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To cite this article: Yu Ivanova *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **597** 012026

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A study on the oxidative coupling of methane over $\text{La}_{2-x}\text{Mg}_x\text{TiO}_4$ catalysts

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Abstract. $\text{La}_{2-x}\text{Mg}_x\text{TiO}_{5-8}$ samples with different content of Mg and La were synthesized by the precipitation from a mixed solution of $\text{Mg}(\text{NO}_3)_2$ and $\text{La}(\text{NO}_3)_3$ in the presence of TiO_2 suspension. The samples were characterized using X-ray diffractometry, mercury porosimetry, and BET techniques. Specific surface area of the samples ranges from 0.1 to 4.17 m^2/g , and pore volume, from 0.005 to 0.023 cm^3/g . Activity and selectivity of the samples in the oxidative condensation of methane (OCM) were measured using a fixed catalyst bed flow quartz reactor. It was demonstrated that samples with $x \leq 0.6$ showed the highest activity toward OCM reaction. This can be explained by a high content of the main active phase $(\text{La},\text{Mg})_2\text{TiO}_{5-8}$ with the layered perovskite structure and a sufficient specific surface area.

1. Introduction

Oxidative condensation of methane (OCM) is one of the promising methods for obtaining the ethane-ethylene mixture directly from natural gas without a complicated step of syngas production. Practical implementation of the process is hindered by the low yield of target products that does not exceed 26% at conversion above 35%, according to experimental data, which is related to the low activity/selectivity of the catalysts.

In this connection, titanium-containing materials with the perovskite structure deserve special attention. Owing to their crystal structure (the closest cubic packing of oxygen ions and metal cations), they possess some unique properties, such as the ability to ionic exchange and intercalation of oxygen ions, high thermal stability, etc. [1, 2] and are promising catalysts for heterogeneous catalysis [3], particularly for the OCM process [4]. The binding energy of oxygen in the perovskite structure plays an important role. Activation of methane starts from cleavage of the C-H bond upon interaction with the oxide surface [5]. Active sites with the strongly bound oxygen decrease the contribution of undesirable processes of complete oxidation of methane, products and semiproducts of oxidative condensation of methane [6].

Of particular interest are oxide systems with the perovskite-like structure containing Mg and La. Individual oxides MgO and La_2O_3 are difficultly reducible and require a large amount of energy to form oxygen vacancies [4]. Systems containing La_2O_3 were successfully employed as catalysts for the OCM process [7-9]. Many researchers noted that the addition of MgO to various oxide systems exerted a beneficial effect on the performance of OCM reaction [10-13]. In [14], active oxygen species in MgO- La_2O_3 mixed oxides of different composition were studied. Strong interactions between MgO and La_2O_3 oxides led to the formation of oxygen vacancies; as a result, an additional type of adsorbed oxygen was produced. This type of adsorbed oxygen is very active toward the low-temperature oxidation of H_2 and



can be used to activate CH₄ at high temperatures under relatively mild conditions of the reaction at 600°C. In [15], La₂TiO₅ oxide with the layered perovskite structure was shown to be highly active; its activity increased upon substitution of lanthanum by strontium.

In our work, the effect of La substitution by Mg in the structure of perovskite-like titanates (La_{2-x}Mg_xTiO_{5-δ}) on their physicochemical and catalytic properties in the oxidative condensation of methane was investigated.

2. Experimental

Precipitation from a mixed solution of Mg(NO₃)₂ and La(NO₃)₃ in the presence of TiO₂ suspension was used to synthesize La_{2-x}Mg_xTiO_{5-δ} samples with a step $x = 0.2$, where x is the degree of lanthanum substitution by magnesium. A 0.5 M solution of (NH₄)₂CO₃ served as a precipitating agent. The precipitation was performed at room temperature until pH became equal to 8–8.5; after that, the precipitate was filtered, washed to pH 7, and dried at 120°C. All the synthesized samples were calcined at 1100°C for 4 hours. The concentration of lanthanum (molar fraction) $C_{La} = La/(La+Mg)$ in the oxides is related with the substitution degree as $x = 2 \cdot (1 - C_{La})$.

Activity and selectivity of the samples in the oxidative condensation of methane were measured using a flow quartz reactor with the diameter 5 mm and a fixed catalyst bed [15]. Conditions of experiments were as follows: temperature $T = 700\text{--}800^\circ\text{C}$; pressure $P = 1$ atm; volume of the catalyst 0.5 ml; catalyst fraction with the grain size 0.25–0.5 mm diluted with 2 g quartz having the grain size 0.25–0.5 mm; and feed space velocity of the reaction mixture (CH₄/O₂/N₂ = 45/11.3/43.7 % (mol.)) 30 l/h. The reaction mixture was sampled and analyzed on LHM-80 and Tsvet-500 chromatographs with thermal conductivity detectors connected in series. The data obtained were used to calculate methane conversion (X_{CH_4}), selectivity (S_{C_2}), and yield (Y_{C_2}) of C₂ products using the following formulas:

$$X_{CH_4} = 1 - \frac{C_{CH_4}}{C_{CH_4}^0} \cdot U \quad (1)$$

$$S_{C_2} = \frac{2 \cdot (C_{C_2H_4} + C_{C_2H_6})}{C_{CO} + C_{CO_2} + 2 \cdot (C_{C_2H_4} + C_{C_2H_6})} \quad (2)$$

$$Y_{C_2} = X_{CH_4} \cdot S_{C_2} \quad (3)$$

where C^0 is the inlet concentration of the corresponding reactant; C is the outlet concentration of the corresponding substance; and U is the ratio of output to input streams.

The specific surface area (S_{BET} , m²/g) was estimated according to BET from thermal desorption of argon. The pore structure was examined by nitrogen porosimetry under pressure using a QUADRASORB evo™ (Quantachrome, USA) instrument.

The phase composition was determined by X-ray diffraction analysis (XRD). Diffraction patterns were obtained on a Bruker D8 (Germany) diffractometer using a CuK_α source ($\lambda = 1.5418$). Each sample was scanned point-by-point with a 0.05° step in the 2θ range from 10 to 70°. The phase composition was revealed by comparing the experimental diffraction patterns with the JCPDS database. The size of coherent scattering region (CSR) was found using the Scherrer formula.

3. Results and Discussion

3.1. Materials characterization

Phase composition and textural characteristics of the samples are listed in Table 1.

According to XRD data, all the synthesized samples contain perovskite-like phases, some samples (at $x < 0.8$) have titania impurities, but single-phase samples are only those with $x = 0$ and 0.8.

A sample with the composition $x = 0$ has a well crystallized La₂TiO₅ structure of layered perovskite. At $x < 0.8$ ($C_{La} > 0.6$), a mixture of the main (La,Mg)₂TiO_{5-δ} and (Mg,Lu)TiO₃ and impurity TiO₂ and MgTiO₃ phases is formed. A sample with the substitution degree $x = 0.8$ ($C_{La} = 0.6$) has reflections of

only one well crystallized phase with the LaTiO_3 perovskite structure [16]. This indicates that at this substitution degree lanthanum and magnesium intercalate into the perovskite-like structure and form a $(\text{La,Mg})\text{TiO}_3$ compound. A sample with $x = 2$ (Figure 1) contains well crystallized MgTiO_3 and Mg_2TiO_4 phases. The SCR sizes of the observed main perovskite-like phases vary in the range of 190-650 Å; single-phase samples have greater CSR sizes.

Table 1. Phase composition, CSR size, specific surface area and pore volume of the synthesized $\text{La}_{2-x}\text{Mg}_x\text{TiO}_{5-\delta}$ samples.

Composition of synthesized $\text{La}_{2-x}\text{Mg}_x\text{TiO}_{5-\delta}$ samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ($\text{cm}^3 \text{g}^{-1}$)	Main phase	CSR (Å)	Impurity phase
La_2TiO_5	1.05	0.018	La_2TiO_5	560	
$\text{La}_{1.8}\text{Mg}_{0.2}\text{TiO}_{5-\delta}$	0.98	0.016	$(\text{La,Mg})_2\text{TiO}_{5-\delta}$ $(\text{La,Mg})\text{TiO}_3$	320 400	TiO_2 , MgTiO_3
$\text{La}_{1.4}\text{Mg}_{0.6}\text{TiO}_{5-\delta}$	4.17	0.023	$(\text{La,Mg})_2\text{TiO}_{5-\delta}$ $(\text{La,Mg})\text{TiO}_3$	190 370	TiO_2 , MgTiO_3
$\text{La}_{1.2}\text{Mg}_{0.8}\text{TiO}_{5-\delta}$	0.10	0.007	$(\text{La,Mg})\text{TiO}_3$	500	
Mg_2TiO_4	1.59	0.005	MgTiO_3 Mg_2TiO_4	650 410	

Specific surface area of the samples ranges from 0.1 to $4.17 \text{ m}^2/\text{g}$, and pore volume, from 0.005 to $0.023 \text{ cm}^3/\text{g}$. A sample with $x = 0.6$ has the highest values of S_{BET} and V_{pore} , whereas the single-phase sample with $x = 0.8$ has the lowest S_{BET} and V_{pore} (Table 1). Overall, non-single-phase samples are characterized by higher specific surface area and pore volume due to their insufficient sintering.

Thus, it was demonstrated that variation of the elemental composition – the La to Mg ratio in $\text{La}_{2-x}\text{Mg}_x\text{TiO}_{5-\delta}$ – makes it possible to synthesize a double oxide with the perovskite structure at $x = 0.8$, or at a molar concentration of lanthanum $C_{\text{La}} = \text{La}/(\text{La}+\text{Mg}) = 0.6$.

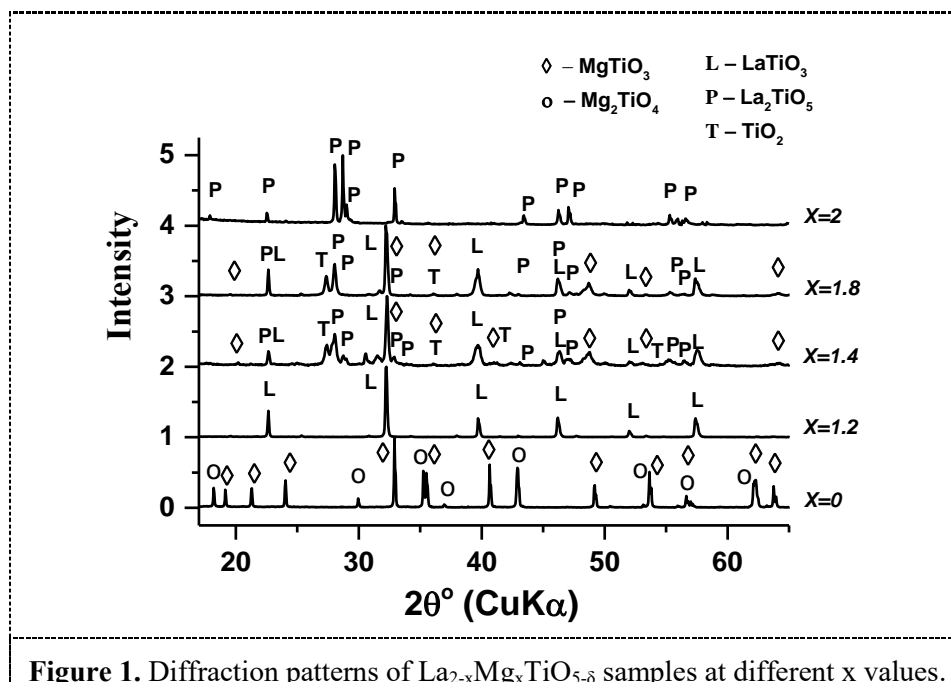


Figure 1. Diffraction patterns of $\text{La}_{2-x}\text{Mg}_x\text{TiO}_{5-\delta}$ samples at different x values.

3.2. Catalytic tests

OCM is a selective process. Products of selective oxidation (ethane and ethylene) are formed along with the deep oxidation products (CO and CO₂).

Dependences of methane conversion (X_{CH_4}), selectivity (S_{C_2}) and yield (Y_{C_2}) of C₂ products on the content of magnesium (x) are displayed in Figures 2 and 3. High activity of the samples was observed for the compositions with $x \leq 0.6$ containing the (La,Mg)₂TiO_{5-δ} phase. Selectivity of the indicated samples (with $x \leq 0.6$) for C₂ products was 55-60%. The highest activity was observed for the samples with $x = 0.4-0.6$.

Overall, an increase in x above 0.6 decreased the methane conversion and C₂ yield; therewith, the (La,Mg)₂TiO_{5-δ} phase was not detected in the composition of the samples. A single-phase La_{1.2}Mg_{0.8}TiO_{5-δ} sample with the LaTiO₃ structure is low active and has a low specific surface area.

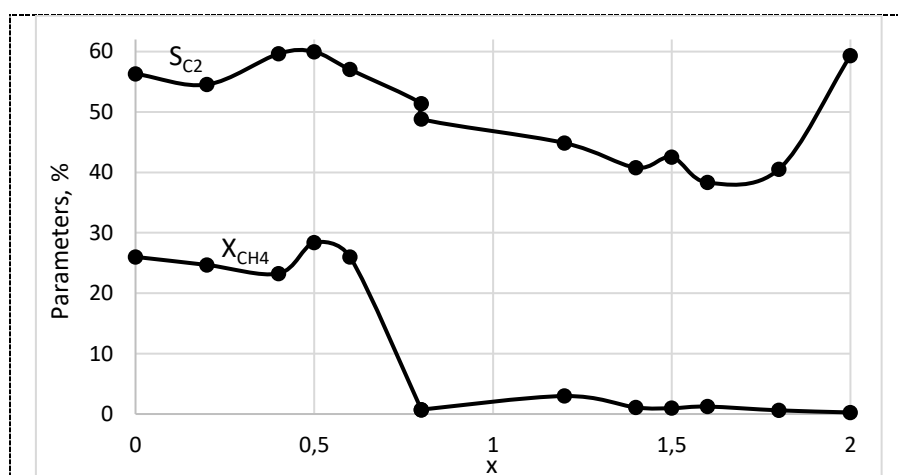


Figure 2. Dependences of methane conversion (X_{CH_4}) and selectivity (S_{C_2}) of C₂ products on the content of magnesium (x) in La_{2-x}Mg_xTiO_{5-δ} oxides. Conditions: gas composition CH₄/O₂/N₂ = 45/11.3/43.7 % (mol.), P = 1 atm.

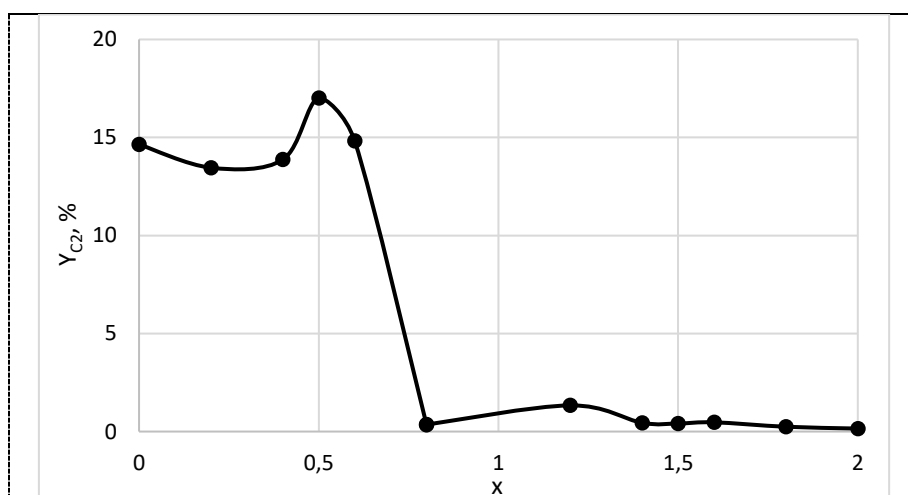


Figure 3. Dependence of the yield (Y_{C_2}) of C₂ products on the content of magnesium (x).

4. Conclusion

$\text{La}_{2-x}\text{Mg}_x\text{TiO}_{5-\delta}$ samples with different content of Mg and La were synthesized. It was shown that the introduction of magnesium (x) leads to the appearance of the perovskite $(\text{La,Mg})\text{TiO}_3$ phase, which content increases with x. The possibility to synthesize a single-phase double oxide system with the $(\text{La,Mg})\text{TiO}_3$ perovskite structure at $x = 0.8$ was demonstrated.

Among the tested samples, those with $x \leq 0.6$ showed the highest activity toward oxidative condensation of methane. This can be attributed to a high content of the main active phase $(\text{La,Mg})_2\text{TiO}_{5-\delta}$ with the layered perovskite structure and a sufficient specific surface area.

Acknowledgments

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

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