

## Partial Oxidation of Methane on Pt-Supported Nanocrystalline Doped Ceria-Zirconia

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### Introduction

Catalytic partial oxidation of methane (POM) into syngas at short contact times using monolithic catalysts is now considered as promising alternative to the traditional steam reforming [1]. Recent research suggests that catalysts comprised of Pt supported on complex fluorite-like oxides favor the so called direct route of methane oxidation into syngas (formation of H<sub>2</sub> and CO as primary products further oxidized into CO<sub>2</sub> and H<sub>2</sub>O depending on process conditions) [2]. This work presents results of research aimed at elucidating effect of the surface/lattice oxygen mobility and reactivity for Pt-supported nanocrystalline Ln<sub>0.3</sub>Ce<sub>0.35</sub>Zr<sub>0.35</sub>O<sub>2-y</sub> (Ln =La, Pr, Gd) catalysts on their performance in POM at short contact times applying a complex of sophisticated kinetic methods. The main attention is paid to elucidation and critical analysis of kinetic (especially, transient) features which might support or reject bifunctional scheme of POM mechanism with a due regard for the Pt-support interaction, oxygen transfer between Pt and surface sites/bulk of nanocrystalline complex oxide supports and effect of realistic reaction feeds on the state of catalyst.

### Experimental

Nanocrystalline fluorite-like oxides Ln<sub>0.3</sub>Ce<sub>0.35</sub>Zr<sub>0.35</sub>O<sub>2-y</sub> (Ln =La, Pr, Gd) were prepared via Pechini route, and Pt was supported by wet impregnation. Parameters characterizing oxygen mobility in nanocrystalline samples with a due regard for fast oxygen diffusion along domain boundaries and Pt-support spillover were estimated from results of <sup>18</sup>O<sub>2</sub> SSITKA experiments [3]. To minimize the heat transfer effect, active composites were supported as thin (10 micron) layers on walls of a separate corundum channel (wall thickness 0.2 mm, triangle side 2.33 mm, channel length 10 mm) [2] and tested in POM at short contact times (5-15 ms) in feeds with

CH<sub>4</sub> content up to 20%, CH<sub>4</sub>/O<sub>2</sub>=2. Transient kinetic experiments were carried out by switching the stream of He to reaction mixture or CH<sub>4</sub> in He. The reactivity of fully oxidized catalyst with respect to CH<sub>4</sub> was evaluated using the TAP system (TAP-1 reactor upgraded with a Stanford Research Systems, SRS RGA300 quadrupole mass spectrometer) and pulse microcatalytic installation combined with a Setaram Sensys DSC TG calorimeter.

### Results/Discussion

For nanocrystalline oxide supports, coefficients of oxygen diffusion (D<sub>interf.</sub> up to 10<sup>-12</sup> cm<sup>2</sup>/s at 700°C) along nanodomain boundaries are by ~3 order of magnitude higher than D values for diffusion within domains. The rate of Pt-support oxygen spillover exceeds by several times the rate of oxygen exchange on Pt sites. Steady-state activity of catalysts in POM correlates with oxygen mobility along domain boundaries (Pr>Gd>La). For completely oxidized surface both TAP and real-pressure pulse studies demonstrated syngas formation along with CO<sub>2</sub> and H<sub>2</sub>O, syngas selectivity increasing with oxygen removal from the catalyst, CO TAP responses being sharp, while those of CO<sub>2</sub> - broad. The average heat of oxygen adsorption as a function of reduction degree varies from ~ 200 kJ/mol on oxidized surface (corresponds to on-top M-O form stabilized on defect sites) to ~ 600 kJ/mol O<sub>2</sub> after removing ~ monolayer of oxygen (corresponds to bridging M<sub>2</sub>O form bound with Ce cations). Rate of CH<sub>4</sub> conversion decreases with reduction degree though remaining high even after monolayer removing due to a fast oxygen diffusion along interfaces. Estimation of rate constants of different steps from results of transient experiments support a direct route of CH<sub>4</sub> selective oxidation into syngas with oxygen-assisted methane activation. This mechanistic feature is related to the strong Pt-support interaction stabilizing in vicinity of domain boundaries highly dispersed oxidic Pt species less active in CH<sub>4</sub> and syngas combustion than metallic Pt clusters. Support activates O<sub>2</sub> molecules and supplies active oxygen species to Pt sites. A high rate of oxygen diffusion on the surface and in the bulk of the support and Pt-support oxygen spillover stabilizes Pt in a well dispersed partially oxidized state while preventing coking at high concentrations of CH<sub>4</sub> in the feed and decreasing activity in reverse water gas shift reaction catalyzed by metallic Pt particles.

Acknowledgements. Support by OCMOL FP7 Project, RFBR-CNRS 09-03-93112 Project and Russian Federal Innovation Agency via the program "Scientific and Educational cadres" is gratefully acknowledged. The Embassy of France in Moscow is gratefully acknowledged for the joint PhD studentship grant of A. Bobin.

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