Potential of Cs as a promoter of Pt/m-ZrO_2 catalysts in the Low Temperature Water-Gas Shift and Ethanol Steam Reforming Reactions

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Presenter : Zahra Rajabi

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Hydrogen Applications

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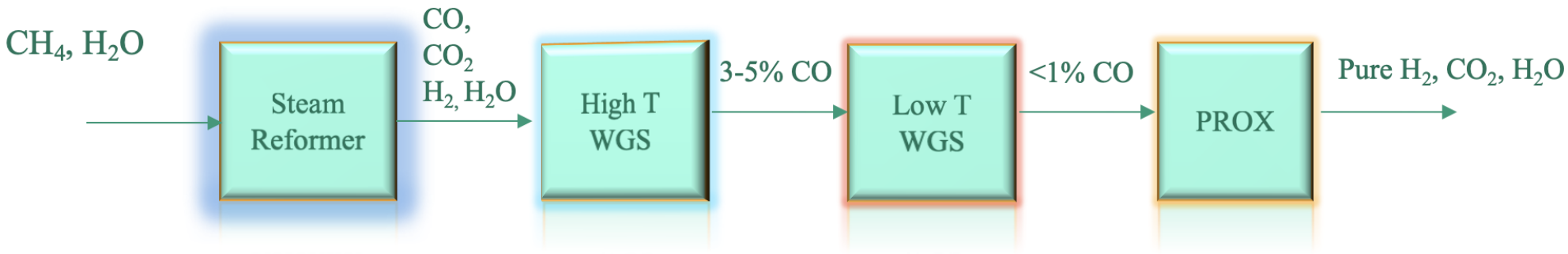
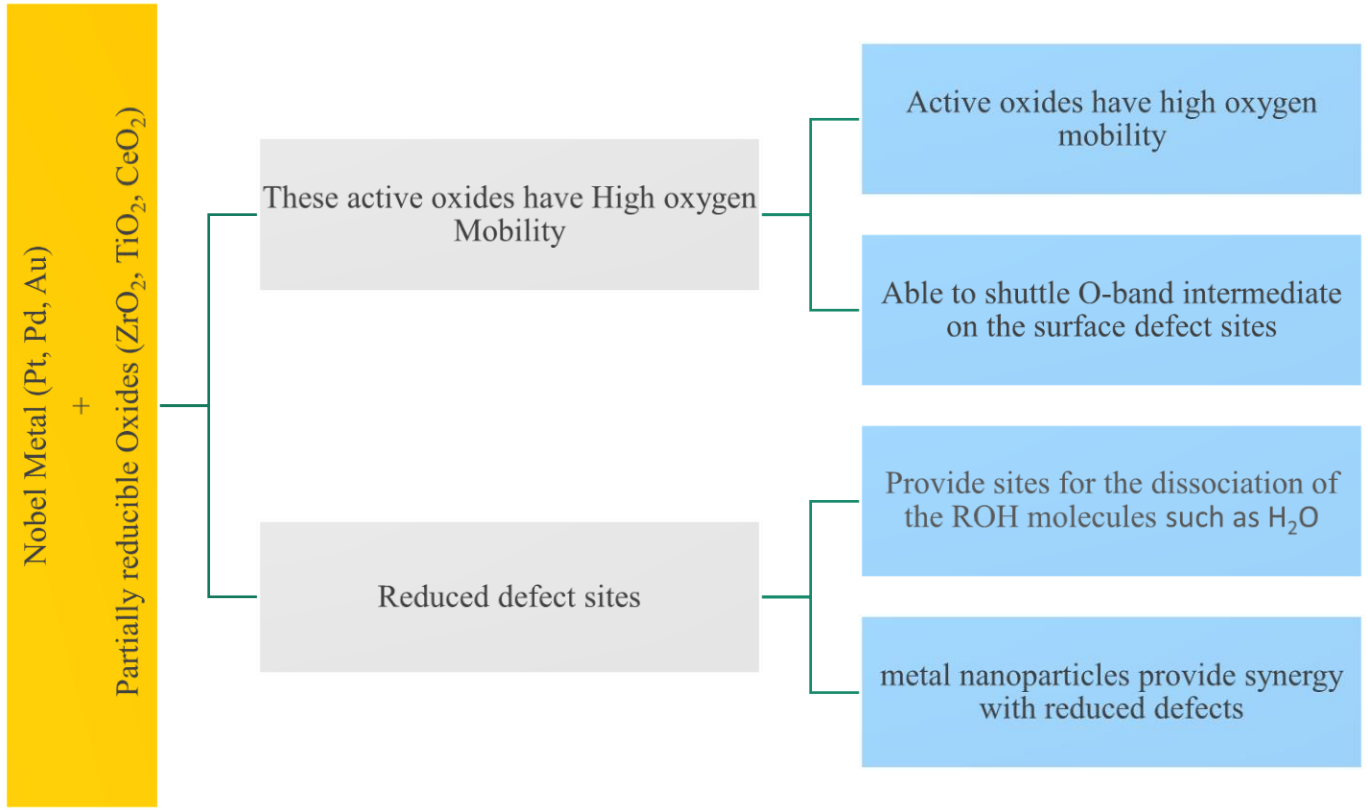
Hydrogen Production Processor



1. Nikolaidis, P. et al . A comparative overview of hydrogen production processes. *Renew. Sustain. Energy Rev.* **2017**, *67*, 597–611
2. Vignatti, C. et al. T.F. Catalytic and DRIFTS study of the WGS reaction on Pt-based catalysts. *Int. J. Hydrogen Energy* **2010**, *35*, 7302–7312.

Catalysts



1. Ratnasamy, C. et al, Water gas shift catalysis. *Catal. Rev.* **2009**, *51*, 325–440.
2. Panagiotopoulou, P. et al, Effect of the nature of the support on the catalytic performance of noble metal catalysts. *Catal. Today* **2006**, *112*, 49–52.

Our Study

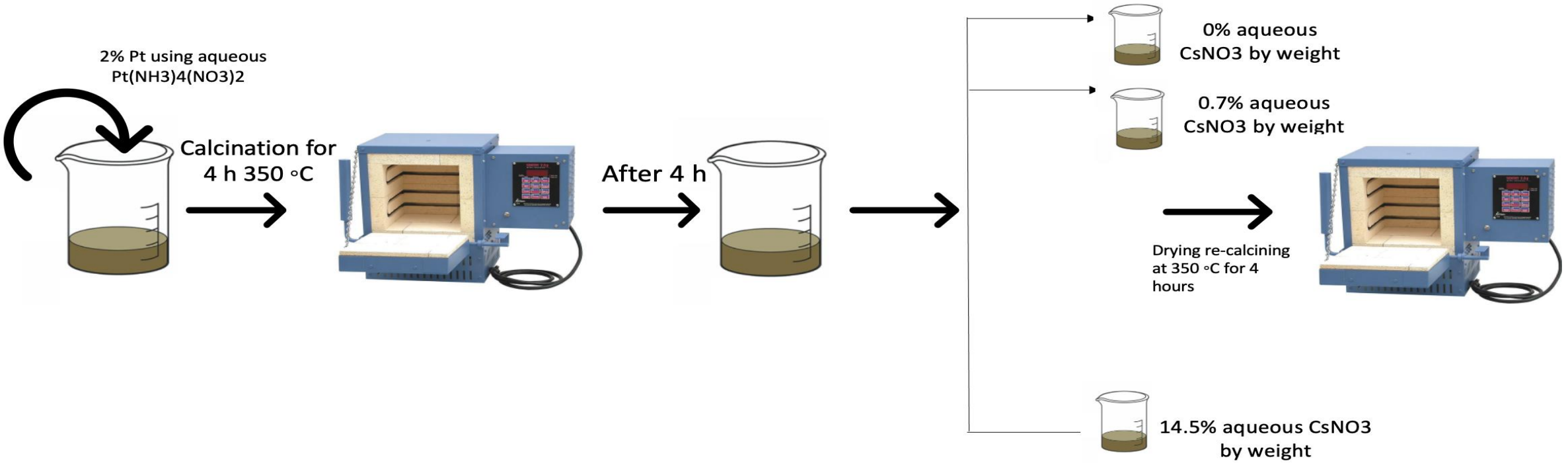
- The effect of Cs as Alkali on Pt/m-ZrO_2 in both LT-WGS and ESR reactions
- The optimal alkalis loading for activity and/or stability.
- Ability to facilitate formate dehydrogenation in WGS reaction and acetate dehydrogenation in ESR reaction

Material and Methods

Material

Name	Brand
Monoclinic phase zirconia	No. 43815, Alfa Aesar, Haverhill, MA, USA
$Pt(NH_3)_4(NO_3)_2$	No. 88960, Alfa Aesar, Haverhill, MA, USA
Aqueous $CsNO_3$	No. 12884, Alfa Aesar, Haverhill, MA, USA

Catalyst Preparation



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Methods

- In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)
- X-ray absorption near edge spectroscopy (XANES)
- Temperature-programmed desorption (TPD)
- Fixed bed catalytic reaction testing

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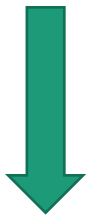
Catalyst Characterization

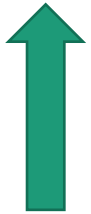
BET surface area

Sample ID	Expected A_S Assuming No Pore Blocking [m^2/g]	Measured A_S (BET) [m^2/g]	Difference between Expected & Measured [m^2/g]
ZrO_2		95.4	
2%Pt/ZrO_2	93.2	89.6	3.6
0.72%Cs-2%Pt/ZrO_2	92.5	88.5	4.0
1.45%Cs-2%Pt/ZrO_2	91.7	84.6	7.1
2.17%Cs-2%Pt/ZrO_2	91.0	85.3	5.7
2.89%Cs-2%Pt/ZrO_2	90.3	86.6	3.7
3.87%Cs-2%Pt/ZrO_2	89.3	86.8	2.5
4.80%Cs-2%Pt/ZrO_2	88.3	78.7	9.6
5.78%Cs-2%Pt/ZrO_2	87.3	74.1	13.2
7.22%Cs-2%Pt/ZrO_2	85.9	69.1	16.8
10.41%Cs-2%Pt/ZrO_2	82.7	62.1	20.6
14.45%Cs-2%Pt/ZrO_2	78.6	54.9	23.7

BJH Pore Volume

Sample ID	V_P (BJH Des) [cm^3/g]
ZrO_2	0.289
$2\%Pt/ZrO_2$	0.272
$0.72\%Cs\text{-}2\%Pt/ZrO_2$	0.259
$1.45\%Cs\text{-}2\%Pt/ZrO_2$	0.249
$2.17\%Cs\text{-}2\%Pt/ZrO_2$	0.246
$2.89\%Cs\text{-}2\%Pt/ZrO_2$	0.251
$3.87\%Cs\text{-}2\%Pt/ZrO_2$	0.256
$4.80\%Cs\text{-}2\%Pt/ZrO_2$	0.238
$5.78\%Cs\text{-}2\%Pt/ZrO_2$	0.229
$7.22\%Cs\text{-}2\%Pt/ZrO_2$	0.211
$10.41\%Cs\text{-}2\%Pt/ZrO_2$	0.197
$14.45\%Cs\text{-}2\%Pt/ZrO_2$	0.177





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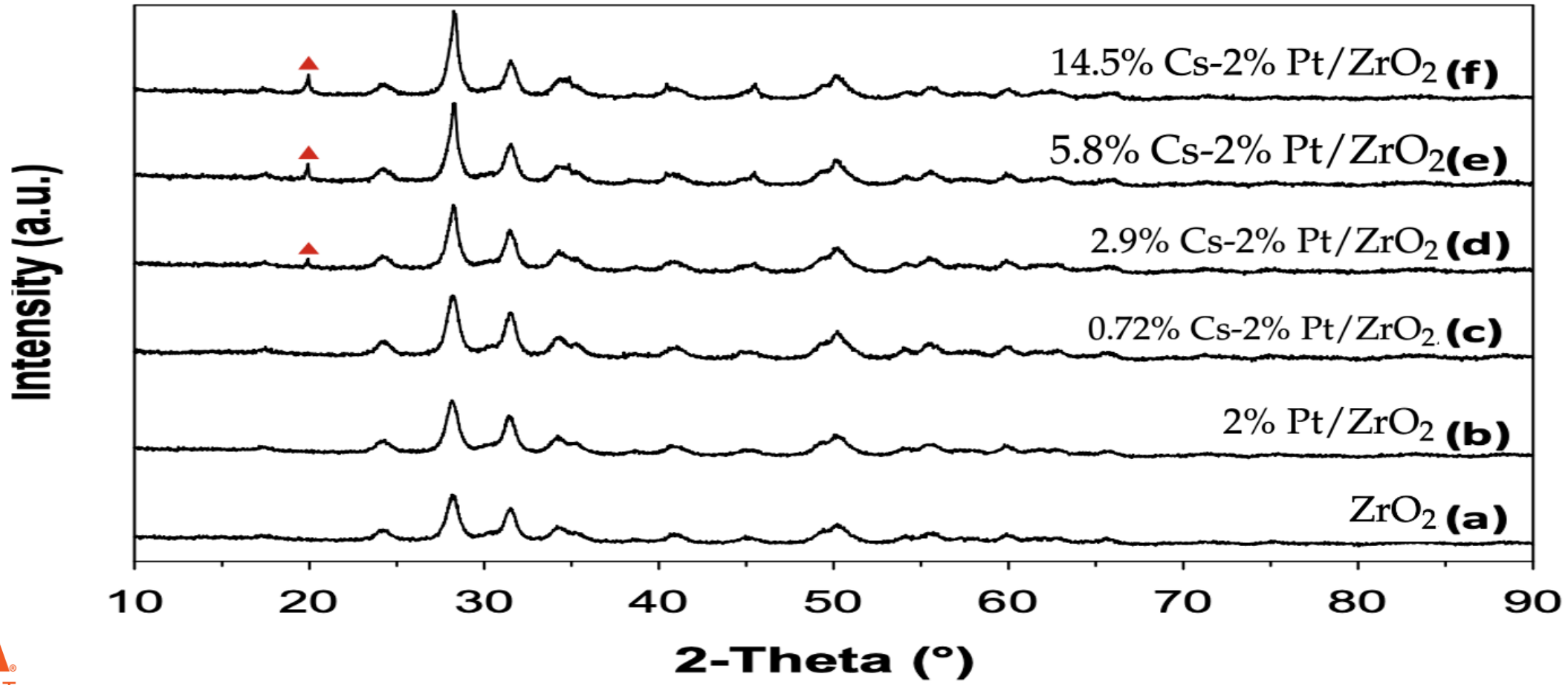
XRD profile



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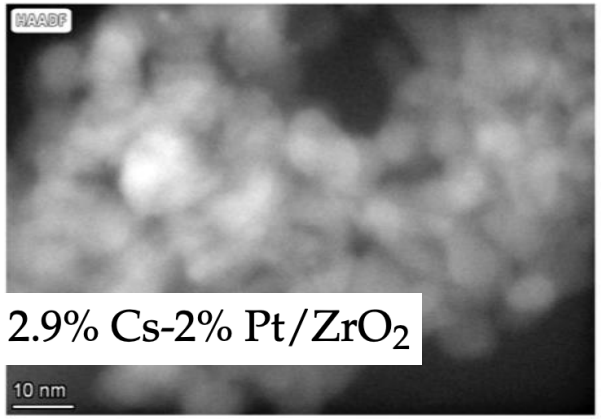

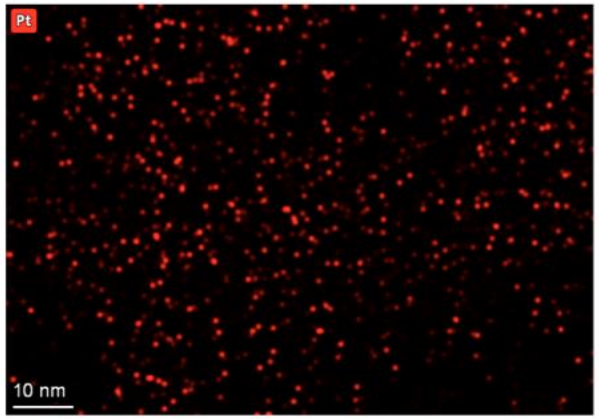

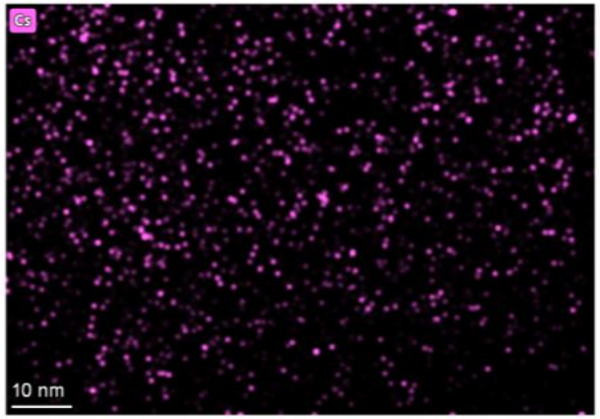

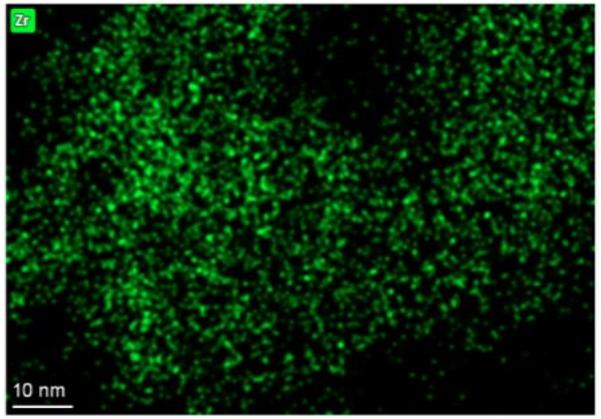

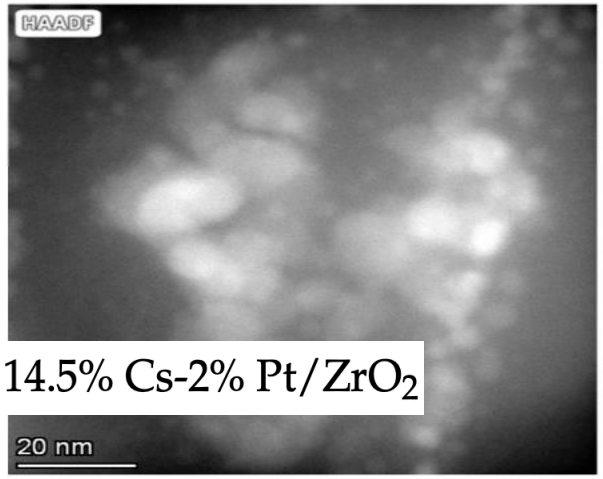

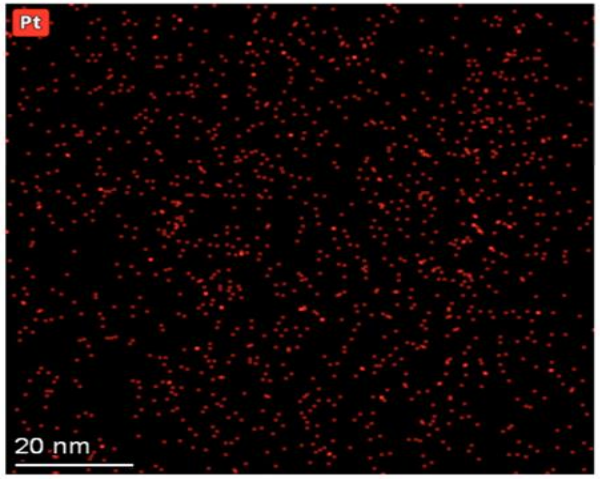

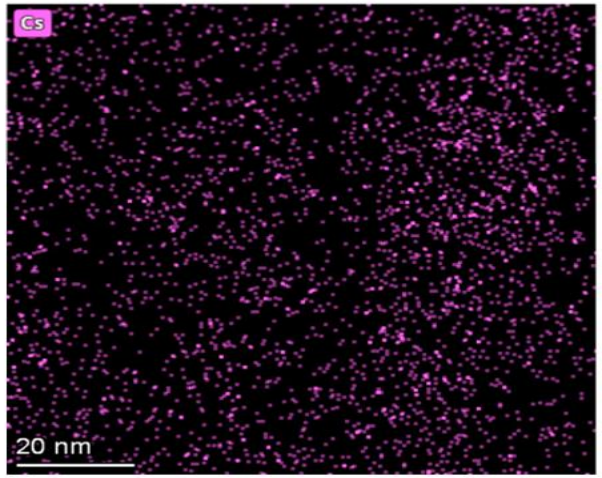

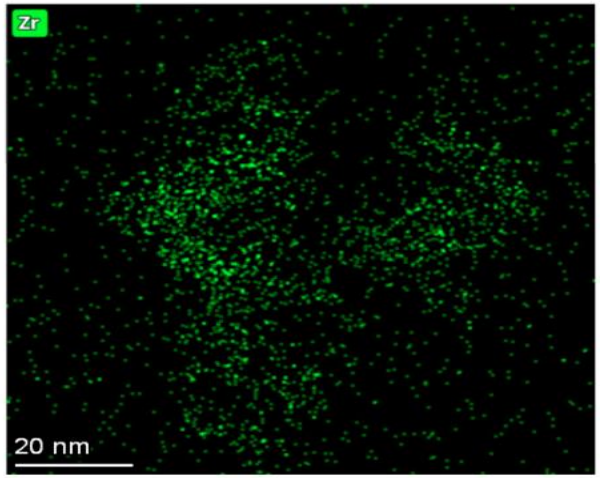

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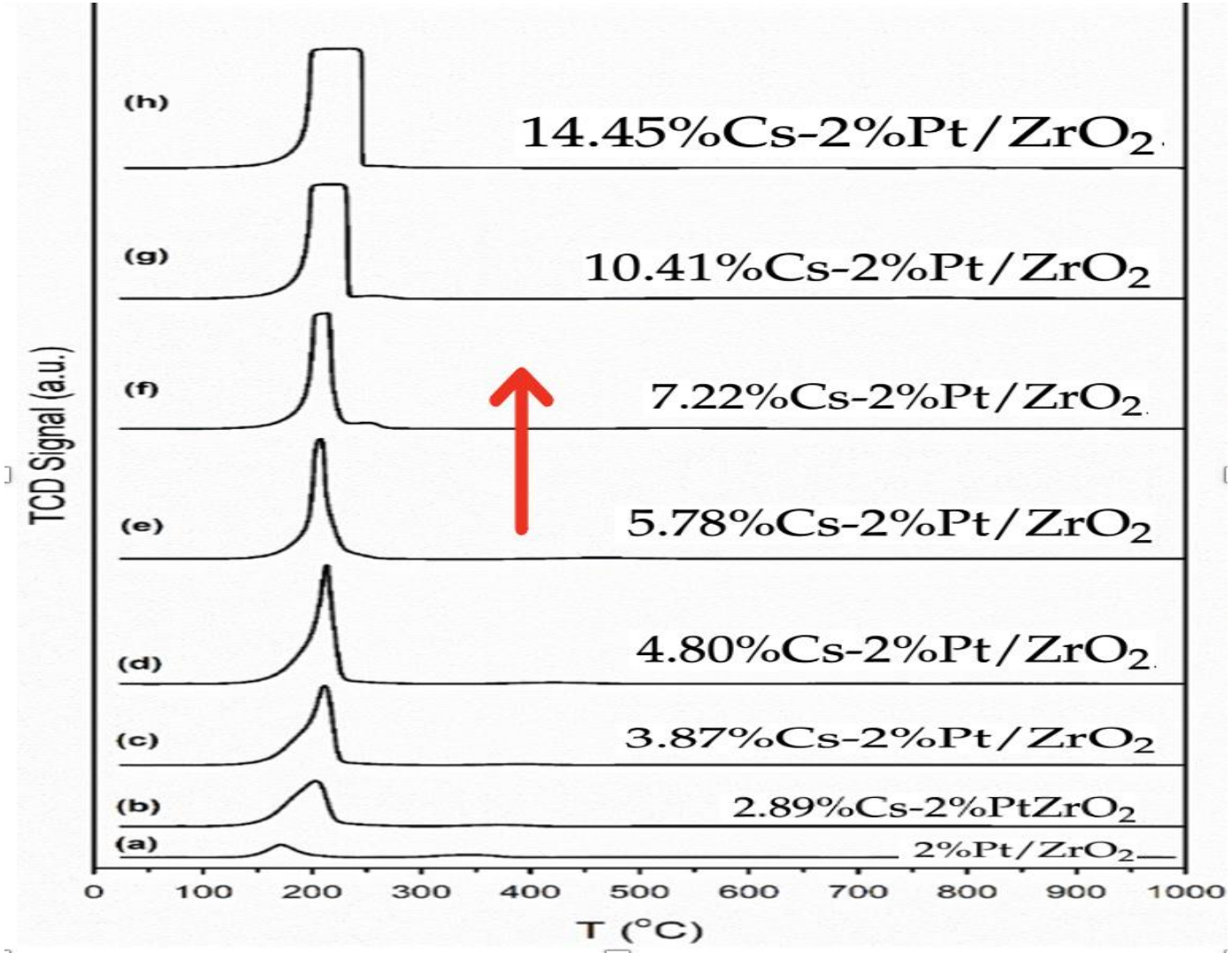
STEM-EDX images

H_2 Temperature-Programmed Reduction (TPR)



EXAFS (Extended X-ray Absorption Fine Structure) data at the L3-edge of Pt

- Average Pt particle size was calculated by using the first atomic shell Pt-Pt coordination number .
- Average Pt^0 particle diameter increases with increase Cs loading
- The dispersion, which is defined as % Pt atoms exposed to the surface, decreases with increase Cs loading.

Sample Description	N Pt-Pt Metal	R Pt-Pt (Å) Metal	e_0 (eV)	σ^2 ($Å^2$)	r-Factor	Est. Number of Atoms *	Est. Diam. (nm) */**	Est. % Disp. (%)
Pt^0 foil	12 (fixed)	2.766 (0.0061)	8.99 (0.657)	0.00537 (0.00045)	0.0094	-	-	-
2%Pt/m-ZrO_2	5.2 (0.44)	2.681 (0.0090)	4.70 (0.612)	0.010 (0.00143)	0.0062	13 →	0.86 0.78 →	92
2.89%Cs-2%Pt/m-ZrO_2	5.3 (0.36)	2.709 (0.0069)	6.15 (0.471)	0.00905 (0.00110)	0.0041	13	0.87 0.79	92
4.80%Cs-2%Pt/m-ZrO_2	6.3 (0.36)	2.725 (0.0057)	6.55 (0.397)	0.00797 (0.00090)	0.0031	22	1.0 0.93	87
5.78%Cs-2%Pt/m-ZrO_2	6.9 (0.51)	2.742 (0.0070)	7.11 (0.507)	0.00660 (0.00110)	0.0054	31	1.1 1.0	84
10.41%Cs-2%Pt/m-ZrO_2	8.2 (0.24)	2.755 (0.0026)	8.32 (0.200)	0.00474 (0.00041)	0.00089	82 →	1.5 1.4 →	73
14.45%Cs-2%Pt/m-ZrO_2	8.0 (0.67)	2.754 (0.0076)	7.38 (0.560)	0.00594 (0.00119)	0.0067	68	1.4 1.3	77

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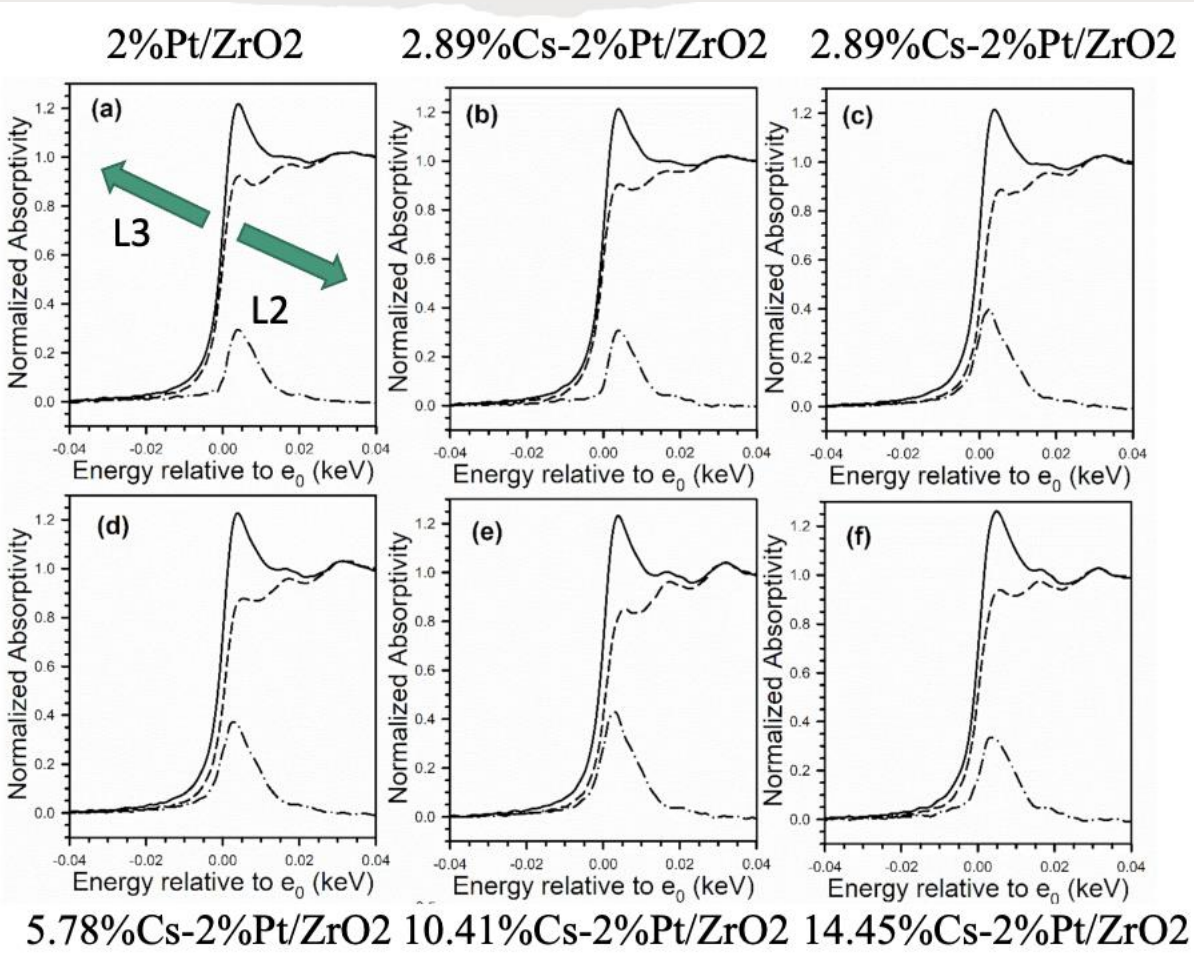
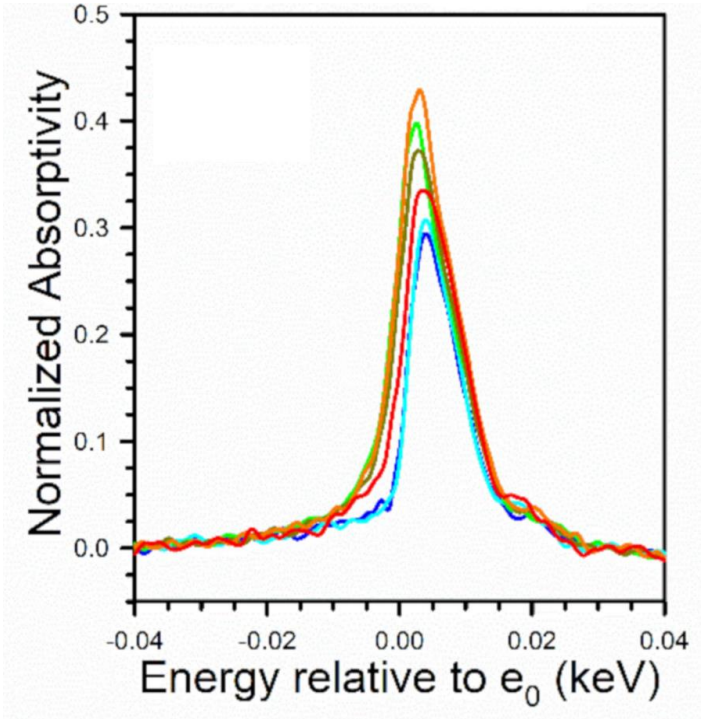
1- Jentys, A. Estimation of mean size and shape of small metal particles by EXAFS. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4059–4063.
2- Marinkovic´, N.S.; Sasaki, K.; Adzic, R.R. Nanoparticle size evaluation of catalysts by EXAFS: Advantages and limitations. *Zaštita 18.Mater.* **2016**, *57*, 101–109.

XANES (X-ray absorption near edge structure) Spectra at the Pt L-3 edge, and L-2 edge

- Overlays of L3–L2 difference spectra, showing an increase in intensity with Cs loading.
- No evidence for e– transfer to Pt from Cs was found, which should result in an opposite trend





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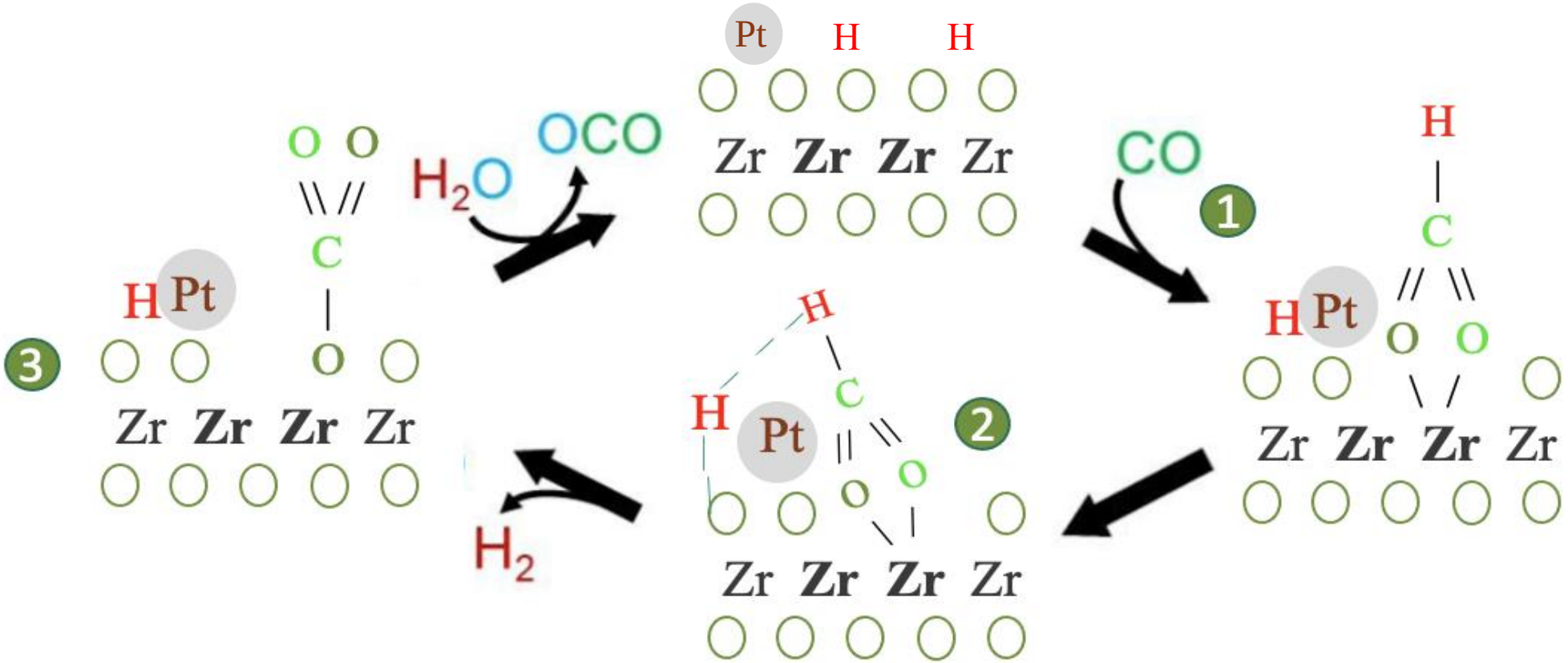
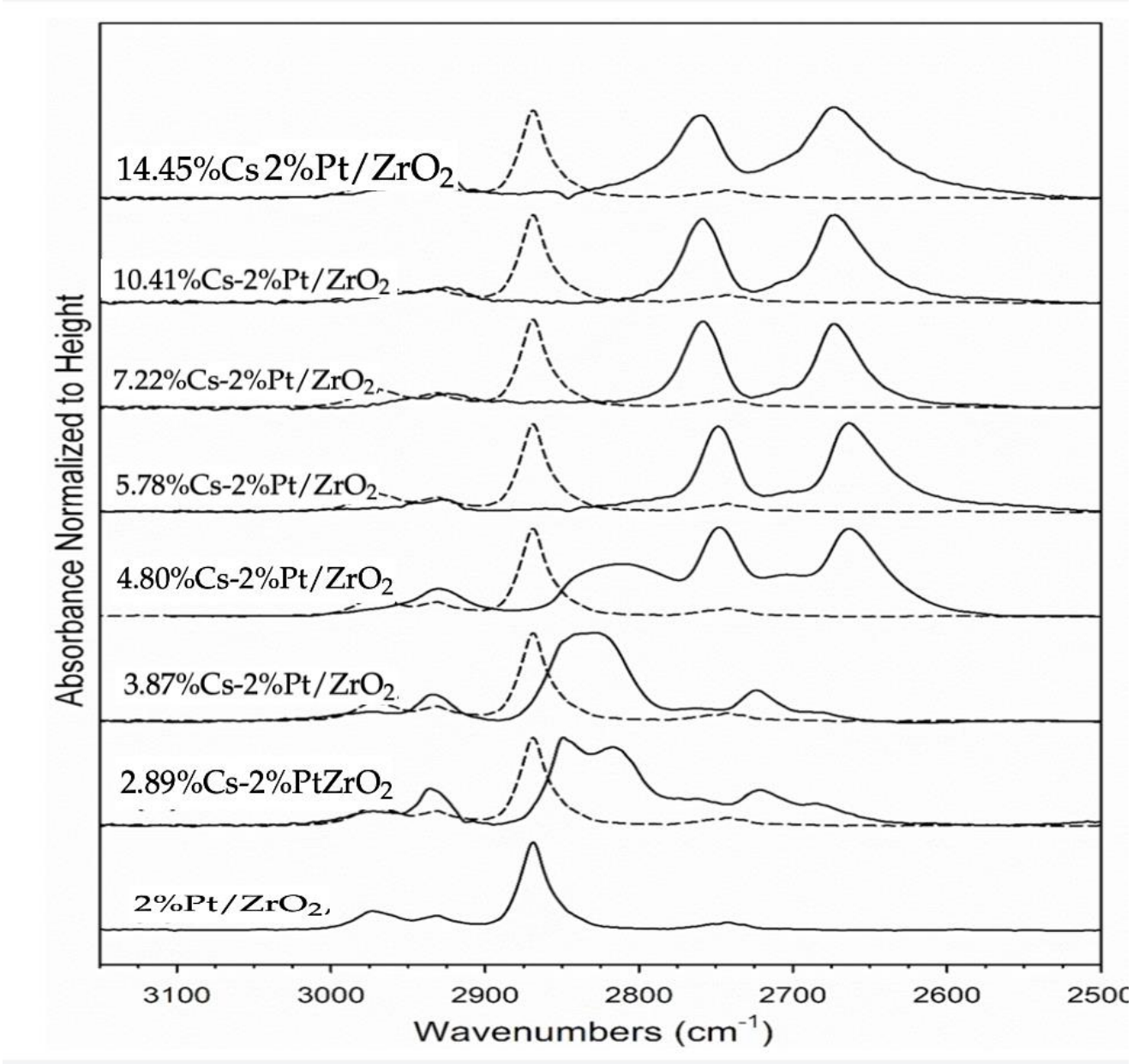
Study of Low Temperature Water Gas Shift Rection (LT-WGS)

Proposed Mechanisms for LT-WGS

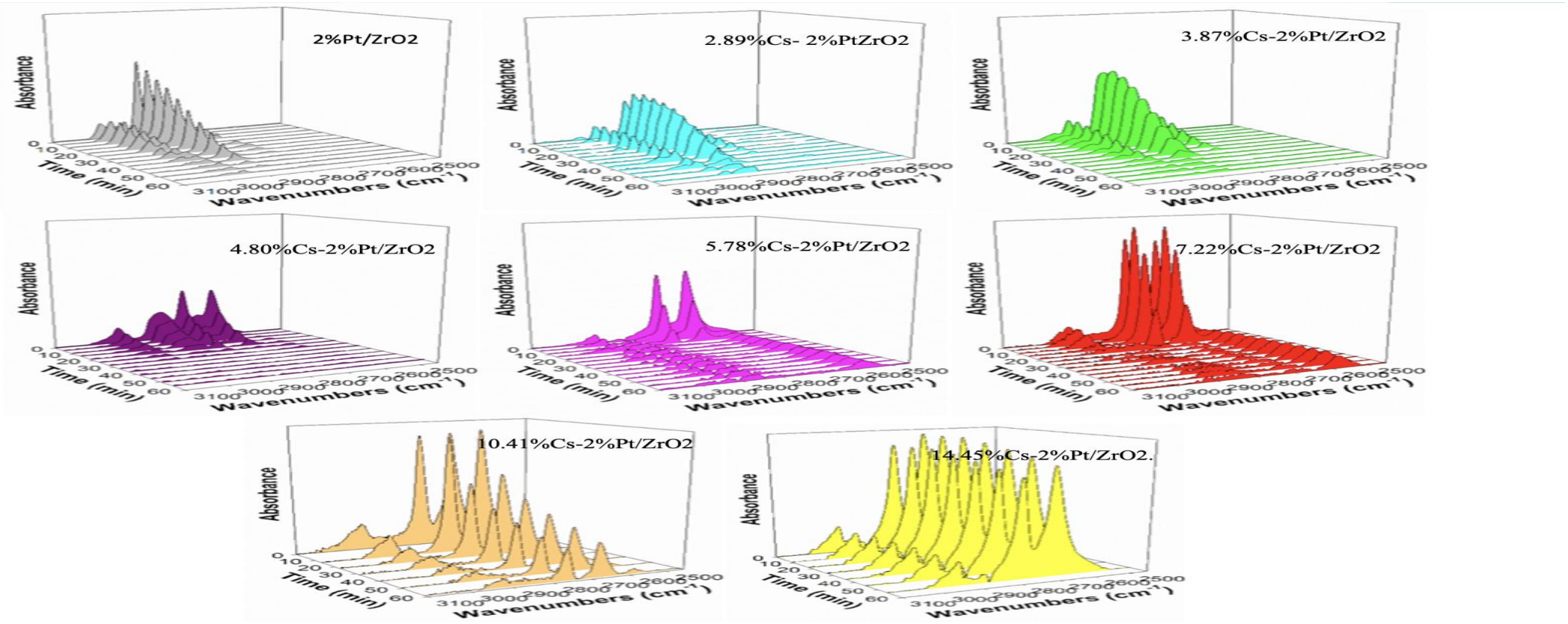


1. Shido, T. et all. Reactant-promoted reaction mechanism for water-gas shift reaction on Rh-doped CeO2. *J. Catal.* **1993**, *141*, 71–78.
2. Wang, Y.X . et all . A systematic theoretical study of the water gas shift reaction on the Pt/ZrO2 interface and Pt (111) *Catal. Sci. Technol.* **2020**, *10*, 876–892.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) LT-WGS



The decomposition of formate through the monitoring of the ν(CH)



DRIFTS results showed an improvement in the forward formate decomposition rate with Cs loading until a maximum rate in the range of 4.80%–5.78%Cs.

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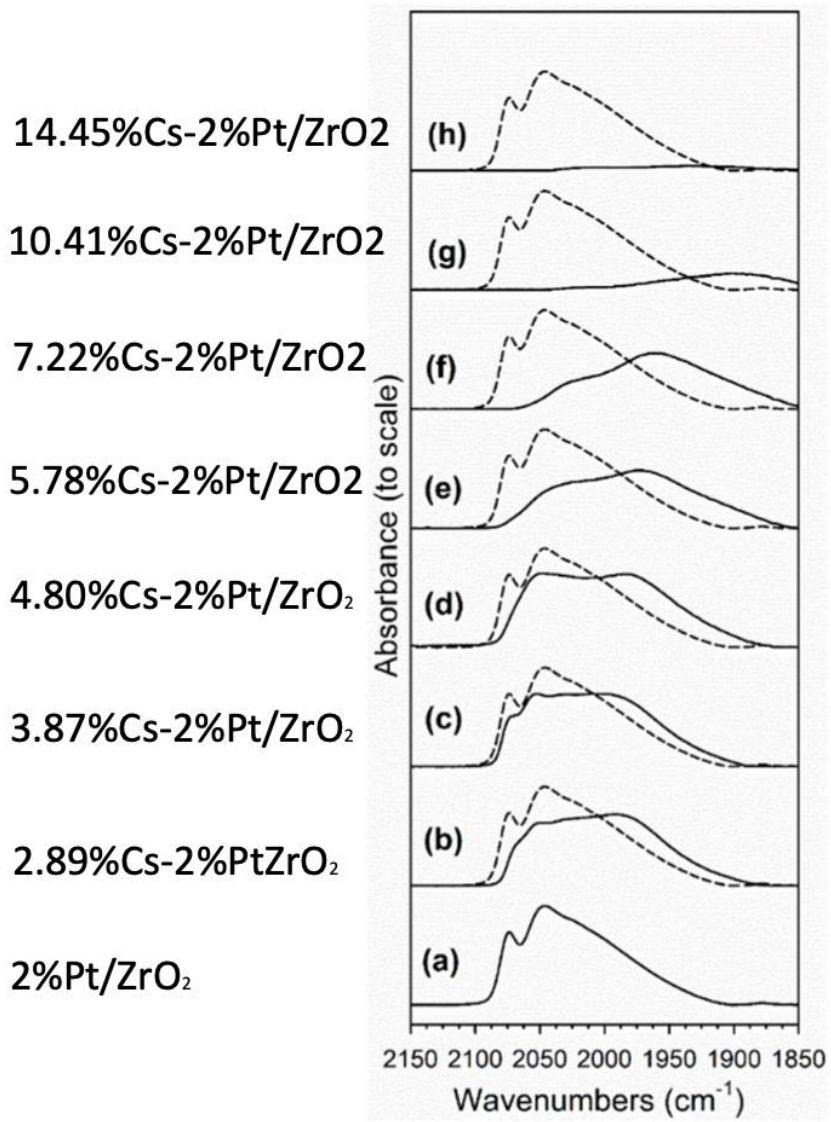
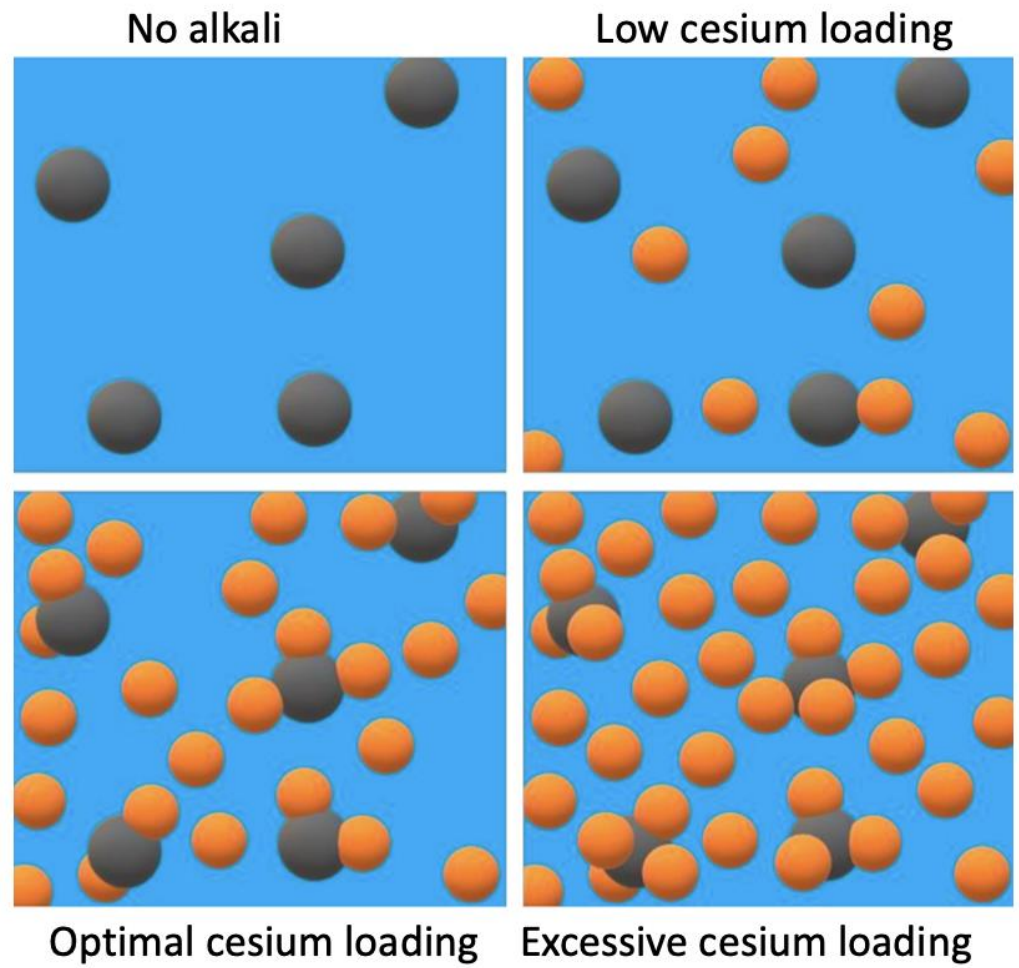
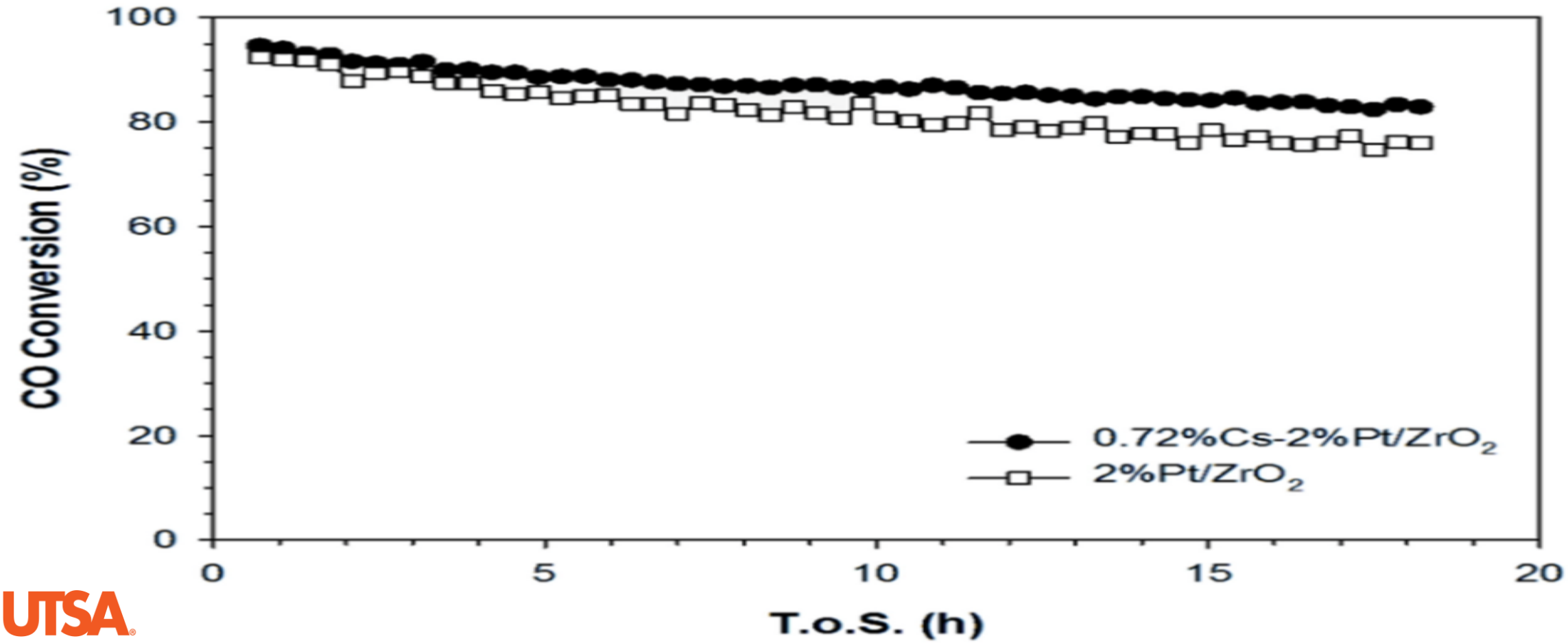

14.45%Cs-2%Pt/ZrO2
10.41%Cs-2%Pt/ZrO2
7.22%Cs-2%Pt/ZrO2
5.78%Cs-2%Pt/ZrO2
4.80%Cs-2%Pt/ZrO2
3.87%Cs-2%Pt/ZrO2
2.89%Cs-2%PtZrO2
2%Pt/ZrO2
(h)
(g)
(f)
(e)
(d)
(c)
(b)
(a)
Absorbance (to scale)
2150 2100 2050 2000 1950 1900 1850
Wavenumbers (cm-1)


No alkali
Low cesium loading
Optimal cesium loading
Excessive cesium loading

Reactor Testing



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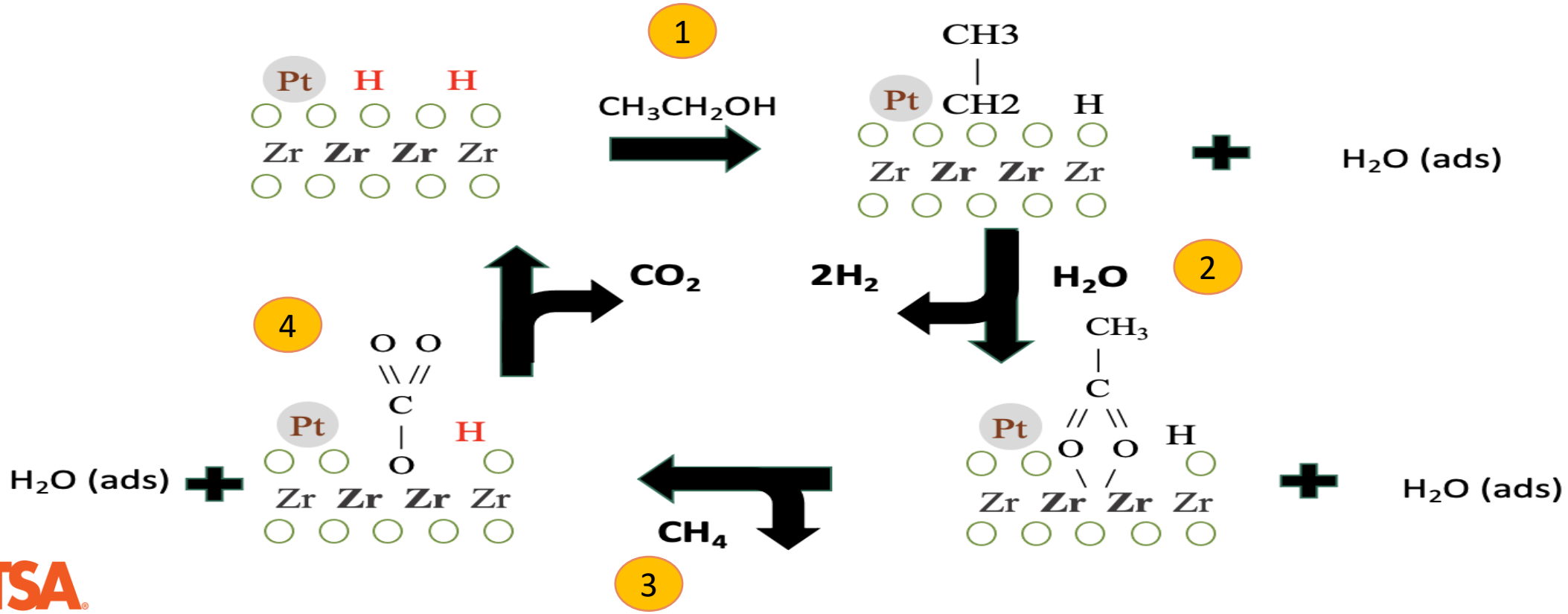
Stability test on 0.72%Cs-promoted and unpromoted Pt/ZrO2 at similar CO conversion

Study of the Ethanol Steam Reforming Reaction (ESR)

Proposed Mechanisms for Ethanol Steam Reforming Reaction



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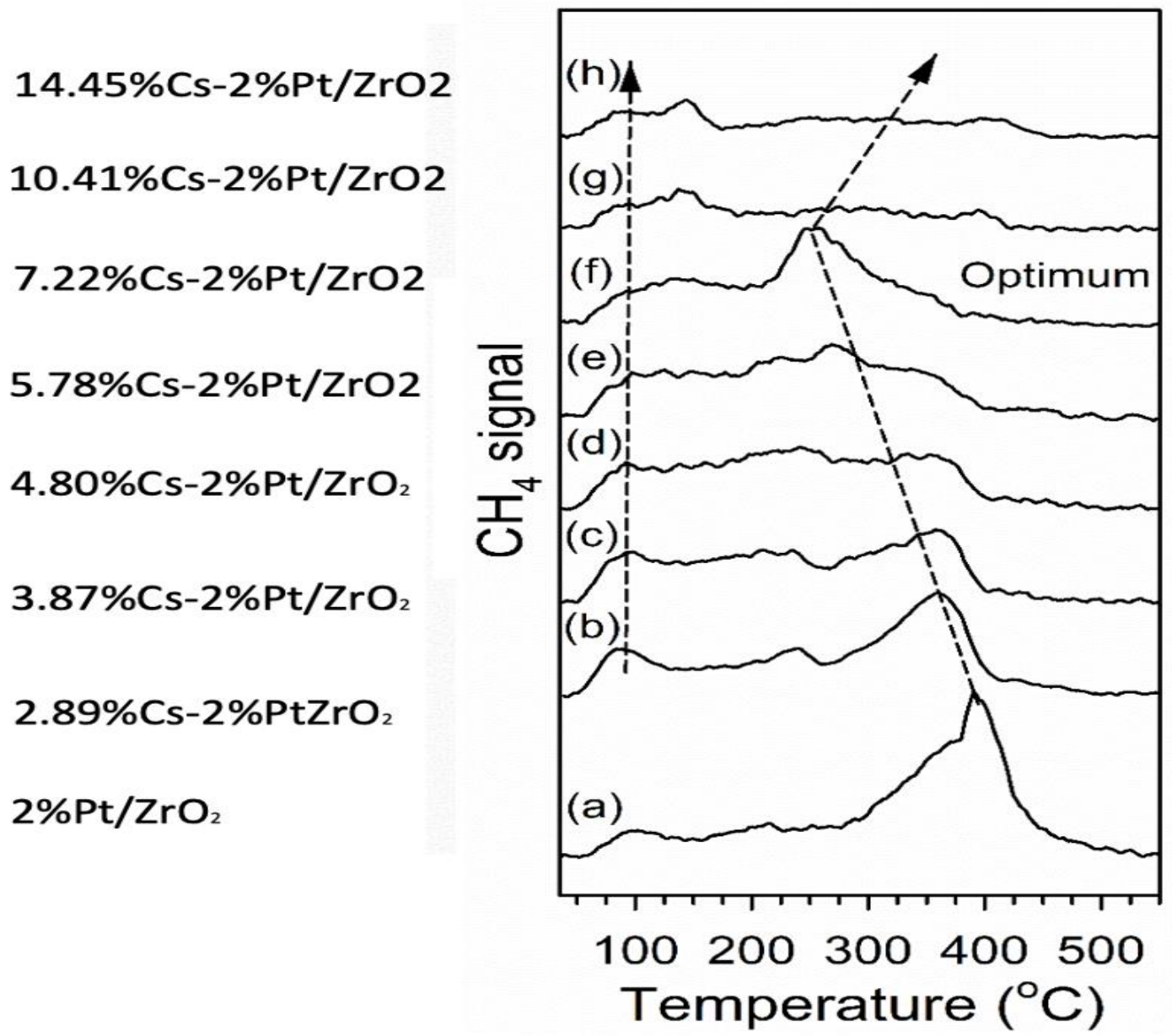
Temperature-Programmed Reaction (TPR) of Ethanol and Water



Reactor test

Catalyst	Conv. C_2H_5OH (%)	C-Selectivity (%)						
		CH_4	CO_2	CO	C_2H_6	C_2H_4	C_3H_6	CH_3CHO
2% Pt/ZrO_2	86.91	45.20 ± 2.26	28.5 ± 1.42	21.16 ± 1.05	0.92 ± 0.04	0.39 ± 0.02	0.34 ± 0.02	3.49 ± 0.34
0.7% Cs-2% Pt/ZrO_2	77.45	48.41 ± 2.42	40.40 ± 2.02	9.44 ± 0.47	0.40 + 0.02	-	-	1.35 ± 0.14
1.5% Cs-2% Pt/ZrO_2	78.42	48.02 ± 2.4	44.66 ± 2.23	6.33 ± 0.32	0.31 ± 0.02	-	-	0.68 ± 0.07
2.9% Cs-2% Pt/ZrO_2	72.95	53.76 ± 2.69	45.62 ± 2.28	-	-	-	-	0.62 + 0.06
5.8% Cs-2% Pt/ZrO_2	63.45	55.74 ± 2.77	43.88 ± 2.17	-	-	-	-	0.68 ± 0.07

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \ (\Delta H_{298}^{\circ} = 173 \text{ kJ/mol})$$

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2 \ (\Delta H_{298}^{\circ} = 55 \text{ kJ/mol}).$$

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Conclution

- Cs promotes the decarboxylation/demethanation pathway over decarbonylation by increasing the basicity of the catalyst and weakening the C–C bond of the acetate intermediate.
- The addition of just 2.9% Cs promoted decarboxylation and virtually nullified the unselective decarbonylation route with a decrease in ethanol conversion of just 16%
- Cs promoter loadings of 3.87% to 7.22% resulted in significant acceleration of the forward formate decomposition in steam at 130 ◦C.

Thank You For Your Attention