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Oxidative coupling of methane in the redox cyclic mode over the $Ag–La_2O_3/SiO_2$ catalytic system

Alexander A. Greish,*[a] Lev M. Glukhov,[a] Elena D. Finashina,[a] Leonid M. Kustov,[a] Jae-Suk Sung,[b] Ko-Yeon Choo[b] and Tae-Hwan Kim[b]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: greish@ioc.ac.ru*
[b] *Korea Institute of Energy Research, Yusunggu, Daejeon 305-343, Republic of Korea. E-mail: thkim@kier.re.kr*

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Synergism of Ag and La_2O_3 in the $Ag–La_2O_3/SiO_2$ catalytic system provides substantial efficiency in oxidative coupling of methane carried out in the redox cyclic mode. Selectivity to C_2 products can be raised by preliminary injection of small amount of hydrogen to the catalyst.

A search for efficient catalysts for oxidative coupling of methane (OCM) is the topical problem in the oxidation catalysis. Numerous catalytic systems on the basis of the metal oxides often possess low selectivity to the target products of OCM, in particular C_2 hydrocarbons, mostly due to complete oxidation of methane as well as C_2 hydrocarbons into carbon oxides.

Application of the redox cyclic mode to OCM can be a solution to enhance OCM selectivity.[1–9] In this case the catalyst should contain mobile lattice oxygen that is able to leave its location in the oxide lattice and then take part in oxidation reactions on the catalyst surface.

In redox mode OCM partial oxidation of methane followed by formation of C_2 hydrocarbons as well as complete oxidation are caused by interaction of methane molecules or intermediates with oxygen species of the catalyst lattice. The lost of lattice oxygen spent in the oxidation reactions is recovered by following feed of air (or oxygen) over the catalyst. Thus, consecutive pulses of air and methane to the catalyst give opportunity to carry out OCM in the redox cyclic mode, *i.e.*, when oxidation and reduction on the catalyst are separated in time and proceed independently.

Noteworthy, if a redox mode is used all oxidation reactions occur in the absence of molecular oxygen in the gas phase, the yield of CO_2 becomes substantially lower. Under conventional conditions of OCM carbon oxides are produced due to participation of molecular oxygen. The literature data[10–14] allow one to suppose, that the catalysts on the basis of rare earths, in particular, lanthanide oxides, are suitable for redox mode OCM.

Addition of metal component (*e.g.*, silver) to the catalyst composition could also increase efficiency of OCM.[15–17] Metallic silver is known to have a good capacity to dissolve oxygen at high temperatures. So, if OCM is carried out in the redox cyclic mode silver can serve as a buffer for mobile oxygen left previously the oxide lattice. Additionally, silver crystallites could store and keep a part of oxygen that is input into the reactor before the pulse of methane.

In the present work OCM in the redox cyclic mode using catalytic system on the basis of Ag and La_2O_3 supported on SiO_2 was studied.† Factors that influence the participation of lattice oxygen in the OCM reaction and selectivity to C_2 products were investigated thoroughly.

Major catalytic reactions that accompany OCM on the catalyst surface and proceed with participation of lattice oxygen can be presented as follows:

Oxidative coupling of methane

1. $2CH_4 + [O] \rightarrow C_2H_6 + H_2O$
2. $C_2H_6 + [O] \rightarrow C_2H_4 + H2O$

Complete oxidation

3. $CH_4 + 4[O] \rightarrow CO_2 + 2H_2O$
4. $C_2H_6 + 7[O] \rightarrow 2CO_2 + 3H_2O$
5. $C_2H_4 + 6[O] \rightarrow 2CO_2 + 2H_2O$

In the redox cyclic mode oxidation and reduction stages of the process are performed in the reverse order. Figure 1 shows a scheme of the gases feed used in the experiments.

During passing air through the catalyst bed the oxide lattice of the catalyst fills its anion vacancies with oxygen. In the next

† Oxidative coupling of methane was carried out in the quartz reactors with a fixed catalyst bed mounted inside a cylindrical furnace. One reactor was of 45 cm length, 5.6 mm i.d., another reactor was of 45 cm length, 3 mm i.d. Reaction temperatures were measured by a thermocouple that was inserted in a jacket inside the reactor. The catalyst sample was placed in the central part of the reactor. In order to minimize gas-phase reactions outside the catalyst bed free space of the reactor was filled with quartz chips or quartz insets.

The temperature was ranged in the 700–800 °C interval.

A setup was destined for injection of alternative pulses of air and methane into the reactor. Pulses of methane were injected into the carrier gas flow with the syringes. The carrier gas was He.

Oxidation recovery of the catalyst was carried out by two methods: (i) injecting of air pulse into the reactor; (ii) passing of inert gas flow containing 0.04–0.05% oxygen over the catalyst bed. In the last case oxidation recovery of the catalyst with loading of 300–500 mg took 10–12 min at 40 cm^3 min^{-1} gas flow rate.

Injections of small quantity of hydrogen (0.02 ml) used in some runs were done 30–60 s before the methane pulse.

At the outlet of the reactor reaction products were caught in the U-shape trap at temperature of liquid nitrogen (–196 °C) and after rapid heating to 150–200 °C they were analyzed by GC on two chromatographic columns packed with Polychrom and Zeolite CaA.

The catalyst samples prepared and tested in the work were as follows: 10% La_2O_3/SiO_2; 3%Ag–10% La_2O_3/SiO_2; 6% Ag–10% La_2O_3/SiO_2; 15% Ag–10% La_2O_3/SiO_2; 6% Ag/La_2O_3.

All samples were prepared by the incipient wetness impregnation method. Grinded silica (KSK, Russia) with 0.25–0.50 mm or 0.09–0.2 mm particles was used as a support. Silica was preliminary washed by a solution of hydrochloric acid and dried. Prepared silica was impregnated with corresponding water solutions of silver nitrate or lanthanum nitrate, or their mixtures. Then the samples were dried at 120 °C for 2 h and calcined at 800 °C for 4 h.

Air	He	CH_4	He	Air	He	CH_4
Oxidation of the catalyst		OCM		Oxidation of the catalyst		OCM
GC analysis		Trapping of products		GC analysis		Trapping of products

Figure 1 The gas supply scheme in the OCM experiments.

step, the catalyst is blown up by the inert carrier gas (*e.g.*, He) for removing molecular oxygen from the reaction zone as well as oxygen species weakly adsorbed on the catalyst surface. The third step of the procedure is input of the methane pulse into the carrier gas flow, and this is the OCM reaction itself. Then a sequence of the gases feed is repeated.

In the redox mode the reaction products are formed due to the interaction of mobile lattice oxygen with methane molecules or intermediate species produced on the catalyst surface. It is very important that under these conditions either OCM or complete oxidation occurs without participation of molecular oxygen.

Note that complete oxidation of methane requires oxygen several times higher than oxidative activation of methane followed by formation of methyl radicals (see equations above). It is reasonable to consider that complete oxidation proceeds with participation of unselective oxygen. The latter is characterized by lower binding energy in the oxide lattice and thus is rather available for methane molecules or intermediate species. There is every reason to suppose that unselective oxygen is either molecular oxygen adsorbed on the catalyst surface or oxygen atoms located on the edges of the oxide lattice.

Oxidative generation of methyl radicals from methane molecules followed by their coupling into C_2 hydrocarbons probably has to occur in the active sites characterized by low concentration of mobile oxygen, and should exhibit higher binding energy in the lattice, *e.g.*, on its planes. Additionally, formation of C_2 hydrocarbons can take place in the locations where the OCM reaction rate is limited by slow diffusion of lattice oxygen (or oxygen dissolved in metallic silver) to outer surface of the catalyst. This can let methyl radicals to stay on the active surface for a relatively long time without next interaction with oxygen species. In turn, it results in increase in opportunity for dimerization (coupling) of methyl radicals into C_2 product.

It is reasonable to suppose that decrease in the concentration of weakly bound oxygen (*i.e.*, unselective oxygen) in the catalyst has to result in increase in selectivity to C_2 hydrocarbons. Lowering of percentage of unselective oxygen can be achieved by passing small amount of hydrogen over the catalyst.

In order to study the influence of silver constituent on catalytic properties of the Ag–La_2O_3/SiO_2 system, such samples as 10% La_2O_3/SiO_2, 3% Ag–10% La_2O_3/SiO_2, 6% Ag–10% La_2O_3/SiO_2 and 6% Ag/SiO_2 were prepared and tested in OCM. The runs with these catalysts were carried out under the identical conditions. Figure 2 presents results of these experiments. To compare the samples in their OCM efficiency, the correlation between C_2 selectivity and the yield of the C_2 products was used.

According to the results such catalysts as 10% La_2O_3/SiO_2, 3% Ag–10% La_2O_3/SiO_2 and 6% Ag–10% La_2O_3/SiO_2 allow one to reach OCM selectivity close to 80–90%. But it takes place just when methane conversion is relatively low: less than 0.5% for 10% La_2O_3/SiO_2, and less than 4% for 3% Ag–10% La_2O_3/SiO_2 and 6% Ag–10% La_2O_3/SiO_2.

Noteworthy, catalytic properties of 3% Ag–10% La_2O_3/SiO_2 and 6% Ag–10% La_2O_3/SiO_2 are very close to each other. Catalytic activity in OCM as well as selectivity to C_2 products of these catalysts exceed essentially those of two other samples, in which either La_2O_3 or Ag alone is supported on silica.

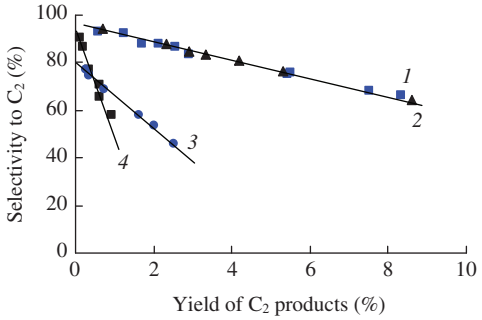

Figure 2 Correlation between selectivity and the yield of C_2 products for OCM carried out in a redox cyclic mode in the runs with (*1*) 3% Ag–10% La_2O_3/SiO_2, (*2*) 6% Ag–10% La_2O_3/SiO_2, (*3*) 6% Ag/SiO_2 and (*4*) 10% La_2O_3/SiO_2. Methane impulse is varied from 0.1 to 6 cm^3; loading of each catalyst, 300 mg; temperature, 750 °C; gas flow rate, 40 cm^3 min^{-1}.

It is important to emphasize that combined action of Ag and La_2O_3 supported on silica enhances both OCM activity and selectivity to the C_2 products. It means that there is a considerable synergetic effect in this case. The curves for 3% Ag–10% La_2O_3/SiO_2 and 6% Ag–10% La_2O_3/SiO_2 samples are located above the corresponding curves for 10% La_2O_3/SiO_2 and 6% Ag/SiO_2. Joint action of Ag and La_2O_3 makes it possible to get the yield of C_2 products of about 9% when OCM selectivity is close to 60%. These values of the C_2 yield as well as OCM selectivity are not available on either 10% La_2O_3/SiO_2 or 6% Ag/SiO_2 catalysts. Increase in silver percentage from 3% to 6% in the Ag–La_2O_3/SiO_2 catalyst system does not practically have effect on the OCM efficiency. It was noticed that total amount of lattice oxygen taking part in oxidation reactions grows if a methane pulse injected into the reactor is increased.

It was found that addition of a small amount of air to the methane pulse resulted in a sharply drop of OCM selectivity. In particular, if 1.6 cm^3 mixture consisted of the equal quantities of methane and air was input over the 6% Ag–10% La_2O_3/SiO_2 catalyst OCM selectivity was about 40%, while in the runs with 0.8 cm^3 methane pulses without air additive OCM selectivity could reach 86%. These results prove that the presence of molecular oxygen in the reaction zone promotes complete oxidation of light hydrocarbons to an essential extent. Thus, molecular oxygen can be considered to be responsible for decrease in OCM selectivity.

The 6% Ag–10% La_2O_3/SiO_2 catalyst was characterized by XRD. XRD pattern of the sample in the 2θ range from 20 to 85° has five diffraction maxima. The most intense reflections were observed at 2θ = 38.14, 44.32, 64.44 and 77.42°. These peaks correspond to the reflections from the different planes Ag crystallites. It means that Ag is in the reduced metallic state. Any peaks associated with the crystalline phase La_2O_3 were not found. It allows one to consider that in our sample the La_2O_3 oxide supported on silica is amorphous and does not form definite crystallite phase which could give corresponding XRD peaks.

Temperature in the interval of 700–800 °C was found to be optimal for OCM proceeding on the catalysts studied. The results showed that the amount of lattice oxygen participating in catalytic reactions lowers with the temperature growth.

Decrease in the gas flow rate does not increase the yield of C_2 hydrocarbons probably because of dilution of injected methane with helium in the reactor volume.

It was found that during starting pulses of methane to the 3% Ag–10% La_2O_3/SiO_2 catalyst the latter enhances its activity in OCM, and the yield of C_2 hydrocarbons becomes several times higher (Figure 3).

It is obvious that training of the catalyst sample occurs in the starting pulses of methane. It can be related with reduction of Ag crystallites followed by formation of the active sites that are

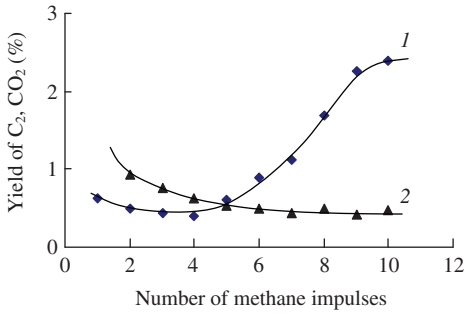

Figure 3 Variation of the yield of C_2 products and CO_2 in the starting pulses of methane during OCM over the 3% Ag–10% La_2O_3/SiO_2 catalyst. Loading of the catalyst, 300 mg; temperature, 750 °C; methane pulse, 0.8 cm^3; gas flow rate, 40 cm^3 min^{-1}.

responsible for OCM proceeding. On the contrary, the yield of CO_2 firstly lowers and then remains at the about constant level, *i.e.*, the rate of complete oxidation does not change.

There was every reason to consider that partial reduction of the Ag–La_2O_3/SiO_2 catalyst before methane pulse has to remove a part of unselective oxygen from the catalyst and thus to cause enhance in OCM selectivity. In order to check this supposition a series of the runs with preliminary injections of small amounts of hydrogen (0.02 cm^3) were carried out (Figure 4). In these runs the 3 mm i.d. reactor was used.

It is clear that preliminary reduction of the catalyst with hydrogen increases reaction selectivity to the C_2 products. However, if the quantity of injected hydrogen is relatively large there is a drop of the catalytic activity in both OCM and complete oxidation, whereas OCM selectivity remains unchanged. It is obvious that large amount of hydrogen is able to remove simultaneously both unselective and selective oxygen species. There is likely an optimal amount of hydrogen injected into the catalyst that is capable of enhancing OCM selectivity.

In general, the catalyst developed can provide 30% yield of C_2 hydrocarbons with 60% OCM selectivity. However, when the yields of C_2 hydrocarbons are lower than 5%, the selectivity can reach 80% and above.

The experiments confirm that formation of the C_2 products (*i.e.*, coupling of methyl radicals) occurs on the active sites that are located either on the silver crystallites or on the boundary between silver and La_2O_3. In this case silver is a carrier of mobile oxygen from La_2O_3 to methane. Meantime, the data evidence that complete oxidation proceeds with participation of nonselective oxygen.

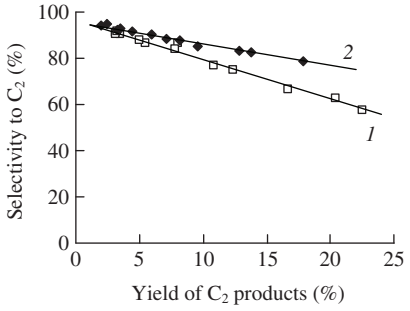

Figure 4 Correlation between selectivity and the yield of C_2 products for OCM in the redox cyclic mode over the 3% Ag–10% La_2O_3/SiO_2 catalyst: (*1*) without preliminary injection of H_2, (*2*) with preliminary injection of 0.02 cm^3 H_2. Methane pulse is varied from 0.1 to 3 cm^3; loading of the catalyst, 300 mg; fraction of the catalyst particles, 0.09–0.20 mm; temperature, 750 °C; gas flow rate, 40 cm^3 min^{-1}.

In summary, the Ag–La_2O_3/SiO_2 system is favourable for carrying out OCM in the redox cyclic mode. This system possesses lattice oxygen capable of leaving the crystal lattice and participating in oxidation reactions accompanying OCM. The lost of mobile oxygen spent in oxidation reactions is recovered by next feed of air to the catalyst.

Combination of Ag and La_2O_3 in the catalyst results in essential synergetic effect and the OCM efficiency. The active sites being responsible for OCM are generated during silver reduction with methane or hydrogen. At the same time proper catalyst reduction increases OCM selectivity. In our opinion, a silver phase is a buffer transferring mobile oxygen from lanthana to methane molecules. In order to achieve high OCM selectivity, it is required to keep reduced state of the catalyst. Rather high efficiency in OCM performed in the redox mode is exhibited by the 3% Ag–10% La_2O_3/SiO_2 catalyst. It allows one to reach the 30% yield of C_2 products with OCM selectivity being close to 65–70%.

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