Carbon Tolerance of Rh-substituted Pyrochlore Catalysts under Low Steam-to-Carbon Ratio for Steam Reforming Conditions

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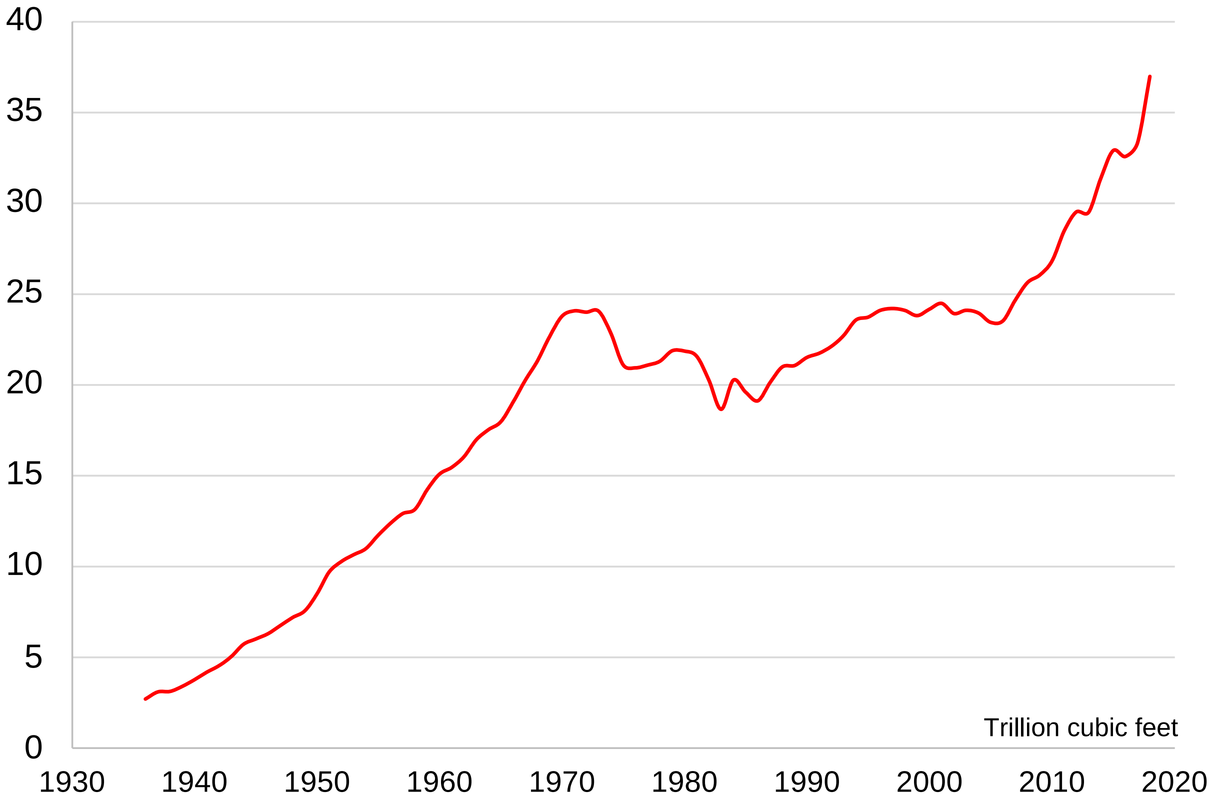
Introduction

NATIONAL ENERGY TECHNOLOGY LABORATORY

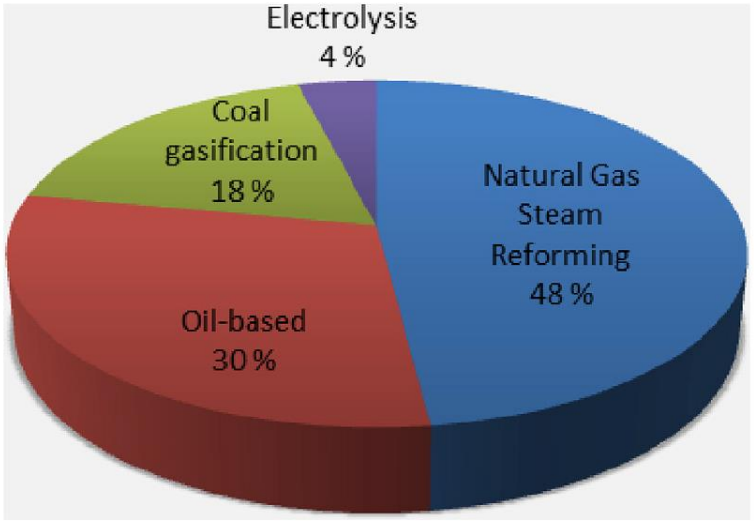
Natural Gas Gross Withdrawals and Production



U.S. EIA, 2018

- Steady increase in natural gas production in the U.S. from 2005- current.

Hydrogen production worldwide, by technology



Voldsund, et al.

- Dependence of methane steam reforming on H_2 production.
- 95% of US H_2 production comes from SMR

Mari Voldsund, Kristin Jordal, Rahul Anantharaman, Int J Hydrogen Energy 2016.

Methane Steam Reforming

Methane Steam Reforming:

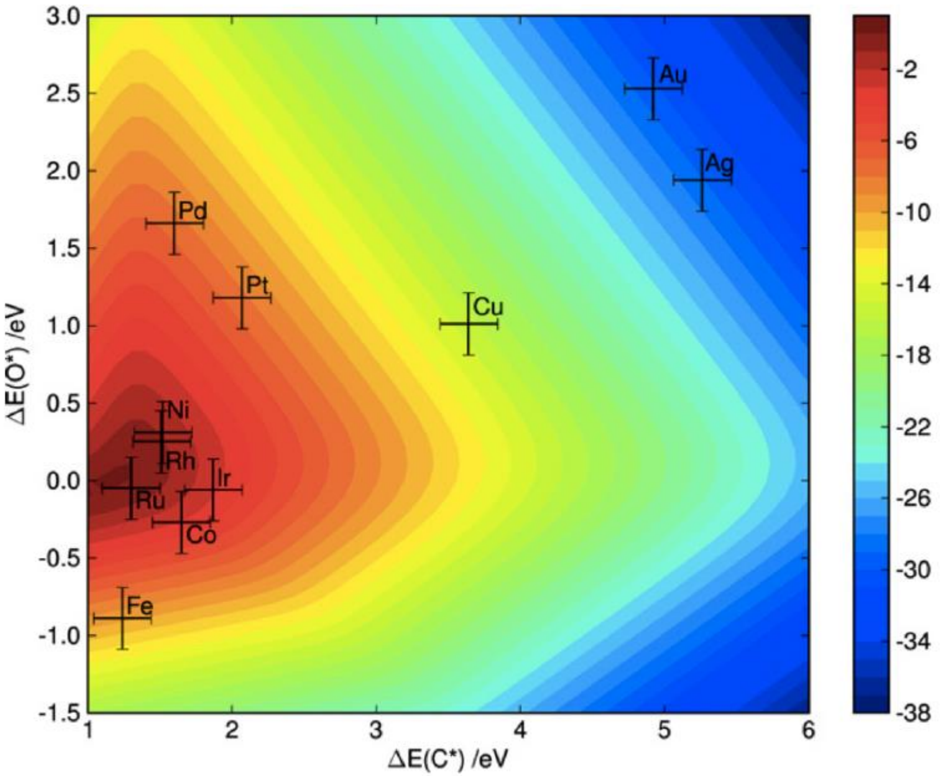
$$CH_{4\,(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$

$$\Delta H_{298K} = +206\ kJ/mol,$$

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

$$\Delta H_{298K} = -41\ kJ/mol$$

- Group VIII transition metal as catalyst
- Activity: Rh, Ru > Ni, Ir >Pt, Pd
- Challenges: Deactivation by sintering; carbon blockage; poisoning by S/As/P etc.

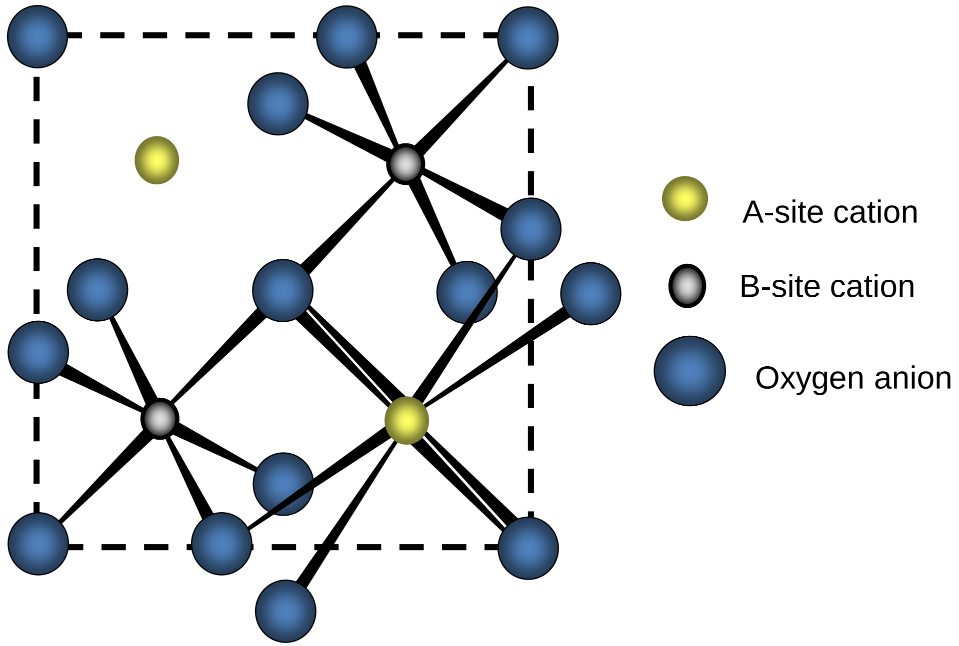


Two-dimensional volcano-plot of the turn over frequency as a function of O and C adsorption energy.

Introduction

Pyrochlore Reforming Catalysts

$(A_2B_2O_7)$



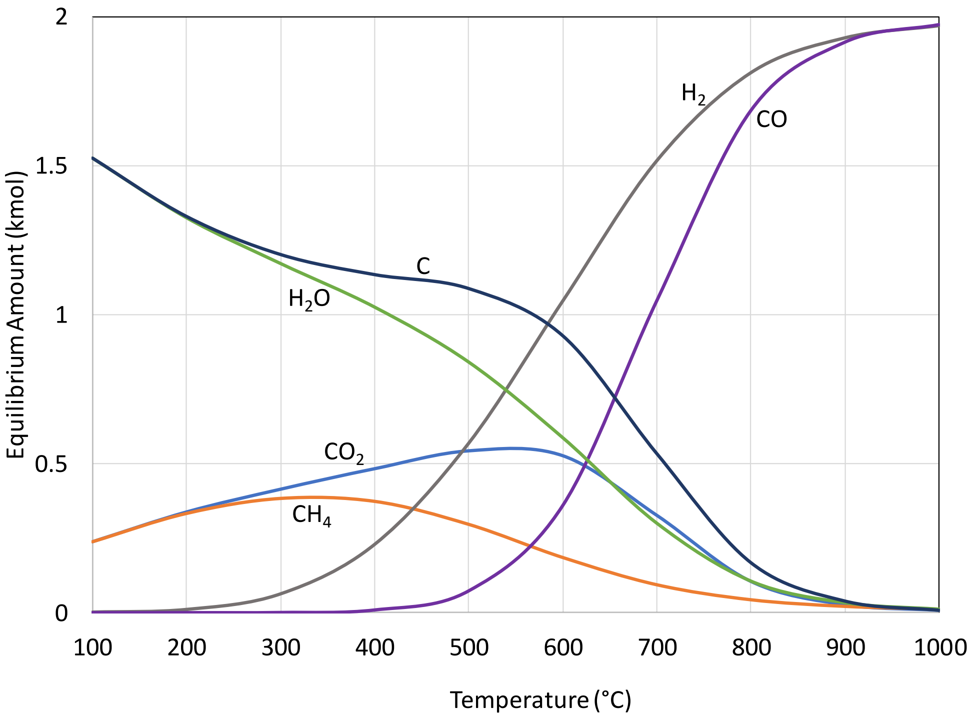
What makes Pyrochlores viable reforming catalysts?

- High chemical and thermal stability [1].
- Mechanical strength to accommodate substitutions [2].
- Active metal can dispersed into small and stable clusters by substitution into the B-site.
- Substitution with lower valence cations in the A-site and/or B-site can create oxygen vacancies, which may increase lattice oxygen-ion mobility to reduce carbon formation.

[1] D. Sedmidubsky, et al., The Journal of Chemical Thermodynamics 37 (2005) 1098.
[2] H. Zhou, et al., Journal of Alloys and Compounds 438 (2007) 217

Project overview

- Develop a pyrochlore catalyst with high carbon tolerance under low steam-to-carbon ratio
- Explore the effect of Y substitution at A site/ B site of the structure
- Determine how Y location influence carbon accumulation and activity



Calculations performed with HSC Chemistry v9.2 using H_2O/CH_4 ratio= 1

- Low steam-to-carbon ratio S/C=1
- Rh substituted $La_2Zr_2O_7$
- Y loadings of 1.5, 4 , 6.5 wt%
- Y at A/B site of structure

Experimental

Pechini Method

Dissolved nitrate salts into DI water (*stirring*)

Aqueous citric acid solution (1.2:1 CA/M ratio)

Heated stirring solution to 70°C

Added Ethylene Glycol (1:1 EG/CA)

Stirring at 70°C for ~8 h

Transparent glassy resin

Polymerization in heating mantle at 130°C

Calcine for 4 h at 900°C

Fresh Catalyst

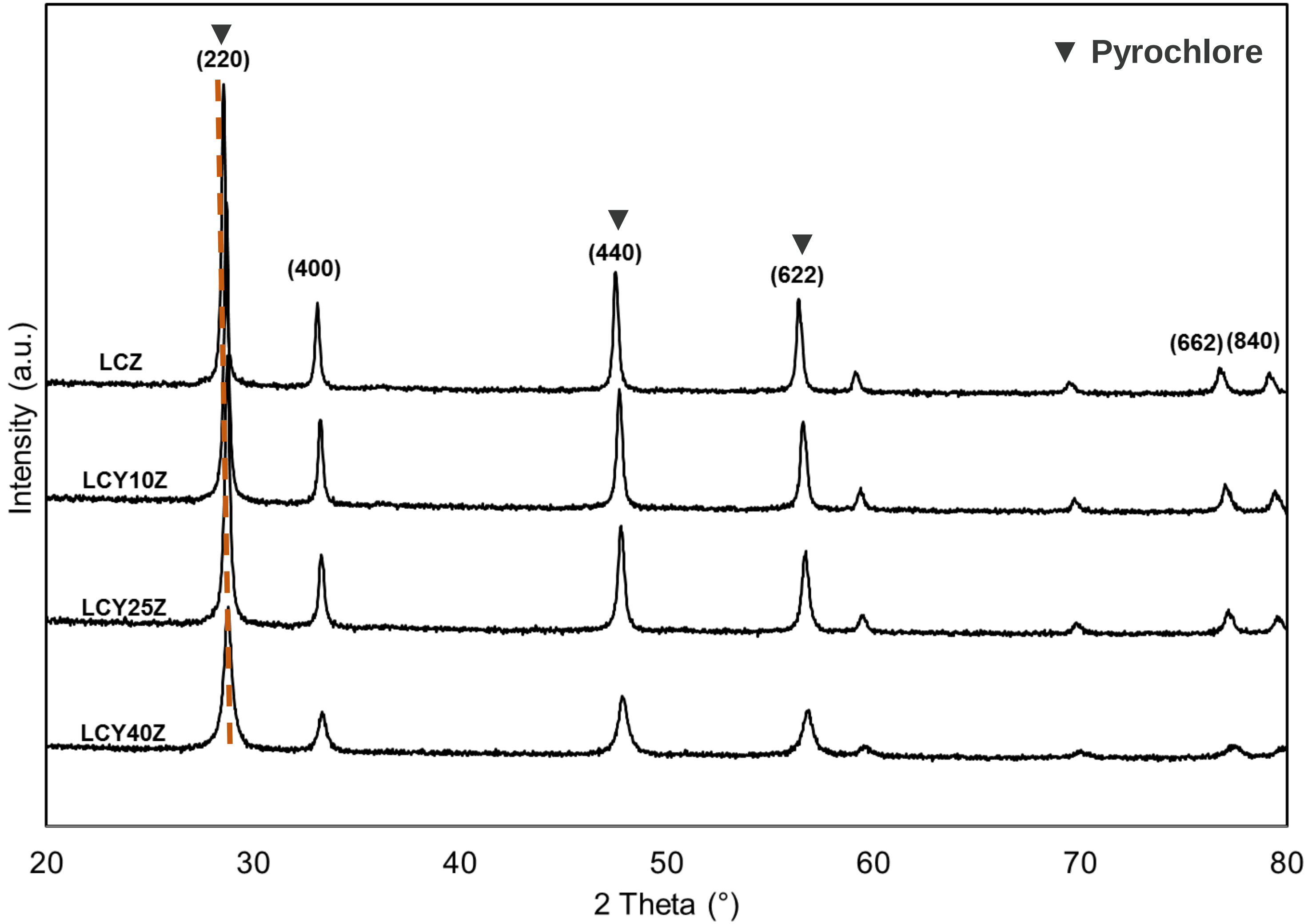
Activity Test

TPSR
Long term activity

Spent Catalyst

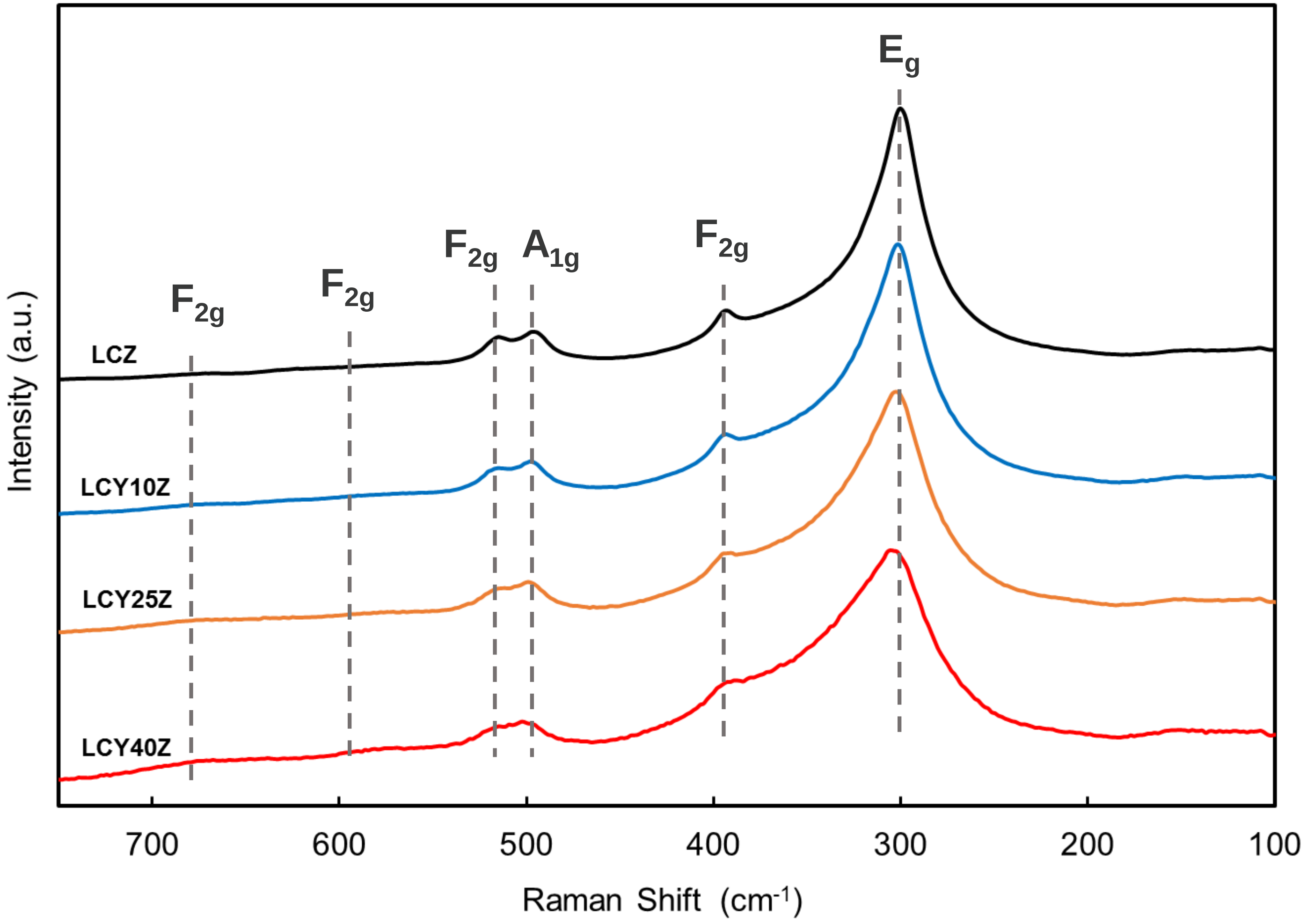
XRD-Crystal structure
TPR- Reducible sites
TPD- Oxygen species
TGA- Carbon analysis
Raman-Oxygen /Carbon
XPS-Surface property

XRD Results-pyrochlore support



- XRD patterns of the freshly calcined $La_{2-x}Y_xZr_2O_7$ supports

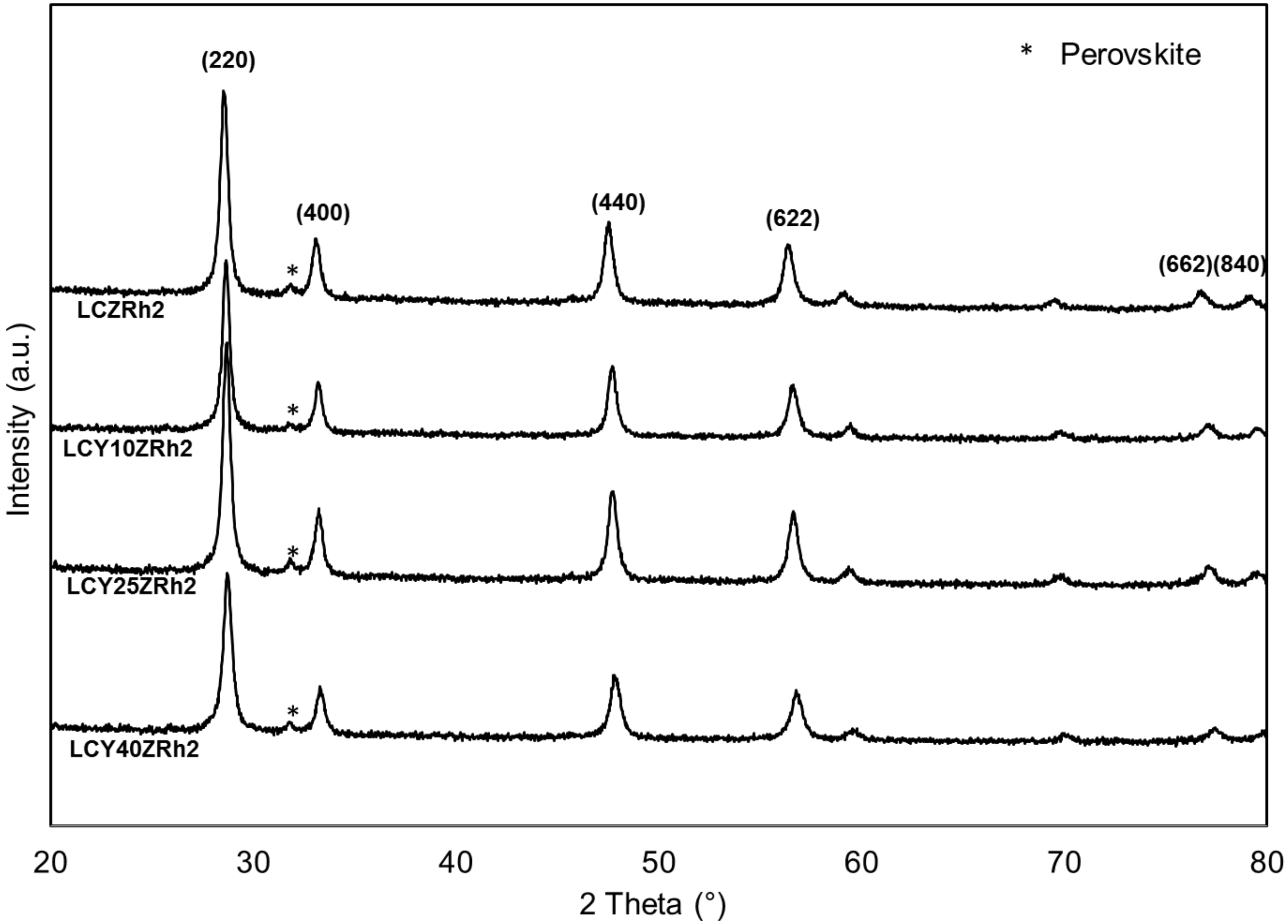
Raman spectroscopy



- 100-750 cm^{-1} , sensitive to oxygen-cation vibrations
- Six Raman active modes for cubic $A_2B_2O_7$ pyrochlores
- **$A_{1g} + E_g + 4F_{2g}$**

Fresh Catalysts

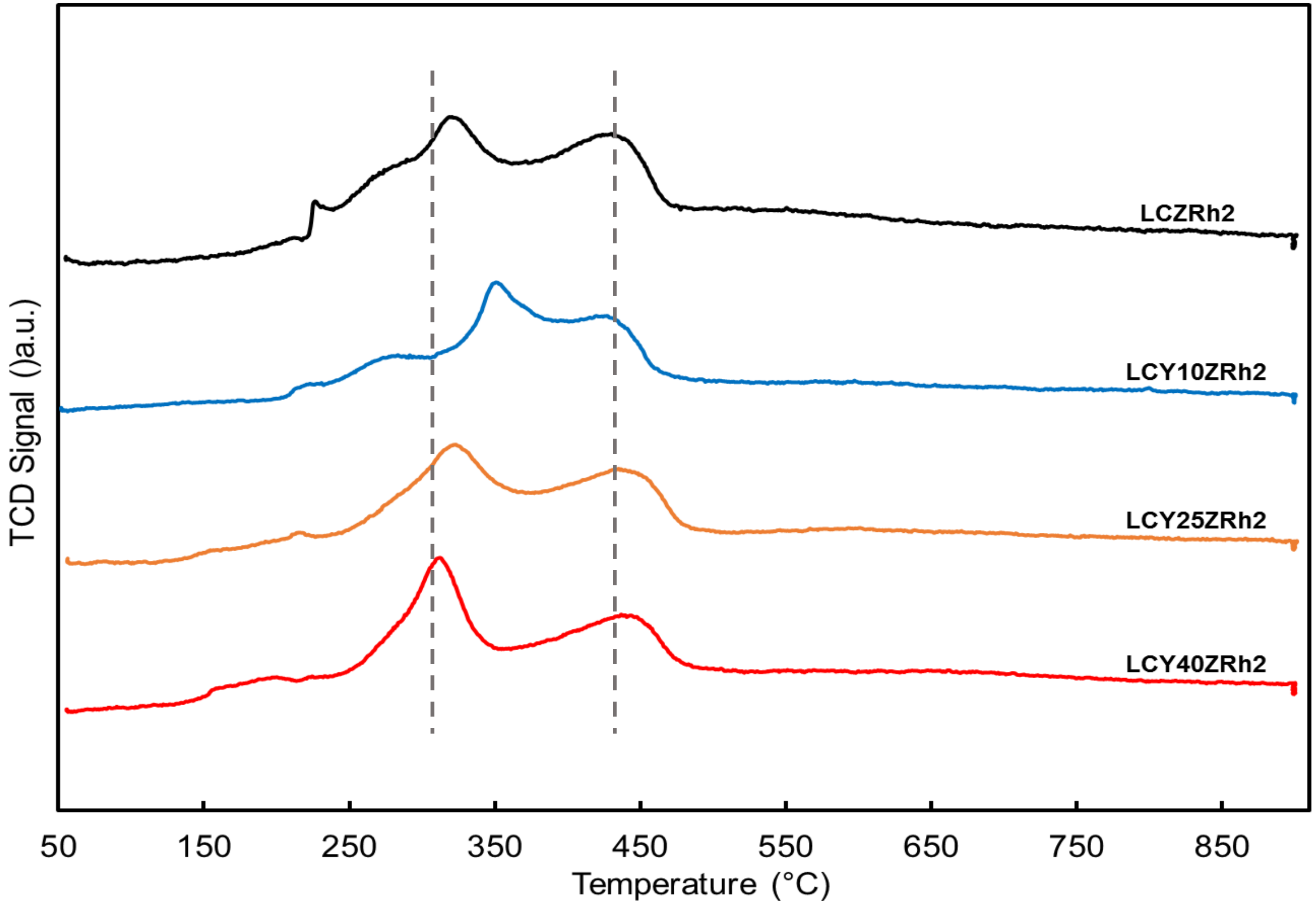
XRD



Perovskite phase $LaRhO_3$

Fresh Catalysts

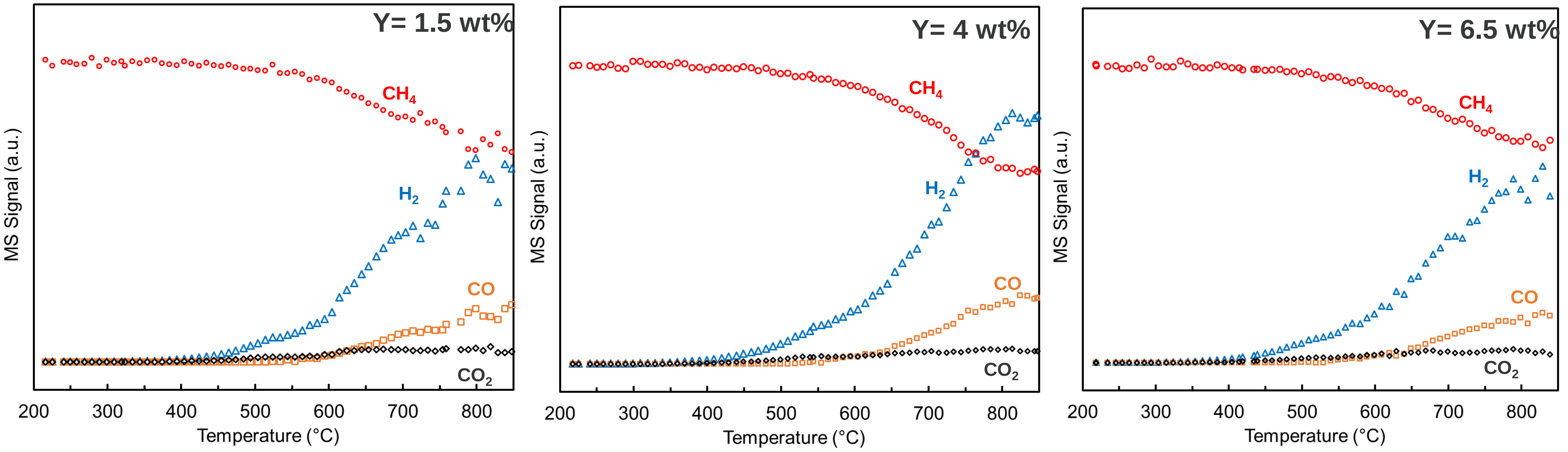
TPR



- Two major peaks observed for reduction of Rh_2O_3 into Rh.
- Lower T peak –reduction of Rh_2O_3 at surface of support.
- Higher T peak– reduction of Rh_2O_3 in the pyrochlore structure.

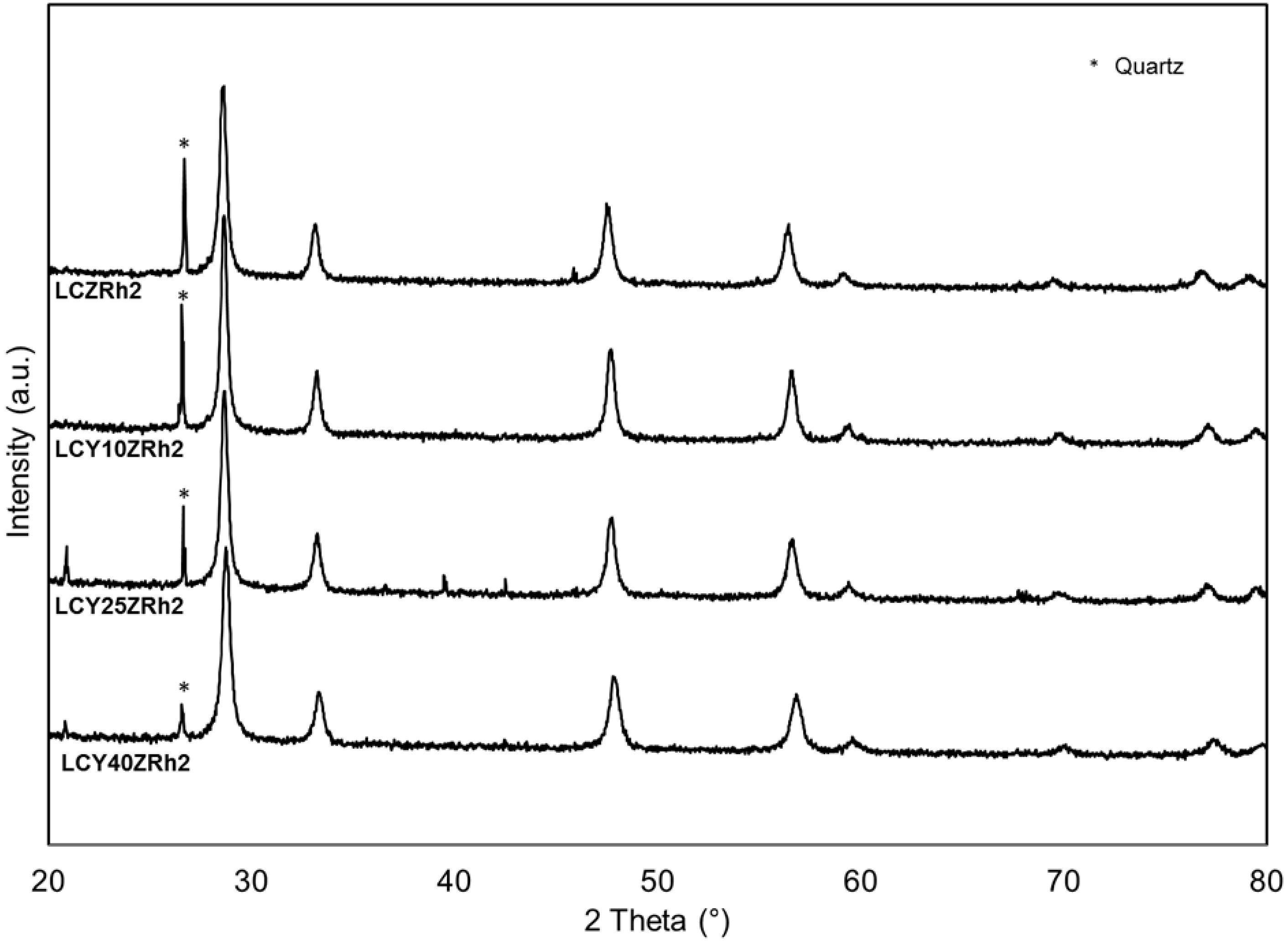
Activity Test

TPSR



- 4% of Y loading enhanced the performance of the catalyst for SMR, while 6.5 % of Y inhibited the performance of the catalyst.

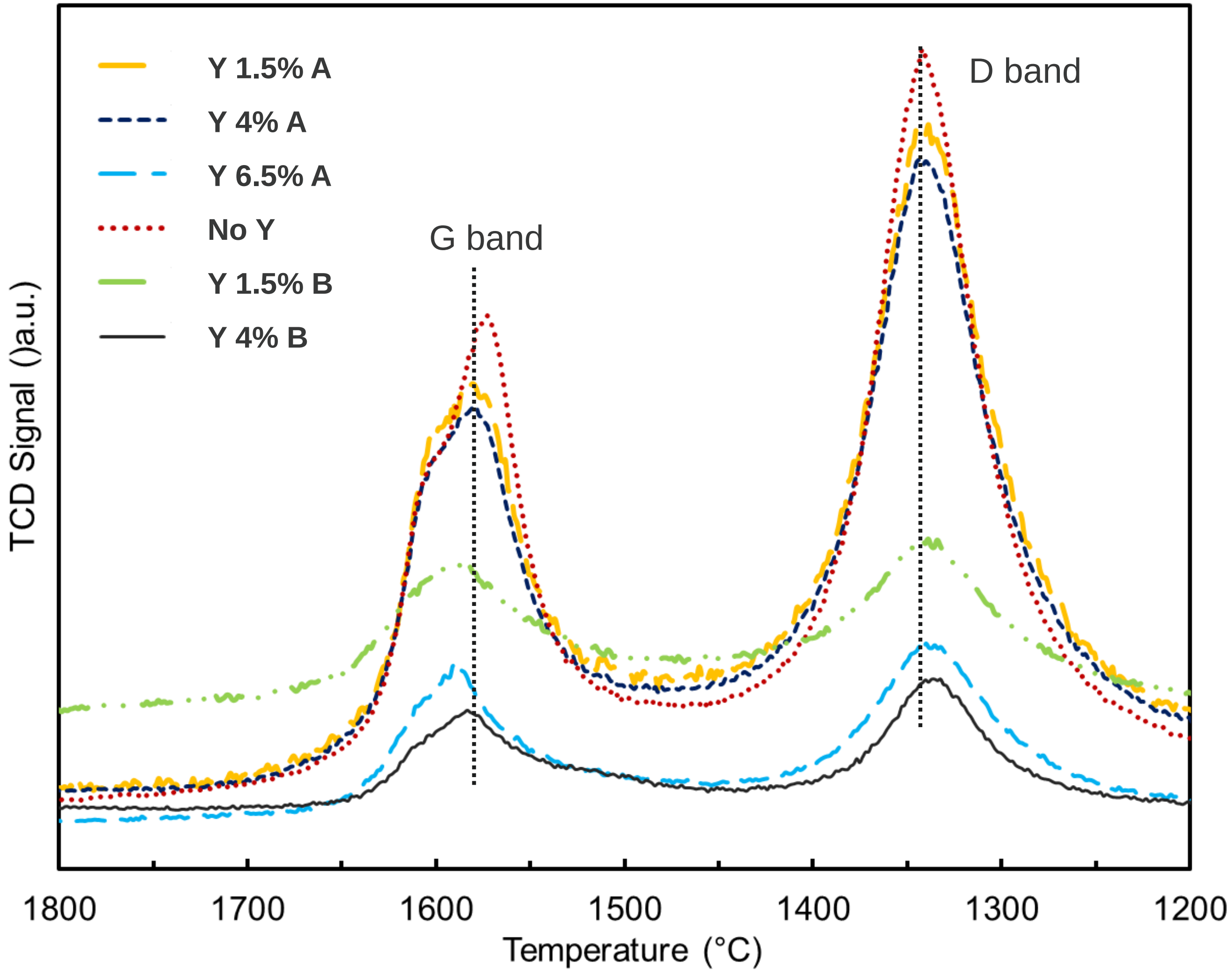
Spent Catalysts



- The catalysts retained their pyrochlore structure.

Spent Catalyst

Raman spectroscopy



- Carbon formation on each catalyst
- Graphitic carbon vs polycrystalline carbon

Catalysts	IG/ID
Y 1.5 % A	0.65
Y4% A	0.66
Y6.5% A	0.89
No Y	0.67
Y 1.5% B	0.91
Y 4% B	0.83

Conclusions

- Y at A site of $A_2B_2O_7$ structure influences the structure of Rh-substituted $La_2Zr_2O_7$, and affects the performance of the prepared catalysts for SMR
- Y at A site with loading of 4 wt% showed optimal performance for SMR, while a further increase of Y loading inhibits the performance of the catalyst, which may be due to distortion of crystal structure caused by Y.
- Y at B site inhibits the performance of the catalysts at low Y loading.

Future study

- Explore substituted Rh dispersion in catalysts by TEM/EDX to further understand Y function in modification of the catalysts.
- Explore other promoters which could help in active metal dispersion in support materials, such as Ce, Nb, W, etc.

Acknowledgment

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Disclaimer

Thank you !