

# Use of crystallite-scale features to predict the reactor-scale performance of a three-way catalyst

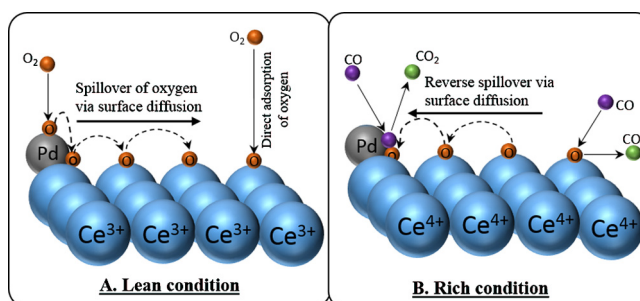
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## HIGHLIGHTS

- Predicted experimental data for a three-way catalyst using crystallite-scale features.
- Incorporated spillover, reverse spillover and direct storage of oxygen.
- Temperature-dependent surface diffusivity used to predict oxygen storage capacity.
- Quantified effect of metal-ceria interfacial perimeter on storage and release kinetics.
- Low values of OSC at low temperatures explained by incomplete catalyst regeneration.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A model incorporating the geometry features, transport, and reactions at the crystallite scale is developed to predict the features of a three-way catalyst during cyclic lean and rich conditions. The reactions on the metal crystallite, metal-ceria interface, and ceria surface are considered and the coupling between these reactions and the spillover processes is incorporated. The crystallite-scale model is integrated with the reactor-scale model to predict the experimental concentration profiles for CO oxidation. It is shown that the dependence of oxygen surface diffusivity on temperature can be used to predict the experimental data. It is quantitatively shown that in addition to the active surface area, the interfacial perimeter plays a key role in the spillover and reverse spillover processes. In agreement with the reported trends, the model predicts that the incomplete regeneration of the catalyst at low temperatures is responsible for the low values of oxygen storage capacity. A low but consistent evolution of CO<sub>2</sub> occurs for low dispersions in contrast to the high amount of CO<sub>2</sub> during the initial few seconds of the rich phase for a high dispersion catalyst. Fundamental insights obtained in the present work are expected to be applicable to other catalysts which involve the spillover effects. To the best of our knowledge, a model which incorporates the geometry features, transport phenomenon and reactions at the crystallite scale and its integration to predict the reactor-scale data under flow conditions for a three-way catalyst has not been reported elsewhere.

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## 1. Introduction

Three-way catalysts (TWCs) can result in a conversion efficiency of up to 95% for the three major pollutants, viz. carbon

monoxide, total hydrocarbons, and nitrogen oxides, when the catalytic converter operates under stoichiometric conditions (Schafer and Basshuysen, 1995). However, under the real driving conditions, the internal combustion engines are operated under highly transient conditions, which cause significant air-fuel ratio variations resulting in the inefficient performance of a TWC (Herz, 1981). Ceria has been used extensively in TWCs to minimize the

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## Nomenclature

$a$	channel width (m)	$R_{Pd,m}$	rate of $m^{\text{th}}$ reaction on the Pd surface (mol/m <sup>2</sup> Pd-s)
$A_{PF}$	atomic packing factor	$R_{\Omega 1}$	hydraulic radius (m)
$C_{ce}^o$	surface concentration of OSC sites (mol/m <sup>2</sup> )	$S_{Ce}$	vacant site on ceria surface
$C_{Pd}$	surface concentration of active Pd sites (mol/m <sup>2</sup> )	$S_{ceria}$	site density of ceria (molecules/m <sup>2</sup> )
$C_{tm}$	total gas concentration (mol/m <sup>3</sup> )	$S_{int}$	vacant site for oxygen adsorption on ceria at Pd-Ce interface
$d$	dispersion (%)	$S_p$	total active Pd area per channel (m <sup>2</sup> )
$D$	catalyst diameter (m)	$S_{Pd}$	vacant Pd site
$D_{Pd}$	diameter of a Pd atom (m)	$t$	time (s)
$D_S$	surface diffusivity of oxygen over ceria (m <sup>2</sup> /s)	$T_{std}$	standard temperature (K)
$GHSV$	gas hour space velocity (h <sup>-1</sup> )	$\bar{u}$	average fluid velocity (m/s)
$I_p$	total interfacial perimeter per channel (m)	$\chi_{j, fm}$	cup-mixing mole fraction of species 'j' in the fluid phase
$k_{c,j}$	external mass transfer coefficient for species j (m/s)	$\chi_{j, wc}$	mole fraction of species 'j' in the washcoat
$k_{i,f}$	rate constant for step 'i' (mol <sup>a</sup> m <sup>b</sup> s <sup>c</sup> )	$\chi_{O_2}^{in}$	inlet mole fraction of O <sub>2</sub>
$L$	monolith length (m)	$\chi_{O_2}^{out}$	outlet mole fraction of O <sub>2</sub>
$m_{cat}$	mass of catalyst (g)	$Z$	axial coordinate (m)
$n_{ch}$	number of monolith channels		
$N_{av}$	Avogadro number		
$N_c$	total number of crystallites per monolith channel		
$N_{Ce_2O_4}$	moles of Ce <sub>2</sub> O <sub>4</sub> (mol)		
$N_{Ce_2O_3}$	moles of Ce <sub>2</sub> O <sub>3</sub> (mol)		
$N_{gs}$	number of gas-solid reactions on the ceria surface		
$N_{Int}$	number of reactions occurring at the Pd-ceria interface		
$N_o$	maximum moles of oxygen stored during experiments (mol)		
$N_{Pd}$	number of reactions occurring on the Pd surface		
$N_{Pd,atom}$	total number of Pd atoms in a crystallite		
$N_{Pd,T}$	total number of moles of Pd in the washcoat per channel (mol)		
$O - S_{Ce}$	species representing oxygen storage on ceria surface		
$O - S_{int}$	species representing oxygen storage on ceria at Pd-Ce interface		
$O - S_{Pd}$	species representing oxygen storage on active metal Pd site		
$OS_t$	oxygen storage capacity (μmol/g)		
$P_{atm}$	atmospheric pressure (Pa)		
$r$	radial position of stored oxygen over ceria (m)		
$R$	universal gas constant (J/mol-K)		
$R_c$	radius of Pd crystallite (m)		
$R_{Ce,m}$	rate of the $m^{\text{th}}$ reaction on the ceria surface (mol/m <sup>2</sup> ceria-s)		
$R_{Ce,m}^{avg}$	average reaction rate over the ceria surface (mol/m <sup>2</sup> ceria-s)		
$R_{eff}$	radius of the region where oxygen can be stored (m)		
$R_{Int,m}$	rate of the $m^{\text{th}}$ reaction at the Pd-ceria interface (mol/m-s)		
		<b>Greek letters</b>	
		$\delta_c$	washcoat thickness (m)
		$\varepsilon_{wc}$	washcoat porosity
		$\nu_{o,m}^{Ce}$	stoichiometric coefficient of oxygen in the $m^{\text{th}}$ reaction on the ceria surface
		$\nu_{o,m}^{Int}$	stoichiometric coefficient of oxygen in the $m^{\text{th}}$ reaction at the interface
		$\nu_{j,m}^{Int}$	stoichiometric coefficient of species j in the $m^{\text{th}}$ reaction at the interface
		$\nu_{j,m}^{Ce}$	stoichiometric coefficient of species j in the $m^{\text{th}}$ reaction on the ceria surface
		$\nu_{j,m}^{Pd}$	stoichiometric coefficient of species j in the $m^{\text{th}}$ reaction on the Pd surface
		$\theta_{j,Pd}$	fractional coverage of surface species j on Pd surface
		$\theta_{v,Pd}$	fraction of vacant Pd sites
		$\theta_{O,Pd}$	fractional coverage of oxygen on Pd surface
		$\theta_{O,Ce}$	fractional coverage of oxygen on ceria
		$\theta_{Ce}$	fraction of vacant ceria sites
		$\theta_{Ce,Int}$	fraction of vacant ceria sites at the Pd/Ce interface
		$\theta_{O,Ce,Int}$	fractional coverage of oxygen on ceria at the Pd/Ce interface
		<b>Superscripts</b>	
		$in$	inlet conditions
		$o$	initial conditions

negative impacts of a variation in the air-fuel ratio by maintaining near stoichiometric conditions (Duprez et al., 2001; Gorte, 2010). This is due to the ability of ceria to store and release oxygen under lean conditions and rich conditions, respectively.

Several research groups performed kinetic modeling studies on the dynamic behavior of a TWC. Holmgren and Andersson (1998) reported experimental data on the amount of isotopic oxygen exchange on ceria-based catalysts and proposed a kinetic model which was able to explain their results. They considered two types of mechanisms for ceria reduction: the fast reduction due to the presence of Pt and the slow reduction in the absence of Pt. They also reported that the rate of exchange increased with an increase in the temperature. The dynamic storage and release of oxygen due to the redox property of ceria was studied by Koltzakis and Stamatielos (1999). Using modeling studies, they showed that the rate of storage is higher than the rate of regeneration.

Rajasree et al. (2004) considered the Fick's second law of diffusion to show that the diffusion of oxygen had a significant role

in the activity of a three-way catalyst. They reported that the formation of CO<sub>2</sub> could take place in the absence of gaseous O<sub>2</sub>, thus highlighting the role of diffusion of oxygen from ceria. Galdikas et al. (2007) modeled the exchange of gas-phase oxygen and oxygen stored in ceria. They also calculated the diffusion coefficients for various temperatures and the activation energy for surface diffusion of oxygen over ceria. In most of the models reported in the literature, a set of reactions related to the oxygen storage and release are assumed and the parameter values are estimated by fitting of the data to the experiments. Even though some of the studies discussed the differing rates of oxygen storage and release depending on their proximity to the active metal, a detailed quantitative analysis has not been reported (Christou and Efstathiou, 2007). Moreover, even though independent studies on the surface diffusion of oxygen on ceria have been done, their integration into a reactor-scale model and explaining the reactor data has not been performed (Galdikas et al., 2004a; Galdikas et al., 2004b).

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