A CRYSTALLITE SCALE APPROACH TO PREDICT OXYGEN STORAGE CAPACITY OF A CERIA-BASED THREE-WAY CATALYST

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Abstract

A crystallite-scale model is used to predict the oxidation and reduction of ceria in a three-way catalyst containing Pd as the catalytically active metal. The model is able to predict the spillover and reverse-spillover of oxygen between the Pd crystallite and ceria surface, and the resulting oxygen storage capacity (OSC). The model is incorporated into a reactor-scale model to predict the transient variation of H_2 concentration during periodic lean and rich cycling experiments as reported by Gong et al. (2017). The formation of CO with H_2 and CO_2 at the reactor inlet is predicted, which confirms the occurrence of reverse water gas shift reaction. It is also predicted that H_2 formation occurs due to the oxidation of ceria by H_2O, thus highlighting the importance of this reaction in kinetic modeling studies. A comparison of the model-predicted rate of spillover and the OSC is performed with H_2 and CH_4 as reductants.
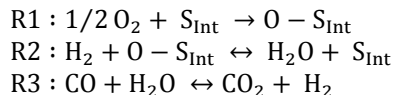
Introduction

A three-way catalyst results in the efficient conversion of CO, hydrocarbons, and NO_x simultaneously under stoichiometric conditions. To maintain stoichiometric conditions on the surface of a three-way catalyst, it is necessary to oxidize ceria in oxygen-deficient conditions and reduce ceria in oxygen-rich conditions. H_2 is an effective reductant for ceria as compared to other species such as CO and hydrocarbons. H_2 reduces the oxidized form of ceria (+4) by the reverse-spillover of oxygen towards the metal/ceria interface. On the other hand, ceria in its reduced state (+3) gets oxidized by the spillover of oxygen from the catalytically active metal through the metal/ceria interface.

Although the oxidation and reduction of ceria is incorporated in various kinetic models, the spillover aspect is not present explicitly. Recently, Gong et al. (2017) developed a model based on the shrinking core approach which considers the spillover and reverse-spillover of oxygen on the ceria surface. However, the effect of metal dispersion was not considered and a constant surface diffusivity was assumed for various temperatures. The crystallite-scale model developed in the present work incorporates the dependence of surface diffusion on the temperature, and the effect of metal/ceria interfacial contact on the rate of spillover and the resultant oxygen storage capacity. The model predictions are validated with the experimental data reported by Gong et al. (2017), who performed lean and rich cycling experiments with various reductants. Consistent with the experimental findings, the model predicts the difference in the reducibility of ceria and the resulting oxygen storage capacity with H_2 and CH_4.

Mathematical model

The surface diffusion of oxygen and its direct storage on the ceria surface is represented by Eq. (1) (Rajbala et al., 2018). The reactor scale model which also incorporates the crystallite scale features is given by Eq. (2). For the catalyst used in the present work, the active metal is Pd. The reactions occurring on the Pd surface, the interfacial reactions on the Pd/ceria interface, and the reactions on the ceria surface are included in the model. A global kinetic approach is used to predict the oxidation and reduction of ceria and is represented by reactions R1 and R2, respectively. The water gas shift reaction is represented by R3.

$R1 : 1/2\, O_2 + S_{Int} \rightarrow O - S_{Int}$
$R2 : H_2 + O - S_{Int} \leftrightarrow H_2O + S_{Int}$
$R3 : CO + H_2O \leftrightarrow CO_2 + H_2$

$$\frac{\partial \theta_{O,Ce}}{\partial t} = \frac{D_O}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \theta_{O,Ce}}{\partial r}\right) + \frac{1}{C_{Ce}^O}\sum_{m=1}^{N_{gs}}\vartheta_{O,m}^{Ce}R_{Ce,m} \quad (1)$$

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$$\frac{\partial x_{j,wc}}{\partial t} = \frac{1}{\varepsilon_{wc}(a+\delta_c)\delta_c}\left\{ak_{c,j}(x_{j,fm}-x_{j,wc})\right.$$
$$+\frac{\pi N_c}{4LC_{tm}}\left[2R_c\sum_{m=1}^{N_{int}}\vartheta_{j,m}^{Int}R_{Int,m}\right.$$
$$+\left(R_{eff}^2-R_c^2\right)\sum_{m=1}^{N_{gs}}\vartheta_{j,m}^{Ce}R_{Ce,m}^{avg}$$
$$\left.\left.+2R_c^2\sum_{m=1}^{N_{Pd}}\vartheta_{j,m}^{Pd}R_{Pd,m}\right]\right\} \qquad (2)$$

Results and discussion

The experimental conditions taken from Gong et al. (2017) were simulated in the present work. They performed lean and rich cycling experiments, the gas compositions of which are given in Table 1. The duration of the lean and rich periods was 60 s each. The crystallite-scale model was incorporated into the reactor-scale model and the resulting equations were solved to obtain the spatio-temporal profile of the concentration and surface coverage of various species. The model-predicted H_2 concentration is plotted in Figure 1 along with the experimental data. Lean phase starts at t=0 s whereas the rich phase starts at t=60 s. It is observed that the model predicts the experimental data quite well. The H_2 breakthrough occurs after 8 s of switching to the rich phase, which confirmed the reduction of ceria as per reaction R2. Further, it is observed that after the breakthrough, H_2 did not reach its inlet value of 2.5 % due to its participation in the reverse water gas shift reaction as per reaction R3.

Table 1. Feed gas composition in the lean and rich cycle

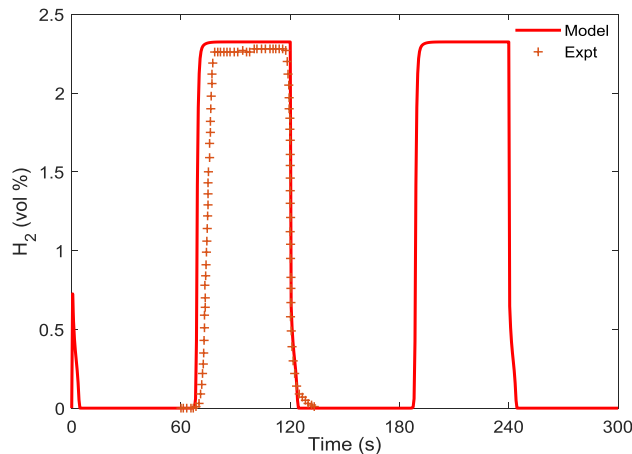|	CO(%)	O_2(%)	H_2(%)	CO_2(%)	H_2O(%)
Lean	0	3	0	5	5
Rich	0	0	2.5	5	5

Figure 1. Comparison of model-predicted and measured H_2 concentration during cycling experiments (T=400 °C).

The outlet concentration of various species such as CO, O_2, CO_2, and H_2O along with H_2 is plotted in Figure 2. In the lean cycle, the delay in the appearance of oxygen at the outlet denotes the storage of oxygen on the Pd surface. After the initial breakthrough, the time taken to reach the inlet O_2 concentration is due to its slow diffusion on the ceria surface. Upon switching to the rich cycle, the formation of CO and a decrease in CO_2 concentration indicates the occurrence of the reverse water gas shift reaction. Additionally, the presence of H_2 in the outlet stream for the initial few seconds of the lean phase and a corresponding decrease in the H_2O concentration shows the oxidation of ceria by H_2O as per the reverse of reaction R2.
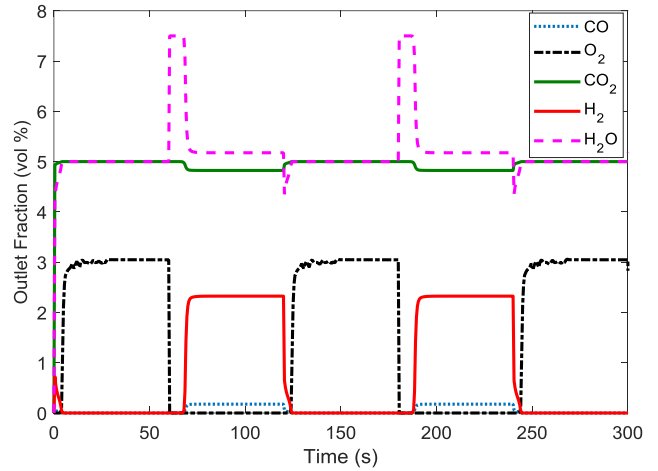

Figure 2. Model-predicted outlet fraction of CO, O_2, CO_2, H_2, and H_2O at the outlet of monolith reactor (T=400 °C).

Conclusions

A crystallite-scale model is developed to predict the spillover and reverse-spillover of oxygen on the surface of ceria during cyclic lean and rich conditions. In agreement with the reported data, the model predicts the temporal variation of the gas-phase concentrations. The dependence of surface diffusivity on the temperature is used to predict the effect of temperature on the oxygen storage capacity. The difference in the reducibility of ceria for different reductants viz., H_2 and CH_4, and the resulting difference in the oxygen storage capacity is predicted. It is shown that the reverse water gas shift reaction to produce CO as well as the oxidation of ceria by water to produce H_2 takes place over the catalyst surface.

References

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