CRYSTALLITE-SCALE MODEL TO PREDICT THE REACTOR-SCALE PERFORMANCE OF SPILLOVER-EXHIBITING AUTOMOTIVE CATALYSTS

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by

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Certificate

This is to certify that the thesis entitled "**Crystallite-scale model to predict the reactor-scale performance of spillover-exhibiting automotive catalysts**" being submitted by **Rajbala** to the Indian Institute of Technology Delhi for the fulfillment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering is a record of bonafide research work carried out by her. She has worked under my supervision and has fulfilled the requirements, which to my knowledge, have reached the requisite standards for the submission of the thesis. The research report and the results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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Abstract

A model incorporating the geometry features, transport, and reactions at the crystallite scale is developed to predict the oxygen storage capacity (OSC) of a Pd-containing three-way catalyst (TWC) during cyclic lean and rich conditions. The reactions on the metal crystallites, metal-ceria interface, and the ceria surface are considered and the coupling between these reactions and the spillover processes is incorporated. The crystallite-scale model is integrated with a monolith reactor model to predict the experimental data of OSC at various temperatures. The dependence of oxygen surface diffusivity on the temperature is used to predict the reported variation of OSC with temperature. 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 TWC at low temperatures is responsible for the low values of OSC. The model predicts the effect of Pd crystallite size, Pd-ceria interfacial contact, and Pd dispersion on the spillover and reverse-spillover of oxygen between Pd and ceria, with CO, H_2, and CH_4 as reductants. Consistent with the experimental findings, the model predicts that H_2 results in a higher OSC than CO and CH_4. The effective surface diffusivity with H_2 is estimated to be higher than that with CO and CH_4, which is attributed to the possible spillover of hydrogen in addition to the reverse-spillover of oxygen.

The extent of hydrogen spillover on two different Pd-based catalysts supported on mesoporous SBA-15 and MCM-41 is quantitatively predicted using a crystallite-scale model, which considers the effect of size and location of crystallites, metal-support interfacial contact, and diffusivity of the adsorbed species on the support surface. The developed model, in combination with a fixed-bed reactor model predicts that in the absence of any reductant in the feed, the NO conversion is higher (=37%) on the SBA-15 supported catalyst as compared to 25% on MCM-41, which is consistent with the reported data in the literature. The difference in

the catalytic activity is ascribed to the different spillover rates of hydrogen on SBA-15 and MCM-41, which is further correlated to the fraction of Pd crystallites present in the support channels. The model is also used to study the effect of cycle time, H_2 concentration, Pd dispersion, and Pd loading on NO reduction under cyclic conditions. Consistent with the literature findings, the model predicts that the Pd surface area and the metal-support interfacial contact increase with an increase in the Pd loading and dispersion, which result in higher spillover and hence increase the NO conversion.

The fundamental insights obtained in the present work are expected to be applicable to other catalytic systems which involve the spillover effects. One such catalyst is a lean NO_x trap which involves spillover of NO_x and/or hydrogen whereas other applications include TWCs for gasoline as the fuel.

सार

क्रिस्टलीय पैमाने पर ज्यामिति सुविधाओं, परिवहन और प्रतिक्रियाओं को शामिल करने वाला एक मॉडल चक्रीय लीन और रिच स्थितियों के दौरान एक Pd-युक्त तीन-तरफा उत्प्रेरक (TWC) की ऑक्सीजन भंडारण क्षमता (OSC) की भविष्यवाणी करने के लिए विकसित किया गया है। धातु क्रिस्टलीय, धातु-सीरिया इंटरफ़ेस, और सीरिया सतह पर प्रतिक्रियाओं को माना गया है, और इन प्रतिक्रियाओं और स्पिलओवर प्रक्रियाओं के बीच युग्मन को शामिल किया गया है। विभिन्न तापमानों पर OSC के प्रायोगिक आंकड़ों की भविष्यवाणी करने के लिए क्रिस्टलीय / क्रिस्टल लाइट - स्केल मॉडल को एक मोनोलिथ रिएक्टर मॉडल के साथ एकीकृत किया गया है।

तापमान के साथ OSC की रिपोर्ट की गई भिन्नता का अनुमान लगाने के लिए तापमान पर ऑक्सीजन की सतह के प्रसार की निर्भरता का उपयोग किया गया है। यह मात्रात्मक रूप से दिखाया गया है कि सक्रिय सतह क्षेत्र के अलावा, इंटरफेसियल परिधि स्पिलओवर और रिवर्स स्पिलओवर प्रक्रियाओं में एक महत्वपूर्ण भूमिका निभाती है। रिपोर्ट किए गए रुझानों के साथ, मॉडल भविष्यवाणी करता है कि कम तापमान पर TWC का अपूर्ण पुनर्जनन OSC के कम मूल्यों के लिए जिम्मेदार है। मॉडल Pd क्रिस्टलीय आकार, Pd- सीरिया इंटरफेसियल संपर्क, और Pd फैलाव और Pd और सेरिया के बीच ऑक्सीजन के रिवर्स-स्पिलओवर पर CO, H_2 और CH_4 के साथ रीडक्टटैंट के रूप में प्रभाव की भविष्यवाणी करता है। प्रयोगात्मक निष्कर्षों के अनुरूप, मॉडल भविष्यवाणी करता है कि H_2 का परिणाम CO और CH_4 की तुलना में अधिक OSC है। H_2 के साथ प्रभावी सतह विवर्तनशीलता CO और CH_4 के साथ की तुलना में अधिक होने का अनुमान है, जो ऑक्सीजन के रिवर्स-स्पिलओवर के अलावा हाइड्रोजन के संभावित स्पिलओवर के लिए जिम्मेदार है।

मेसोपोरस एसबीए - १५ और एमसीएम -४१ पर समर्थित दो अलग-अलग Pd-आधारित उत्प्रेरकों पर हाइड्रोजन स्पिलओवर की मात्रा एक क्रिस्टलीय-स्केल मॉडल का उपयोग करके मात्रात्मक रूप से भविष्यवाणी की जाती है, जिसमे क्रिस्टलीट के आकार और स्थान के प्रभाव, धातु-समर्थन इंटरफेसियल संपर्क और समर्थन सतह पर अड़सोरबड प्रजातियों के प्रसार माना गया है। वर्तमान मॉडल, एक फिक्स्ड-बेड रिएक्टर मॉडल के साथ संयोजन में भविष्यवाणी करता है कि फ़ीड में किसी भी रिडक्टेंट की अनुपस्थिति में, एसबीए-१५ समर्थित उत्प्रेरक पर NO रूपांतरण अधिक (=३७%) और एमसीएम - ४१ पर कम (=२५ %) है। यह साहित्य में रिपोर्ट किए गए डेटा के अनुरूप है। उत्प्रेरक गतिविधि में अंतर एसबीए - १५ और एमसीएम - ४१ पर हाइड्रोजन के अलग-अलग स्पिलओवर दरों पर अंकित है, जो कि समर्थन चैनलों में मौजूद Pd क्रिस्टलीट्स के अंश से संबंधित है। मॉडल का उपयोग चक्र के समय, H_2 एकाग्रता, Pd फैलाव, और चक्रीय परिस्थितियों में Pd लोडिंग का NO रीडक्टशन पर होनेवाले प्रभाव का अध्ययन करने के लिए भी किया जाता है। साहित्य के निष्कर्षों के अनुरूप, मॉडल भविष्यवाणी करता है कि Pd सतह क्षेत्र और धातु-समर्थन इंटरफेसियल संपर्क Pd लोडिंग और फैलाव में वृद्धि के साथ बढ़ता है, जिसके परिणामस्वरूप उच्च स्पिलओवर होता है और इसलिए NO रूपांतरण में वृद्धि होती है।

वर्तमान कार्य में प्राप्त मौलिक अंतर्दृष्टि अन्य उत्प्रेरक प्रणालियों पर लागू होने की उम्मीद है जिसमें स्पिलओवर प्रभाव शामिल है। ऐसा एक उत्प्रेरक एक लीन NOx ट्रैप है जिसमें NOx और / या हाइड्रोजन का स्पिलओवर शामिल है जबकि अन्य अनुप्रयोगों में ईंधन के रूप में गैसोलीन के लिए TWCs शामिल हैं।

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Nomenclature

a	channel width (m)
A_b	cross-sectional area of the catalyst bed (m^2)
A_P	area of catalyst particle (m^2)
A_{PF}	atomic packing factor
C_{ce}^o	surface concentration of ceria sites (mol/m^2)
C_S^o	surface concentration of support sites (mol/m^2)
C_{Pd}	surface concentration of active Pd sites (mol/m^2)
C_{tm}	total gas concentration (mol/m^3)
d	dispersion (%)
D	catalyst diameter (m)
D_{Pd}	diameter of a Pd atom (m)
$D_{O,S}$	surface diffusivity of oxygen on ceria surface (m^2/s)
D_o	pre-exponential factor for calculating surface diffusivity of oxygen on ceria (m^2/s)
$D_{H,S}$	surface diffusivity of hydrogen on support surface (m^2/s)
D_j	diffusivity of species ‘j’ in gas phase (m^2/s)
D_P	diameter of catalyst particle (m)
E_s	activation energy for surface diffusion of oxygen on ceria (kJ/mol)
f_{PdIn}	fraction of Pd crystallites present inside the support channels
f_{PdOut}	fraction of Pd crystallites present outside the support channels
GHSV	gas hour space velocity (h^{-1})
$H - S_k$	hydrogen adsorbed on site k (k = Pd, Pd-support interface)
I_P	total interfacial perimeter per channel (m)

$k_{c,j}$	external mass-transfer coefficient for gaseous species ‘j’ (m/s)
$k_{m,Ce}$	kinetic rate constant for reaction ‘m’ occurring on ceria surface $(mol/m^2.s)$
$k_{m,Pd}$	kinetic rate constant for reaction ‘m’ occurring on Pd surface $(mol/m^2.s)$
$k_{m,Int}$	kinetic rate constant for reaction ‘m’ occurring at Pd-support interface $(mol/m.s)$
L	monolith length (m)
L_b	length of fixed bed reactor (m)
L_{Pd}	palladium loading (wt %)
m_{cat}	mass of catalyst (g)
$M_{w,Pd}$	molar mass of Pd (g/mol)
N_o	maximum moles of oxygen stored during experiments (mol)
N_{Av}	Avogadro number
n_{ch}	number of channels in monolith reactor
N_c	total number of crystallites per monolith channel
$N_{Ce_2O_4}$	moles of Ce_2O_4 (mol)
$N_{Ce_2O_3}$	moles of Ce_2O_3 (mol)
$N_{Pd,atom}$	total number of Pd atoms in a crystallite
N_{Ce}	number of gas-solid reactions on the ceria surface
N_{Int}	number of reactions occurring on the support at the Pd-support interface
N_{Pd}	number of reactions occurring on the Pd surface
$N_{Pd,T}$	total number of moles of Pd in the washcoat per channel (mol)
$N_{H,m}$	maximum moles of hydrogen stored on the support surface
$N_{H,S}$	number of moles of hydrogen on the support surface
$N_{O,Pd}$	number of moles of oxygen adsorbed on Pd surface

$N_{O,Ce}$	number of moles of oxygen adsorbed on ceria surface
$N_{P,vol}$	number of catalyst particles per unit volume of fixed bed reactor (m^{-3})
OSC	oxygen storage capacity (μmol/g)
$O - S_k$	oxygen adsorbed on site k (k = Pd, ceria, and Pd-ceria interface)
P_{atm}	atmospheric pressure (Pa)
r	radial coordinate on support surface (m)
r^*	dimensionless radial coordinate
R	ideal gas constant (J/mol.K)
Re_j	Reynolds number for gaseous species 'j'
R_c	radius of a Pd crystallite (m)
R_{eff}	radius of the region where oxygen/hydrogen can be stored (m)
$R_{m,Ce}$	rate of the m^{th} reaction on the ceria surface ($mol/m^2\ ceria.s$)
$R_{m,Int}$	rate of the m^{th} reaction at the Pd-support interface ($mol/m.s$)
$R_{m,Pd}$	rate of m^{th} reaction on the Pd surface ($mol/m^2\ Pd.s$)
$R_{m,Ce}^{avg}$	average rate of m^{th} reaction on the ceria surface ($mol/m^2\ ceria.s$)
$R_{\Omega 1}$	hydraulic radius (m)
$R_{m,PdIn}$	rate of m^{th} reaction occurring on the Pd crystallites present inside the channel ($mol/m^2.s$)
$R_{m,PdOut}$	rate of m^{th} reaction occurring on the Pd crystallites present outside the channel ($mol/m^2.s$)
Sc_j	Schmidt number for gaseous species 'j'
S_{Ce}	vacant site on ceria surface
Sh_j	Sherwood number for gaseous species 'j'
S_{Int}	support site for hydrogen/oxygen adsorption at the Pd-support interface

S_{Pd}	vacant site on Pd surface
S_P	total active Pd area per channel (m^2)
t	time (s)
τ_d	diffusion time (s)
τ_c	residence time (s)
τ_r	reaction time (s)
$\tau_{r,OInt}$	characteristic reaction time for consumption of oxygen at interface (s)
$\tau_{r,OPd}$	characteristic reaction time for consumption of oxygen on Pd surface (s)
$\tau_{r,OCe}$	characteristic reaction time for consumption of oxygen on ceria surface (s)
T	solid temperature (K)
T_{std}	standard temperature (K)
$\bar{u}$	average fluid velocity (m/s)
u_s	superficial velocity (m/s)
$X_{j,fm}$	cup-mixing mole fraction of species 'j' in the fluid phase
$X_{j,wc}$	mole fraction of species 'j' in the washcoat
$X_{j,f}$	fluid-phase mole fraction of gaseous species 'j'
$X_{j,p}$	mole fraction of species 'j' in the pores of the catalyst particle
$X_{O_2,in}$	inlet mole fraction of O_2
$X_{O_2,out}$	outlet mole fraction of O_2
z	axial coordinate (m)
Greek letters	
δ_c	washcoat thickness (m)
ΔG	Gibbs free energy (J/mol)
ΔH	standard heat of reaction (J/mol)

ΔS	entropy change ($J/mol.K$)
ε_b	void fraction of the catalyst bed
ε_p	porosity of the catalyst particle
ε_{wc}	washcoat porosity
θ_{Ce}	fraction of vacant sites on ceria surface
$\theta_{H,Int}$	fractional coverage of hydrogen on the support at the Pd-support interface
$\theta_{H,PdIn}$	coverage of hydrogen adsorbed on Pd crystallites present inside the support channels
$\theta_{H,PdOut}$	coverage of hydrogen adsorbed on Pd crystallites present outside the support channels
$\theta_{H,S}$	fractional coverage of hydrogen on the support surface
θ_{Int}	fraction of vacant support sites at the Pd-support interface
$\theta_{j,Pd}$	fractional coverage of surface species 'j' on Pd surface
$\theta_{O,Ce}$	fractional coverage of oxygen on ceria surface
$\theta_{O,Ce}^{avg}$	average fractional coverage of oxygen on ceria surface
$\theta_{O,Int}$	fractional coverage of oxygen on ceria at the Pd-ceria interface
$\theta_{O,Pd}$	fractional coverage of oxygen on Pd surface
$\theta_{v,Pd}$	fraction of vacant sites on Pd surface
$\theta_{v,PdIn}$	fraction of vacant Pd sites present inside the support channels
$\theta_{v,PdOut}$	fraction of vacant Pd sites present outside the support channels
$\vartheta_{Ce}^{j,m}$	stoichiometric coefficient of species 'j' in the m^{th} reaction on the ceria surface
$\vartheta_{Ce}^{O,m}$	stoichiometric coefficient of adsorbed oxygen in the m^{th} reaction on the ceria surface
$\vartheta_{Int}^{j,m}$	stoichiometric coefficient of species 'j' in the m^{th} reaction at the interface

$\vartheta_{Int}^{H,m}$ stoichiometric coefficient of adsorbed hydrogen in the mth reaction at the Pd-support interface

$\vartheta_{Int}^{O,m}$ stoichiometric coefficient of adsorbed oxygen in the mth reaction at the Pd-ceria interface

$\vartheta_{Pd}^{j,m}$ stoichiometric coefficient of species 'j' in the mth reaction on the Pd surface

$\vartheta_{Pd}^{H,m}$ stoichiometric coefficient of adsorbed hydrogen in the mth reaction on the Pd surface

ν_o volumetric flow rate (m^3/s)

Superscripts

$^\circ$ initial conditions

in inlet conditions

Abbreviations

FOS	Fractional oxidation state
GC	Gas chromatography
HCs	Hydrocarbons
MS	Mass spectrometer
MAS	Magic angle spinning
NMHC	Non-methane hydrocarbon
NMR	Nuclear magnetic resonance
OSC	Oxygen storage capacity
OER	Oxygen exchange rate
SCR	Selective catalytic reduction
TAP	Temporal analysis of products
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TPD	Temperature programmed desorption
TPO	Temperature programmed oxidation
TPR	Temperature programmed reduction
TPSR	Temperature programmed surface reaction
TWC	Three-way catalyst
TOSC	Total oxygen storage capacity
XPS	X-ray photoelectron spectroscopy