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Oxidative coupling of methane in the redox cyclic mode over the catalysts on the basis of CeO_2 and La_2O_3

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, 71-2 Jangdong, Yusunggu, Daejeon 305-343, Republic of Korea. E-mail: jssung@kier.re.kr*

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The 1% CeO_2, 9% La_2O_3/SiO_2 and 2% CeO_2, 8% La_2O_3/SiO_2 catalysts show reliable efficiency in the OCM reaction, as well as stable work in the redox cyclic mode. Selectivity to C_2 products remarkably increases if preliminary reduction of the catalyst by a small amount of hydrogen is used.

Oxidative coupling of methane (OCM) is one of the challenges in natural gas processing. A search for efficient oxidation catalysts for the OCM process remains the topical problem in the oxidation catalysis. Now, many attempts to increase the efficiency of this process are made. One of the ways to enhance the OCM selectivity consists in alternating feeding of methane and oxygen to the catalyst. Earlier, this approach has been applied both for OCM[1–5] and other processes.[6–9]

If OCM occurs over an oxide catalyst, the lattice of the catalyst can supply its oxygen for oxidative conversions of methane accompanying OCM. Then, formation of the reaction products, such as C_2 hydrocarbons and CO_2, proceeds from the interaction of methane molecules with lattice oxygen. As a result, reduction of the oxygen content in the catalyst composition takes place. The lost of lattice oxygen in the catalyst is recovered by the following re-oxidation procedure. Thus, using consecutive reduction and oxidation stages in OCM allows one to carry out this process in the so-called redox cyclic mode. The main feature of this mode is that oxidation recovery of the catalyst and oxidative methane conversions are separated in time and are performed in the alternating flows.

The absence of molecular oxygen in the reaction zone is favourable for lowering the yield of carbon dioxide that is a product of complete oxidation of both methane and C_2 products produced in OCM. As a result, the OCM selectivity to C_2 products can be enhanced.

Earlier, it was found that the $Mn–Na_2WO_4/SiO_2$ catalyst is rather suitable for OCM performed in the redox cyclic mode.[1,2] The main reason is that the $Mn–Na_2WO_4/SiO_2$ catalyst includes two transient metals that are capable to take part in reduction–oxidation reactions due to changing their valency.

The goal of this work was searching the catalysts for the OCM process carried out in the redox cyclic mode. This mode can be realized if the catalyst consists of a metal oxide that provides its lattice oxygen for oxidative activation of methane molecules followed by cleavage of C–H bonds. In this case, the OCM efficiency must depend on the dynamics of oxygen supply from the oxide lattice for oxidation conversions on the catalyst surface.

Recently,[10–14] the catalytic properties of rare earth element oxides in the OCM reaction were studied. It was shown that the catalysts on the basis of La_2O_3 and CeO_2 oxides and their compositions exhibited high activity in this reaction. We decided to study the opportunity of using similar catalysts for carrying out the OCM process in the redox cyclic mode. For our study, a series of catalysts on the basis of La_2O_3 and CeO_2 supported on silica have been prepared.

Investigations were focused on the study of the factors that effect the contributions of oxidative reactions resulting, on one hand, in the formation of C_2 hydrocarbons and, on the other hand, in the formation of CO_2. Also there was the intention to find the proper reaction conditions that would be most suitable for increasing the OCM selectivity.[†]

To perform the redox cyclic testing of the catalysts in the OCM process, air and methane gases are injected into the reactor as separate pulses in the inert gas flow (Figure 1). In this case, methane passes over the previously oxidized catalyst bed in the

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[†] The experimental setup for the study of the OCM reaction in a redox cyclic mode made it possible to inject alternating pulses of air and methane into the catalytic reactor, followed by GC analysis of the reaction products.

The carrier gas was He. Air and methane pulses were injected by syringes. Methane pulses were introduced to the oxidized catalyst. After the reaction products were removed from the reactor, the catalyst was reoxidized by the air pulse.

The amount of oxygen required for recovery of the catalyst after OCM can be introduced by feeding the inert gas (He) containing 0.04–0.05% of oxygen to the catalyst bed for 10–15 min.

The catalytic reactor was a quartz tube with 5.6 mm or 2.5 mm i.d. and 45 cm length. To minimize the free space in the reactor, quartz chips or insets were used. This allowed us to reduce an opportunity of gas-phase reactions in the space out of the catalyst bed.

At the outlet of the reactor, the reaction products were collected in a U-shape trap at the temperature of liquid nitrogen (–196 °C), and after fast heating to 150–200 °C they were analyzed by gas chromatography. GC analysis was performed on two chromatographic columns packed with Polychrom and Zeolite CaA. The temperature range of the process was 700–850 °C.

The following catalyst samples were prepared and tested in this work: 10% La_2O_3/SiO_2; 1% CeO_2, 9% La_2O_3/SiO_2; 2% CeO_2, 8% La_2O_3/SiO_2; 10% CeO_2, 90% La_2O_3 (bulk).

All supported catalysts were prepared by impregnation of grinded silica with a particle size 0.25–0.5 mm with appropriate metal nitrates solutions followed by drying at 120 °C and calcination in dry air at 800 °C. The bulk $CeO_2–La_2O_3$ catalyst was prepared by co-precipitation of oxalates of La and Ce using dropwise addition of an oxalic acid solution to a solution of $La(NO_3)_3$ and $Ce(NO_3)_3$. Then the sample was dried at 120 °C and calcined at 800 °C.

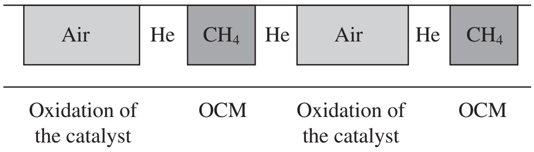

Figure 1 The gas supply in the OCM experiments.

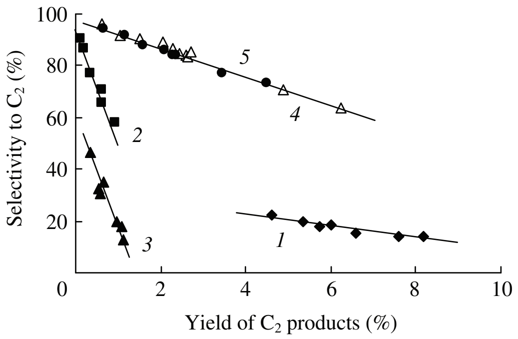

Figure 2 Correlation between OCM selectivity and the yield of C_2 products for the catalysts tested in the redox cyclic mode at 800 °C. Loading of each catalyst, 300 mg; methane pulse is changed from 0.1 to 6 cm^3; gas flow rate, 40 cm^3 min^{-1}. (*1*) 10% CeO_2/SiO_2; (*2*) 10% La_2O_3/SiO_2; (*3*) 10% CeO_2–90% La_2O_3 (bulk); (*4*) 1% CeO_2, 9% La_2O_3/SiO_2 and (*5*) 2% CeO_2, 8% La_2O_3/SiO_2.

absence of molecular oxygen in the gas phase. After reaction products were removed from the reactor, the catalyst was re-oxidized by introducing an air pulse. The amount of air needed for entire re-oxidation (recovery) of the catalyst depends on the amount of oxygen lost by the catalyst during oxidative conversions of methane.

In the absence of molecular oxygen in the reaction zone, the lattice of the oxide catalyst delivers oxygen atoms to activate methane molecules for the OCM reaction. In this case, methyl radicals are produced from methane molecules due to their interaction with mobile oxygen atoms of the catalyst lattice. Certainly, at high temperatures of the process a part of lattice oxygen can be removed from the catalyst and takes part in oxidation reactions and thus in the following formation of all reaction products. The lost of lattice oxygen spent in oxidation reactions is recovered by re-oxidation of the catalyst. The processes of oxygen evolution from metal oxide and next recovery of anion vacancies appeared after oxidation reactions can be presented in a general way by the following equations:

$$Me_2O_3 \rightarrow Me_2O_{3-x} + x[O]_{surf.};$$

$$Me_2O_{3-x} + x[O]_{gas} \rightarrow Me_2O_3.$$

Participation of lattice oxygen in the oxidation reactions accompanying OCM on the catalyst surface can be presented as follows:

Coupling of methane
$$2CH_4 + [O] \rightarrow C_2H_6 + H_2O;$$

Partial oxidation of ethane
$$C_2H_6 + [O] \rightarrow C_2H_4 + H_2O.$$

Noteworthy the amount of oxygen required for conversion of methane to CO_2 (complete oxidation) exceeds several times the amount consumed in the reactions of formation of such products as ethylene or ethane. For example, the reaction of complete oxidation of methane demands four times more oxygen than oxidative activation of methane molecules followed by the formation of ethane.

Taking this into account, it is very important to know the factors that can change the ratios of presented oxidation reactions in favour of C_2 hydrocarbons formation. It is most likely that the formation of CO_2 is related with the participation of mobile oxygen which has a lower binding energy in the oxide lattice, *i.e.* with nonselective oxygen.

It is well known that CeO_2 oxide can be a supplier of lattice oxygen for different oxidation reactions, *e.g.*, oxidation of light hydrocarbons. Its lattice oxygen is rather mobile. There was intension to check the properties of CeO_2 as an oxygen supplier for the OCM reaction carried out in the redox cyclic mode.

Therefore, the 10% CeO_2/SiO_2 catalyst was chosen as the initial sample for investigation of main features of OCM carried out in a redox cyclic mode. The use of the CeO_2/SiO_2 catalyst in OCM was expected to result in relatively high yields of C_2 hydrocarbons.

The very first experiments with the CeO_2/SiO_2 catalyst showed that this catalyst possesses a certain amount of mobile lattice oxygen that takes part in both methane conversion to C_2 and CO_2 (Figure 2, plot *1*). But this catalyst exhibits a very low selectivity in OCM because the complete oxidation of methane to CO_2 prevails, although after the following re-oxidation procedure the catalyst recovers entirely its activity. The data allow us to conclude that the CeO_2/SiO_2 catalyst is not suitable for OCM carried out in a redox cyclic mode.

It was decided to lower remarkably the content of CeO_2 in the catalyst composition and replace it with such an oxide as La_2O_3. The latter is known to possess less pronounced oxidation properties than CeO_2. The maximum positive valency of Ce is 4+, while that of La is only 3+. The total molar amount of the rare earth element oxide in the catalyst composition was the same, *i.e.*, 10%. Such samples as 1% CeO_2, 9% La_2O_3/SiO_2 and 2% CeO_2, 8% La_2O_3/SiO_2 were prepared and tested also in the redox cyclic mode of OCM. The data show that these catalysts are also able to supply their lattice oxygen for oxidative conversions of methane (Figure 2, plots *4*, *5*). Moreover, the 1% CeO_2, 9% La_2O_3/SiO_2 and 2% CeO_2, 8% La_2O_3/SiO_2 catalysts exhibit proper oxidative properties and high stability. With the use of these catalysts it is possible to approach the OCM selectivity higher than 85–90%, but in the case when the yield of C_2 products does not exceed 2–3% (Figure 2, plots *4*, *5*).

The amount of lattice oxygen of these catalysts taking part in oxidation reactions increases with reaction temperature, likely due to increasing oxygen mobility in the oxide lattice at high temperatures. According to experimental data, when injecting of 3 ml methane pulses, the increase in temperature from 700 to 800 °C results in about double increase in the amount of converted methane, from 0.8 to 1.7 μmol. Meantime, in the 800–850 °C temperature range, the quantity of mobile oxygen changes insignificantly.

Note that the total amount of formed CO_2 practically does not depend on the volume of the methane pulse. It allows us to suppose that in the catalyst there is a fixed quantity of nonselective oxygen that takes part in complete oxidation.

In most of the runs, the ethylene portion in the C_2 products does not exceed 45–50%. This indicates that a relatively small amount of lattice oxygen participates in partial oxidation of ethane.

The data obtained lead to a conclusion that in the catalyst there are two types of lattice oxygen delivered for such oxidation reactions as OCM and complete oxidation. These types of oxygen can be considered as selective and nonselective oxygen. Selective oxygen takes part in OCM only, while nonselective oxygen participates in complete oxidation and partial oxidation of ethane to ethylene. These types of oxygen differ by the binding energy in the oxide lattice. Selective oxygen is characterized by a larger binding energy than nonselective oxygen.

Dilution of injected methane with helium results in a decrease in the OCM selectivity and increase in the yield of CO_2. The 1% CeO_2, 9% La_2O_3/SiO_2 catalyst starts to work stable after a few pulses of methane, *i.e.*, its surface must be somewhat reduced.

In comparison with the supported catalyst, the bulk sample 10% CeO_2–90% La_2O_3 was prepared and tested (Figure 2, plot *3*). It was found that the presence of CeO_2 in the bulk 10% CeO_2–90% La_2O_3 catalyst results in a sharp drop of the selectivity to C_2 products, it was about 15–25% at 1% yield of C_2 products. There is a large slope in the dependence of the OCM selectivity on the yield of C_2 products. When the amount of injected methane is reduced, there is a sharp drop of the OCM selectivity. It is obvious that lattice oxygen in the CeO_2 oxide is rather mobile and relatively easy leaves the crystal lattice for participation in oxidation reactions. However, one should take into account that the bulk density of the bulk 10% CeO_2–90% La_2O_3 catalyst exceeds essentially that of the supported 1% CeO_2, 9% La_2O_3/SiO_2 catalyst. It means that at equal loadings of the bulk and supported catalysts, the accessible surface area of the first catalyst is remarkably lower than that of the second one. In any case, one can consider that the bulk catalyst is inferior to the supported sample in its activity in OCM.

It was interesting to check the catalytic activity of La_2O_3 supported on SiO_2, *i.e.* La_2O_3/SiO_2.

Some results obtained in the runs with the 10% La_2O_3/SiO_2 catalyst are presented in Figure 2 (plot *2*). It can be noticed that the 10% La_2O_3/SiO_2 catalyst allows one to reach a 80–90% selectivity to C_2 products but when the methane conversion to C_2 hydrocarbons is lower than 1%. Injection of small pulses of methane at 800 °C gives the yield of C_2 hydrocarbons no more than 2%. Increasing the reaction temperature leads to a sharp drop of the catalyst productivity in oxidation reactions.

Thus, introduction of a small additive of CeO_2 to La_2O_3/SiO_2 system allows one to get a catalyst that exhibits a higher selectivity in OCM than initial La_2O_3/SiO_2. A plot of the selectivity *vs.* the C_2 yield becomes more flat, *i.e.*, with a less pronounced slope.

According to our results, the catalysts with a mixture of La_2O_3 and CeO_2 oxides taken in ratios 9:1 or 8:2 make it possible to reach a relatively high selectivity to C_2 products in OCM performed in the redox cyclic mode. These values of the OCM selectivity are obtained when we use small pulses of methane. In this case, a large part of methane undergoes complete oxidation and is converted into CO_2. C_2 products formed previously in OCM can burn also giving an additional amount of CO_2 but the contribution of the former process in the total formation of CO_2 is more remarkable. One reason of the foreground burning of methane under these conditions may be dilution of the methane pulse with inert gas. Really, OCM is known to be a reaction of a second order. Therefore, a decrease in the partial pressure of methane in the reaction zone results in a decrease of the possibility of OCM and corresponding lowering of the C_2 yield. In order to decrease the dilution of methane pulse with He, it was decided to use the reactor with a diameter of 2.5 mm.

Our expectations were met. The dependence of the OCM selectivity on the yield of C_2 products became more flat (Figure 3). The catalyst shows a rather good stability.

It is clear that, in order to increase the OCM selectivity, it is necessary to decrease the content of nonselective oxygen in the catalyst. To do that we injected a small amount of hydrogen (0.04 cm^3) directly before each methane pulse. The data show (Figure 3, plot *2*) that preliminary introduction of hydrogen (for reduction of the catalyst) leads to essential increase of the OCM selectivity.

It is a very important result. This confirms once more that in the catalyst sample there are two types of mobile lattice oxygen, *i.e.* weakly and strongly bound oxygen atoms. Injection of a small amount of hydrogen directly before the methane pulse reduces the content of weakly bound oxygen that leads to an increase in the OCM selectivity.

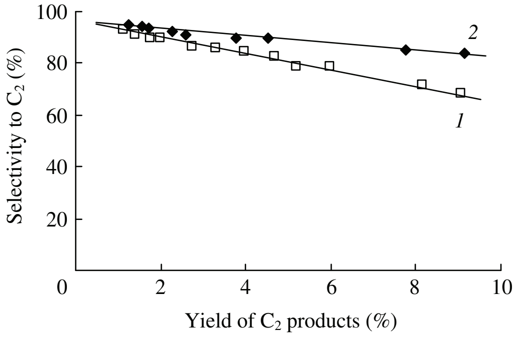

Figure 3 Correlation between the OCM selectivity and the yield of C_2 products for the 2% CeO_2, 8% La_2O_3/SiO_2 catalyst at 800 °C in the reactor of 2.5 mm i.d. Loading of the catalyst, 300 mg; methane pulse is changed from 0.1 to 6 cm^3; gas flow rate, 40 $cm^3\,min^{-1}$. (*1*) Without injecting of hydrogen; (*2*) with preliminary injecting of hydrogen.

Extrapolation of the curve *2* in Figure 3 to the larger values of the C_2 yield allows one to consider that under our conditions the 2% CeO_2, 8% La_2O_3/SiO_2 catalyst is able to give the yield of C_2 hydrocarbons at the level of 30% when the OCM selectivity is close to 65–70%.

Thus, the data show that the catalysts consisted of the La_2O_3 and CeO_2 oxides provide the opportunity to carry out the OCM process in the redox cyclic mode. A general feature of this process is the supply of lattice oxygen of the catalyst for oxidation reactions proceeding on the catalyst surface.

The best results are found on 1% CeO_2, 9% La_2O_3/SiO_2 and 2% CeO_2, 8% La_2O_3/SiO_2 catalysts, in particular when the process is carried out in the narrow catalytic reactor and with preliminary injection of a small amount of hydrogen. Preliminary reduction of the catalyst by hydrogen decreases the surface concentration of non-selective oxygen. This results in an increase in the selectivity to C_2 products.

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