

Characterization of the dynamic oxygen migration over Pt/CeO₂-ZrO₂ catalysts by ¹⁸O/¹⁶O isotopic exchange reaction

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Abstract

To characterize the oxygen mobility over metal supported catalysts on a dynamic and in situ base, ¹⁸O/¹⁶O isotopic exchange reaction combined with CO oxidation was designed and exemplified on three kinds of three way catalysts of Pt/CeO₂-ZrO₂ (CZ-O, CZ-D and CZ-R). The obtained oxygen diffusion coefficients, oxygen release rate, and oxygen storage capacity were discussed and correlated with XRD spectra and other physical parameters. It was found that the oxygen mobility and oxygen storage capacity were parallel to the structural homogeneity of Zr introduction into the CeO₂ frame work, and decreased as: CZ-R > CZ-D > CZ-O. These results indicated that this combined isotopic exchange technique could be used to quantify the surface and bulk oxygen mobility, the oxygen storage capacity and oxygen release rate over the metal supported catalysts, and could be employed as a meaningful probe into the nature of CeO₂-ZrO₂ oxygen storage material. The oxygen mobility is also another important indicator for the development of oxygen storage materials.

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1. Introduction

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 oxygen storage system [1–5], oxygen storage capacity (OSC) is currently used as the key parameter for evaluating the performance of an oxygen storage material, and has been taken as the most important parameter for the development of an oxygen storage material. Besides the static oxygen storage capacity, the dynamic oxygen mobility or oxygen diffusivity plays a very important role on the efficient oxygen storage capacity and the oxygen storage/release rate, or the oxygen amount that could be actually stored and released during the transient period in the practical catalytic process. The oxygen mobility and oxygen storage capacity are both important parameters for the formulation of a real catalysts or making a new catalyst recipe. As a matter of fact, most published papers were concerned with the static

oxygen storage capacity, while the oxygen mobility, especially on the surface and in the bulk of the oxides, had been scarcely investigated and discussed, more rarely on an in situ and dynamic base.

For studying the spillover of chemisorbed species, isotopic exchange reaction had been taken as a useful technique. Hall and Lutinski [6] and Carter et al. [7] had 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 [8]. Quantitative measurements of surface diffusivities were carried out by Conner and co-workers [9,10] by means of a spatially-resolved FTIR apparatus. In 1987, Duprez and co-workers developed a method of isotopic exchange for the study of surface mobility [16–19], and systematically studied the supported metal catalysts and some mixed oxides [11–18]. In 2002, C.T. Au had conducted a qualitative study on the oxygen mobility over Ce_{0.6}Zr_{0.35}Y_{0.05}O₂ (CZY) – supported noble metal catalysts with oxygen isotopic exchange reaction [20].

In this 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

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surface to the bulk of the support, we applied $^{18}\text{O}/^{16}\text{O}$ isotopic exchange (IE) reaction technique onto three catalysts of $\text{Pt}/\text{CeO}_2\text{-ZrO}_2$, which have the same Ce/Zr ratio of 1:1 but a different structure. One improvement we made was to combine CO oxidation with the IE reaction, thus enabled the previous IE reaction technique to accomplish 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 IE reaction results with XRD and other physical parameters, we tried to reveal the relationship between the structure and the actual oxygen mobility, to gain a deeper insight and understanding to the oxygen storage materials. This hopefully give us some useful hints for the actual catalyst formulation and optimization of the efficient oxygen storage capacity of an oxygen storage material to its theoretical limit, thus to enhance the performance of the automotive three way catalysts.

2. Experimental

2.1. Catalyst preparation

In this research, three different types of $\text{CeO}_2\text{-ZrO}_2$ (CZ-O, CZ-D, and CZ-R) with the same Ce/Zr molar ratio of 1 were synthesized [29], respectively. CZ-O was prepared by precipitation of $\text{Zr}(\text{OH})_4$ on a fine ceria powder (ANA KASEI Co. Ltd., 99.9% purity, specific surface area of $120\text{ m}^2/\text{g}$) using hydrolysis of $\text{ZrO}(\text{NO}_3)_2$ with aqueous NH_3 . 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 at 500°C for 3 h in air. CZ-D was prepared by the mechano-chemical reaction of CeO_2 and ZrO_2 powder with high energy ball milling. Thereafter, Pt (1.0 wt.%) was supported by conventional

impregnation using $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ as platinum precursor and then calcined at 500°C for 3 h in air.

2.2. Characterization

The specific surface areas were measured by N_2 adsorption, one point BET method on Micro Sorb 4232II (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 $\text{CeO}_2\text{-ZrO}_2$ oxides were determined by Sherrer equation from XRD spectra (RINT2200, Rigaku Co. Ltd., with Cu $\text{K}\alpha$ radiation).

2.3. Isotopic exchange reaction

As shown in Fig. 1, the isotopic exchange reaction experiments were carried out in a re-circulated reactor (ca. 100 cm^3), which was coupled to a mass spectrometer (UL-VAC QMS). The vacuum connection to the mass spectrometer was thermo-regulated so as to maintain a constant pressure of 1.2×10^{-6} Torr, while the pressure in the reaction loop was 50 Torr. Under the experimental conditions, the vacuum connection produces a negligible decrease of the total micro-reactor pressure (1.0 Torr for 4.0 h at 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, first reduced under hydrogen atmosphere at 500°C for 20 min, and then oxidized under oxygen atmosphere at 500°C for 60 min. After the above pretreatment, evacuated the system for one hour with the sample at 500°C , and then cooled the sample down to the reaction temperature. IE reaction was started after a 50 Torr dose of pure $^{18}\text{O}_2$ (99.2% of ^{18}O , ICON) was introduced, and the whole system got stabilized. The masses of 32 ($^{16}\text{O}_2$), 34 ($^{18}\text{O}^{16}\text{O}$), 36 ($^{18}\text{O}_2$) and 28 (N_2 , to detect a possible leak) were continuously monitored by the mass spectrometer, thus,

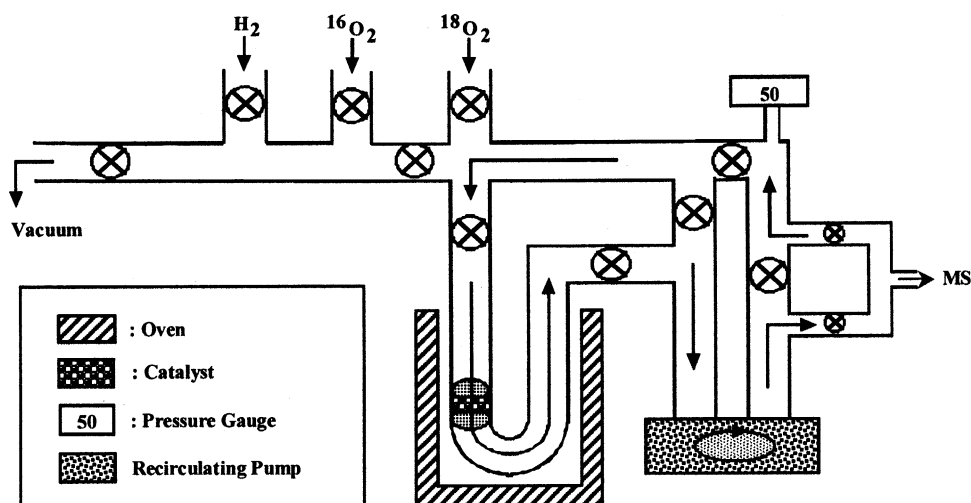


Fig. 1. Isotopic exchange reaction apparatus.

the partial pressure variation of the oxygen 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 isotopic exchange reaction, 22.5 Torr of pure CO was introduced into the reaction loop and then conducted CO oxidation 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 the produced C^{16}O_2 and $\text{C}^{16}\text{O}^{18}\text{O}$ was calculated as OSC, and the oxygen release rates were derived from the resulting slopes of C^{16}O_2 and $\text{C}^{16}\text{O}^{18}\text{O}$ with time.

3. Principle and mathematics

3.1. Mechanism with the isotopic exchange reaction

Boreskov and Novakova [20,21] classified three types of exchange reaction on the oxide surfaces. (1) The homo-exchange (or equilibration) occurs without any participation of the ^{16}O atoms of the oxide, and the isotopic oxygen fraction in the gas phase remains constant during the exchange reaction. (2) Simple hetero-exchange that occurs with the participation of only one oxygen atom of the oxide. (3) Multiple hetero-exchange that occurs with the participation of two oxygen atoms of the oxide. According to Winter's study over a great number of oxides [22], type 3 exchange is rarely encountered, and most oxides follow type 2 exchange. For the metal supported catalysts in this work, the isothermal isotopic exchange belongs to type 2 exchange, the simple hetero-exchange.

Measurements of surface mobility can be carried out by hetero-exchange on the metal-supported catalysts. The metal particles are regarded as portholes for ^{18}O atoms, acting as the donors of mono-atomic oxygen species. The mechanism with $^{18}\text{O}/^{16}\text{O}$ isotopic exchange reaction includes the following several steps: (1) $^{18}\text{O}_2$ molecules adsorb and dissociate on the metal particles; (2) ^{18}O atoms transfer from the metal to the support or spillover step; (3) ^{18}O atoms migrate on the top surface of the support and go further into the bulk of support; (4) ^{18}O atoms exchange with ^{16}O atoms of the support; (5) ^{16}O and ^{18}O atoms back-spillover and recombine to $^{16}\text{O}^{18}\text{O}$ or $^{16}\text{O}_2$ molecules, and desorb from the catalyst surface.

3.2. Reaction rate of the isotopic exchange

Under certain conditions, the coefficients of surface and of bulk oxygen diffusion could be quantified. The mathematical equations used to determine these parameters are discussed in this section.

The rate of exchange (R_E) is the first parameter which can be determined in the isothermal isotopic exchange reaction (ISIE). From the partial pressure values, we can first define the ^{18}O atomic fraction α_g^t in gas phase at each time t as:

$$\alpha_g^t = \frac{(1/2)P_{34}^t + P_{36}^t}{P_{36}^t + P_{34}^t + P_{32}^t} \quad (1)$$

The rate of exchange, R_E , equals to the rate of disappearance of ^{18}O from the gas phase, therefore it was possible to determine R_E by Eq. (2):

$$R_E = -N_g \frac{d\alpha_g^t}{dt} = N_s \frac{d\alpha_s^t}{dt} \quad (2)$$

where N_g and N_s are the total number of oxygen atoms in gas phase and the number of exchangeable oxygen atoms at the oxide surface, respectively. R_E (in atoms per square meter and per time unit) can be obtained by Eq. (3):

$$R_E = -\frac{N_A P_T}{SR} \left(\frac{V_r}{T_r} + \frac{V_c}{T_c} \right) \frac{d\alpha_g^t}{dt} \quad (3)$$

where N_A is the Avogadro's number, P_t the total pressure, S the oxide BET area (m^2), R the ideal gas constant, V_r and V_c the volumes of the heated and unheated zones of the reactor, respectively, and T_r and T_c the temperatures of the heated and unheated zones of the reactor, respectively.

3.3. Coefficients of oxygen surface and bulk diffusion

When the surface migration is the rate determining step of oxygen migration, the rate of exchange depends both upon the coefficient of surface diffusion (D_s) and the specific perimeter (I_o) of the particles are considered as circular sources of oxygen atom species. Previously used by Kramer and Andre [23], Cavanagh and Yates [8], and Duprez and Miloudi [24], the number of atoms diffused at the beginning of exchange reaction, N_e^t , would amount to:

$$N_e^t = 4NrC_{18\text{O}}\sqrt{\pi D_s t} \quad \text{with } I_o = N(2\pi r) \quad (4)$$

where C^{18}O , r , and I_o are the concentration of isotopic ^{18}O , the radius, and the circumference of the metal particles (N particles per m^2), respectively.

This model is applicable if the concentration of ^{18}O on the metal particles remains constant during the experiment. So in the case of isotopic exchange reaction, this model could only be used at the start of exchange reaction when ^{18}O concentration, C^{18}O , equals to the oxygen surface concentration on metal surface particles. Under these conditions, the coefficient of surface diffusion could be calculated by the following Eq. (5):

$$D_s = \left(\frac{\pi}{4} \right) \left(\frac{S_1}{C_{18\text{O}}^* I_o} \right)^2 \quad \text{with } S_1 = \frac{dN_e^t}{d\sqrt{t}} \quad (5)$$

where S_1 is the initial slope of the curve representing the variation of N_e^t as the function \sqrt{t} .

For the bulk oxygen diffusion phenomenon, we can determine the coefficient of oxygen bulk diffusion, D_B , according to Kakioka's model [25] as the following Eq. (6):

$$\ln(\alpha_g^t - \alpha_s^0) = -\frac{\rho S}{N_g} \sqrt{\frac{4D_B}{\pi}} \sqrt{t} + \ln(\alpha_g^\infty - \alpha_s^0) \quad (6)$$

where ρ and S are the density and the surface area of the sample, N_g is the total amount of oxygen atoms in gas phase, respectively, and α_g^t , α_g^0 , α_g^∞ are respectively, the atomic fractions of ^{18}O in gas phase at time t , in solid phase at time $t = 0$, and in gas phase at equilibrium.

The measurement of the final slope S_2 (when the surface is reaching the exchange equilibrium) of the curve representing $-\ln(\alpha_g^t - \alpha_s^0 / \alpha_g^\infty - \alpha_s^0)$ versus \sqrt{t} allows us to calculate the coefficient of bulk oxygen diffusion:

$$D_B = \left(\frac{\pi}{4}\right) \left(\frac{S_2 N_g}{\rho S}\right)^2 \quad (7)$$

4. Results and discussions

4.1. Structural characterization of CeO_2 - ZrO_2 oxides

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

The physical parameters with the CeO_2 - ZrO_2 solids are listed in Table 1. The XRD patterns shown as in Fig. 2 indicated that CZ-O is a mixture of a cubic CeO_2 phase and a tetragonal ZrO_2 phase, and CZ-D and CZ-R are the mono-phasic $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution with a cubic structure. Upon 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 $\delta < 0.07$ [27]. In such a phase, Ce and Zr ions are distributed

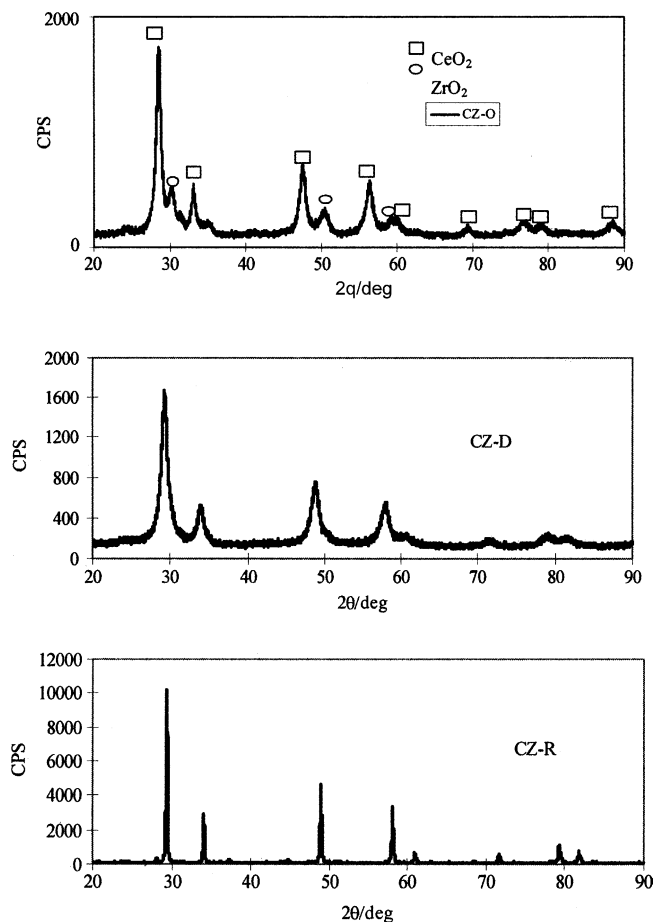


Fig. 2. XRD patterns of the three CeO_2 - ZrO_2 oxides.

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 that structure, Ce ions and Zr ions have similar arrangement to that of pyrochlore-type structure [26,27]. XRD pattern of CZ-R corresponds to $\kappa\text{-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$. This result indicates that Zr ions were homogeneously substituted in to 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 [28]. 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 measured by EDX analysis during TEM observations [29]. The Ce/Zr ratio for CZ-R was almost constant at 1.0, while this ratio varied between 0.2 and 1.4 for CZ-D. This result indicated that the distribution of Zr ions into CeO_2 framework in CZ-D was not as homogeneous as in CZ-R. To summarize, the homogeneity of Zr introduction into the CeO_2 framework decreased as: CZ-R > CZ-D > CZ-O. Nagai et al. [30] had also verified the structures of these 3 oxides by Ce K-edge and Zr K-edge X-ray absorption fine structure (XAFS).

Table 1
Physical parameters of the catalysts

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

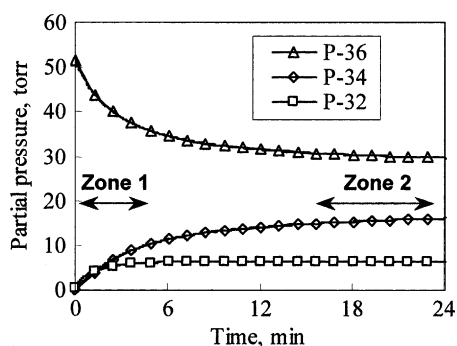


Fig. 3. Partial pressure evolution during IE reaction on CZ-R at 460 °C.

4.2. Isotopic exchange reaction rates and oxygen diffusion coefficients

As a matter of fact, CO oxidation method has been conventionally used to characterize the oxygen storage material [15], 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 , $^{18}\text{O}/^{16}\text{O}$ isotopic exchange reaction could be employed as a dynamic and in situ probe to characterize the oxygen mobility. Moreover, if one can erase the effect from the supported metal and the size of the support oxide, $^{18}\text{O}/^{16}\text{O}$ isotopic exchange reaction could be used to access the nature of oxygen storage materials themselves, the surface and bulk oxygen diffusion.

The partial pressure curves of three molecules evolved along with the exchange reaction were plotted as in Fig. 3. If we take the data obtained on Pt/CZ-R at the reaction temperature of 460 °C as an example, the adsorption and decomposition of oxygen molecules on Pt metals would be the fast step, or we could regard the diffusion of oxygen atoms to the top surface through the bulk of oxide would be the control step. This could be also verified by the homo-exchange results. The initial reaction region is referred as zone 1 corresponding to the surface diffusion, and the reaction region approaching equilibrium is referred as zone 2 ascribing to the bulk diffusion.

How much is the contribution of the surface and the bulk of the oxide to the total actual oxygen storage and release during the transient period has been under argument and dis-

cussion for many years. The results obtained from isotopic exchange reaction are believed to provide a quantitative evidence to clarify this issue. IE reaction rates and oxygen diffusion coefficients at 411 °C are listed in Table 2. The surface diffusion rate for CZ-R (R_E^0) is nearly four times larger than the bulk diffusion rate or the equilibrium IE rate (R_E^∞), while it is 3.8 times larger for CZ-D, and 26 times larger for CZ-O. These results implied that, the OSC contribution from the 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 derivation of the diffusion coefficients could be regarded as a kind of opening of the black box, that is, to take off the influences caused by the supported noble metals, the size and the dispersions of metal particles, and the grain size of the support oxides, that are included in the formula (4), (5), and (7). This quantitative evaluation of the diffusion coefficients is very important and useful for estimating the actual oxygen storage and release performance, and is also very crucial for making a new catalyst recipe and the catalyst formulation, especially for the transient period. Therefore, these coefficients could be counted as a very meaningful indicator for the further development of the oxygen storage materials.

If correlated the initial reaction rate or surface diffusion rate with the structures of three kinds of CZ oxides, the result for CZ-D seemed a little bit abnormal, that is, the surface diffusion seemed not parallel to the structure homogeneity. The metal particle size, the metal dispersion, and the homo-exchange reaction results on CZ-D are used to make this question clear. Homo-exchange reaction is conducted with the initial equal-mole ratio of $^{18}\text{O}_2$ and $^{16}\text{O}_2$, being regarded to reveal the activity and the property of the supported metals. The homo exchange results on three CZ catalysts at different temperatures are shown in Fig. 4. CZ-D has the highest metal dispersion and smallest metal particle size among the three catalysts. The homo-exchange results showed that, the activation energy is in the order of CZ-D (172 kJ/mol) > CZ-O (67 kJ/mol) > CZ-R (19 kJ/mol). It indicates that the oxygen adsorption and decomposition on Pt/CZ-D is somehow restricted, the oxygen on CZ-R is the most active among the three samples, and metal particle size is favorable for the homo-isotopic exchange reaction. Therefore, when compared with the other two catalysts, the initial exchange reaction rate or surface diffusion rate on

Table 2
IE reaction rates and oxygen diffusion coefficients at 411 °C

Catalysts	Pt/CZ-R	Pt/CZ-D	Pt/CZ-O
Initial IE reaction rate, R_E^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_E^∞ atoms ($\text{S}^{-1} \text{g}^{-1}$)	3.55×10^{17}	1.029×10^{17}	5.7321×10^{16}
Surface diffusion coefficient, D_s ($\text{m}^2 \text{S}^{-1}$)	2.98×10^{-13}	1.48×10^{-18}	4.23×10^{-19}
Bulk diffusion coefficient, D_B ($\text{m}^2 \text{S}^{-1}$)	4.33×10^{-19}	1.20×10^{-20}	7.77×10^{-22}

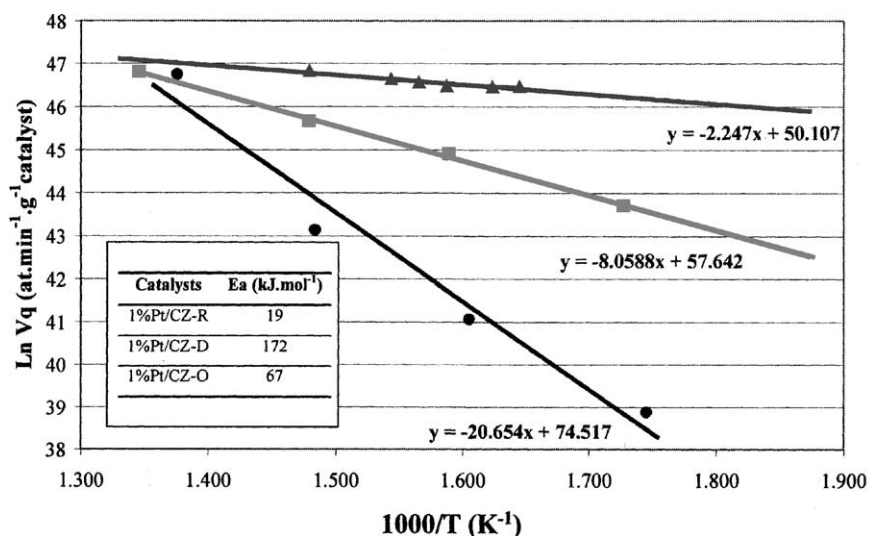


Fig. 4. Homo-exchange reaction on three catalysts.

CZ-D is the smallest. This is reasonable if take the physical parameters of the supported metal into consideration, although the surface diffusion coefficients are also closely related with the structure of the oxides, and parallel to the homogeneity of Zr introduction into the CeO₂ frame work.

4.3. OSC performance and the role of Zr

Following the ¹⁸O/¹⁶O isotopic exchange reaction, CO was introduced into the reaction system to conduct CO oxidation, as shown in Fig. 5. From the CO oxidation results, the oxygen storage capacity and the oxygen release rate were derived as shown in Figs. 6 and 7, respectively. It is well know that, OSC and oxygen release rates are the overall performance for the property of oxygen storage materials, which including the factors of the supported metal and oxygen storage material itself. IE reaction used in this research is initially to characterize the oxygen mobility. However, with the combination of the subsequent CO oxidation, the performance of oxygen storage/release could also be accessed.

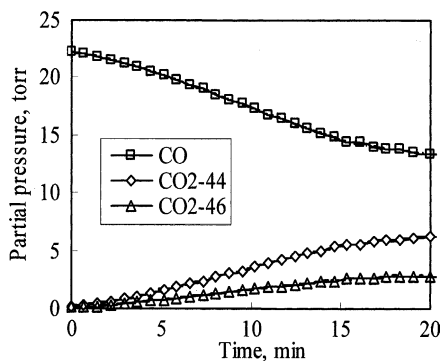


Fig. 5. Subsequent CO oxidation at 500 °C after IE reaction on CZ-R at 460 °C.

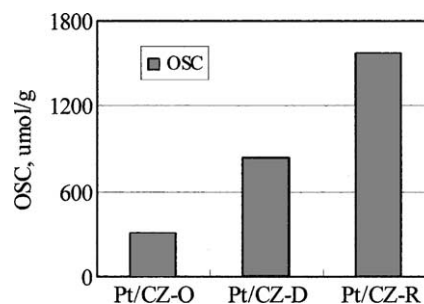


Fig. 6. Oxygen storage capacity (OSC) measured by subsequent CO oxidation at 500 °C.

Therefore, this combined IE reaction method is being a compact characterization technique, and is believed to be a very useful indicator for the development of a more efficient oxygen storage material. Moreover, the obtained OSC and oxygen release rates on the three CZ materials were well matched with the results measured by TGA method [28,31], and are in good agreement with the oxygen mobility and the structural homogeneity of Zr into the frame work of the oxides, as CZ-R > CZ-D > CZ-O. This verified the correct-

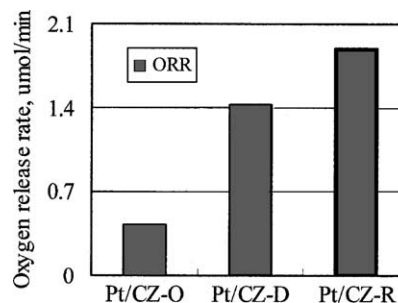


Fig. 7. Oxygen release rate (ORR) at 500 °C.

Table 3
Oxygen diffusion coefficient in CeO₂-ZrO₂ oxides

Oxides	CeO ₂	Ce _{0.15} Zr _{0.85} O ₂	ZrO ₂
D_s at 300°C (10^{-19} m ² s ⁻¹)	21	33	2
E_a (kJ/mol)	41	39	49
D_B at 300°C (10^{-23} m ² s ⁻¹)	12	53	41
E_a (kJ/mol)	15	10	14

ness and the reliability of this improved characterization method.

In the oxygen storage/release process, the roles of noble metal and cerium are commonly taken as the promoter and the oxygen storage material, however, what kind of role is played by Zirconium atoms? So far, Zirconium atoms are conventionally regarded to contribute to the enlargement of the lattice space, thus to facilitate the migration of oxygen atoms. In addition to the reported space effect, we propose a new insight or concept to the role of zirconium, “carrier role”. That is, zirconium atoms in the frame work help to “capture” oxygen atoms and “transfer” them to cerium atoms. Based on our isotopic exchange reaction, the oxygen diffusion coefficients of the pure CeO₂, Ce_{0.15}Zr_{0.85}O₂ oxide and the pure ZrO₂ were measured and listed in Table 3. The results clearly indicated that, the surface diffusion coefficient of CeO₂ is much higher than that of ZrO₂, while the bulk diffusion coefficient is smaller than that of ZrO₂ in the case of. The CeO₂-ZrO₂ 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 further investigation, such as applying it to other oxides with isotopic exchange reaction technique. The improvement of bulk diffusivity by addition of another component will be a novel and meaningful approach for the development of more efficient automotive three way catalysts.

5. Conclusions

Through the combination with CO oxidation, ¹⁸O/¹⁶O isotopic exchange reaction has been upgraded to a compact technique to enable a quantitative measurement of oxygen surface and bulk mobility, as well as the efficient OSC and the oxygen release rate on a dynamic and in situ base. The measured oxygen storage capacity was in good agreement with those obtained by the conventional TGA method. The oxygen diffusion coefficient closely relates to the structure of oxygen storage materials. The oxygen surface and bulk diffusivity, OSC efficiency and the oxygen release rates showed good consistency with the homogeneity of the Zr distribution into the oxide framework, as CZ-R > CZ-D > CZ-O. Oxygen diffusion coefficients measure on CeO₂, ZrO₂ and CeO₂-ZrO₂ hinted 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 propose that zirconium atoms play a role as carriers for the oxygen transfer. From all the above results, we can conclude that, our isotopic exchange system can be used as a very valuable characterization technique for the oxygen spillover rate both on the surface and in the bulk of the oxide, the dynamic oxygen release rate and OSC, and also a direct probe to access the nature of the oxygen storage material. The new insight into the oxygen storage mechanism is hopefully a meaning indicator for the further development of more efficient oxygen storage materials.

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