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To cite this article: Yu Ivanova et al 2019 J. Phys.: Conf. Ser. 1145 012024

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# Study of oxidative coupling of methane over Sr<sub>2-x</sub>La<sub>x</sub>TiO<sub>4</sub> materials

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**Abstract.** Strontium titanate  $Sr_2TiO_4$  was synthesized by various methods (coprecipitation, precipitation on titania, and citrate method). The samples were characterized using X-ray diffractometry, mercury porosimetry, and BET techniques. Obtained materials had a perovskite-like structures, good crystallinity and specific surface areas of 0.6 to 3  $m^2/g$ . The catalytic activity to oxidative coupling of methane was determined at the temperature range of 700–900°C. The highest yield of  $C_2$  hydrocarbons was observed with the samples prepared by co-precipitation with K<sub>2</sub>CO<sub>3</sub>. Samples of Sr<sub>2-x</sub>La<sub>x</sub>TiO<sub>4</sub> catalyst synthesized by co-precipitation were examined. The highest the activity was established for  $Sr_{2-x}La_xTiO_4$  at the stoichiometric range of lanthanum content x (La) = 0.8-1.8.

#### 1. Introduction

Oxidative coupling of methane (OCM) is a promising method for the direct conversion of natural gas to an ethane-ethylene mixture with avoided stage of synthesis gas generation. The practical implementation of the process is constrained due to a low yield of the target products (no more than 35% at the conversion of more than 35% and selectivity 65-75% [1, 2]. The theoretical calculations [3, 4] demonstrate the limit yield in the OCM process which is 36% of ethane and ethylene in total. Therefore, a primary problem is the search for effective catalytic systems to improve the yield of the target products. OCM is a heterogeneous-homogeneous process: active sites of the catalyst provide the methane activation, i.e. the formation of methyl radicals CH<sub>3</sub><sup>•</sup> to be further recombined in the gas phase to produce C<sub>2</sub>-hydrocarbons [5, 6]. The OCM catalyst must feature a minor oxidative activity in order to activate effectively methane but to make a minimal contribution to hydrocarbon oxidation.

Oxides of alkali and alkali earth metals, as well as of La, W, Mn, Ti, Al, Ce, Sm, Zn, Zr are most often used in the active components of catalysts for methane activation, and  $SiO_2$ , MgO, La<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, BaO, CaO, SrO as supports [7]. In the recent years, there is a growing interest in perovskite-like structures; their stability often makes them more effective than one-components systems. In addition, they can be modified to affect the bond energy of oxygen in the oxide structure and, hence, their activity. It was shown [8] that the oxide system Sr<sub>2</sub>TiO<sub>4</sub> prepared mechanochemically and calcined at 1100°C can be used as the bases for promising OCM catalysts operating at 850–900°C. Lanthanumbased catalysts with the perovskite structure (LaXO<sub>3</sub>, X = Al, Fe, or Ni) also show good activity to OCM [9]. Mixed oxide systems with the perovskite structure comprising several components, such as SrO and La<sub>2</sub>O<sub>3</sub>, active to OCM are of interest. The preparation procedure also can influence the catalyst activity. Perovskites usually are prepared by sintering at high temperatures. For example, Sr<sub>2</sub>TiO<sub>4</sub> is synthesized by sintering of stoichiometric quantities of TiO<sub>2</sub> and SrCO<sub>3</sub> at 1100–1400°C.

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doi:10.1088/1742-6596/1145/1/012024

Search for new methods for the synthesis as an alternative to solid-state method [10] is aimed at the preparation of catalysts with predetermined properties (chemical and phase composition, microstructure, thermal stability, optimal texture, etc.) to influence the process efficiency (a combination of a high methane conversion and selectivity to ethylene and ethane).

The present study was focused on the influence of the procedure for preparation of strontium titanate with the structure of layered perovskite  $Sr_2TiO_4$  on physicochemical and catalytic properties of the catalyst for methane condensation coupling. The catalytic activity to methane condensation coupling was studied with samples of  $Sr_{2-x}La_xTiO_4$  with different degrees of strontium substitution (x) prepared by precipitation.

# 2. Experimental part

### 2.1. Material preparation

Various procedures were used for synthesis of stoichiometric catalytic system Sr<sub>2</sub>TiO<sub>4</sub>. The precursor - hexachlorotitanic acid H<sub>2</sub>TiCl<sub>6</sub> - was prepared by mixing TiCl<sub>4</sub> and concentrated HCl; the solution was diluted with distilled water to reach the required concentration. Sample (P1) was prepared by precipitation from the mixed solution of H<sub>2</sub>TiCl<sub>6</sub> and Sr(NO<sub>3</sub>)<sub>2</sub>, 0.5 M K<sub>2</sub>CO<sub>3</sub> solution being the precipitator. The precipitation was achieved at room temperature to reach pH 9.5, than the precipitate was filtered out, washed to reach pH 7 and dried at 120°C. Samples (S1) and (S2) were prepared by precipitation of strontium nitrate in the presence of titania under the action of precipitators 0.5M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and 0.4M K<sub>2</sub>CO<sub>3</sub>, respectively. The precipitation was achieved at room temperature to reach pH 8–8.5, than the precipitate was filtered out, washed to reach pH 7 and dried at 120°C. Sample (C1) – Sr<sub>2</sub>TiO<sub>4</sub> was prepared by the citrate method using citric acid (CA). Excess citric acid was added to the solution of  $Sr(NO_3)_2$  and  $H_2TiCl_6$  at the molar ratio (Sr+Ti):CA = 1:3. The solution was evaporated at 200°C using a sand bath to obtain a black viscous solid resin, then the resin was annealed in a muffle furnace at 300°C for an hour to form a black solid mass to be crushed to powder. Substituted samples  $Sr_{2-x}La_xTiO_4$  (x = 0-2) were prepared the same way as sample S2. All the prepared samples were calcined at 900°C for 4 hours and then at 1100°C for another 4 hours. Reagents used in the synthesis had a chemical purity of at least 99% (Nevareaktiv, Vecton, Solikamsk Magnesium Plant, Russia).

# 2.2. Catalytic tests

A fixed catalyst bed flow setup was used for experimental determination of the activity to oxidative methane coupling and the catalyst selectivity. A mixture of reactants (CH<sub>4</sub> and O<sub>2</sub> in N<sub>2</sub>) was fed from a balloon through a gas regulator to a reactor with the catalyst under close to atmospheric pressure. The quartz reactor was heated using high-temperature electric oven with the fluidized sand bed. Samples of the reaction mixture were drawn behind the reactor and fed on-line to series-connected chromatographs LHM-80 (Chromatograph, Russia) and Tsvet-500 (Tsvet, Russia) equipped with thermal conductivity detectors. Helium was used as the gas carrier. The test conditions were as follows:  $T = 700-900^{\circ}$ C, P = 0.1 MPa, catalyst loading 0.5 ml, ratio CH<sub>4</sub>:O<sub>2</sub> = 4:1 in the methane-air mixture contact time 0.06 s. The heat exchange was improved by adding quartz grains to the equisized catalyst. The reaction mixture was fed at the rate of 30 L/h.

The impact of internal diffusion was estimated theoretically for S1 sample. It was obtained that oxygen diffusion inside the catalyst pores does not affect the reaction rate, it can be concluded that the reaction occurs in the kinetic regime.

# 2.3. Material characterization

XRD technique was used for determining the phase compositions. Diffraction patterns were acquired using a Bruker D8 diffractometer (Bruker, Germany) with  $CuK_a$  ( $\lambda = 1.5418$ ) radiation by scanning samples in 0.05° steps in the 2 $\theta$  range of 10° to 70°. The phase composition was determined by comparing the experimental diffraction patterns to the JCPDS database. The FullProff program

doi:10.1088/1742-6596/1145/1/012024

package was used for calculating the structural parameters. High pressure mercury porosimetry with an AutoPore IV 9500 V1.09 instrument (Micromeritics, USA) was used for studying the porous structure of the catalysts. The BET method by nitrogen adsorbtion with Sorbi N.4.1 (Meta, Russia) instrument with reproducibility 0.5% was used for measuring the specific surface area of the samples.

# 3. Results and discussion

#### 3.1. Characterization

Reflections typical of the perovskite-like structure 14/MMM were observed in diffraction patterns of  $Sr_2TiO_4$  (figure 1A). The samples were well crystalline with the coherent scattering regions (CSR) of 500 to 610 Å. The lattice constants of all the samples are close to literature data [11]. Sample (C1) prepared by the citrate method produces low-intense reflections of impurity phase  $Sr_4ClO_6$  formed during burning of the organic constituent of the organometallic complex precursor (Table 1). Different precipitators, (NH<sub>3</sub>)<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub> (samples S1 and S2) influence the crystallite size, specific surface area and porous structure. The catalysts under study were prepared by different methods and differ in their specific surface areas and porous structures (table 1). Values of coherent scattering area  $d_{XRD}$  calculated by the Scherrer. Specific surface area,  $S_{sp}$ , increases in the series: C1 < P1 < S2 < S1, while the average pore size, in contrast, increases in the series S1 < S2 < P1 < C1.



**Figure 1.** XRD analysis of the prepared samples: a)  $Sr_2TiO_4$ : l - P1, 2 - S1, 3 - S2, 4 - C1; b,c)  $Sr_2$ .  $_xLa_xTiO_4$ : l - (x = 0), 2 - (x = 0.2), 3 - (x = 0.4), 4 - (x = 0.6), 5 - (x = 0.8), 6 - (x = 1.0).

Consequently, the applied methods allow preparing practically single-phase well crystalline strontium titanates with the layer perovskite structure, which differ in the specific surface areas (0.6–3 m<sup>2</sup>/g), average pore sizes (0.22–1.59  $\mu$ m), and, seemingly, defect structures.

XRD data on samples with substitution degree x from 0.2 to 0.6 (Figure 1B) indicate, apart from the main phase of Sr<sub>2</sub>TiO<sub>4</sub>, the presence of a minor impurity of the TiO<sub>2</sub> phase (rutile P42/MNM) and the phase of La<sub>2</sub>O<sub>3</sub> (P3-M1). An increase in x up to 0.8–1 results in the appearance of perovskite SrTiO<sub>3</sub> and in a total disappearance of layer perovskite Sr<sub>2</sub>TiO<sub>4</sub> in the sample with x = 1.0. SrTiO<sub>3</sub> along with La<sub>2</sub>O<sub>3</sub> becomes the main phase in the samples at x = 1-1.2. The further increase in the proportion of lanthanum leads to the formation of phase La<sub>2</sub>TiO<sub>5</sub> (x = 1.4) that becomes the main phase upon an increase in the molar fraction of La at x = 1.6-2 while the phase of SrTiO<sub>3</sub> fades away. At the range of large substitution degrees (x > 1.4), there is the phase of lanthanum oxycarbonate La<sub>2</sub>O<sub>2</sub>(CO<sub>3</sub>) that is accounted for by the ability of La<sub>2</sub>O<sub>3</sub> to adsorb readily CO<sub>2</sub> and to interact with it [12].

Inspection of positions of main reflections of the crystal structure  $Sr_2TiO_4$  ( $\theta = 31.35^\circ$  and  $32.57^\circ$ ) shows the shift of maxima of reflection intensities towards the low angle reaction at x = 0.1-0.8 (Figure 1C). This may mean that lanthanum atoms enter the crystal structure of  $Sr_2TiO_4$  to substitute for Sr atoms; in view of the fact that the La<sup>3+</sup> radius (0.819 Å) is longer than that of Sr<sup>2+</sup> (0.683 Å), the lattice constants increases to cause the shift of the reflections. From literature data, it is practically difficult to obtain a material with the SrLaTiO<sub>4</sub> structure because of the considerable difference in the atomic coordination in the SrO<sup>0</sup> and LaO<sup>+</sup> layers that results in a strong stress in the internal electric field in the material bulk [13].

**Table 1.** Textural and structural properties of the samples.

Sample	Average pore size (µm)	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	Lattice constants a = b, d <sub>XRD</sub> (Å) c (Å)	)
P1	0.86	$0.8\pm0.004$	3.8886 12.6014 550	
<b>S</b> 1	0.22	$3 \pm 0.015$	3.8871 12.5991 610	
S2	0.47	$1.3 \pm 0.0065$	3.8854 12.5891 500	
C1	1.59	$0.6 \pm 0.003$	3.8856 12.5810 560	





**Figure 2.** Pore volume distribution vs pore radius in samples of Sr<sub>2</sub>TiO<sub>4</sub>.

**Figure 3.** Influence of reaction temperature on the yield of C<sub>2</sub> hydrocarbons  $Y_{C2}$ : 1 - P1, 2 - S1, 3 - S2, 4 - C1.

# 3.2. Catalytic activity of $Sr_2TiO_4$ samples. Effect of preparation method

Results obtained by testing  $Sr_2TiO_4$  samples are illustrated in figures 3–5. Figure 3 shows the experimental temperature dependence of the yield  $Y_{C2}$  of  $C_2$  hydrocarbons (ethane, ethylene) over the prepared  $Sr_2TiO_4$  catalysts. With all the catalysts, the yield increases as the reaction temperature rises in the range of 799 to 900°C. However, at above 800°C catalyst P1 provided a higher yield equal to 13.7% (at 25.4% conversion and 53.8% selectivity) that is almost two times as high as that over catalysts S1 and S2 and 3 times as high as that over catalyst C1. On the other hand, the catalysts under study provide some different relative selectivity to ethylene  $S_{C2H4}/S_{C2}$  (Figure 4). With catalyst C1, ethane is only formed at low temperatures but ethylene at above 850°C, the relative selectivity  $S_{C2H4}/S_{C2}$  being 29.3% at 900°C. With the other catalysts, the relative concentration of ethylene is 30–40% over the whole temperature range under study.





**Figure 4.** Influence of reaction temperature on the relative selectivity to ethylene  $S_{C2H4}/S_{C2}$ : I - P1, 2 - S1, 3 - S2, 4 - C1.

**Figure 5.** Dependence of process performance at 800°C on specific catalyst surface area: l – methane conversion  $X_{CH4}$ , 2 – selectivity to C<sub>2</sub> hydrocarbons S<sub>C2</sub>, 3 – ten-fold yield of C<sub>2</sub> hydrocarbons  $Y_{C2}$ .

The direct proportionality between the methane conversion and specific surface area is observed with the catalysts whose specific surface areas  $S_{sp}$  range between 0.6 and 1.3 m<sup>2</sup>/g. The further increase in  $S_{sp}$  up to  $\beta_{0.3}$  m<sup>2</sup>/g does not cause noticeable increase in the activity (Figure 5). The dependence of the selectivity on conversion is typical of the reaction of partial oxidation of hydrocarbons; it decreases as the conversion increases due to oxidation of the products to carbon oxides. The constant yields of C<sub>2</sub> hydrocarbons equal to ca. 8.6% at ca. 15.5% conversion and ca. 41% selectivity are observed at 800°C over the catalysts with  $S_{sp} = 1.3-3.0$  m<sup>2</sup>/g.

# 3.3. Catalytic activity of $Sr_{2-x}La_xTiO_4$ samples

The studies of the influence of the degree of substitution (x) of lanthanum for strontium in  $Sr_{2-x}La_xTiO_4$  on the catalytic properties revealed non-monotone variations in the activity, the highest activity being characteristic of the catalysts with x = 0.8-1 (Figure 6). The activity of oxides SrO [14] and  $La_2O_3$  [14, 15], both individual and supported, to the reaction (OCM) is under discussion in literature. At a low substitution degree (x  $\leq 0.8$ ), Sr atoms are bonded to the perovskite structure and do not make individual contribution to the reaction (OCM). The substitution of lanthanum for strontium makes the layer perovskite structure disarranged and leads to the formation of individual

oxide phases of La<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and, probably, SrO. It is difficult to identify SrO reflections in the XRD patterns of multiphase samples because they are overlapped by reflections from perovskite phases  $Sr_2TiO_4$  and  $SrTiO_3$ . From literature data, the combined action of La and Sr produces a synergistic effect that gives high  $S_{C2} = 68\%$  [16]. The high activity of the samples with large substitution degrees x = 0.8-1.8 can be, probably, accounted for by the presence of two phase, La<sub>2</sub>O<sub>3</sub> and SrO, simultaneously at the optimal disperse distribution relative to each other.



**Figure 6.** Methane conversion as a function of x in  $Sr_{2-x}La_xTiO_4$ . Reaction conditions:  $CH_4/O_2/N_2 = 45/11.3/43.7 \text{ mol }\%$ , P = 1 atm,  $T = 800^{\circ}C$ .

## 4. Conclusion

The studies were focused on  $Sr_2TiO_4$  samples prepared by different methods such as co-precipitation from an aqueous solution, precipitation from an aqueous solution in the presence of TiO<sub>2</sub> suspension under the action of various precipitators, as well as formation of titanium and strontium complexonates with citrate ligands. From XRD data, all the oxide samples under study were well crystalline and structured as layer perovskites with CSR of 500 to 610 Å. Their specific surface areas varied from 0.6 to 3 m<sup>2</sup>/g and average pore size from 0.22 to 1.59 µm. It was demonstrated that the largest surface area and the least average pore size are characteristic of the samples prepared by precipitation with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> from the aqueous solution in the presence of TiO<sub>2</sub>, and the smallest surface area and the largest average pore size are typical of the samples prepared through the formation of titanium and strontium complexonates with citrate ligands.

The catalytic activity of the samples to oxidative methane coupling was determined at 700–900°C. The samples prepared by co-precipitation (sample P1) or precipitation by  $K_2CO_3$  in the presence of TiO<sub>2</sub> suspension (sample S2) were shown to be most active under the used experimental conditions.

The influence of substitution of La for Sr on the physicochemical and catalytic properties was studied with the catalyst based on strontium titanate with the layer perovskite structure prepared by co-precipitation. An increase in the activity was established for  $Sr_{2-x}La_xTiO_4$  at the stoichiometric range of lanthanum content x (La) = 0.8–1.8. This fact may be accounted for by the presence of hexagonal phase of La<sub>2</sub>O<sub>3</sub> with crystallite of optimal size, as well as probable impurity of poorly crystalline SrO.

### Acknowledgments

This work was conducted within the framework of the budget project AAAA-A17-117041710090-3 for Boreskov Institute of Catalysis.

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