

EXAFS analysis for Pt/CeO₂ catalysts active for partial oxidation of methaneRajaram Bal^{1,*} and Takehiko Sasaki²¹ Refinery Technology Division, CSIR- Indian Institute of Petroleum,
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1 Introduction

Natural gas or mainly methane is considered to be an alternative source of future fuel due to its very high abundance on earth. After decades of research methane steam reforming (SRM) is established as the one and only large scale commercial process for syngas production. Partial oxidation of methane (POM) is considered to be an alternative for SRM from energy and economic point of view, produces synthesis gas with H₂/CO ratio 2. Because of exothermic nature of POM reaction, the process is capable of synthesis gas production at much lower temperature.

Here, we are reporting the EXAFS characterization of Pt-nanoparticles supported CeO₂ mesoporous spheres for POM. The catalyst was highly active and stable for more than 60 h at 800 °C. Bimodal nature of pores of the catalyst was found to be the reason for superior activity of the catalyst [1].

2 Experiment

Pt-CeO₂ mesoporous spheres were prepared by two step synthesis technique. First, CeO₂ mesoporous spheres with bimodal pore structure were prepared by solvo-thermal method and then Pt-nanoparticles were deposited over prepared CeO₂ surface by following a newly developed method as reported elsewhere [1]. EXAFS measurements of Pt-L_{III} edge were carried out at KEK-IMMS-PF BL9C.

3 Results and Discussion

Recently we have reported Pt-nanoparticles supported CeO₂ nanocrystals (2Pt-CeO₂^{PS}) with very high POM activity [2]. The catalyst was prepared by a two-step synthesis method and controlled deposition of Pt-particles led to formation of very small (1.54 nm, from metal dispersion) and highly selective Pt-nanoparticles formation. Here, we have prepared Pt-CeO₂^{MS} catalyst with similar two-step method but the difference was synthesis of support and its properties. Previous report was about 20-60 nm of CeO₂ crystals (Surface area 88.7 m²/g) but here in this report we will be discussing about 150 nm mesoporous spheres comprised of about 5-15 nm of CeO₂ particles (Surface area 182 m²/g). The best and most advantageous feature of the support (CeO₂^{MS}) and the catalyst (2Pt-CeO₂^{MS}) was its bimodal pore structure and very high surface area, which led to even much smaller Pt-particles (1.27 nm) formation and much more selective Pt-CeO₂^{MS} catalyst for POM reaction [3].

EXAFS analysis was done for Pt L_{III}-edge to analyze the local environment of 2Pt-CeO₂^{MS-F} and 2Pt-CeO₂^{MS-S} catalyst. F and S represent fresh and spent, respectively. Figure 1a and 1b shows the EXAFS Fourier transforms of 2Pt-CeO₂^{MS-F} and 2Pt-CeO₂^{MS-S} catalysts. Table 1 shows structural parameters for 2Pt-CeO₂^{MS-F} catalyst and 2Pt-CeO₂^{MS-S} catalyst. The parameters were obtained by curve fitting of Pt L_{III}-edge spectra of both the catalysts. EXAFS spectra of 2Pt-CeO₂^{MS-F} catalyst showed presence of Pt-oxide with Pt-O bond distance 0.1995 nm and co-ordination number 2.4. 2Pt-CeO₂^{MS-F} catalyst also showed presence of metallic Pt with Pt-Pt bond distance 0.2787 nm and co-ordination number 5.9. So, 2Pt-CeO₂^F catalyst contains both Pt-oxide and metallic Pt species. Presence of metallic Pt-species was unusual but our recent study revealed that use of hydrazine and CTAB could have been the reason for such observation [2]. Use of hydrazine reduced Pt-ions to metallic Pt during Pt-deposition and during calcination although all the particles are supposed to be oxidized but presence of CTAB which produced hydrogen species could have reduced some of the oxidized Pt-species back to its metallic form. 2Pt-CeO₂^{MS-S} catalyst also showed presence of both Pt-oxide and metallic Pt species. In this case, Pt-O bond distance was 0.2002 nm and co-ordination number 1.1, whereas Pt-Pt bond distance of metallic Pt particles were 0.2765 nm and co-ordination number 5.8. Presence of Pt-oxide in 2Pt-CeO₂^{MS-S} catalyst was due to re-oxidation of metallic Pt-species during catalysis.

Table 1: Summary of the EXAFS fitting results for the fresh and spent Pt catalysts^a

	Path	R (10 ⁻¹ nm)	CN	DW (10 ⁻⁵ nm ²)	ΔE ₀ (eV)	R _f (%)
Fresh	Pt-O	1.995±0.011	2.4±0.6	2.5±1.9	10.6±1.7	1.5
	Pt-Pt	2.787±0.012	5.9±0.4	5.5±1.7		
Spent	Pt-O	2.002±0.013	1.1±0.4	0.42±2.1	9.1±2.0	1.6
	Pt-Pt	2.765±0.008	5.8±1.1	5.5±1.0		

^a Fitting was conducted in the range Δk: 3–12.5 (10⁻¹ nm) and ΔR: 1.2–3.0 (10⁻¹ nm). Amplitude reducing factor S₀² was set as 0.95

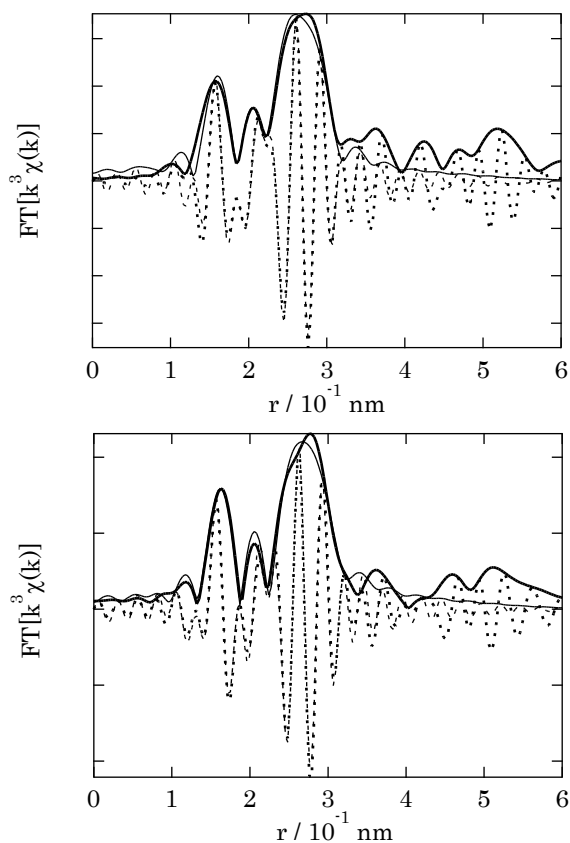


Figure 1: (a) (Upper panel) k^3 -weighted Fourier transform of Pt-L_{III} edge EXAFS for the fresh 2Pt-CeO₂^{MS} catalyst. Amplitude and imaginary part are traced by thick curve and thin curve, respectively. Observed data are shown with solid lines and fitting data are shown with dotted lines. (b) (Lower panel) k^3 -weighted Fourier transform of Pt-L_{III} edge EXAFS for the spent 2Pt-CeO₂^{MS} catalyst. Amplitude and imaginary part are traced by thick curve and thin curve, respectively. Observed data are shown with solid lines and fitting data are shown with dotted lines.

In summary, CeO₂ mesoporous spheres prepared by solvo-thermal method showed bimodal nature of pore size distribution. Bimodal nature of CeO₂ mesoporous spheres provided very high surface area. Pt-nanoparticles were deposited over the prepared CeO₂ mesoporous spheres by controlled deposition method, which showed very high Pt-dispersion. Very high Pt-dispersion of prepared Pt-CeO₂ catalyst was the result of Pt-deposition method in presence of morphology controlling agent CTAB and capping agent hydrazine. In addition, smaller pores of support CeO₂ mesoporous spheres, which provided high surface area improved Pt-dispersion. High OSC and bimodal nature of the catalyst highly improved catalytic activity by lowering the ignition temperature and protecting Pt-particles residing inside the smaller pores of the catalyst. Pt-particles residing inside the smaller pores of the catalyst were protected from sintering and rapid molecular transportation through larger pores highly influenced POM

activity and stability of the catalyst. Different characterization techniques revealed high metal-support interaction, which highly enhanced the metal-support interfacial surface area and improved activity and stability of the catalyst during POM. Superior activity and stability of the catalyst was due to catalysts bimodal nature, smaller catalyst particles, high OSC and high metal-support interactions.

References

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