Study of the kinetic regularities of the oxidative methane coupling over Sr-La$_2$O$_3$ material

R Petrov, S Reshetnikov, Yu Ivanova and L Isupova

Boreskov Institute of Catalysis SB RAS, 5 Lavrentieva Avenue, Novosibirsk 630090, Russian Federation

E-mail: petrov@catalysis.ru

Abstract. Sr-La$_2$O$_3$ material was prepared by incipient wetness impregnation of La$_2$O$_3$ with an ammonia solution of strontium nitrate. The material was characterized using XRD and BET techniques. The influence of temperature (450–630°C) and contact time (0.02–0.06 s) on the kinetics of oxidative coupling of methane (OCM) was studied in an isothermal reactor. A schematic of the OCM process over the Sr-La$_2$O$_3$ catalyst was suggested. The experimental results obtained in the range of very low conversions (0.25–8.5%) led to conclude about concurrent formation of primary OCM products which are ethane (C$_2$H$_6$) and carbon oxides (CO, CO$_2$).

1. Introduction

The traditional methods for methane processing to liquid hydrocarbons are based on complex multistage processes that need solid investments. It seems more rational to use the methods (without the stage of synthesis gas generation) such as oxidative coupling of methane (OCM) to form C–C bonds. In the OCM process, methane is oxidized over a catalyst at high temperature (> 550°C) to form target products (ethane and ethylene) and side products (carbon oxides) [1, 2]. Numerous studies in the field did not lead as yet to the practical implementation of the process because of the insufficient yields of C$_2$ hydrocarbons, the reason being the low performance (selectivity, stability) of the catalysts used. At the same time, the studies are in progress.

The intensive studies led to establish that many oxide systems are active at the temperature range between 700 and 850°C. They can be notionally classified into the following groups: alkali earth metal oxides modified with ion metal ions [3]; rare earth metal oxides as well as mixed oxides of alkali earth and rare earth metals [4–6]; complex oxides comprising manganese oxide [7–9]. Economically, the catalysts which are active at the low temperature region (500–650°C) are most promising. The catalysts based on mixed compounds of alkali earth and rare earth elements are effective in this temperature region. They comprise mainly of lanthanum oxide promoted with alkali earth metals such as Sr or Mg [10, 11]. For example, recent studies have demonstrated that the Sr-La$_2$O$_3$ based materials are highly active to OCM [12–14].

OCM is a heterogeneous-homogeneous process. It is commonly accepted that the catalyst role is mainly to accelerate the homogeneous process owing to generation of methyl radicals on the catalyst surface and their release to the gas phase [15–18]. Hence, the studies of OCM regularities over various heterogeneous catalysts are of urgent importance.

The present work was aimed at studying the influence of temperature and contact time on the catalytic activity of Sr-La$_2$O$_3$ and the elucidation of the reaction pathway.
2. Experimental part

Sr-La$_2$O$_3$ catalyst was prepared by incipient wetness impregnation of the La$_2$O$_3$ fraction obtained through decomposition of La(NO$_3$)$_3$·6H$_2$O in air at 700°C for 10 hours. An ammonia solution of strontium nitrate was used as the precursor of the active component. The sample was dried at 100°C for an hour and calcined in air at 300°C for another hour and at 700°C for 4 hours. Reagents used in the synthesis had a chemical purity of at least 99% (Fabricator: Nevareaktiv, Vector; Russia).

High pressure mercury porosimetry with AutoPore IV 9500 V1.09 instrument (Micromeritics, USA) was used for studying the porous structure. BET surface area was determined by nitrogen desorption. XRD technique was used for determining the phase composition. Diffraction patterns were acquired using a Bruker D8 diffractometer (Bruker, Germany) with CuKα (λ = 1.5418) radiation by scanning samples in 0.05° steps in the 2θ range of 10° to 70°. The phase composition was determined by comparing the experimental diffraction patterns to the JCPDS database. The FullProf program package was used for calculating the structural parameters.

A fixed catalyst bed flow setup (figure 1) was used for experimental determination of methane and oxygen conversions and selectivities to the products (ethane, ethylene, carbon monoxide and dioxide) of the OCM reaction. A mixture of reactants (46 mol % CH$_4$ and 11.5 mol % O$_2$ in N$_2$) was fed from balloon 1 through gas regulator 2 to reactor 3 with the catalyst under close to atmospheric pressure. The quartz reactor was heated using electric oven 4 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 5 (Chromatograph, Russia) and Tsvet-500 6 (Tsvet, Russia) equipped with thermal conductivity detectors. Helium was used as the carrier gas. Gases (CO$_2$ and C$_2$ hydrocarbons) were separated in a column with polymer sorbent HayeSep, and H$_2$, O$_2$, N$_2$, CH$_4$ and CO in a similar column with 5A zeolite at the column temperatures of 60 and 90°C, respectively. Gases used in the mixture of reactants preparation and chromatographic analysis had a chemical purity of at least 99% (Fabricator: Chistie Gazi; Russia).

The OCM process was studied under the following conditions: $T = 450–630^\circ$C, catalyst loading 0.5 ml, ratio CH$_4$O$_2$ = 4 in the methane-air mixture, contact time 0.02–0.06 s. The heat exchange was improved by adding quartz grains to the equisized catalyst (0.25–0.5 mm). The reaction mixture was fed at the rate of 30–100 L/h.

![Figure 1. Set-up diagram of the catalytic oxidative coupling of methane including balloon (1), gas regulator (2), reactor with the catalyst (3), high temperature oven (4), LHM-80 chromatograph (5), Tsvet-500 chromatograph (6), data processing unit (7).](image-url)

The catalyst activity often is determined using a mixture of methane and oxygen [15, 16]. In this case the highly exothermic process causes problems in providing near-isothermal conditions even in a laboratory reactor. In testing catalyst samples, different total heat effects are characteristic of the catalysts with different activities and selectivities; hence, the temperature profiles will differ to hinder interpretation of the data obtained. In order to decrease influence of temperature changes and to
provide correct comparison of the catalyst properties (activity, selectivity), the activity was determined in a low-concentrated mixture containing almost half nitrogen.

Dilution of the reaction mixture with nitrogen and of the catalyst with inert quartz provided the close to isothermal conditions of the kinetic experiments.

3. Results and discussion

3.1. Material characterization

XRD studies (figure 2a) revealed that prepared Sr-La$_2$O$_3$ catalyst consists of La$_2$O$_3$ (P3-M1 hexagonal structure) and of SrO phases. Well faceted crystallites of the La$_2$O$_3$ support are 295 Å in size. Lattice constants of La$_2$O$_3$ (a = 3.9374 and c = 6.1275) calculated using the PowderCell 2.4 program package are slightly different from the literature data (a = 3.9379, c = 6.1729) [19], probably, because of the modification with strontium ions.

![XRD pattern (CSR - La$_2$O$_3$ = 295 Å)](image)

**Figure 2.** XRD pattern (CSR - La$_2$O$_3$ = 295 Å) (a) and pore size (r) distribution (b) for the Sr-La$_2$O$_3$ material. $V_p$ is pore volume, $r$ is radius of pore.

Isotherms of low temperature nitrogen adsorption and desorption were used for determining the specific surface area, porosity and pore size distribution. The adsorption isotherms were described by the BET equation. The data on pore size distribution (figure 2b) shows mainly the presence of macropores (0.16 μm in average size) and a small portion of 3–30 nm mesopores. Such a pore size distribution indicates the possibility of the influence of internal diffusion of reactants through the porous grain on the process of methane oxidation [20]. Therefore, it is important for kinetic studies to obtain catalytic data in kinetic regime (free of the influence of the external and internal diffusion).

3.2. Analysis of influence of diffusion resistance

The correct studies on the influence of contact time on the kinetic regularities need the reaction to proceed in the kinetic regime where the external and internal diffusion does not affect the reaction. Such approach requires additional experiments or theoretical consideration.

The influence of external diffusion resistance was studied in additional experiments on the influence of the gas flow rate on methane conversion at a constant contact time. The required contact time was provided through proportional variations in the flow rate and in the volume of the loaded catalyst. It was established that the gas flow rate should be no less than 3 L/h under the reaction conditions.
conditions. When so, the external diffusion does not influence the reaction. The further studies were carried out at the gas flow rate more than 3 L/h.

The influence of pore-diffusion resistance in the catalyst grains on the OCM process was analyzed by the method proposed by Wagner [20]:

$$ F_s = \frac{d_z^2 \cdot R_{\text{max}}}{4 \cdot D_{\text{eff}} \cdot c} < 1 $$  \hspace{1cm} (1)

where $F_s$ is the modified the Thiele module; $D_{\text{eff}}$ is the coefficient of effective diffusion of reactants inside catalyst grain, m$^2$/s; $d_z$ is the catalyst particle diameter, m; $R$ is the maximal reaction rate, mol/(mol·s); $c$ is the initial concentration of the reactant, mol/mol.

To check criterion (1) needs determination of reaction rate $R$ from experimental data and calculation of the effective diffusion coefficient $D_{\text{eff}}$.

The maximal reaction rate was calculated from the first order equation using the following experimental data: $T = 630^\circ$C, contact time 0.06 s, initial reaction mixture 46 mol % CH$_4$ and 11.5 mol % O$_2$, rest N$_2$; conversion of oxygen $X_{O_2} = 81.7\%$ and of methane $X_{CH_4} = 16.9\%$. With deficient oxygen in the initial reaction mixture, the reaction rate $R$ was calculated from the oxygen concentration. In the said conditions, $R = 3.27$ mol/(mol·s).

The effective diffusion coefficient was determined as follows [20]:

$$ D_{\text{eff}} = \frac{\epsilon}{\xi} D_M $$  \hspace{1cm} (2)

where $\epsilon$ is porosity of catalyst grains, $\xi$ is pore tortuosity, $D_M$ is the molecular diffusion coefficient.

While the dilutant was nitrogen in a great proportion, the coefficient of oxygen diffusion in nitrogen was taken as $D_M$.

The reaction mixture comprised non-polar components (O$_2$, N$_2$, CH$_4$), and the coefficient of molecular diffusion $D_M$ was calculated by the Fuller, Schettler, Giddings method [21]:

$$ D_M = \frac{10^{-7} \cdot T^{1.73} \cdot \sqrt{\frac{1}{M_{N_2}} + \frac{1}{M_{O_2}}}}{P \cdot (V_{N_2}^{0.333} + V_{O_2}^{0.333})^2} $$  \hspace{1cm} (3)

where $D_M$ is coefficient of molecular diffusion of oxygen in nitrogen, m$^2$/s; $T$ is temperature, K; $M_{N_2}$, $M_{O_2}$ are molecular weights of nitrogen and oxygen, g/mol; $V_{N_2}$, $V_{O_2}$ are diffusion volumes of nitrogen and oxygen.

Insertion of parameters $V_{N_2}$=17.9, $V_{O_2}$ = 16.6 to formula (3) gives $D_M = 1.44 \cdot 10^{-4}$ m$^2$/s. The porous structure of the catalyst grains makes the effective diffusion coefficient far lower than the molecular coefficient. From the porosimetry data on Sr-La$_2$O$_3$, $\epsilon$ equals 0.34. While coefficient $\xi$ changes between 2 and 7 [20], the average ratio $\epsilon/\xi = 0.1$ was chosen for calculations, i.e. $D_{\text{eff}} = 0.1 \cdot D_M$. When we insert the obtained quantities to (1), then we have $F_s = 0.122 < 1$. Criterion (1) is satisfied, hence the oxidative methane condensation using 0.25-0.5mm catalyst particles proceeds in the kinetic region.

### 3.3. Catalyst activity testing

Figures 3, 4 illustrate experimental data on the selectivity to target (C$_2$H$_6$, C$_2$H$_4$) and side (CO, CO$_2$) products and methane conversion $X$ as functions of methane conversion and temperature. At $X < ~6\%$ and temperature of 600$^\circ$C (figure 3), an increase in the methane conversion does not cause changes in the selectivity to carbon monoxide and dioxide but the selectivity to the target products increases (figure 3). The experimental results obtained in the range of very low conversions (less than 0.25%) are an unambiguous evidence of the concurrent formation of the target and side products from methane. This conclusion agrees with the data obtained with Mn/Na$_2$WO$_4$/SiO$_2$ and La/Ce catalysts [22, 23].
Figure 3. Dependence of the selectivity to reaction products from methane conversion at 600°C. Contact time 0.02-0.06 s.

As temperature rises, oxygen and methane conversions, as well as selectivities to ethane and ethylene, increase (figure 4A). The selectivity to carbon monoxide decreases but that to carbon dioxide increases due to oxidation of CO to CO₂. The selectivity to ethane starts increasing at a lower temperature than the selectivity to ethylene (figure 4B). This is an indication that the activation energy is higher for the formation of ethane than for the formation of ethylene. Ethane is the primary product of the OCM process (figures 3, 4B), it consumed in reactions of dehydrogenation and oxidative dehydrogenation to give ethylene:

\[ C_2H_6 = C_2H_4 + H_2 \]  \hspace{1cm} (4)  
\[ 2 C_2H_6 + O_2 = 2 C_2H_4 + 2 H_2O \]  \hspace{1cm} (5)  

This conclusion agrees with the data obtained with the Mn/Na₂WO₄/SiO₂ catalyst [24].

Figure 4. Temperature dependences of oxygen and methane conversions (A) and of selectivity to products (B). Contact time 0.06 s.

Hence, the reaction pathway (figure 5) can be presented as:
Figure 5. Schematic of the OCM reaction over Sr-La$_2$O$_3$ catalyst.

The suggested pathway includes the routes of methane oxidation to the target ethane (C$_2$H$_6$) and side products – carbon oxides (CO, CO$_2$), the formation of ethylene (C$_2$H$_4$) from ethane through dehydrogenation by reaction (4) and through oxidative dehydrogenation by reaction (5), and oxidation of ethane and ethylene to carbon dioxide.

4. Conclusion
Sr-La$_2$O$_3$ material was prepared by incipient wetness impregnation of La$_2$O$_3$ with an ammonia solution of strontium nitrate. XRD studies revealed that the Sr-La$_2$O$_3$ material comprises of La$_2$O$_3$ (P3-M1 hexagonal structure) and of SrO phases. Crystallites of the La$_2$O$_3$ support are well faceted. The data on pore size distribution indicate the presence of pores of 0.16 μm in average size mainly.

Kinetic studies of the process of oxidative coupling of methane (OCM) were carried out using 0.25-0.5 particles of the synthesized material at 450–630°C and contact time between 0.02 and 0.06 s under close to isothermal conditions. The data obtained at low methane conversions allowed the pathway of methane transformation to be determined and the schematic of OCM process over the synthesized catalyst to be suggested. The schematic includes the routes of methane oxidation to form ethane and carbon oxides, the formation of ethylene from ethane (through dehydrogenation and oxidative dehydrogenation reactions), and oxidation of ethane and ethylene to carbon dioxide.

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