

16th International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov, CCE 2015

Manganese Catalysts to Obtain Olefins from C₁-C₄ Alkanes

S.I. Galanov^{a,c*}, O.I. Sidorova^a, M.A. Gavrilenko^b, O.B. Frants^{a,c}, V.O. Nekhoroshev^{a,c},
Y.D. Korolev^{a,c}, A.V. Egoshina^b *

^aTomsk Polytechnic University, Lenin ave. 30, Tomsk, 634050, Russia

^bTomsk State University, Lenin ave., 36, Tomsk, 634050, Russia

^cInstitute of High Current Electronics SB RAS, 2/3, Akademicheskoy Ave., Tomsk, 634055, Russia

Abstract

Oxidative transformations of C₁-C₄ alkanes into olefins on oxide manganese catalysts were under study. We also studied oxidative coupling of methane (OCM) into ethylene on deposited and applied on the silicon dioxide catalysts. We studied the influence of chemical composition of catalyst and promoters on the OCM. Adding a little amount of ethane and propane hydrocarbons to methane allows increasing the concentration of ethylene in gases and significantly increasing productivity in ethylene. The study also shows the impact of the amount of manganese and promoters applied on SiO₂ on the yield of olefins during the conversion of C₃-C₄ alkanes.

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Peer-review under responsibility of Tomsk Polytechnic University

Keywords: Manganese catalysts, oxidative coupling of methane, C₁-C₄ alkanes

1. Introduction

Reactions of receiving olefins from gaseous alkanes apart from receiving olefins in petro-chemistry can be also important in the process GTL (gas-to-liquid)^{1,2}. The formation of olefins is possible from methane and its higher homologues according to the following reactions:

1. Oxidative coupling of methane $2\text{CH}_4 + \text{O}_2 = \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$ ³.

* Corresponding author. Tel.: +7-960-975-9711

E-mail address: galanov@xf.tsu.ru

2. Dehydration of ethane into ethylene $\text{C}_2\text{H}_6 + 0,5\text{O}_2 = \text{C}_2\text{H}_4 + \text{H}_2\text{O}$ ⁴.
3. Paraffins $\text{C}_3\text{--C}_4$ dehydrate and crack to the mixture of olefins (ethylene, propylene, butylene) ^{5,6}.

There are two possible processes of olefins synthesis from alkanes:

1. Continuous – the oxidizer (oxygen or air) is supplied together with hydrocarbons into the reactor ^{3,7}.
2. Cyclic – the catalyst is synchronically the reagent; the hydrocarbons conversion occurs because of oxygen from the catalyst lattice with further reoxidation during air flush with the oxidizer, i.e. air. The advantages of the cyclic process are the following: air is the oxidizer, explosion safety, the possibility to organise a recycle ^{2,8,9}.

The requirements set for the catalysts of oxidation of hydrocarbons in cyclic process are the following:

- catalyst stability in a wide range of temperature
- capacity of the element with mixed valence in the composition of the catalyst to form stable oxides in variable oxidation degrees
- capacity of the catalytic system for fast and effective regeneration (reoxidation), which means regeneration of its catalytic activity.

Manganese oxide systems because of high mobility of lattice oxygen are applied as catalysts in oxidative processes, where cation additives of alkali metals are used as promoters ^{2,3,6,7,10}.

The objective of this paper is to determine the optimal chemical composition of the catalyst, chemical nature of promoting additive, conditions of conducting cyclic process to obtain high yield of olefins from alkanes.

2. Material and Methods

The paper includes the usage of manganese catalysts, which are deposited and applied to a carrier. Deposited samples of catalysts were prepared in the following way: estimated amounts of nitrates of manganese (II), lithium and phosphorous acid or sodium phosphate were dissolved in distilled water, and then the solution was evaporated during agitating until a smooth paste was obtained; dried at 200 °C during two hours, the obtained mass was calcinated for seven hours at 900 °C. The composition of the obtained catalysts was in accordance with the following formula: $(y)\text{Me}_3\text{PO}_4 \cdot (100-y)\text{MnO}_x$, where (y) expresses molar ratio of phosphate Me (of lithium or sodium) and the manganese oxide in the catalytic system (as %), while the oxygen coefficient (x) can vary in the range of 1.5-2. Applied catalytic systems were obtained with infiltration of $\gamma\text{-Al}_2\text{O}_3$ or SiO_2 granulas (fraction 0.25-0.5 mm) with an estimated amount of $\text{Mn}(\text{NO}_3)_2$ and promoting additive: Na_3PO_4 , $\text{Na}_2\text{B}_4\text{O}_7$, NaOH , Na_2WO_4 , Na_3VO_4 . The obtained mass was dried at 150 °C for six hours and calcinated for 7 hours at 900 °C. Quantitative estimation of alkali metals in the samples was conducted with X-ray fluorescent energy-dispersive spectrometer Oxford ED-2000 (UK, Oxford Instruments) ¹¹.

Catalytic properties of the contacts were studied on continuous catalytic unit with a fixed bed of catalyst in the range of temperature from 600 to 850 °C. The conditions of the experiment with separate input of reagents varied in the range: catalyst bulk volume was 3.9-7.9 cm³, contact time was from 1 to 3.5 sec. The operation cycle of the catalytic reactor is the following. The air flush the heated up reactor with nitrogen, feeding of hydrocarbon has on the catalyst (the cycle of olefins operation) from two to ten minutes, air flush the reactor with nitrogen was two minutes, the cycle of reoxidation of the catalyst (air flush) from 2 to 10 minutes, which corresponded with the time of olefins operation cycle, air flush the reactor with nitrogen was 2 minutes and then the cycles were repeated. The temperature in the isothermal conditions was preserved to a high accuracy of ± 0.1 °C.

The analysis of initial gases and reaction products was chromatographic. We used gas chromatograph Kristall-5000.1 with 2 thermal conductivity detectors and a flame ionization detector for this analysis.

To separate gaseous mixture, we used the following chromatographic columns: 1) a 4 m long packed column with sorbent NaX (60/80 mesh) to detect and identify: hydrogen, oxygen, nitrogen, methane and carbon monoxide (carrier gas Ar); 2) a 1.5 m long packed column with sorbent Carbosieve S-II (60/80 mesh) to detect and calculate the concentration of carbon dioxide (carrier gas He); 3) a 50 m long capillary column HP-PLOT $\text{Al}_2\text{O}_3(\text{KCl})$ to separate and detect hydrocarbons $\text{C}_1\text{--C}_5$. The temperature of the column oven was 80 °C. The calculation of the concentrations of the components of gaseous mixture was according to the method of absolute calibration in the program "Chromatech Analytic 2.5" ^{12,13}.

3. Result and Discussion

The oxidation of hydrocarbons in cyclic regime is non-stationary, which means that the interaction of hydrocarbon molecule with the oxygen on the catalyst surface with the formation of radicals, and their further transformation on the surface of the catalyst and in the gaseous phase^{1,14,15}. Correspondingly, the effectiveness of catalysts in cyclic regime apart from selectivity in the formation of olefins and hydrocarbons conversion is determined by the operation cycle duration and depends on the surface and bulk properties of oxygen in catalyst (the diffusion rate of oxygen from the volume of the catalyst lattice and the rate of the interaction of surface oxygen with hydrocarbon and reaction products).

When we used methane as raw hydrocarbon, the rate-limiting step of the process is the activation of the methane molecule with the formation of methyl radicals, which then recombine on the catalyst surface and in the gaseous phase with the formation of ethane, which then transforms into ethylene. Thus, yield of ethylene depends both on the primary activation of methane and secondary reactions of ethane. According to table 1, methane conversion, selectivity to ethylene and correspondingly yield of ethylene for deposited catalysts increase along the increase of temperature and contact time. Sodium phosphate suits best as promotor because if compared with lithium sample quite a high yield of ethylene can be obtained at the temperature of 800 °C.

To increase catalysts performance, and above all structural performance, it is preferred to use oxide systems applied on the carrier. Usage of aluminum oxide as a carrier leads to the decrease of selectivity to C₂ hydrocarbons up to 0.5%, in this case manganese applied systems perform as catalysts of deep oxidation. Usage of SiO₂ type CSC as a carrier allows obtaining selective catalysts of oxidative dimerization of methane (table 2).

Table 1. Catalytic properties of deposited manganese systems

Catalyst	Reactor temperature, °C	Contact time, s	Methane conversion, mol %	Selectivity, %		Ethylene yield, %
				C ₂ hydrocarbons	Ethylene	
6 % mol Li ₃ PO ₄ /MnO _x	800	1	3.8	88.0	26.0	1.0
	800	2	5.8	84.0	36.1	2.1
	850	1	7.4	82.5	41.5	3.1
	850	1.5	9.8	76.4	44.4	4.3
	850	2	11.6	68.9	42.3	4.9
6 % mol Na ₃ PO ₄ /MnO _x	800	1	7.1	79.2	25.9	1.9
	800	2	9.9	75.0	34.9	3.5

Table 2. Catalytic properties of the applied manganese systems with 2% composition with promotor as 17.4% MnO_x/SiO₂

№	Promotor	Reactor temperature, °C	Methane conversion, %	Selectivity, %		Ethylene yield, %
				C ₂ hydrocarbons	Ethylene	
1	Na ₃ PO ₄	750	3.4	100	43.0	1.5
		800	3.5	100	51.8	1.8
		850	9.2	93.9	54.3	5.0
2	Na ₂ B ₄ O ₇	750	4.6	55.7	13.2	0.6
		800	11.2	35.0	29.3	3.3
		850	30.6	17.7	13.5	4.1
3	NaOH	750	1.3	100	13.8	0.18
		800	2.0	100	42.1	0.84
		850	3.0	100	29.1	0.87
4	Na ₂ WO ₄	750	3.8	60.3	26.9	1.02
		800	11.5	28.8	27.1	3.1
		850	12.9	29.9	21.5	2.8
5	Na ₃ VO ₄	750	2.9	59.4	25.5	0.74
		800	3.8	27.7	11.3	0.43
		850	5.6	20.2	9.8	0.6

It can be inferred from table 2 that anion of the promoting additive significantly influences activity and selectivity of the applied catalysts. For example, usage of NaOH as a promotor allows obtaining C2-hydrocarbons with 100% selectivity but the methane conversion is low and ethylene yield is correspondingly low (table 2, sample 3). Samples 2 and 4, which were promoted with sodium tetraborate and tungstate with high methane conversion increasing alongside the temperature increase (table 2), demonstrate low selectivity to products. The optimal promotor is sodium phosphate (table 2, sample 1).

There is a significant increase of productivity in ethylene (table 3) when ethane and propane are added to methane of higher hydrocarbons. The increase of productivity, caused by feeding C2-C3 hydrocarbons into the system, is not proportional to their concentration and is much higher.

Table 3. The concentration of ethylene in reaction gases ($C_{C_2H_4}$, vol %) and catalyst productivity P in ethylene under various compositions of raw hydrocarbons

Composition of raw hydrocarbons, vol %	Reactor temperature, °C	Contact time, s	$C_{C_2H_4}$, vol %	P , g of ethylene/g of catalyst · h
97,3-CH ₄ ; remaining N ₂	740	1	1.2	0.10
	780	1	1.9	0.13
	800	1	2.9	0.15
94,9-CH ₄ ; 2,4-C ₂ H ₆ ; remaining N ₂	740	1	2.5	0.31
	780	1	2.8	0.32
	800	0.4	2.8	0.33
93,7-CH ₄ ; 2,4-C ₂ H ₆ ; 1,2-C ₃ H ₈ ; remaining N ₂	740	0.2	4.5	1.07
	780	1	5.2	1.16
	800	1	5.3	1.21

Thus, using methane-ethane-propane mixture with the concentration of higher hydrocarbons of 3.6 % vol. under similar conditions increases productivity in ethylene by ten times compared with pure methane. According to the following works^{1,13}, the main function of the catalyst in the OCM is to generate methyl radicals, which means to initiate radical reaction leading to the formation of ethane, ethylene and CO_x.

Correspondingly, feeding higher homologues of methane with energies of dissociation of bond C–H 97 kcal/mol for ethane and propane, C–C bond for ethane is 84 and for propane is 82 kcal/mol, while C–H bond dissociation in case of methane is 102 kcal/mol¹⁶, contributes to a more effective generation of radicals, leading to the increase of productivity in ethylene (table 3)⁶. Usage of propane-butane mixture (propane is 70 mol.%, the rest is butane) as raw hydrocarbon allows obtaining a much higher yield of olefins (fig. 1) with deposited catalyst of 6 mol % Na₃PO₄/MnO_x.

On the deposited catalyst, there are mostly reactions of oxidizing cracking, and, therefore, there is a predominant yield of ethylene, the product of cracking of C3-C4 hydrocarbons over dehydration products, i.e. propylene and butylenes, yield of non-selective oxidation CO_x is low, figure 1. On the applied catalyst 2%-Na₃PO₄/17.4%-MnO_x/SiO₂, high yield of olefins is obtained at much lower temperatures, the yield of dehydration products, i.e. propylene and butylenes, is much higher than for a deposited catalytic system (fig. 2).

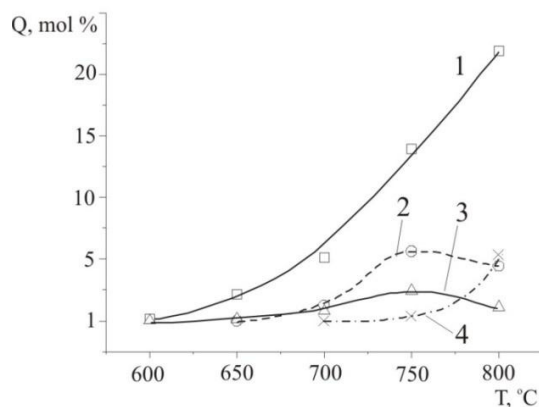


Fig. 1. Correlation of yield of ethylene (1), propylene (2), butylenes (3), CO₂ (4) and the temperature. Catalyst 6 mol % Na₃PO₄/MnO_x

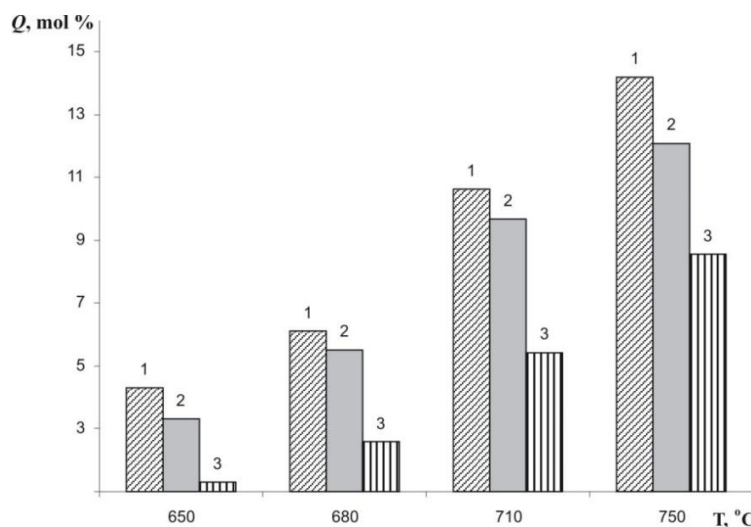


Fig. 2. Correlation of yield of ethylene (1), propylene (2), butylenes (3) and the temperature. Catalyst 2%-Na₃PO₄/17.4%-MnO_x/SiO₂

For a two-step conversion of hydrocarbons into synthetic liquid hydrocarbons, a high content of higher olefins in the raw product is optimal for the second step, i.e. oligomerization because of higher reaction capability of C3-C4 olefins if compared with ethylene. The study of amount variation for the applied active component MnO_x for SiO₂ (fig.3) demonstrated that optimal content of manganese oxides is 17 %. The increase of the content of active component leads to decrease of olefins yield because of the increase of the rate of deep oxidation of hydrocarbons to CO_x. The decrease in the content of active component in the catalyst leads to the decrease of olefins yield because of low rate of raw hydrocarbons transformation (fig. 3).

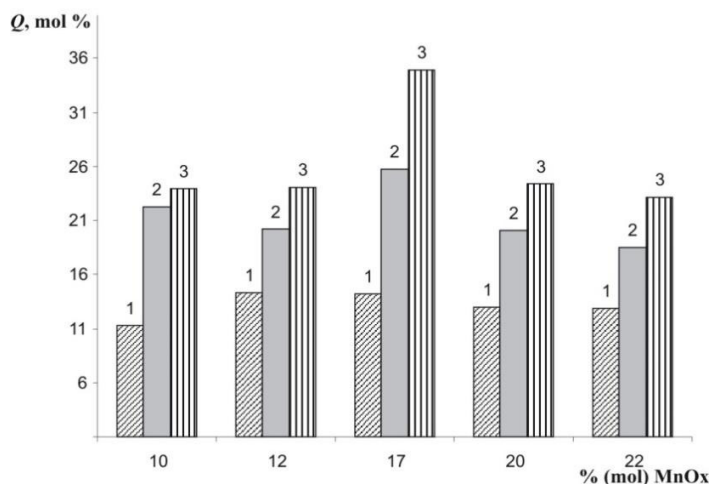


Fig. 3. Correlation of total olefins yield and the content of the active component MnOx applied on SiO₂. Reactor temperature: 1) 680; 2) 710; 3) 750 °C. Contact time 1 sec.

When we used the mixture of C1-C4 hydrocarbons with the methane content of 60-70 vol %, the rest C2-C4 hydrocarbons, the concentration of olefins in reaction gases can be up to 25-30 mol.% in one reactor passage. According to the applied technologies of alkanes C₂+ oligomerization, we can obtain petrol and diesel fuel, but the ratio of petrol to diesel fuel can vary in a wide range^{1,2,17}. After oligomerization of olefins in fuels, unreacted alkanes return into the cycle, where they mix with the initial hydrocarbons.

4. Conclusion

1. It was shown by experiment that the optimal catalyst for the transformation of C1-C4 alkanes and their mixtures into olefins in cyclic process can be the 2%-Na₃PO₄/17.4%-MnOx/SiO₂ system, where methane and its higher homologues convert into olefins with high extent of efficiency.
2. The temperature of reactor of hydrocarbon gases conversion into olefins depends on the chemical content of the raw materials, for gases with high content of CH₄ the optimal temperature is 800-850 °C, for gases with high content of C3-C4 alkanes this temperature is 730-770 °C.
3. To obtain ethylene with low content of C3-C4 olefins it is necessary to use deposited manganese catalysts.

Acknowledgements

The authors acknowledge funding for this research by the Russian Government Program «Science» of Tomsk Polytechnic University, grant No. 4.1187.2014/K. This work was performed as part of the Program for the Competitive Growth of Tomsk State University and Tomsk State University Academic D.I. Mendelev Fund Program in 2015.

References

1. Lunsford J.H. Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21 st century. *Catalysis Today* 2000; **63**: 165–174.
2. Baliban R.C., Elia J.A., Floudas Ch.A. Novel Natural Gas to Liquids Processes: Process Synthesis and Global Optimization Strategies. *AIChE Journal* 2013; **59**: 505-531.
3. Malekzadeh A., Dalai A.K., Khodadadi A., Mortazavi Y. Structural features of Na₂WO₄-MO_x/SiO₂ catalysts in oxidative coupling of methane reaction. *Catalysis Communications* 2008; **9**: 960–965

4. Bodke A.S., Bharadwaj S.S., Schmidt L.D. The Effect of Ceramic Supports on Partial Oxidation of Hydrocarbons over Noble Metal Coated Monoliths. *Journal of catalysis* 1998; **179**: 138-149
5. Wang H., Zhao Zh., Zhang Zh. Duan A., Xu Ch. Selective oxidation of propane to oxygenates over mesoporous SBA-15-supported potassium catalysts. *Journal of Porous Materials* 2008; 221-229.
6. Usachev N.Ya., Kharlamov V.V., Belanova E.P., Starostina T.S., Krukovsky I.M. Oxidative processing of light alkanes: state and prospects. *Rossiyskiy khimicheskiy zhurnal* 2008; **LII**: 22-31.
7. Dedov A.G., Makhlin V.A., Podlesnaya M.V., Zyskin A.G., Loktev A.S., Tyunjaev A.A., Nipan G.D., Koltsova T.N., Ketsko V.A., Kartasheva M.N., Moiseev I.I. Kinetics, mathematical modeling, and optimization of the oxidative coupling of methane over a LiMnW/SiO₂ catalyst. *Theoretical Foundations of Chemical Engineering* 2010; **44**: 1-11.
8. Sofranko J.A., Leonard J.J., Jones C.A. The oxidative conversion of methane to higher hydrocarbons. *Journal of catalysis* 1987; **103**: 302-310.
9. Li K., Wang H., Wei Y., Yan D. Transformation of methane into synthesis gas using the redox property of Ce-Fe mixed oxides: Effect of calcinations temperature. *International journal of hydrogen energy* 2011; **36**: 3471-3482.
10. Wu J., Zhang H., Qin S., Hu Ch. La-promoted Na₂WO₄/Mn/SiO₂ catalysts for the oxidative conversion of methane simultaneously to ethylene and carbon monoxide. *Applied Catalysis A: General* 2007; **323**: 126-134.
11. Galanov S.I., Sidorova O.I. Effect of a precursor on the phase composition and particle size of the active component of Ni-ZrO₂ catalytic systems for the oxidation of methane into syngas. *Russian of physical chemistry A* 2014; **88**: 1629-1636.
12. Galanov S.I., Sidorova O.I. Combined conversion of methane into syngas on Ni/MgO-Cr₂O₃ catalysts. *Russian Journal of Applied Chemistry* 2014; **87**: 1435-1441.
13. Korolev Y.D., Frants O.B., Landl N.V., Kasyanov V.S., Galanov S.I., Sidorova O.I., Kim Y., Rosocha L.A., Matveev I.B. Propane oxidation in a plasma torch of a low-current nonsteady-state plasmatron. *IEEE Trans. Plasma Sci.* 2012; **40**: 535-542.
14. Arutyunov V.S. *Oxidizing conversion of natural gas*, Krasand, Moscow, 2011.
15. Korolev Y.D., Frants O.B., Landl N.V., Geyman V.G., Kasyanov V.S. Methane Oxidation in a Low-Current Nonsteady-State Plasmatron. *IEEE Trans. Plasma Sci.* 2014; **42**: 1615-1622.
16. Morrison P., Boil R. *Organic Chemistry*, Allyn and Bacon, Inc., Boston, 1970.
17. Velichkina L.M., Gossen L.P. Environmental Aspects of Technical Catalysis in Petroleum Chemistry (A Review). *Petroleum Chemistry* 2009; **49**: 445-453.