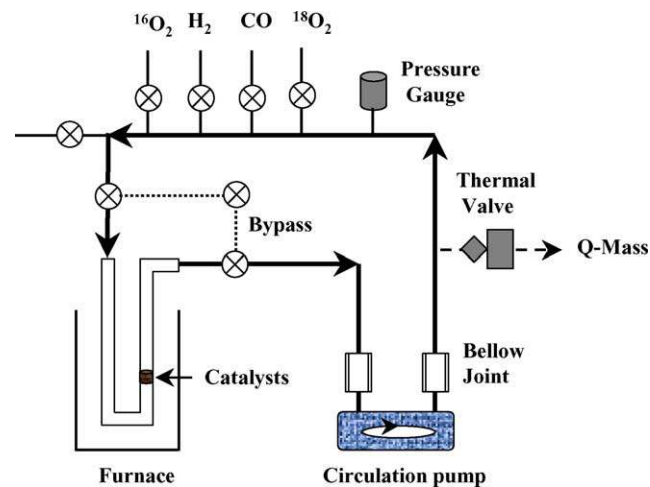


Fig. 1. Scheme of ¹⁶O/¹⁸O exchange reaction system.

isotopomers, P-36 ($^{18}\text{O}_2$), P-34 ($^{18}\text{O}^{16}\text{O}$), and P-32 ($^{16}\text{O}_2$) were continuously recorded at the temperature of reaction. The total pressure (P-36, P-34, and P-32) remained virtually constant.

2.4. Subsequent CO oxidation

Following the above isotopic exchange reaction, 22.5 Torr of pure CO was introduced into the reaction loop and then oxidation was conducted at 500 °C. The partial pressure variations of C^{16}O (P-28), $\text{C}^{16}\text{O}^{16}\text{O}$ (P-44) and $\text{C}^{16}\text{O}^{18}\text{O}$ (P-46) were continuously monitored until the reaction reached an equilibrium. The integration of C^{16}O_2 and $\text{C}^{16}\text{O}^{18}\text{O}$ was taken as OSC, and the oxygen release rates were derived from the resulting slopes of C^{16}O_2 and $\text{C}^{16}\text{O}^{18}\text{O}$.

3. Results and discussions

3.1. Structures of the CeO_2 - ZrO_2 supports

For the automotive exhaust catalyst, spillover has been developed into a workable concept instead of simply being used to explain a certain phenomenon. For a multi-component catalytic system, such as our metal supported automotive catalysts, to develop a spillover process, at least two distinct phases are needed, namely a donor of the spillover species and an acceptor for this species. These two phases can be in intimate proximity (co-gelled, co-precipitated or one phase impregnating the other) or even simply physically ad-mixed. The analysis and understanding of the structure and the closeness of different components or phases will be very beneficial to picture the spillover process and gain insight into the nature and the functioning of the involved components or materials of automotive catalyst.

Physical properties concerning our CeO_2 - ZrO_2 solids are listed in Table 1. From XRD patterns in Fig. 2, CZ-O was shown to be a mixture of a cubic CeO_2 phase and a tetragonal ZrO_2 phase. CZ-D and CZ-R were shown to be monophasic $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution with a cubic structure. After high-temperature reduction, CeO_2 - ZrO_2 oxide transforms into a pyrochlore-type $\text{Ce}_2\text{Zr}_2\text{O}_{7+\delta}$ phase with $\delta < 0.07$ [15]. In such a phase, Ce and Zr ions are distributed in an ordered arrangement. $\kappa\text{-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ was obtained by mild oxidation of the pyrochlore-type structure. In the last structure, Ce ions and Zr ions have similar arrangement to that

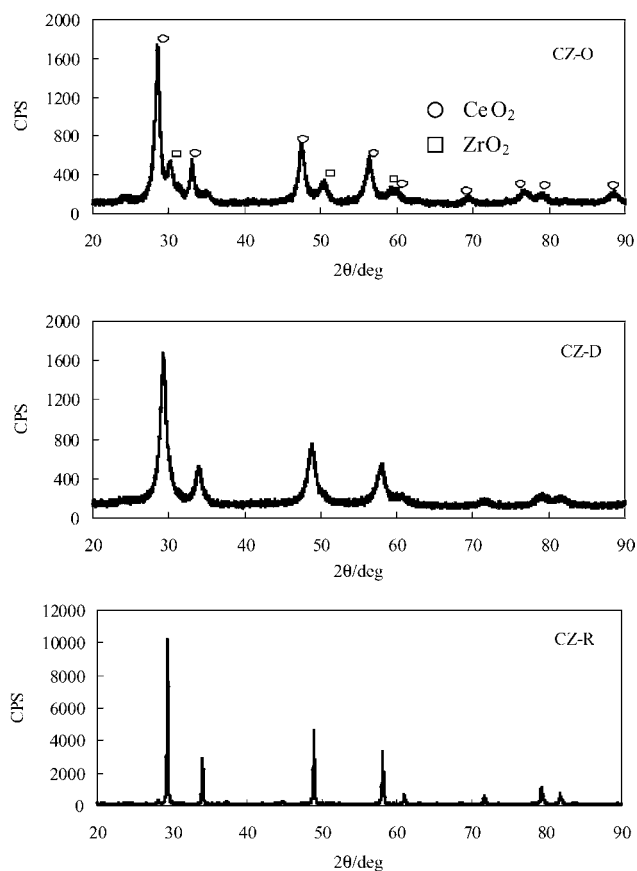


Fig. 2. XRD patterns of the three CeO_2 - ZrO_2 oxides.

of pyrochlore-type structure [15]. XRD pattern of CZ-R almost corresponds to $\kappa\text{-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$. This result indicates that Zr ions were homogeneously substituted in the CeO_2 lattice. CZ-D was also found to have a cubic phase structure. It shows that CZ solid may easily be prepared by high energy ball milling [16]. In the case of CZ-D, due to peak broadening, it is difficult to estimate how homogeneous Zr ions are introduced. Peak broadening could originate either from the small particle size or from a non-homogeneous solid solution. Ce/Zr atomic ratios were determined by EDX analysis during TEM observations [14], although the Ce/Zr ratio for CZ-R is almost constant at 1.0, but this ratio varies between 0.2 and 1.4 for CZ-D. This result means that the distribution of Zr ions into CeO_2 framework in CZ-D is not as homogeneous as in CZ-R. To summarize, the homogeneity of Zr introduction into the CeO_2 framework decreases as: CZ-R > CZ-D > CZ-O. Nagai et al. [17] have verified

Table 1
Summary of the three-model catalysts and their physical parameters

Catalysts	CeO_2 - ZrO_2 preparation	Surface area ($\text{m}^2 \text{g}^{-1}$)	Metal dispersion (%)	Metal particle size (nm)	Oxide grain size (nm)
1% Pt/CZ-O	Precipitation	104	23	5.2	10
1% Pt/CZ-R	HTR	3	2	59	200
1% Pt/CZ-D	Ball milling	37	59	2	20

HTR: high-temperature reduction at 1200 °C by CO.

the structures the three oxides by Ce K-edge and Zr K-edge X-ray absorption fine structure (XAFS).

3.2. Oxygen mobility measured by isotopic exchange reaction

As a matter of fact, CO oxidation method has been conventionally used to characterize the oxygen storage material [18], although it is just a kind of overall estimation of the oxygen storage capacity instead of the oxygen mobility. Considering the basics of the $^{18}\text{O}/^{16}\text{O}$ isotopic exchange reaction, the reaction process and route are the same as those of the oxygen in the exhaust on automotive catalysts. With the labeling function of isotopic oxygen of ^{18}O , the $^{18}\text{O}/^{16}\text{O}$ isotopic exchange reaction could be employed as a dynamic and in situ probe to characterize the oxygen mobility. Moreover, if one can erase the factors from the supported metal and support particle size, the isotopic exchange reaction could be used to access the nature of oxygen storage materials themselves, and for the surface and bulk oxygen diffusion.

The results obtained on Pt/CZ-D at 450°C were employed to exemplify the IE reaction. The partial pressure curves of three molecules evolved along with the exchange reaction was plotted in Fig. 3(A). At 450°C , the adsorption and decomposition of oxygen molecules on Pt metals would be the fast step, thus the diffusion of oxygen atoms to the top surface from the bulk of oxide would be the control step. The initial reaction region is referred to as Zone 1 corresponded with the surface diffusion, and the reaction region approaching equilibrium is referred to as Zone 2 ascribed to the bulk diffusion.

The contribution from the surface and from the bulk of the oxide to the actual oxygen storage and release during the transient period has been under argument and discussion for many years. The results from isotopic exchange reaction are believed to provide some quantitative evidence to clarify this issue. The derivation of the diffusion coefficients are a kind of opening of the black box, that is, to erase the influences caused by the supported noble metals, the size and the dispersions of metal particles, and the grain size of the support oxides [11]. IE reaction rates and oxygen diffusion coefficients at 410°C are listed in Table 2. The surface diffusion rate for CZ-R (R_c^0) is nearly four times larger than the bulk diffusion rate or the equilibrium IE rate (R_c^∞), while it is 3.8

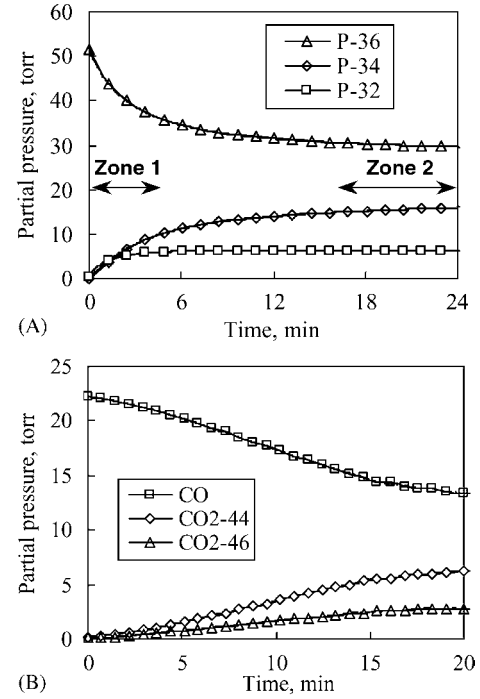


Fig. 3. (A) Partial pressure evolution along with IE reaction on Pt/CZ-D at 450°C . (B) Partial pressure evolution along with the subsequent CO oxidation (500°C) on Pt/CZ-D after IE reaction at 450°C .

times larger for CZ-D, and 26 times larger for CZ-O. These results indicated that the contribution from bulk could also be counted as an important part in the total oxygen storage and release performance. As listed in Table 2, the derived surface and bulk oxygen diffusion coefficients of CZ-R are apparently larger than those of CZ-D and CZ-O. The surface and bulk diffusion coefficients relate closely with the nature and the structure of the oxygen storage material. The quantitative evaluation of the diffusion coefficients is very important and useful, to estimate the oxygen storage and release performance, which are very crucial for making a new catalyst recipe and the catalyst formulation, especially for the transient period.

The initial reaction rate or surface diffusion rate for CZ-D seemed a little bit abnormal when correlated with the structures of three kinds of CZ oxides. The parameters of metal particles and the metal dispersion of CZ-D, and the homo-exchange reaction results could be used to clarify this

Table 2
Isotopic exchange reaction rates and oxygen diffusion coefficients at 410°C

Catalysts	Pt/CZ-R	Pt/CZ-D	Pt/CZ-O
Initial IE reaction rate, R_c^0 (atoms $\text{s}^{-1} \text{g}^{-1}$)	1.504×10^{18}	3.899×10^{17}	1.578×10^{18}
Equilibrium IE reaction rate, R_c^∞ (atoms $\text{s}^{-1} \text{g}^{-1}$)	3.55×10^{17}	1.029×10^{17}	5.73217×10^{16}
Surface diffusion coefficient, D_S^a ($\text{m}^2 \text{s}^{-1}$)	2.98×10^{-13}	1.48×10^{-18}	4.23×10^{-19}
Bulk diffusion coefficient, D_B^b ($\text{m}^2 \text{s}^{-1}$)	4.33×10^{-19}	1.20×10^{-20}	7.77×10^{-22}

^a D_S : surface diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), S: surface.

^b D_B : bulk diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), B: bulk.

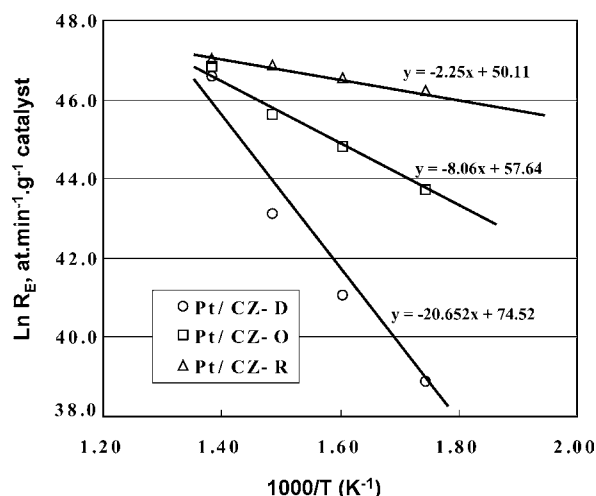


Fig. 4. Homo-exchange reaction on three-model three-way catalysts.

question. Homo-exchange reactions were conducted with the initial equal-mole ratio of ^{18}O and ^{16}O , being regarded to reveal the activity and the performance of the supported metals. The homo-exchange results on three CZ catalysts at different temperatures are shown in Fig. 4. The activation energies could be also derived from Arrhenius equation, as Pt/CZ-D (172.0 kJ/mol) > Pt/CZ-O (67.0 kJ/mol) > Pt/CZ-R (19.0 kJ/mol). If correlated with the metal particle sizes, we would find that the bigger metal particle favors homo-isotopic exchange reaction. The activation energy on Pt/CZ-D was the highest among the three catalysts. Compared with the other two catalysts, the oxygen adsorption and decomposition on Pt/CZ-D was somehow restricted, thus the initial reaction rate or surface diffusion rate for CZ-D is the smallest.

3.3. Dynamic oxygen storage/release performance and a new insight to the role of Zr atoms played in oxygen storage/release process

Following the above $^{18}\text{O}/^{16}\text{O}$ isotopic exchange reaction, CO was introduced into the system to conduct CO oxidation, as shown in Fig. 3(B). The oxygen storage capacity and the oxygen release rate were derived as shown in Fig. 5. It is well known that OSC and oxygen release rates are conventionally employed as the tools to evaluate the performance of oxygen storage materials. IE reaction is very useful to measure or characterize the oxygen mobility instead of the OSC. Through combining with CO oxidation, our designed IE system also enabled us to access the OSC performance. The obtained OSC and oxygen release rates on the three CZ materials were well matched with the results measured by TGA method [16,19], and are in good correspondence with the oxygen mobility and the structural homogeneity of Zr into the frame work of the oxides, as CZ-R > CZ-D > CZ-O (Table 3).

It is well known that the roles of noble metal and cerium played in the oxygen storage/release process are the pro-

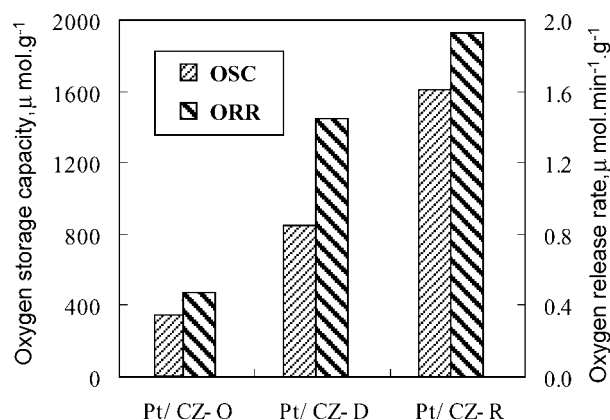


Fig. 5. OSC and ORR measured by subsequent CO oxidation at 510 °C.

Table 3
Measured oxygen diffusion coefficient in CeO_2 , ZrO_2 , and $\text{CeO}_2\text{-ZrO}_2$ oxides

Oxides	CeO_2	$\text{Ce}_{0.15}\text{Zr}_{0.85}\text{O}_2$	ZrO_2
Surface diffusion coefficient, D_s , at 300 °C ($\times 10^{-19} \text{ m}^2 \text{ s}^{-1}$)	21	33	2
Surface diffusion activation energy, E_a (kJ mol $^{-1}$)	41	39	49
Bulk diffusion coefficient, D_B , at 300 °C ($\times 10^{-23} \text{ m}^2 \text{ s}^{-1}$)	12	53	41
Bulk diffusion activation energy, E_a (kJ mol $^{-1}$)	15	10	14

moter and the oxygen storage material. What kind of role has been played by Zr? So far, Zr is conventionally regarded to contribute to the enlargement of the lattice space, thus facilitating the migration of oxygen atoms. In addition to the reported space effect, we propose the new insight or concept to the role of Zr, “carrier role”. That is, Zr in the frame work helps to “capture” oxygen atoms and “transfer” them to Ce atoms. Referring to the oxygen diffusion coefficients in $\text{CeO}_2\text{-ZrO}_2$ oxides based on the method of the isotopic exchange reaction, this is clearly indicated that surface diffusion coefficients on CeO_2 is much higher than on ZrO_2 , while it is smaller than ZrO_2 in the case of bulk diffusion. The $\text{CeO}_2\text{-ZrO}_2$ solid solution gives both a much higher surface and bulk diffusion coefficient. Moreover, we think, at higher temperatures, oxygen atoms are being shared by the whole oxide, instead of being fixed or restricted in some certain positions of the frame work. This assumption still needs to be verified by applying this isotopic exchange reaction technique to other oxides. The improvement of bulk diffusivity by addition of another component will be a meaningful approach for developing more efficient automotive three-way catalysts.

4. Conclusions

Through the combination with CO oxidation, $^{18}\text{O}/^{16}\text{O}$ isotopic exchange reaction had been upgraded to a compact

technique for quantifying the oxygen migration on the surface and in the bulk of the oxides, the efficient OSC and the oxygen release rate of the oxygen storage materials. The measured oxygen surface and bulk diffusivity, oxygen storage capacity and the oxygen release rates showed a good consistency with the homogeneity of the Zr distribution into the oxide framework, as CZ-R > CZ-D > CZ-O. The oxygen storage capacity at 500 °C was in a good match with those obtained by the conventional TGA method. Oxygen diffusion coefficients measured over CeO₂, ZrO₂ and CeO₂-ZrO₂ hinted to us an insight to the mechanism for the oxygen storage, where oxygen species are mobile in the oxide support. In addition to the contribution to the space effect, we proposed that zirconium atoms play a role as carriers for the oxygen transfer, although further investigation is needed. The oxygen diffusion coefficient relates closely to the nature of oxygen storage materials. This new insight into the oxygen storage mechanism is hopefully a valuable approach for the development of more efficient oxygen storage materials. We expect that this improved isotopic exchange can be used as a useful probe to access directly the oxygen spillover rate on the surface and in the bulk of the oxide, the dynamic oxygen storage capacity and oxygen release rate.

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