Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

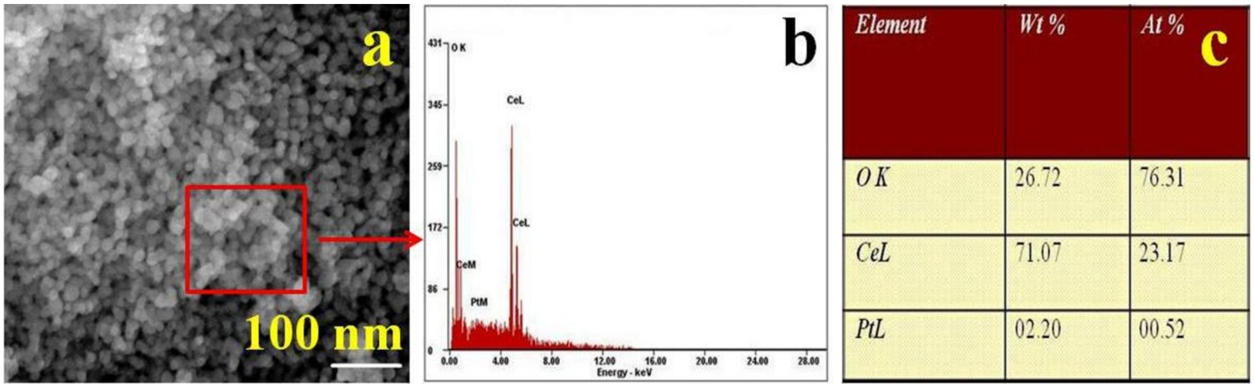
Partial Oxidation of Methane to Synthesis Gas over Pt Nanoparticles Supported on Nanocrystalline CeO_2 Catalyst

Rajib Kumar Singha,[a] Shilpi Ghosh,[a] Shankha Subhra Acharyya,[a] Aditya Yadav,[a] Astha Shukla,[a] Takehiko Sasaki,[b] Anna Maria Venezia,[c] Chandrashekar Pendem [a] and Rajaram Bal*[a]

[a]Nanocatalysis Area, Refining Technology Division, CSIR-Indian Institute of Petroleum, Dehradun 248005, India. Fax: +91 135 2660202; Tel: +91 135 2525917.

[b]Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, Kashiwanoha, Kashiwa-shi, Chiba 277-8561, Japan.

[c]ISMN-CNR, Via Ugo La Malfa 153, 90146 Palermo, Italy.



Element	*Wt %*	*At %*
O K	26.72	76.31
CeL	71.07	23.17
PtL	02.20	00.52

Fig. S1. (a) SEM image of 2Pt-CeO_2^{PS} catalyst, (b) EDAX of the indicated portion of the sample and (c) Elemental composition obtained from the EDAX analysis.

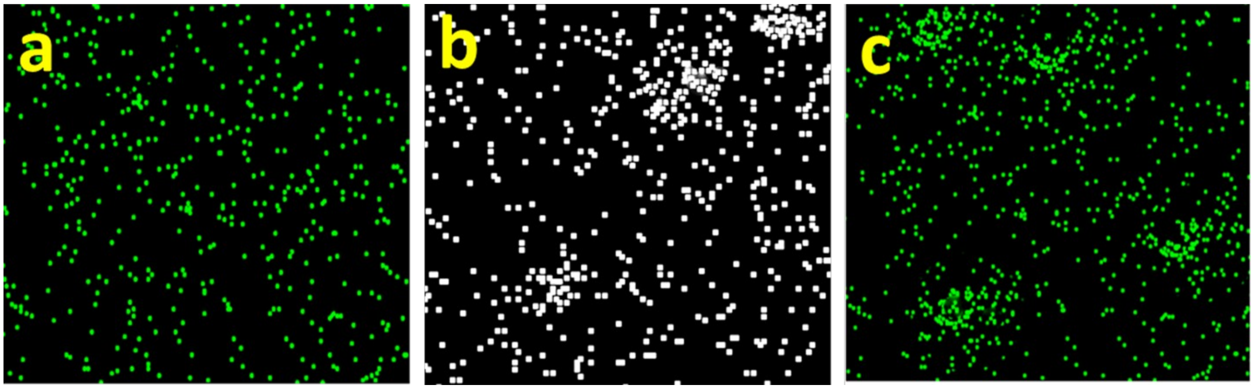


Fig. S2. Elemental mapping of Pt from SEM analysis, (a) 2Pt-CeO_2^{PS}, (b) 2Pt-CeO_2^{Imp} and (c) 2Pt-CeO_2^{PSCom} catalyst.

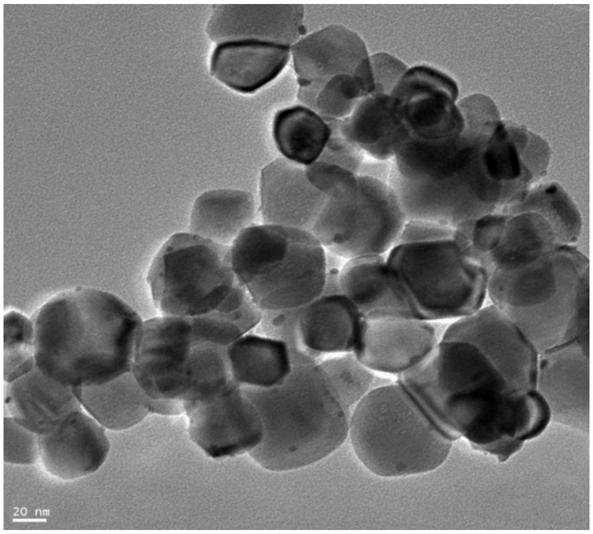


Fig. S3. TEM image of the prepared 2Pt-CeO_2^{PS} catalyst.

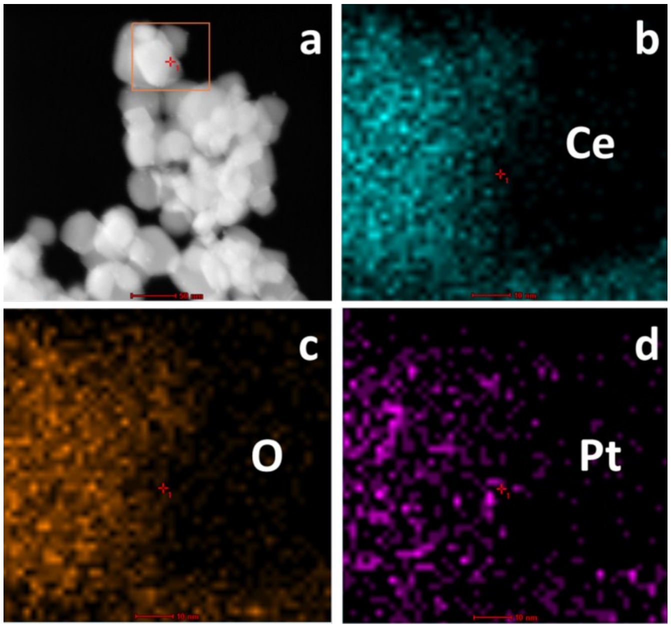


Fig. S4. Elemental mapping of the prepared 2Pt-CeO_2^{PS} catalyst.

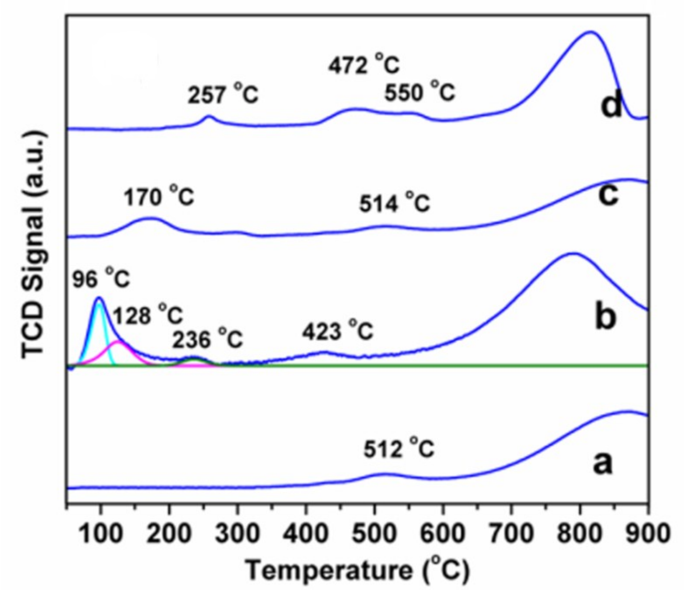


Fig. S5. CO-TPR of (a) CeO2HT, (b) 2Pt-CeO_2^{PS}, (c) 2Pt-CeO_2^{PSCom} and (d) 2Pt-CeO_2^{Imp} catalyst.

The reduction behavior of CeO_2^{HT}, 2Pt-CeO_2^{PS}, 2Pt-CeO_2^{PSCom} and 2Pt-CeO_2^{Imp} catalysts was also examined through CO-TPR by monitoring the CO consumption and the production of CO_2. The corresponding patterns are shown in Fig. 4(ii). CO can also be used as a reducing agent to characterize the reducibility of the catalyst.[1, 2] CO reduces the surface CeO_2 at lower temperatures as compared to H_2 because the adsorbed H_2 needs to be dissociated to achieve the reduction of Pt or CeO_2, whereas, CO can directly reduce the surface oxygen in CeO_2.[1] We believe that due to the small size of Pt particle, it is easier to reduce the Pt species compared to the bigger Pt particles for other catalysts. In case of Pt-CeO_2^{Imp} (Fig. 4(ii)d), two reduction peaks appeared around 472 °C due to bulk Pt-oxide species and 550 °C due to surface layer reduction of CeO_2.[3]

References:

1. H. Zhu, Z. Qin, W. Shan, W. Shen and J. Wang, J. Catal., 2004, 225, 267.
2. J. Bilik, P. Pustejovska, S. Brozova and S. Jursova, Scientia Iranica B, 2013, 20(2), 337.
3. A. Scarabello, D. D. Nogare, P. Canu and R. Lanza, App. Catal. B: Environmental, 2015, 174, 308.

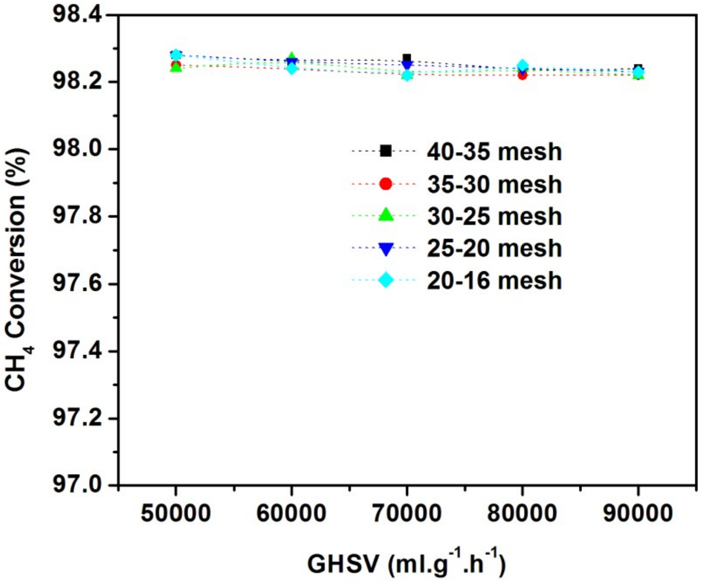


Fig. S6 Effect of pellet size and GHSV.

Reaction condition: catalyst (120 mg) diluted with ground quartz, Temperature (800 °C), $O_2 : CH_4$: He = 1:1:7 (feed ratio), Pressure (1 atm.).

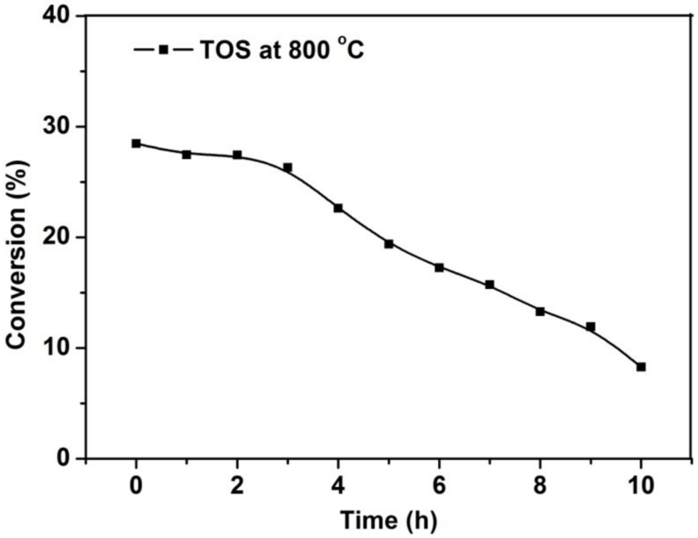


Fig. S7. Effect of TOS over 2Pt-CeO$_2^{\mathrm{Imp}}$ catalyst at 800 °C.

Reaction condition: Pressure (1atm), GHSV (80000 mlg^{-1}h^{-1}), Feed ratio (O$_2$:CH$_4$:He = 1:2:7).

Mass and Heat Transfer Calculations for Partial oxidation of methane upon 2Pt-CeO$_2^{\mathrm{PS}}$ catalyst at 800 °C

For PBR reaction mode (10 O$_2$ / 20 CH$_4$ / 70 He) with respect to Methane

Mears Criterion for External Diffusion

If $\frac{-r_A'\rho_b R n}{k_c C_{Ab}} < 0.15$, then external mass transfer effects can be neglected.

$-r_A'$ = reaction rate, kmol/kg-cat · s

n = reaction order

R = catalyst particle radius, m

ρ_b = bulk density of catalyst bed, kg/m^3

=(1-ϕ) (ϕ= porosity or void fraction of packed bed)

ρ_c = solid catalyst density, kg/m^3

C_{Ab} = bulk gas concentration of A, kmol/m^3

k_c = mass transfer coefficient, m/s

$\dfrac{-r_A'\rho_b R n}{k_c C_{Ab}}$ = [1.91 × 10^{-04} kmol-C_3/kg-cat.s × 1000] [367 kg/m^3][5.3 × 10^{-5} m][0.75]/([1.02 m/s] × [0.0508 kmol/m^3])= **5.3774 x 10^{-2} < 0.15 {Mears for External Diffusion}**

Weisz-Prater Criterion for Internal Diffusion

If $C_{WP} = \dfrac{-r'_{A(obs)}\,\rho_c R^2}{D_e C_{As}} < 1$**, then internal mass transfer effects can be neglected.**

-r'$_{A(obs)}$ = observed reaction rate, kmol/kg-cat · s

R = catalyst particle radius, m

ρ_c = solid catalyst density, kg/m^3;

D_e = effective gas-phase diffusivity, m^2/s

$= \dfrac{D_{AB}\phi_p \sigma_c}{\tau}$ where

D_{AB} = gas-phase diffusivity m^2/s; ϕ_p = pellet porosity; σ_c =constriction factor; τ =tortuosity.

C_{As} = gas concentration of A at the catalyst surface, kmol-A/m^3

$C_{WP} = \dfrac{-r'_{A(obs)}\,\rho_c R^2}{D_e C_{As}}$ = [1.91 × 10^{-04} kmol-C^3/kg-cat.s × 1000] × [4.777 x 10^3 kg-cat/m^3] × [5.3 × 10^{-5} m]^2 / ([3.74 × 10^{-4} m^2/s] × [0.0508 kmol-C3/m^3]) = **0.85 < 1**

{Weisz-Prater Criterion for Internal Diffusion}

Mears Criterion for External (Interphase) Heat Transfer

$$\left|\frac{-\Delta H_r(-r_A')\rho_b R E}{h_t T_b^2 R_g}\right| < 0.15$$

[-52 kJ/mol × (-1.91 × 10^{-04} kmol/kg-cat.s) × 1000 × 367 kg-cat/m^3 × 5.3 x 10^{-5} m× 65.75 kJ/mol] / [5.325 kJ/m^2.K.s × 1073^2 K^2 × 8.314 ×10^{-3} kJ/mol.K] = 2.49 × 10^{-4} < 0.15

{Mears Criterion for External (Interphase) Heat Transfer}

Mears Criterion for Combined Interphase and Intraparticle Heat and Mass Transport (Mears, 1971)

$$\frac{-r'_A R^2}{C_{Ab} D_e} < \frac{1 + 0.33\gamma\chi}{\left|n - \gamma_b \beta_b\right|(1 + 0.33 n\omega)}$$

$$\gamma = \frac{E}{R_g T_s};\ \gamma_b = \frac{E}{R_g T_b};\ \beta_b = \frac{(-\Delta H_r) D_e C_{Ab}}{\lambda T_b};\ \ \chi = \frac{(-\Delta H_r) - r'_A R}{h_t T_b};\ \ \omega = \frac{-r'_A R}{k_c C_{Ab}}$$

γ = Arrhenius number; β_b = heat generation function;

λ = catalyst thermal conductivity, W/m.K;

χ = Damköhler number for interphase heat transport

ω = Damköhler number for interphase mass transport

$\frac{-r'_A R^2}{C_{Ab} D_e}$ = [1.91 × 10^{-04} kmol/kg-cat.s × 1000 × (5.3 × 10^{-5})^2 m^2]/[0.0508 kmol/m^3 × 3.74 × 10^{-4} m^2/s] = 2.82 ×10^{-5} < 3

{Mears Criterion for Interphase and Intraparticle Heat and Mass Transport }