



Dynamic oxygen storage modeling in a three-way catalyst for natural gas engines: A dual-site and shrinking-core diffusion approach



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ABSTRACT

A dual-site oxygen storage model was developed to predict the dynamic oxygen storage on a Pd/Rh/CeZrO_x TWC catalyst. Two oxygen storage sites (surface and sub-surface) were used to describe two distinct regimes of the oxygen storage process. A shrinking core diffusion model was applied on the sub-surface site to predict slow oxygen storage and depletion. It is found that water gas shift and steam reforming reactions play significant roles in determining the oxygen storage capacity (OSC) and they were included in the model. A methodology of OSC measurement was designed to quantify the OSC with distinct reductants over a temperature window of 250 °C to 650 °C for model development. The amount of OSC with different reductants were compared. The reducibility of the reductants on OSC decreased in the order of H₂ > CO > CH₄. The amount of OSC showed a slight temperature dependency when using H₂, followed by CO and CH₄ in the temperature from 250 °C to 450 °C. However, similar amount of OSC was observed when the temperature was above 450 °C regardless of the reductants. With the dual-site OSC model, the dynamic oxygen storage capacities with various reductants could be correctly predicted.

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1. Introduction

1.1. Oxygen storage components in TWC

Three-way catalytic converter (TWC) has been widely and successfully utilized in stoichiometric gasoline and natural gas engines to control pollutants such as carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x) in the last decades [1,2]. It is well known that a TWC has a maximum conversion efficiency in a narrow window around stoichiometric air fuel ratio (AFR), where all the major pollutants can be simultaneously reduced. Maintaining the AFR around the stoichiometric condition is quite challenging. In real world operating conditions, deviation from the stoichiometric conditions (fuel cut and acceleration) were often encountered. Therefore, oxygen storage components (Cerium or Cerium and Zirconium solution) were introduced in the TWCs for effective AFR control. The main function of OSC is to act as an oxygen buffer to extend the operating window of the AFRs and help to curb emission breakthrough. With the aid of oxygen storage components, better performance can be achieved by dithering such that the AFR is targeting to a specific mean value rather than holding to that

value constantly. Also, CO and NO conversions can be enhanced when AFR switches between lean and rich exhaust composition [2,3]. The secondary benefits including promotion of the water gas shift (WGS) and steam reforming reactions, increasing the thermal stability of the support, improving precious metal dispersion, were extensively reviewed in the literature [4,5].

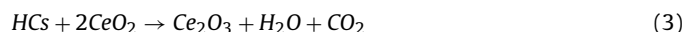
It is well established that the dynamic OSC is a result of reduction of ceria at rich and reoxidation of ceria at lean. A large number of studies on the reduction of CeO₂ have been collected by temperature programmed reduction (TPR) measurements on ceria containing materials [6–8] as well as ceria supported precious metals catalysts [7,9,10], which provide insights into temperature dependent interactions between reductants and CeO₂. These TPR studies indicated that there are multiple steps of ceria reduction depending on the catalyst temperature. For ceria supported precious metal catalysts, the reduction of ceria occurs firstly on the precious metal and ceria interface at low temperatures (~350 K) [7,11] and progressively takes place on the sub-surface at higher temperatures through migration of oxygen vacancies [12]. Bulk ceria reduction was observed at very high temperature (~1100 K) [7]. It was also found that the reducibility of the ceria is essentially determined by the textural and morphological properties of ceria [4,13]. For example, a higher reducibility of ceria was observed on the cubic structure ceria compared to the tetragonal and monoclinic ceria, which was attributed to a higher oxygen mobility on the cubic

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Nomenclature

A_i	Pre-exponential factor
E_i	Activation energy (kJ/mol)
θ_i	CeO ₂ coverage of the i^{th} site
$R_{i,surf}$	Reaction rate of specie i at the PGM/ceria surface site (mole/m ³ -s)
$R_{i,sub}$	Reaction rate of specie i at the sub-surface site (mole/m ³ -s)
C_i	Concentration of specie i (mole/m ³)
Ω_i	Site density of the i^{th} site (mole/m ³)
k_{if}	Reaction rate constant of the i^{th} forward reaction (m ³ /mole-s)
k_{ib}	Reaction rate constant of the i^{th} backward reaction (m ³ /mole-s)
$k_{i,eff}$	Effective reaction rate constant of the i^{th} reaction (m ³ /mole-s)
$K_{i,eq}$	Equilibrium constant of i^{th} reaction (–)
K_i	Adsorption equilibrium constants (–)
ΔG	Change of gibbs free energy (kJ/mol)
ΔH	Change of enthalpy formation (kJ/mol)
ΔS	Change of entropy formation (kJ/mole-K)
l_D	Diffusion rate scale (s/m)
d_p	Diameter of CeO ₂ particle (m)
D	Diffusion coefficient of oxygen from surface to sub-surface (m ² /s)
OS_t	Cumulative oxygen storage at time t (μ mole O/g catalyst)
SV	Space velocity at standard condition (1/s)
P	Ambient pressure (Pa)
R	Universal gas constant (J/mole-K)
T	Catalyst temperature (K)
m_{cat}	Mass of the catalyst (g)
V_{cat}	Volume of the catalyst (m ³)
r_t	Radius of total ceria particle (m)
r_s	Radius of sub-surface ceria particle (m)

structure [14]. Also, the degree of CeO₂ reduction at reducing conditions depends on the type of reductant and temperature. Eqs. (1)–(3) shows the OSC reduction reactions under reducing conditions using H₂, CO and HCs as reductants.



Under oxidizing conditions, oxygen is stored by filling up the oxygen deficient sites on the precious metal as well as the most active ceria surface. In the meantime, oxygen lattice on the surface ceria can diffuse into the sub-surface ceria and bulk ceria through intermediates O₂[–] (superoxide) and O₂^{2–} (peroxide) in the process of O₂ dissociation [15]. Diffusion can be a rate limiting factor of dynamic OSC in fast redox cycling experiments [6]. Eq. (4) shows the global reaction when O₂ is exposed to the reduced ceria under oxidizing conditions.



1.2. Modeling activities towards OSC

Since TWC catalyst performance is strongly correlated to the dynamic OSC, development of a dynamic OSC model is very crucial for modeling the TWC catalyst performance behaviors. There is a number of OSC models available in the literature, which include

simplified control-orientated models, global kinetic models as well as detailed microkinetic models. Brinkmeier et al. lumped oxygen storage and release into a single global reaction in the TWC model, which was able to predict the dynamic lambda signal of a commercial TWC [16]. Similarly, a control-orientated OSC model was developed by Kumar et al. [17] to simulate the oxygen storage in a TWC by lumping all the reducing species into one single representative specie. Koltsakis et al. is one of the pioneer researchers who first incorporated a global OSC model into TWC modeling in order to improve the model accuracy during transient conditions [18]. Later on, the OSC model was extended by considering H₂, CO and HCs as reducing species and O₂ and NO as oxidizing species [19]. This extended OSC model was extensively used in the modeling of TWC by many other researchers [20–22]. Surprisingly, most of the OSC models did not take into account of the effect of H₂O and CO₂, which were founded to be weaker oxidizers of Ce₂O₃ compared to O₂. Holder et al. incorporated the OSC reactions with H₂O and CO₂ independently in his model, however, thermodynamic consistency was not discussed [23]. Moller et al. [24] is probably the first researcher to systematically investigate the effects of H₂O and CO₂ on the OSC in TWCs through experiments and modeling. In his work, the effects of H₂O and CO₂ on OSC was experimentally observed and modeled, however, WGS reaction was not modeled independently but lumped into his OSC model. In most of detailed microkinetic TWC models [25–27], kinetics of oxygen storage and release on ceria were not included at all but lumped together with the kinetics of precious metals. Some microkinetic TWC models [28–30] were found to be able to predict the dynamic performance of TWC by incorporating an additional oxygen storage site beside the precious metal site. In normal operation of TWC, the single OSC site modeling approach was adequate to capture the TWC performance without taking into account of the slow oxygen storage due to oxygen lattice diffusion. However, in some circumstances such as fuel cut events, the oxygen storage can be significantly higher compared to the normal dithering due to the extra oxygen storage on the subsurface or in bulk ceria.

In the present study, a dynamic oxygen storage model was developed in a TWC for natural gas engines. Thermodynamically consistent kinetics were presented and discussed which take into account the effect of H₂O and CO₂. Model validations on the experimental OSC data collected on a tube flow reactor was discussed.

2. Experiments

2.1. Catalyst

The catalyst used in this study was a three way catalyst containing precious metals supported on ceria/zirconia (CeZrO_x). The catalytically active material was coated on a cordierite monolith with a cell density of 400 cells per square inch (cps) and wall thickness of 0.102 mm. The catalyst was de-greened by 5% O₂ in presence of 5% CO₂ and 5% H₂O at 650 °C for 1 h. No specific pretreatment was carried on the catalyst sample. Oxygen storage capacity (OSC) measurements were performed on the de-greened sample with a diameter of 1/4 inch and a length of 1 inch.

2.2. Methodologies of OSC measurements

A fix-bed quartz tube reactor system was used for the OSC measurements. All the simulated exhaust concentration were introduced by MKS mass flow controllers from three different gas banks. Lean gas bank consists of O₂ and N₂. Rich gas bank consists of different reductants, such as H₂, CO or CH₄. Common bank consists of CO₂ and H₂O. Helium was used as the carrier gas for all the other gases. A fast switching valve was used to switch

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