

Development of a crystallite scale model for oxygen storage and release dynamics in a three way catalyst

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Highlights

- Developed a crystallite scale model for automotive three way catalyst containing ceria
- Quantified effect of interfacial perimeter on storage and release kinetics
- Predicted oxygen storage and release by spillover, reverse spillover and direct storage
- Predicted oxygen storage capacity by temperature-dependent surface diffusivity

1. Introduction

The internal combustion engines operate under highly transient conditions, which causes a significant variation in the air-fuel ratio, thus affecting the performance of a three way catalyst (TWC). Ceria has been used extensively in TWCs to obtain high conversions of pollutants under transient conditions. This is due to the ability of ceria to store and release oxygen under lean conditions and rich conditions, respectively.

In this work, a crystallite scale model is developed and integrated into a monolith reactor model to explain the experimental data on the oxygen storage and release [1]. The surface reactions on Pd, interfacial reactions at the metal-ceria interface and the reactions involving gas phase species with ceria are considered in the model. The oxygen storage by spillover during lean conditions and its release during rich conditions by reverse spillover is predicted by the model. Simulations with various active metal dispersions are performed, which highlights the role of Pd-Ce interfacial perimeter in the kinetics of storage and release.

2. Methods

The experimental data was obtained from Gong et al. [1], who performed lean and rich cycling experiments over a three way catalyst containing precious metals supported on ceria/zirconia. They reported the oxygen storage capacity for various temperatures using CO as the reductant during the rich phase. Based on their experimental findings, a crystallite scale model is developed [2, 3]. One-dimensional radial diffusion of oxygen over ceria and the reaction of oxygen stored on ceria with the gas phase reductants is assumed to take place, which results in Equation (1), as follows:

$$\frac{\partial \theta_o}{\partial t} = \frac{D_o}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_o}{\partial r} \right) + \frac{1}{C_{ceria}^o} \sum_{m=1}^{N_{gs}} \vartheta_{o,m}^{Ce} R_{Ce,m} \quad R_C \leq r \leq R_{eff} \quad (1)$$

θ_o in Eq. (1) is the fractional coverage of stored oxygen at a particular radial position, D_o is the surface diffusivity of stored oxygen in the ceria phase, C_{ceria}^o is the surface concentration of the oxygen storage sites and N_{gs} is the total number of gas-solid reactions, i.e., the reactions involving the gas phase species and stored oxygen on ceria. $R_{Ce,m}$ represents the rate of the m^{th} reaction on the ceria surface, whereas $\vartheta_{o,m}^{Ce}$ represents the stoichiometric coefficient of oxygen in the m^{th} reaction on the surface. R_C is the radius of Pd crystallite and R_{eff} is the radius over which oxygen gets stored on the ceria phase. Continuity of flux of the diffusing species viz. oxygen is used to obtain the boundary condition at the Pd-ceria interface and is represented by Eq. (2), as follows:

$$-D_o \frac{\partial \theta_o}{\partial r} = \frac{1}{C_{ceria}^o} \sum_{m=1}^{\alpha} \vartheta_{o,m}^{Int} R_{Int,m} \quad \text{at } r = R_C \quad (2)$$

$R_{Int,m}$ in Eq. (2) represents the rate of the m^{th} reaction at the Pd-Ceria interface and $\vartheta_{o,m}^{Int}$ represents the stoichiometric coefficient of oxygen in the m^{th} reaction at the interface.

3. Results and discussion

The model equations were solved to simulate the cyclic operation of the TWC catalyst with lean and rich times of 60 s each. The lean phase contained 3% O₂ whereas the rich phase contained 2.5% CO at the inlet. 5% H₂O and 5% CO₂ at the inlet were common to both the phases. The time variation of the concentration of CO, O₂ and CO₂ at the outlet is shown in Figure 1. It is observed that the outlet concentration of O₂ did not reach its inlet concentration until 30 seconds into the lean phase. This phenomenon is due to the direct storage of oxygen on ceria and the spillover of oxygen through Pd-Ce interface towards ceria through surface diffusion. The former is represented by the 2nd term on the RHS of Eq. (1), whereas the latter is represented by Eq. (2). During the rich conditions, additional CO₂ formation occurs despite the absence of O₂ in the feed. This is due to the reverse spillover of stored oxygen from the ceria surface.

Temperature-dependent surface diffusivities were used to predict the oxygen storage and release behavior. The simulated values of cumulative oxygen storage capacity (OSC) for different surface diffusivities are plotted in Figure 2 along with the experimental data. It is observed that the model predicts the temporal trends of the oxygen storage behavior. It was also found that the kinetics of the reactions played a minor role in the predictions. Simulations were performed for various values of Pd dispersion and it was found that high dispersion resulted in a high interfacial perimeter. This resulted in an increased rate of spillover and reverse spillover and hence a faster storage and regeneration of the catalyst.

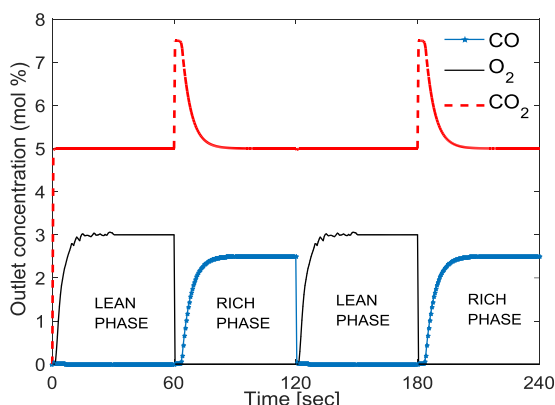


Figure 1. Mole fraction of CO, O₂ and CO₂ at the outlet of monolith reactor during cyclic conditions (Lean time = 60 s, Rich time = 60 s)

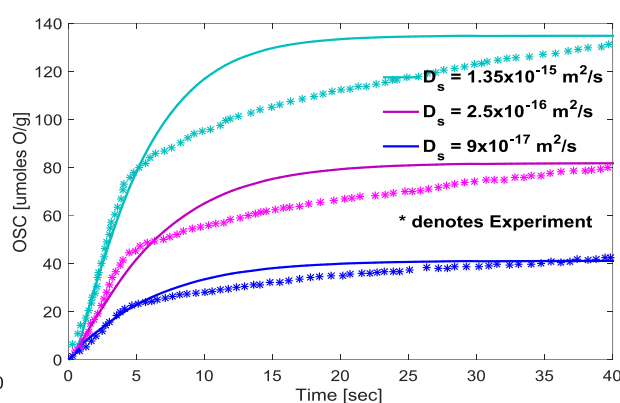


Figure 2. Comparison of the time variation of experimental and simulated oxygen storage capacities for various temperatures/surface diffusivity

Conclusions

A crystallite scale model is developed and integrated into a monolith reactor model to predict the storage and release of oxygen on a TWC catalyst containing ceria. The oxygen storage by spillover during lean conditions and its release during rich conditions by reverse spillover is predicted by the model. It is shown that the trends in the data can be explained by the temperature-dependent surface diffusivities, and the kinetics of the reactions may not play a major role. The contribution of various mechanisms of oxygen storage such as the surface reactions on Pd, interfacial reactions at the metal-ceria interface and the reactions involving gas phase species with ceria is quantified. It is shown that high dispersion results in high values of interfacial perimeter, which increases the role of spillover and reverse spillover during storage and reduction.

References

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Keywords

Crystallite scale model; Ceria; Spillover; Surface diffusion