

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

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**OCTOBER 2020**

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

by

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*Submitted*

*in fulfilment of the requirements of the degree of Doctor of Philosophy*

*to the*



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**OCTOBER 2020**

## 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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## Acknowledgements

First and foremost, I would like to express my sincere gratitude and intense respect to my advisor **Prof. Divesh Bhatia** who has helped and encouraged me at all stages of my Ph.D. work. His time-to-time guidance and immense knowledge helped me a lot in doing the successful research work. I would like to give special thanks to him for removing my terror towards the code development and for always being ready for the clarification of my technical doubts. Definitely, under his guidance my writing and presentation skills got improved a lot.

Besides my supervisor, I would like to express deep gratitude to my SRC member, Prof. Ravi P singh for always motivating me. His positive feedback during my SRC presentations always encouraged me towards my Ph.D. work. I would like to express my sincere thanks to my SRC chairperson Prof. K. K. Pant and department expert Prof. Sreedevi upadhyayula for their suggestions, support and encouragement. The knowledge they conveyed me throughout the Ph.D. helped me a lot in the formation of thesis. I would like to thank IIT Delhi for providing me place for research work. I would like to thank MHRD for providing me financial support for conducting the research.

I would like to thank Prof. Ralph T. Yang from the University of Michigan and Dr. Jian Gong from Cummins for providing additional information on the experimental data.

I would like to thank my family members. First and foremost, I would like to thank my mummy, papa and bhaiya for always motivating me, believing me, and making me feel superior than anyone. I would like to thank my younger brothers, Gautam and Durgesh for always being ready for helping me.

I would like to thank my husband Dr. Rakesh kumar for being the best husband and always be the reason for smile on my face. Due to you only, every one used to say that how you could be so happy during the Ph.D. I would like to thank my mother-in-law and father-in-law, for never

creating pressure for anything. Due to your support, I am able to successfully handle the married and Ph.D. life.

Now, I would like to express my thanks to my lab mates and friends who make my life so easy during my Ph.D. stay. First, I would like to thank Karan Malik for always being available for any kind of help either technical or personal. None of the schematic diagram in my paper is complete without the help of Karan Malik. I would like to thank Dr. Suverna Trivedi for always being my bestie and motivating me. I would like to thank Dr. Deepali Chugh for encouraging me for my work. She always inspired me for taking the great step. I still remember that, I want to submit the abstract in two reputed conferences NASCRE-4 and NAM-26 and I had only one work for submission. At that time, she suggested me about my two work and I got oral presentation in both conferences. I would like to thank Dr. Karan Gupta for helping me during the learning stage of MATLAB.

I would like to give special thanks to Priyanka, my neighbour, my gossip partner, and my best friend. She never let me to miss the breakfast. I really enjoyed the morning tea and leg pulling of Navdeep (Sarkari Naukri). I would like to thank Neh Nupur for always believing me and inspiring me. I would like to thank Sunita for always inviting me for dinner in her house. I would like to thank Anika mam, for inviting all the lab members at home for yummy and delicious food.

I would like to thank Marvi Kaushik my junior, my friend. I really enjoyed her company at the end phase of my Ph.D. She really cares me a lot, whenever I get ill. Marvi helped me a lot when I suffered from chicken pox at last stage of my Ph.D. Marvi and Priyanka made my life so easy during the phase of chicken pox, and my first trimester pregnancy. Both of them never let me miss my family in difficult situations.

I would like to thank Dwijraj for always bringing the chicken dishes made in various flavour, yummy chocolates, home-made cakes for every one birthday. Even Brabeque nation is failed before the dishes made by Dwijraj. I would like to thank Pranav for always be the hope for everyone in technical discussion and for cracking the jokes in the lab. I would really like to thank Pranav and Dwijraj for making the good lab environment. I would like to thank my neighbour lab members Dr. Rajeev Gautam, Dr. Biju mam, Mansu Kapoor, Dr. Jay Pandey for always being ready for help. Thankyou Rajeev sir for always treating me like your child. I always miss your lunch prepared by you and Jyoti mam. At the end, I would like to thank myself for completing my thesis work by holding the tag of marriage and pregnant women, and never get frustrated by any type of hurdles obtained in life.

## 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<sub>2</sub>, and CH<sub>4</sub> as reductants. Consistent with the experimental findings, the model predicts that H<sub>2</sub> results in a higher OSC than CO and CH<sub>4</sub>. The effective surface diffusivity with H<sub>2</sub> is estimated to be higher than that with CO and CH<sub>4</sub>, 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 इंटरफेस, 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 सीरिया के बीच ऑक्सीजन के रिवर्स-स्पिलओवर पर CO, H<sub>2</sub> और CH<sub>4</sub> के साथ रीडक्टेंट के रूप में प्रभाव की भविष्यवाणी करता है। प्रयोगात्मक निष्कर्षों के अनुरूप, मॉडल भविष्यवाणी करता है कि H<sub>2</sub> का परिणाम CO और CH<sub>4</sub> की तुलना में अधिक OSC है। H<sub>2</sub> के साथ प्रभावी सतह विवर्तनशीलता CO और CH<sub>4</sub> 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, जिसमें क्रिस्टलीय के आकार और स्थान के प्रभाव, धातु-समर्थन इंटरफेसियल संपर्क और समर्थन सतह पर अडसोर्बड 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 रीडक्टेंट 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 क्रिस्टलीय के अंश से संबंधित है। मॉडल का उपयोग चक्र के समय, H<sub>2</sub> एकाग्रता, Pd फैलाव, और चक्रीय परिस्थितियों में Pd लोडिंग का NO रीडक्शन 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 NO<sub>x</sub> ट्रेप है जिसमें NO<sub>x</sub> 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 ( $k = Pd, Pd\text{-support interface}$ )                     |
| $I_p$       | 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 <sup>2</sup> .s) |
| $k_{m,Pd}$    | kinetic rate constant for reaction 'm' occurring on Pd surface (mol/m <sup>2</sup> .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 <sub>2</sub> O <sub>4</sub> (mol)                                             |
| $N_{Ce_2O_3}$ | moles of Ce <sub>2</sub> O <sub>3</sub> (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 ( $\mu mol/g$ )                                                                    |
| $O - S_k$        | 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<br>( $mol/m^2$ . s)  |
| $R_{m,PdOut}$    | rate of $m^{th}$ reaction occurring on the Pd crystallites present outside the channel<br>( $mol/m^2$ . 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)                                                                    |
| $\tau_d$        | diffusion time (s)                                                          |
| $\tau_c$        | residence time (s)                                                          |
| $\tau_r$        | 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   |                                                                             |
| $\delta_c$      | washcoat thickness (m)                                                      |
| $\Delta G$      | Gibbs free energy (J/mol)                                                   |
| $\Delta H$      | standard heat of reaction (J/mol)                                           |

|                         |                                                                                             |
|-------------------------|---------------------------------------------------------------------------------------------|
| $\Delta S$              | entropy change (J/mol. K)                                                                   |
| $\varepsilon_b$         | void fraction of the catalyst bed                                                           |
| $\varepsilon_p$         | porosity of the catalyst particle                                                           |
| $\varepsilon_{wc}$      | washcoat porosity                                                                           |
| $\theta_{Ce}$           | 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                                      |
| $\theta_{Int}$          | 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         |

|                                              |                                                                                                             |
|----------------------------------------------|-------------------------------------------------------------------------------------------------------------|
| $\vartheta_{\text{Int}}^{\text{H},\text{m}}$ | stoichiometric coefficient of adsorbed hydrogen in the $m^{\text{th}}$ reaction at the Pd-support interface |
| $\vartheta_{\text{Int}}^{\text{O},\text{m}}$ | stoichiometric coefficient of adsorbed oxygen in the $m^{\text{th}}$ reaction at the Pd-ceria interface     |
| $\vartheta_{\text{Pd}}^{\text{j},\text{m}}$  | stoichiometric coefficient of species ‘j’ in the $m^{\text{th}}$ reaction on the Pd surface                 |
| $\vartheta_{\text{Pd}}^{\text{H},\text{m}}$  | stoichiometric coefficient of adsorbed hydrogen in the $m^{\text{th}}$ reaction on the Pd surface           |
| $v_o$                                        | volumetric flow rate ( $\text{m}^3/\text{s}$ )                                                              |
| Superscripts                                 |                                                                                                             |
| ◦                                            | 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        |