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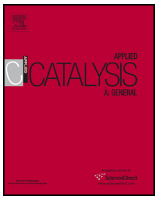

Oxidative methane coupling over Mg, Al, Ca, Ba, Pb-promoted $SrTiO_3$ and Sr_2TiO_4: Influence of surface composition and microstructure

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ABSTRACT

Mg, Al, Ca, Ba, Pb-substituted titanates $SrTi_{1-x}A_xO_3$ (A = Mg, Al, Ca, Ba, Pb, $x = 0.1$) and $Sr_2Ti_{1-x}A_xO_4$ (A = Mg, Al, $x = 0.1$) were synthesized using mechanochemical method (sintering at 1100 °C in air for 4 h) and tested in oxidative coupling of methane (OCM) at 850 and 900 °C. The obtained samples were double-phase samples consisting of Mg, Ca, Ba substituted perovskite ($SrTiO_3$) and "layered" perovskite – (Sr_2TiO_4 or $Sr_3Ti_2O_7$). In case of Al and Pb, it was shown that these cations most probably did not replace Ti in the perovskite structure and formed the $Sr_3Al_2O_6$ and $SrPbO_3$ individual phases. The most active samples were Mg- and Al-doped $SrTiO_3$ and Sr_2TiO_4, which in their mixture with inert quartz particles showed C_2 yield up to 25% and C_2 selectivity around 66%. Microstructure analysis of Mg-substituted titanates revealed that under reaction conditions the "layered" perovskite decomposed releasing (Sr, Mg)O mixed oxide segregated to the surface. The samples characterized by the highest surface content of the (Sr, Mg)O oxide, which was estimated by IR CO_2 adsorption, demonstrated both the highest activity in methane activation and the highest rate of methyl radical generation to the gas phase. The influence of the (Sr, Mg)O segregation on the formation of active oxygen species is discussed.

1. Introduction

For about 30 years the scientists are looking for a way of how to commercialize of oxidative methane coupling reaction (OCM) and to produce ethane and ethylene directly from natural gas. Among the difficulties encountered are both to overcome high heat emissions at 750–900 °C and to find a highly selective catalyst [1]. In spite of the numerous studies, the known OCM catalysts do not reach the required 80% C_2 selectivity and 30% methane conversion for a single pass and there still exists a crucial need for a selective catalyst.

It was shown that OCM was the heterogeneous–homogeneous reaction and the catalytic effect of OCM catalysts was to generate methyl radicals to the gas phase [2–4] and not to promote their heterogeneous oxidation on the surface [5,6]. Thus, among the properties of the catalysts the most important are both low oxygen mobility and presence of surface oxygen ion-radicals [7–9], being the active sites for methyl radical generation. Therefore, simple, complex or mixed oxides of alkaline, alkaline-earth and rare-earth elements traditionally showed high activity in OCM [1,10–15]. Another active system, which was found by Fang et al. [16], was a combination of alkaline element with transition metal oxide, for example, W-Na-Mn/SiO_2 [17–22]. Some authors showed that mixture of the rear earth oxides or their modification with the noble metals resulted in high activity in OCM because of the synergetic effects [23,24]. However, homogeneous reactions give rise to the limiting upper bound on the yield of C_2 hydrocarbons corresponding approximately to 28% [25]. To reach this level active catalyst should not only effectively generate methyl radicals, but also promote their efficient recombination in the gas phase. Thus, the active catalysts should be multicomponent and include in their composition both an active phase (for methyl radical generation) and an inert phase (for methyl radical recombination).

The active component of the composite catalyst can be considered to be perovskite-like oxide systems (ABO_3) because of appropriate structure, which allows us to create electronic defects

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Abbreviations: XRD, X-ray diffraction; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy; DDPA, differential dissolution phase analysis; OCM, oxidative coupling of methane.

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and oxygen vacancies by doping in A and B sublattices and thus to influence the concentration of active surface sites. The second reason is that in perovskites individual oxides of Sr, Ba and La can easily segregate to the surface, thus increasing the concentration of oxygen ion-radicals and modifying the surface properties of perovskites. Moreover, perovskites possess both high thermal and chemical stability, which make them promising materials for design of composite catalysts. Recently Fakhroueian et al. have studied $Ba_{0.5}Sr_{0.5}TiO_3$ substituted with Li, Na, Mg and have shown that doping increases the catalytic activity of titanates [26]. However, the reasons of this still remained unclear. In this work we attempted to determine what governs high activity of substituted titanates in OCM. The aim of this work was to synthesize Mg, Al, Ca, Ba, Pb substituted $SrTiO_3$ and Sr_2TiO_4 samples and to identify how the phase composition and the microstructure of the samples influence catalytic activity.

2. Experimental

2.1. Catalyst preparation

$SrTi_{0.9}A_{0.1}O_3$ (A = Mg. Al, Ca, Ba, Pb) and $Sr_2Ti_{0.9}B_{0.1}O_4$ (B = Mg, Al) samples were prepared by mechanochemical method [27] using $SrCO_3$, TiO_2, MgO, $BaCO_3$, CaO, Al_2O_3 (obtained by decomposition of $Al(NO_3)_3{\cdot}9H_2O$ at 600 °C), PbO_2 (obtained from decomposition of $Pb(NO_3)_2$ at 600 °C), all being of chemical pure grade or pure for analysis grade. Stoichiometric amounts of these compounds were mixed and intensively milled for 3 min in a planetary mill APF-5 under the following conditions: air atmosphere, steel drums of 25 cm^3 volume, steel ball of 5 mm in diameter, mass of the power 15 g, balls to power weight ratio is equal to 3–4:1, basic disk rotation speed 850 rpm, acceleration 40 g. To obtain the final catalyst the mechanically treated powder was tabletted and then calcined in air at 1100 °C for 4 h. Mechanochemical method is favorable for preparation of the sintered materials with low surface area, which is necessary to reduce the secondary surface process of total oxidation in the pores.

2.2. Catalyst characterization

The crystalline phases in the samples were identified by X-ray diffraction. X-ray diffractograms were recorded using CuK_α monochromatic radiation in a range between 15 and 80° 2θ with a step 0.02° and were analyzed by Rietveld full-profile method using FullProf program. In the Rietveld refinement, the contributions of both the $K_{\alpha1}$ (λ = 1.54056 Å) and $K_{\alpha2}$ (λ = 1.54439 Å) radiations were considered, and the intensity ratio of $K_{\alpha2}/K_{\alpha1}$ was fixed to 0.5. Diffraction line profiles were approximated by Pseudo-Voigt function. The refined instrumental and structural parameters were: zero shift, scale factor, background polynomial parameters, unit cell parameter, FWHM and shape parameters. High-temperature diffraction experiments were performed on a Bruker D8 diffractometer using Anton Paar high-temperature X-ray chamber.

Differential dissolution phase analysis (DDPA) was used to analyze the phase composition, the cation stoichiometry and the arrangement of the phases in the samples. The samples were loaded in a microreactor and dissolved in the solvent flow with the composition changing from the lower toward the higher acidity in the following order: H_2O (heating from 22 to 90 °C) → hydrochloric acid solution ($HCl{:}H_2O = 1{:}10$, 90 °C) → mixture of acids ($HNO_3{:}HCl{:}H_2O = 1{:}1{:}1$, 90 °C). The outlet solution analysis was carried out by an atomic emission spectroscopy using BAIRD spectrometer.

X-ray photoelectron spectra were recorded on a SPECS (Germany) spectrometer using a hemispherical PHOIBOS-150-MCD-9 analyzer (AlK_α radiation, $h\nu$ = 1486.6 eV, 200 W). The binding energy (BE) scale was calibrated using the positions of the peaks of $Au4f_{7/2}$ (BE = 84.0 eV) and $Cu2p_{3/2}$ (BE = 932.67 eV) core levels. The binding energies of detected peaks were calibrated by the position of the C1s peak (BE = 284.8 eV) corresponding to the surface hydrocarbon-like deposits (C—C and C—H bonds). Survey spectra were recorded at the analyzer pass energy of 50 eV, and the narrow spectral regions – at 20 eV. The ratios of surface atomic concentrations of the elements were calculated from the integral intensities of the photoelectron peaks corrected by the corresponding atomic sensitivity factors based on the Scofield's photo-ionization cross sections [28].

Transmission Electron Microscopy (TEM) micrographs were obtained with a JEM – 2010 instrument (lattice resolution 1.4 Å, acceleration voltage 200 kV). The local elemental composition was analyzed using an energy-dispersive EDX spectrometer equipped with the Si(Li) detector (energy resolution 130 eV).

The surface carbonate species were studied by CO_2 adsorption using IR spectroscopy. For IR experiments, a disk of the sample (1 cm × 2 cm, 20–40 mg) was placed in an IR cell and pretreated at 500 °C in vacuum during 1 h. After cooling to a room temperature, the sample was exposed to different amounts of CO_2 using an injector until the saturation was reached. IR spectra were collected in a range 400–6000 cm^{-1} with the resolution 4 cm^{-1} and the accumulation of 100 scans using Shimadzu FTIR-8300 infrared spectrometer. The total amount of carbonate species was calculated from the integral intensity of the IR bands using the integral coefficient of absorption 10 cm/μmol.

2.3. Catalytic tests

The catalytic activity in oxidative methane coupling (OCM) was measured in a fixed-bed quartz tube reactor (5 mm i.d.) at 850–900 °C and ambient pressure. The temperature of the catalyst was measured with chromel–alumel thermocouple adjusting the outer surface of the reactor at the middle of the catalyst bed. Gas mixture consisted of CH_4, O_2 and He was introduced in the reactor using flow mass controllers. Reactant and product concentrations were analyzed by on-line gas chromatograph with Porapack Q (i.d. = 3 mm, l = 3 m) and CaX (i.d. = 3 mm, l = 2 m) columns using a thermal conductivity detector. The reaction products were ethane, ethylene, water, CO, hydrogen and CO_2. Water was removed from the probe with SiO_2 trap. A blank run (quartz tube filled with only inert SiO_2 particles (0.25–0.5 mm in size)) showed no conversion at the reaction conditions. The conditions of catalytic activity measurement were the following:

1) Screening tests: 0.020–0.030 g of the catalyst, corresponding to the volume of 0.02 ml (particles of 0.25–0.5 mm in size), were mixed with 0.08 ml of inert quartz (particles of 0.25–0.5 mm in size) and held on the quartz filter. Total flow rate was 4.2 cm^3/s, corresponding to the contact time in normal τ = 0.024 s. Reaction mixtures were $20\%CH_4 + 5\%O_2$ in He and $10\%CH_4 + 5\%O_2$ in He. Activity at different CH_4/O_2 ratios (from 8 to 2) were studied at the content (vol.%) of methane in the reaction mixtures varied from $40\%CH_4 + 5\%O_2$ in He to $10\%CH_4 + 5\%O_2$ with the flow rate varied from 2 to 8.3 cm^3/s, corresponding to the contact time τ = 0.05–0.012 s.
2) Tests at different catalyst/quartz ratio: the sample (0.015–0.15 cm^3) were mixed with the inert quartz particles in such a way that the total volume was equal to 0.15 cm^3. Catalytic activity was measured in the reaction mixtures – $20\%CH_4 + 5\%O_2$ in He and $10\%CH_4 + 5\%O_2$ in He at flow rate 8.3 cm^3/s and contact time τ = 0.018 s.