ELSEVIER

Catalysis Today 42 (1998) 211–215

CATALYSIS TODAY

Interaction of carbon dioxide with methane on oxide catalysts

O.V. Krylov[a,*], A.Kh. Mamedov[b], S.R. Mirzabekova[b]

[a]N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina. 4, Moscow 117977 GSP-1, Russian Federation
[b]Yu.G. Mamedaliev Institute of Petrochemical Processes, Azerbaijan Academy of Sciences, ul. Telnova 30, Baku 370604, Azerbaijan

Abstract

Catalytic interaction of methane with carbon dioxide with the formation of syngas $CO+H_2$ over manganese oxide containing catalysts was studied. 5%Ca–12%Mn–O/Al_2O_3 was proved to be the most effective one. At 870°C and space velocity of 900 h^{-1} the conversion degree of methane was 83.1%, that of CO_2 was 62.7%, and the H_2-selectivity was 76.5%. The mechanism of methane interaction with Mn-containing catalyst and that of the catalyst reoxidation by CO_2 and by O_2 was investigated. It turned out that much less of oxygen was introduced into catalyst during oxidation by CO_2 than by oxygen. The conversion of CH_4 into C_2-hydrocarbons takes place under non-stationary conditions. A thermoneutral process of syngas production on Mn-oxide catalyst was proposed using a combination of endothermic CH_4+CO_2 and exothermic CH_4+O_2 reactions. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Carbon dioxide; Methane; Ca–Mn–O/Al_2O_3

1. Introduction

The direct interaction of methane with CO_2 or "dry" methane reforming

$$CH_4 + CO_2 = 2CO + 2H_2, \quad \Delta H = 209.3\,\mathrm{kJ/mol}, \tag{1}$$

has been intensively studied on metallic catalysts by many workers [1–3]. This reaction is very attractive from the industrial point of view, because it leads to the synthesis gas of the ratio $CO:H_2=1:1$. Such a mixture is necessary, for example, for the synthesis of dimethyl ether, the "fuel of the 21st century", as it was claimed on the last conference on the natural gas conversion (South Africa, November 1995). Both reagents are cheap and one may hope to work out large-scale processes on their basis. Besides that, syngas of any composition can be obtained by combining reaction (1), steam reforming of methane (2), and oxygen reforming (3)

$$CH_4 + H_2O = CO + 3H_2, \quad \Delta H = 76.6\,\mathrm{kJ/mol}, \tag{2}$$

$$2CH_4 + O_2 = 2CO + 4H_2, \quad \Delta H = -49.0\,\mathrm{kJ/mol}. \tag{3}$$

Some other reactions proceed on the metal catalysts during their interaction with CH_4 and CO_2:

$$CH_4 + 2CO_2 = C + CO_2 + 2H_2, \quad \Delta H = 641.1\,\mathrm{kJ/mol}, \tag{4}$$

$$CH_4 + 3CO_2 = 4CO + 2H_2O, \quad \Delta H = 330.6\,\mathrm{kJ/mol}, \tag{5}$$

---

*Corresponding author.

PII S0920-5861(98)00094-7

$$2CH_4 + CO_2 = C_2H_6 + CO + H_2O,\quad \Delta H = 16.7\,\mathrm{kJ/mol}, \tag{6}$$

$$CO_2 + H_2 = CO + H_2O,\quad \Delta H = 42.3\,\mathrm{kJ/mol}. \tag{7}$$

All these reactions (4)–(7) are endothermic and proceed at high temperatures (600–900°C). At 800°C, ΔG for the reactions (4), (5), and (7) is negative and for reaction (6) it is positive but not very high. The equilibrium yield of C_2H_6 in reaction (6) at 800°C is 13%, which is fairly large. Nickel catalysts are most often employed for syngas formation, but they are poisoned by reaction (4). Noble metals, especially iridium and ruthenium are active catalysts and are not poisoned by carbon, but they are expensive.

In this paper we propose oxide catalysts for reaction (1). They are less active, than metals, but they are stable in catalytic conditions. Some data on the mechanism of the reaction are presented. We are also trying to construct a thermoneutral process by a combination of endothermic and exothermic reactions.

2. Experimental

All catalysts were prepared by impregnation of SiO_2 or Al_2O_3 with nitrates of different metals, followed by drying at 100–140°C over 4 h and calcination at 800–900°C. The details of experimental procedure are given in papers [4,5]. The catalysts prepared on the basis of both SiO_2 and Al_2O_3 do not strongly differ by their surface areas (69 and 34 m^2/g, respectively). This shows that the differences in catalytic properties of these systems are not due to surface area influence.

The catalytic experiments were performed in silica reactors of 0.7 cm diameter. The pulse method was also used in a reactor of 0.15 mm diameter. The amount of catalyst was 4 cm^3, the grains were 0.05–0.4 cm in size; the space velocity was varied from 900 to 5000 h^{-1}.

3. Results

In order to find the most effective catalyst and to elucidate the characteristics of catalyst selection, we carried out a study of the effect of modifying additives on the catalyst [4]. Modification of Ni by different additives, such as Cu, Cr, Fe, Mn oxides, etc. changes its properties in CH_4+CO_2 conversion. The best effect was obtained when manganese oxide was used as modifying additive. Fig. 1 shows results of the study of CO_2 pulse interaction with catalysts coked in methane. Upon increase of Mn content the degree of CO_2 conversion increases and the coking decreases.

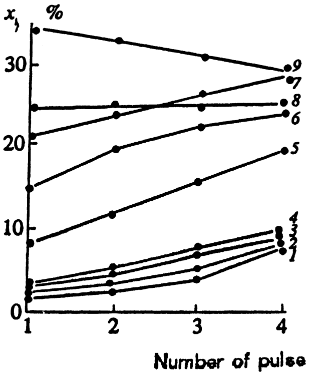


Fig. 1. CO_2 interaction with the catalysts coked in CH_4 in pulse regime at 800°C. Dependence of the CO_2 conversion degree on the number of pulse: 1 – 12%Ni/Al_2O_3; 2 – (5%Ba+12%Ni)/Al_2O_3; 3 – (5%Ca+12%Ni)/Al_2O_3; 4 – (5%Ca+2%Cu+12%Ni)/Al_2O_3; 5 – (5%Ca+2%Mn+12%Ni)/Al_2O_3; 6 – (5%Ca+5%Mn+12%Ni)/Al_2O_3; 7 – (5%Ca+10%Mn+12%Ni)/Al_2O_3; 8 – (5%Ca+12%Mn+12%Ni)/Al_2O_3; 9 – (5%Ca+12%Mn)/Al_2O_3.

Further investigation showed that the catalyst can work without any metallic component (curve 9 in Fig. 1). Under stationary conditions the 5%CaO–12%Mn–O/Al_2O_3 catalyst proved to be the most effective. This catalyst has a stable activity and in the steady state functions for a longer time than the catalyst (12%MnO+5%CaO+12%Ni)/Al_2O_3. These data are shown in Table 1. In the initial non-steady state the C_2-hydrocarbons yield was 9% at 850°C. It increased up to 13% with decrease of the pretreatment temperature.

An XRD study shows that the oxidized Mn-phases – Mn_2O_3 and Mn_3O_4 promote total methane oxidation; the reduced phases – MnO and $MnCO_3$ assist methane conversion into syngas; intermediate phases, where O^- stabilization is possible, promote methane oxidative coupling. When the initial phases are completely reduced, the formation of C_2H_6 and C_2H_4 decreases

Table 1
Conversion of methane with CO_2 in stationary state conditions on the catalyst: 5%Ca–12%Mn–O/Al_2O_3, space velocity 900 h^{-1}

T (°C)	Initial mixture		Composition of products (%)				Conversion (%)		H_2 selectivity
	CH_4	CO_2	CO	H_2	CO_2	CH_4	CH_4	CO_2	
870	43	57	49.7	30.6	14.7	5.1	83.1	62.7	76.5
890	49	51	56.4	37.4	3.5	2.3	91.8	89.1	80.1
920	47	53	55.6	40.3	3.6	0.6	97.8	89.3	84.1
930	43	57	56.8	42.4	2.4	0	100	94.6	84.6

Table 2
Interaction of CH_4, O_2 and CO_2 with the 13%Na–17%Mn–O/SiO_2 catalyst and the CH_4+CO_2 stationary reaction

Consecutive processes	Results
Reducing interaction of CH_4 at 800°C with the catalyst treated by air at 800°C during preparation	Initial CH_4 conversion is 24%, initial C_2-selectivity is 21%
Steady-state reaction CH_4+O_2 (air) at 765–785°C and 3600 h^{-1}	CH_4 conversion is 60.7–89.4%, low C_2-selectivity equal to 16–17%
Reduing reaction of CH_4 after the steady-state reaction and air treatment	Initial CH_4 conversion equal 17.4%, increase of C_2-selectitivity up to 90%, oxygen capacity equal to 512 μmol/g
Reoxidation of the reduced catalyst by CO_2	Starting at 700°C, CO formation, the oxidation rate is 50 times less than that of reduction
Reducing reaction of CH_4 with the catalyst, reoxidized by CO_2	Initial CH_4 conversion is 4–5%, initial C_2-selectivity is 39–41% and constant, oxygen capacity equal to 76.2 μmol/g
Steady-state CH_4+CO_2 reaction at 805–900°C	CH_4 conversion is 60% at 805°C, traces of C_2, CO selectivity is 85%, 100% CO+H_2 at 900°C
Reoxidation of the catalyst by air and interaction with CH_4	Initial CH_4 conversion is 8%, decrease of CO_2 conversion four times, decrease C_2 conversion two times, this means an increase of C_2-selectivity

and only conversion to syngas, reaction (1), takes place.

We studied the processes of separate interaction of CH_4, O_2 and CO_2 with the catalysts: 13%Na–17%Mn–O/SiO_2 (I), 2%Na–17%Mn–O/SiO_2 (II) and 13%K–17%Mn–O/SiO_2 (III). The sequence of the processes and the main results are shown in Table 2.

These data allow to conclude that: (1) the CO_2 activation takes place on the reduced surface, most probably, on MnO; (2) the steady-state reaction (1) does not follow the alternating redox mechanism and proceeds on this reduced phase; (3) the complete oxidation $CH_4+2O_2 \rightarrow CO_2+2H_2O$ does not take place; (4) the oxygen capacity in the reoxidation by CO_2 is seven times less than in the oxidation by O_2, which means that the carbonate fragments formed block the access to O_2 accepting; (5) comparison of H_2 formation rate in steady state conditions (3×10^{-3} mol/g h) and during the reduction of the catalyst by CH_4 (1.7×10^{-3} mol/g h) shows that they are close to each other; (6) the rate of CO_2 interaction with the reduced surface is higher than the rate of reduction.

The rate of reoxidation of the catalyst (II) is one order of magnitude higher than that of the catalyst (I). An increase of Na at the surface leads, probably, to the coverage of the more stable carbonates. CO_2 desorption from the catalyst (II) starts at 550°C, from the catalyst (I) only at 700°C. At low Na concentrations the reoxidation of the reduced Na–Mn–O catalyst by CO_2 proceeds with CO formation, at high Na concentrations more stable carbonates CO_3^{2-} are formed which take part in C_2 hydrocarbons formation. The rate of catalyst (III) reoxidation and that of CO formation from CO_2 is three times higher than in the case of catalyst (I).

Another catalyst – La–Mn–O/SiO_2 exhibits even almost 100% C_2-selectivity after its treatment by CO_2 and subsequent admission of CH_4 at 800°C, whereas CO is not formed. The La–MnO/Al_2O_3 catalyst was somewhat less selective. The process

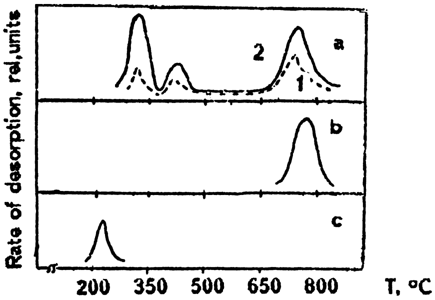


Fig. 2. CO_2 thermodesorption from the manganese containing catalysts: (a) Mn–O/SiO_2, 1 – after H_2 pretreatment, 2 – without pretreatment; (b) Cr–Mn–O/SiO_2; (c) Cr–O/SiO_2.

of C_2-hydrocarbons formation takes place, probably, via the interaction of CH_4 with carbonate fragments:

$$2CH_4 + CO_3^{2-} \rightarrow C_2H_6 + CO + H_2O + O^{2-} \qquad (8)$$

The oxygen bond strength in the catalysts was determined by thermodesorption. Fig. 2 shows CO_2 thermodesorption spectra for three catalysts. Three peaks, i.e. three types of oxygen sites, were observed for the Mn–O/SiO_2, which was pretreated in CO_2: at 335°C, 445°C and 750°C with activation energies 92±8, 225±9, and 290±10 kJ/mol, correspondingly. Pretreatment in H_2 (curve 1 in Fig. 2) decreases the oxygen capacity of these sites, but does not change their properties. For Cr–Mn–O/SiO_2 only one high temperature peak is observed (Fig. 2(b)). But this catalyst leads to only reaction (5) of CO+H_2O formation. Thus, Cr^{3+} reoxidizes Mn^{2+} to Mn^{3+} or Mn^{4+}, which lead to complete oxidation. Syngas formation takes place with the participation of an oxygen site of moderate strength (moderate basicity). One low temperature peak was observed on Cr–O/SiO_2. (Fig. 2(c)) containing catalyst.

4. Discussion

The essential requirement for the correct selection of the oxide system is its ability to accept and to activate CO_2. The acid nature of CO_2 necessitates the employment of a catalytic system with basic properties. However, alkali and alkaline earth oxides, which form stable carbonates, are not effective. Moderately strong bases forming carbonates with reduction of CO_2 are needed. Such requirements are met with manganese oxides and apparently some lanthanide oxides. Their acid and redox properties may be changed by adding other oxides. The Ca–Mn–O/SiO_2 catalyst turned out to be selective and stable against coking during syngas formation, but less active, than metal catalysts.

The above described results allow to propose the following scheme of syngas formation by dry methane reforming on manganese oxide catalysts:

$$CH_4 + MnO \rightarrow MnO\ldots C + 2H_2 \qquad (9)$$

$$CO_2 + MnO \leftrightarrow MnCO_3$$

$$MnCO_3 + MnO\ldots C \rightarrow 2MnO + 2CO$$

$$MnCO_3 + H_2 \rightarrow MnO + CO + H_2O$$

$$MnO\ldots C + H_2O \rightarrow MnO + CO + H_2$$

The intermediate carbonates here perform transport functions with respect to oxygen. The following equation for the reaction rate results from scheme (9)

$$r = \frac{k_1 P_{CH_4}}{1 + (1/k_2k_3)(P_{CO}^2/P_{CO_2}) + k_2P_{CO_2}}, \qquad (10)$$

where P_{CH_4}, P_{CO}, P_{CO_2} are the partial pressures of CH_4, CO, and CO_2, respectively, k_1, k_2, and k_3 are the rate constants of the reaction in scheme (9). This equation was confirmed by experimental data. The interaction of $MnCO_3$ with MnO…C (virtually, the reverse Boudouard reaction) is a fast reaction and the constant k_3 is high.

For the metal catalyst Eq. (11) was proposed [6]

$$r = \frac{k_1 P_{CH_4}}{1 + aP_{H_2O}/P_{H_2} + bP_{CO}}, \qquad (11)$$

where k_1, a and b are constants. This equation and other equations proposed for metals differ from Eq. (10) by the absence of the term kP_{CO_2}.

One of the drawbacks of the dry methane reforming is its endothermicity. Our data presented in Table 2 allow to propose an overall process, which includes endothermic and exothermic reaction

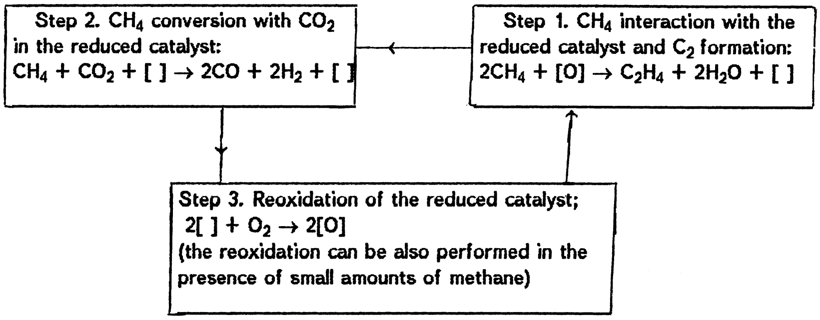
$$3CH_4 + CO_2 + 2O_2 = C_2H_4 + 2CO + 2H_2 + 2H_2O \qquad (12)$$

The endothermic reaction of syngas formation can be compensated here by exothermic oxidative methane coupling. The thermoneutrality can be reached by adding some amounts of CH_4 in the reoxidation step. Additive of methane establishes an optimal degree of catalyst reduction and secures additional heat evolution.

Another possibility of the thermoneutral process:

$$(1+2x)CH_4 + CO_2 + xO_2 \rightarrow 2(1+x)CO + 2(1+2x)H_2 \qquad (13)$$

has been realized by us on Ni–Mn–O/MgO in the "tube in tube" reactor. The CH_4+O_2 reaction took place in the external tube and the reaction CH_4+CO_2 – in the internal tube. At 800°C the CH_4 and CO_2 conversion was close to 80–85% and the CO:H_2 ratio was close to 1.



Step 2. CH_4 conversion with CO_2 in the reduced catalyst:
$CH_4 + CO_2 + [\ ] \rightarrow 2CO + 2H_2 + [\ ]$

Step 1. CH_4 interaction with the reduced catalyst and C_2 formation:
$2CH_4 + [O] \rightarrow C_2H_4 + 2H_2O + [\ ]$

Step 3. Reoxidation of the reduced catalyst;
$2[\ ] + O_2 \rightarrow 2[O]$
(the reoxidation can be also performed in the presence of small amounts of methane)

5. Conclusion

Manganese oxide containing supported catalysts are selective in the reaction CH_4+CO_2 with syngas formation at high temperatures (800–900°C) and stable against coking. A study of alternating stepwise interaction of the catalyst with CH_4 and CO_2 allows to propose the mechanism of the reaction with participation of intermediate carbonate $MnCO_3$. In the non-stationary state condition the oxidative coupling of methane also proceeds. It was proposed to use these results for development of a thermoneutral process of methane oxidation.

References

[1] J.H. Rostrup-Nielsen, J.H.B. Hansen, J. Catal. 144 (1993) 38.
[2] A. Erdohelyi, J. Czerenyi, E. Papp, F. Solymosi. Appl. Catal. A 105 (1994) 205.
[3] P.D.F. Vernon, M.L.H. Green, A.K. Cheetham, A.T. Ashcroft, Catal. Today 13 (1992) 417.
[4] S.R. Mirzabekova, A.Kh. Mamedov, V.S. Aliev, O.V. Krylov, React. Kinet. Catal. Lett. 47 (1992) 159.
[5] O.V. Krylov, A.Kh. Mamedov, Russ. Chem. Rev. 64 (1995) 877.
[6] I.I. Bodrov, L.O. Apelbaum, Kinet. Katal. 8 (1967) 379.