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Ethanol selective oxidation into syngas over Pt-promoted fluorite-like oxide: SSITKA and pulse microcalorimetry study

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ABSTRACT

Catalysts based on oxides with a high lattice oxygen mobility and reactivity are known to be able to efficiently transform ethanol into syngas by selective oxidation. Mechanism of this reaction over $Pt/Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ catalyst was studied by using SSITKA and pulse microcalorimetry. The rate–determining step is C—C bond rupture in ethanol/acetaldehyde molecules, while C—H bond breaking in the ethanol dehydrogenation step proceeds easily. The mechanism is described by step-wise red–ox scheme including ethanol oxidative decomposition on Pt sites with participation of bridging oxygen species (with the heat of adsorption ~ 550 kJ/mol O_2) located at Pt-oxide interface followed by fast reoxidation of reduced support sites by O_2. Rapid oxygen migration from the oxide sites to Pt provides conjugation between these steps, thus suppressing coking.

1. Introduction

Biofuels derived from renewable feedstocks can be used as a source of hydrogen for fuel cells as well as syngas for chemical industry. Ethanol is the most widespread biofuel with the annual production rate of 84.5 billion L in 2011 [1]. Syngas production by ethanol steam reforming on traditional catalysts is hampered by their rapid deactivation due to coking. This problem can be solved by using catalysts based on oxides with a high lattice oxygen mobility and reactivity able to transform ethanol into syngas by selective oxidation or oxidative steam reforming ($Pt/CeZrO_2$, Ir/CeO_2, Pt/ZrO_2, Ru or Pd/Y_2O_3 etc) [2–9]. However, to provide a high yield of syngas in these processes with a lot of steps occurring at the oxide sites or metal-support interface [3–11], characteristics of complex oxide supports and supported metals are to be properly tuned. At present such crucial characteristics mainly remained to be clarified at the best semi-qualitatively, which makes such a task at least demanding. Thus, such important characteristics of ceria (ceria-zirconia) –based oxide supports as oxygen mobility and oxygen storage capacity are mainly determined for the initial oxidized state [7,12], while they can be quite different in the partially reduced steady-state [13]. Hence, it is not clear whether surface diffusion of the reactive oxygen species to the metal-support interface is sufficiently fast to provide their supply required for the efficient consumption of activated fuel species –acetaldehyde or acetate complexes [2,10,11] to prevent coking. If this is so, a simple red-ox scheme of ethanol partial oxidation with independent stages of ethanol and oxygen transformation on the metal and oxide sites, respectively, conjugated by the surface oxygen diffusion can be applied [13]. Similarly, the surface oxygen bonding strength in the steady-state conditions of ethanol partial oxidation has not yet been estimated, though it is well known to be much higher in stationary conditions of red-ox reactions (methane dry reforming, etc [14]) than for the initial oxidized state. Moreover, even the nature of the rate limiting stage in ethanol transformation remains to be a matter of debate: it is assumed to be either dehydrogenation of molecularly adsorbed ethanol [15], formation and diffusion of

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Abbreviations: SSITKA, steady state isotope transient kinetic analysis; WGS, water gas shift; TEM, transmission electron microscopy; XRD, X-ray diffraction; EDX, energy dispersive X-ray spectroscopy.

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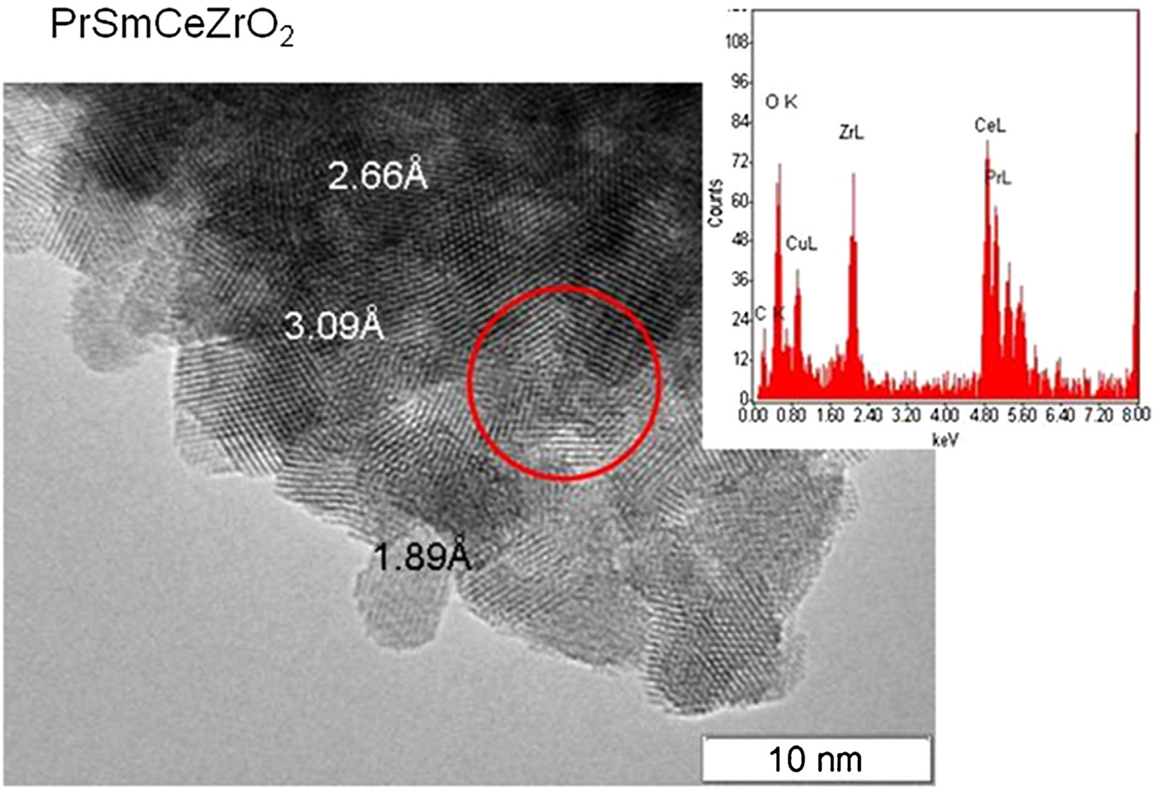
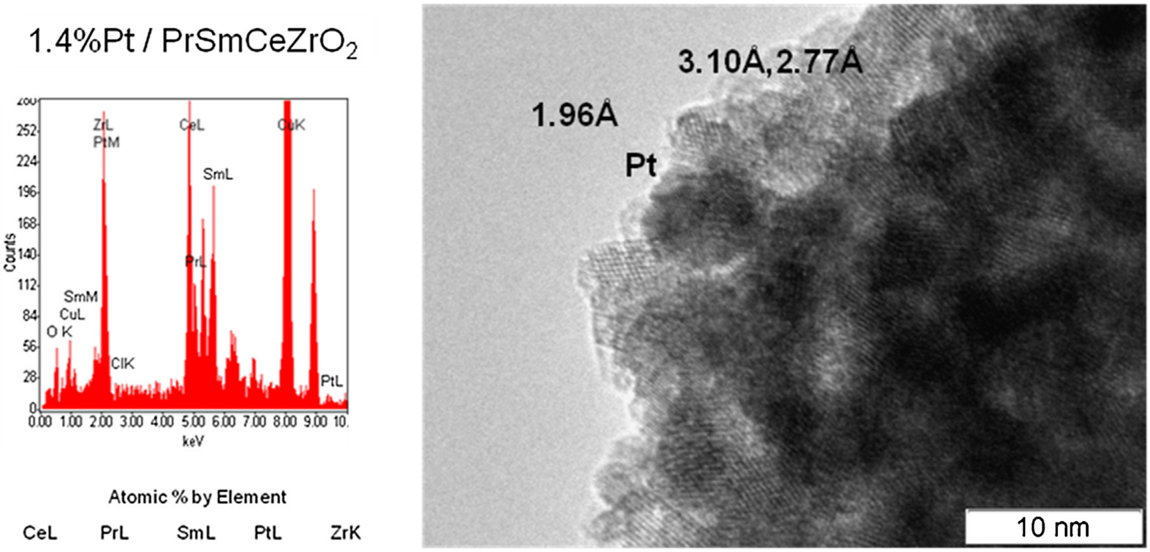


Fig. 1. TEM image of as prepared mixed oxide. Interplanar distances are shown. EDX spectrum of selected area is given in the inset.



Atomic % by Element

CeL	PrL	SmL	PtL	ZrK
44.09	14.64	16.49	0.53	24.24

Fig. 2. TEM image of as prepared catalyst sample.

acetate species along the ceria surface [7] or scission of the C—C bond in partially dehydrogenated species (acetates, acetaldehyde, etc) [10,11].

Hence, this paper presents results of research aimed at elucidation of these critically important points of mechanism of ethanol selective oxidation into syngas for the case of Pt supported on doped ceria-zirconia oxide (Pt/$Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$) by using combination of advanced techniques –pulse microcalorimetry and isotope kinetic transients.

2. Experimental

2.1. Catalysts preparation and characterization

$Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ fluorite-like oxide was prepared by polymerized complex precursor (Pechini) route and calcined in air at 900 °C for 2 h [16]. Pt (1.4 wt.%) was supported via incipient wetness impregnation with H_2PtCl_6 solution followed by drying and calcination at 700 °C for 2 h in air.

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