**Supplementary Information**

**Spectroscopic and Kinetic Insights into the Methane Reforming over Ce-pyrochlores**

**Disha Jain[[1]](#footnote-1)\*, Shreya Saha**

Department of Chemical Engineering

Indian Institute of Science, Bangalore 560012, India

**H2 Temperature Programmed Reduction**



**Figure S1.** TPR profiles of bare pyrochlore oxides

Figure S1 depicts that Ce2Zr2O7 shows the lowest H2 uptake/ OSC. The lower OSC of Ce2Zr2O7 than Ce2Zr2O8 indicating that the amount of oxygen content is lower in synthesized Ce2Zr2O7 samples, thus corroborating XPS results. The amount of H2 consumption Ce2Zr2O7, Ce2Zr2O8 and Ce2Ti2O7 in was found to be 83, 169 and 135 μmol O/g, respectively.



**Figure S2.** TPR profiles of samples containing Pt at Ce and Zr site, respectively

Figure S2 shows the comparison of the H2 reduction profile of Ce2Zr1.96Pt0.04O7-δ and Ce1.96Pt0.04Zr2O7-δ. It is evident from the figure that the substitution of Pt on Ce site does not have synergistic influence on the extent of reduction of the oxide. The OSC of Ce2Zr1.96Pt0.04O7-δ and Ce1.96Pt0.04Zr2O7-δ was found to be 270 and 36 μmol O/g, respectively.

**CO Temperature Programmed Desorption**



**Figure S3.** CO TPD profile of Ce2Zr1.96Pt0.04O7-δ

**Catalytic Studies**

 

**Figure S4.** Comparison between the (a) Conversion, (b) Reaction rate of 20% and 3% CH4 with CH4:CO2 -1 over Ce2Zr1.96Pt0.04O7-δ; Reaction conditions- GHSV = 38120 h-1, Wcat = 100 mg



**Figure S5.** Comparison variation in fractional CH4 conversion with temperature for DRM over Ce2Zr1.96Pt0.04O7-δ and 4% Pt/ Ce2Zr2O7; Reaction conditions- GHSV = 38120 h-1, Wcat = 100 mg

**DRIFTS Studies**





**Figure S6.** DRIFT spectra recorded upon exposure of CH4, CO2 and CH4+CO2 on Ce2Zr1.96Pt0.04O7-δ at (a) 30 °C, (b) 350 °C, (c) 450 °C; (d) CH4+CO at different temperatures

**Derivation of rate equation** **for Ce2Zr1.96Pt0.04O7-δ**

 (R-1)

 (RDS) (R-2)

 (R-3)

 (R-4)

 (R-5)

 (R-6)

 (R-7)

 (R-8)

 (R-9)

 (R-10)

 (R-11)

By writing pseudo steady state approximation, the adsorption of CH4 and H2 on Pt at equilibrium can be given as

 (E-1)

 (E-2)

where, and represents the fractional coverage of sites which are covered by CH4 and H species, respectively, and denotes the fraction of unoccupied Pt sites. DRIFTS study exhibited the presence of the adsorbed CO2 (step 5) as well as the formation of carbonates (step 4) over the catalyst surface. The kinetic studies suggested that there is no competition between CH4 and CO2 for the same site (Pt). Therefore, it was assumed that CO2 adsorption occurs on the oxide vacancy present near Pt. On the basis of previous reports and DRIFTS, the interaction of CO2 with lattice oxygen leading to carbonate formation was also integrated in the reaction mechanism. The generation of formates can be attributed to the interaction between adsorbed CO2 on the oxide vacancy (neat Pt) and H species adsorbed on Pt site.

 (E-3)

 (E-4)

 (E-5)

 (E-6)

For C-Pt species,

 (E-7)

The site balance for Pt and support is as follows

 (E-8)

 (E-9)

 (E-10)

 (E-11)

where and refers to the fraction of vacant site (oxide vacancy) and sites occupied by O species, respectively. , and denotes the fraction of site occupied adsorbed CO2, carbonate and formate species, respectively. and represents the fraction of Pt site occupied by adsorbed CO and carbon, respectively. Assuming, the dissociation of CH4 to be rate determining step, the final rate expressions was found to be

 (E-12)

In the range of temperature under study, the reaction is far from equilibrium and thus the forward reaction was dominant. Hence, it is assumed that the dependence of reaction rate on reverse reaction rate parameters is negligible and the kinetic parameters of the forward reaction were sufficient to describe the kinetics. Thus, the above expression reduces to

 (E-13)

1. \* Corresponding author : disha@iisc.ac.in [↑](#footnote-ref-1)