CHEMICAL ENGINEERING TRANSACTIONS

VOL. 70, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Timothy G. Walmsley, Petar S.Varbanov, Rongxin Su, Jiří J.Klemeš

ISBN978-88-95608-67-9; **ISSN** 2283-9216

DOI: 10.3303/CET1870320

Heat Generation by Catalytic Environmentally Friendly Combustion of Methane

Zauresh T. Zheksenbaeva[a,b], Svetlana A. Tungatarova[a,b,*], Tolkyn S. Baizhumanova[a], Rabiga O. Sarsenova[a], Kaysar Kassymkan[a]

[a]D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, 142 Kunaev str., Almaty, 050010, Kazakhstan
[b]Al-Farabi Kazakh National University, 71 al-Farabi ave., Almaty, 050040, Kazakhstan
tungatarova58@mail.ru

It is known that environmentally friendly flameless combustion of hydrocarbons without formation of nitrogen oxides is an important way to dispose of natural gas. In this regard, the development of energy-saving and environmentally friendly catalytic combustion technologies of light hydrocarbons for heating of greenhouses and use of formed CO_2 for carbon dioxide additional fertilizing of plants is the aim of the present work. Polyoxide heat resistant (up to 1,473 K) highly efficient Mn-containing catalysts for deep oxidation of methane and propane-butane in vapor-air mixture have been developed. Prototype of catalytic heat generator was created for ecologically clean methane and propane-butane burning. Pilot testing of catalytic heat generator for heating of greenhouses were conducted and carbon dioxide fertilizing of plants by combustion products of propane-butane mixture was carried out. It was shown that the Mn catalyst contains crystalline CeO_2 and nanoparticles of Mn_2O_3 (d = 30 - 40 Å) using BET, XRD, TEM and ESDR methods. Its amount decreases by heating to 1,173 K through a partial interaction with rare earth elements with the formation of La(Ce)MnO_3, $CeAlO_3$, then hexaaluminate $LaMnAl_{11}O_{19}$ at 1,273 - 1,473 K, which are active in oxidation of CH_4 to CO_2. Such phase composition is main condition for optimum deep oxidation of CH_4.

1. Introduction

Light gaseous hydrocarbons have special significance among the organic fuels. They are used in form of household and motor fuel or burned as waste gas in the "torch". In this case, a potential source of energy is lost and ozone layer of the Earth is destroyed. Therefore, the problem of their efficient processing and using for various technological purposes is relevant.

Flameless catalytic combustion of natural and oil gases without the formation of nitrogen oxides is a promising way to utilization of natural methane and other alkanes to produce heat, carbon dioxide and products for organic synthesis (CO, H_2). Calculating the cost of heat produced during deep methane combustion in a pilot plant showed that it is lower than cost of coal-fired boiler heat. Catalytic oxidation of CH_4 to CO_2 in order to generate heat is a promising way to dispose of mine, ventilation and burnt in flares methane. Catalytic combustion is fundamentally different from thermal combustion, as occurs on the surface of solid catalysts without the flame selectively to CO_2 at much lower temperatures, which prevents the formation of nitrogen oxides and other pollutants. Stringent requirements to catalysts of deep oxidation of CH_4 and other light hydrocarbons to CO_2 are imposed. They should have a high thermal stability up to 1,473 - 1,573 K, mechanical strength, high activity and selectivity.

Known industrial polyoxide and spinel Cu-, Cr-, Mn-, Ni-, and Co-containing catalysts, which are used for cleaning waste gas from harmful substances, are not thermally stable. Their phase transformations take place together with simultaneous decrease in the activity of catalysts. It is known that ttotal surface of oxide Ni-Cu and Pt catalysts used in oxidation of CH_4 and C_3H_8-C_4H_{10} decreases sharply after their heating at 1,473 K, which leads to a significant reduction in catalyst activity. Sintering processes of carrier and additional dispersion of oxides under certain conditions can occur with increasing of processing temperatures of the supported oxide

Please cite this article as: Zheksenbaeva Z.T., Tungatarova S.A., Baizhumanova T.S., Sarsenova R.O., Kassymkan K., 2018, Heat generation by catalytic environmentally friendly combustion of methane , Chemical Engineering Transactions, 70, 1915-1920 DOI:10.3303/CET1870320

catalysts. Mn/Al_2O_3 catalyst (Tsyryul'nikov, 1996) was the most thermally stable (up to 1,273 K), high efficient in the combustion of alkanes, but then its activity sharply decreased.

Therefore, the development of catalysts for complete combustion of light alkanes (C_1-C_4) aimed at improving the thermal stability due to modification of carriers and active phases (perovskites (Vereshchagin et al., 2015), hexaaluminates (Popova et al., 2003)) are particularly relevant. Recently, heat exchange has been widely studied in such systems (Kukulka et al., 2016) as well as Co firing (Barmina et al., 2016), solid oxide fuel cell-based trigeneration systems (Tippawan et al., 2016), hybrid-heating systems (Schumm et al., 2016), on the base of biomass (Goryunov et al., 2016), model-based analysis of novel heat engines for low-temperature heat conversion (Knoke et al., 2017). It was investigated the thermodynamic properties of methane combustion (Acampora et al., 2017) and relationship on CO_2, energy consumption and economic growth (Kushairi et al., 2018).

In this regard, the purpose of work is the creation of energy-efficient and environmentally friendly catalytic technology for combustion of gaseous hydrocarbon fuel to heat the greenhouses and the use of produced CO_2 for carbon dioxide plant nutrition.

2. Experimental

New approaches to the synthesis of thermally stable multicomponent oxide catalysts were used for the development of catalysts for combustion of light alkanes in heat generators. Granulated θ-Al_2O_3 (S = 100 m^2/g), modified by 2 % Ce, forming surface $CeAlO_3$ perovskite resistant to 1,373 K was used as a carrier. The rare earth elements (REE) (La, Ce) and alkali-earth elements (AEE) (Ba, Sr) were entered into the composition of supported polyoxide catalysts based on 3d metals (Ni, Cu, Cr, Mn) for the formation of perovskite-like structures and spinels on the surface Oxide catalysts were promoted with Pt and Pd (0.05 %) to increase the activity and thermal stability.

The catalysts were prepared by capillary impregnation of alumina by mixed aqueous solutions of metal nitrates on water capacity with subsequent drying at 453 - 473 K (4 - 5 h) and calcination at 873 K (1 - 1.5 h) in air. The catalyst activity was determined in oxidation of CH_4 in flow type installation at atmospheric pressure in tubular quartz reactor with fixed catalyst bed at 673 - 973 K. Catalyst was placed in the central part of reactor and quartz wool placed above and below the catalyst bed. Temperature was measured by a thermocouple inserted in a jacket of the reactor. The study of deep oxidation of CH_4 (0.5 - 4 %) was carried out by varying the space velocity from 10 to 20×10^3 h^{-1} and O_2 concentrations from 2 to 20 % (Popova et al., 2003).

The phase composition of catalysts was determined by X-ray diffractometer DRON-4.7, Co – anode, 25 kV, 25 mA, 2θ – 5–80° (XRD). The morphology, particle size and chemical composition were investigated using transmission electron microscope EM-125K at 80,000 times magnification by the replica method with extraction using microdiffraction (TEM). The surface of catalysts was determined by the BET method on the low temperature N_2 adsorption using the Accusorb apparatus (Micromeritics, USA). Spectra of diffuse reflection of catalysts were recorded in the air as the composition of the catalysts became more complicated on the Shimadzu UV-300 instrument in the IR SB RAS using a standard attachment for reflection in the 240-800 nm region (ESDR).

3. Results and Discussion

Table 1 shows the data obtained at the oxidation of 0.5% CH_4 in air at GHSV = 10×10^3 h^{-1} on the synthesized catalysts after heating at 873 K and 1,473 K. It is seen that after heating the catalyst at 873 K for 1 h at 973 K provided 85 – 99 % conversion of methane. Catalysts (heating at 873 K, 1 h) at 973 K can be arranged in a series of degree of oxidation: AP-56 (100 %), NiCuCr + Pd (99 %), NiCuCr + Pt (96 %), MnREEAEE/2 % Ce/θ-Al_2O_3 (92 %), NiCuCr/2 % Ce/θ-Al_2O_3 (91 %), MnREEAEE + Pd (90 %), MnREEAEE + Pt (85 %). The contact based on Ni-Cu-Cr/2 % Ce/θ-Al_2O_3, close by effectiveness to known commercial Pt contact AP-56 (0.56% Pt) is the most effective catalyst for the oxidation of methane at 973 K.

Due to the fact that the catalysts in combustion process of CH_4 can undergo significant over heating (1,473 K), they lose their activity. Therefore, synthesized contacts were heated in air first at 873 K for 1 h, then sequentially 5 h at 1,073, 1,273, 1,373, and 1,473 K.

Heating at high temperatures are affected differently on the degree of oxidation of CH_4 on different catalysts. Table 1 shows that the heating of catalysts at 1,473 K resulted in significant reduction of the surface of all catalysts. Warming has no negative effect on the degree of oxidation of CH_4 on MnREEAEE catalysts up to 1,373 K. Only upon heating at 1,473 K there was a slight decrease in α_{CH4} (maximum 10 %) in contrast to the Pt/Al_2O_3 (AP-56) contact, the effectiveness of which decreased sharply especially after 1,373 K. As a result of this α_{CH4} reached 60 % at 973 K, and only 10 % at 773 K. Activity of MnREEAEE contact decreases slightly for the initial and heated contacts at 973 K (by 2-7%). Sharp decrease in the degree of conversion of CH_4 occurred after warming since 1,373 and especially at 1,473 K for Ni-Cu-Cr catalyst, which reached 63 % at 973 K, and at 773 K dropped up to 0.

Table 1: Oxidation of 0.5 % CH_4 at GHSV = 10×10^3 h^{-1} in air at 773 and 973 K after heating at 873 K and 1,473 K

Catalyst	Active phase, %	α_{CH_4} after heating at 873/1,473 K, %		S, m^2/g before and after heating
		773 K	973 K	
MnREEAEE	7.00	39/14	92/88	62.9/3.1
MnREEAEE +Pd	7.50	31/16	90/81	56.4/3.6
MnREEAEE +Pt	7.60	40/17	85/86	51.1/2.8
AP-56 (0.56 % Pt)	0.56	54/10	100/60	119.6/2.9
NiCuCr	9.0	38/0	91/63	61.3/2.2
NiCuCr + Pd	9.5	45/0	99/58	60.0/2.1
NiCuCr + Pt	9.5	50/12	96/62	53.5/2.2

A comparative study of oxide catalysts of methane combustion to CO_2 has been shown that the MnREEAEE/2% Ce/θ-Al_2O_3 is the most thermally stable up to 1,473 K catalyst (not promoted by Pd and Pt) which provides 92-88% oxidation of CH_4 at 973 K and GHSV = 10×10^3 h^{-1}.

Figure 1 shows the effect of heating temperature on oxidation of 0.5% CH_4 to CO_2 at 973 K over the MnREEAEE/2 % Ce/θ-Al_2O_3 catalyst, as well as on oxide Ni-Cu-Cr and Mn/Al_2O_3 (IC-40) catalysts.

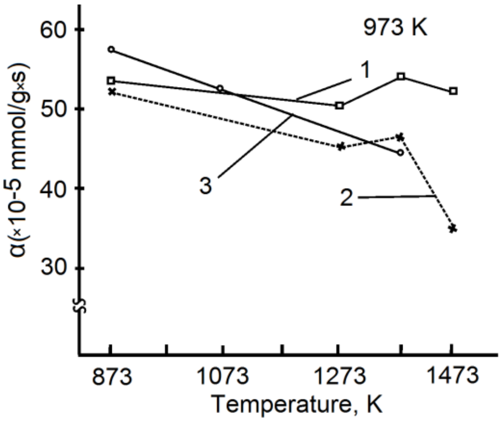

Figure 1: Effect of temperature on specific rate of oxidation of 0.5 % CH_4 on the catalysts: 1 - MnREEAEE/2 % Ce/θ-Al_2O_3, 2 - Ni-Cu-Cr/2 % Ce/θ-Al_2O_3, 3 - Mn/Al_2O_3, IC-40

Heating of the MnREEAEE/2 % Ce/θ-Al_2O_3 catalyst in air up to 1,473 K does not have a negative effect on the specific rate of oxidation of 0.5 % CH_4 at 973 K and GHSV = 10×10^3 h^{-1} in contrast to industrial Mn/Al_2O_3 (IC-40) (Tsyryul'nikov, 1996) oxide catalyst and Ni-Cu-Cr/Al_2O_3. The rate of CH_4 oxidation at 973 K in air on MnREEAEE catalyst heated to 1,473 K is (52 - 54) × 10^{-5} mmol g^{-1} s^{-1}. It was determined that more significant drop in the rate of oxidation from 52×10^{-5} to (33 - 35) × 10^{-5} mmol g^{-1} s^{-1} is observed on the Ni-Cu-Cr-catalyst. Degree of CH_4 conversion is reduced from 58×10^{-5} to 47×10^{-5} mmol g^{-1} s^{-1} after heating at 1,273 K on the IC-40 catalyst.

Study of changes in the phase and surface composition of MnREEAEE/2 % Ce/θ-Al_2O_3 in the heating process using XRD, TEM, BET, ESDO were conducted to determine the causes of its thermal stability. The presence of θ-Al_2O_3 and a certain amount of α-Al_2O_3, crystalline CeO_2, X-ray amorphous Mn_2O_3 clusters was determined in the initial MnREEAEE/2 % Ce/θ-Al_2O_3 catalyst after heating at 873 K in air. It was shown that the concentration of crystalline CeO_2 in catalyst increases with heating. The formation of α-Al_2O_3 increases sharply at temperatures above 1,273 K. This process is accompanied by a slight decrease in the specific surface at temperatures up to 1,273 K and its sharp decrease to 2.5 m^2 g^{-1} at 1,473 K. The nanoparticles of metal oxides (d = 20 - 100 Å), as well as larger dense aluminate type AB_2O_4 and ABO_3 particles (d = 100 - 200 Å) are formed after heat treatment at 873 K of multicomponent oxide MnREEAEE catalysts according to the TEM analysis and electron diffraction. Interaction of elements with the carrier θ-Al_2O_3 occurs at increase of temperature in spite of its protection by Ce ($CeAlO_3$) to form larger Ba and Sr aluminates (d > 200 Å) and $LaMnAl_{11}O_{19}$ hexaaluminates (d = 70 - 100 Å).

The analysis of TEM images and microdiffraction data showed that the oxide fine particles of Mn (Mn_2O_3), Ba, Sr, Ce (d = 30-40 Å) and semi-transparent dense particles of the aluminates of different composition ($LaAlO_3$, $CeAlO_3$ with signs of faceting, d = 70 - 100 Å) are available in the initial 7.5 % Mn-REE-AEE catalyst supported on 2 % Ce/θ-Al_2O_3, (heating temperature - 873 K), Figure 2.

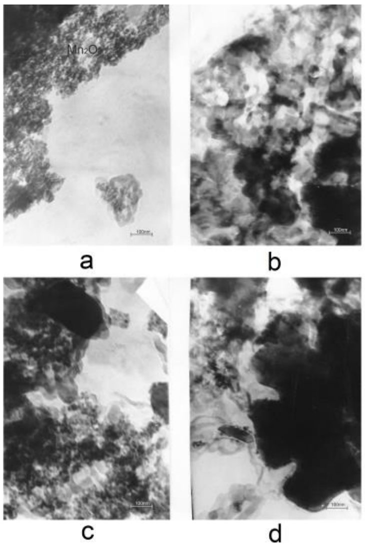

Figure 2: TEM images (× 160,000 times) of the 7.5 % MnREEAEE/2 % Ce/θ-Al_2O_3 catalyst: a - after heating at 873 K, b - after promotion by Pt and heating at 873 K, c - after promotion by Pd and heating at 873 K, d - after heating of the previous sample at 1,273 – 1,473 K

Fine particles (d = 50-100 Å) of the oxide clusters of Ba, Ce, La, Pt, Sr, Mn_2AlO_4 and accumulations of translucent lamellar prisms (d = 100 - 200 Å), as well as flocculent formation, consisting of a mixture of Mn_2AlO_4, LaPt, Mn_3O_4, $LaMnAl_{11}O_{19}$, $SrAl_{12}O_{19}$, $BaMnO_4$ are seen in the sample promoted by Pt, Figure 2b. There are also small particles (100 - 200 Å) of oxide, medium and large translucent particles of Mn_2AlO_4 and $CeAlO_3$ aluminates and large translucent formations of $Sr_3Al_{32}O_{51}$, $LaMnAl_{11}O_{19}$, $SrMnO_3$ in the sample promoted by Pd, Figure 2c. Heating of Mn-catalysts promoted by Pt and Pd at 1,373 – 1,473 K causes the considerable increase as oxide, and aluminate particles. Sr, Mn, and Ce aluminates, as well as mixed $Ba(MnO_4)_2$ oxides are appeared, Figure 2d. According to TEM analysis, the nanoparticles of metal oxides or their mixtures are formed in polyoxide MnREEAEE catalysts after decomposition of the metal nitrates at 873 K. BaMn-mixed oxides and $LaMnAl_{11}O_{19}$ hexaaluminates appear at elevated temperatures up to 1,473 K and at promotion by Pt and Pd.
Electronic spectra of diffuse reflection (ESDR) of Mn catalysts supported on Al_2O_3 are shown in Figure 3.

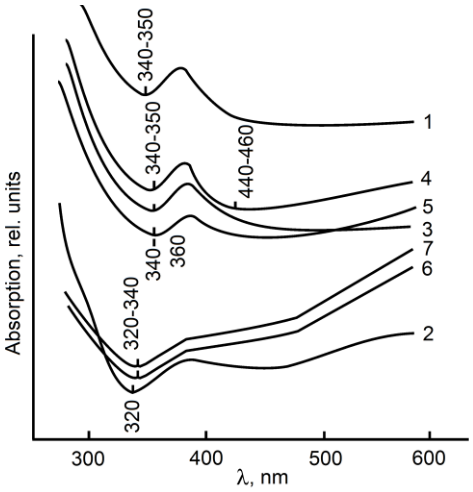

Figure 3: The ESDR of Mn catalysts supported on Al_2O_3 without additives (1, 2) and with additions of AEE oxides (3), REE oxides (4, 7) and mixtures of REE and AEE oxides (5, 6): 1,3,4,5 – heating temperature 873 K; 2, 6, 7 – heating temperature 1,173 K

It was shown that heating of the Mn/Al_2O_3 catalyst at 873 K leads to a strong increase in absorption. Non-structural absorption occurs at absorption bands over 400 nm, and below 400 nm (maximum at 340-350 nm, spectrum 1) is observed in the visible region. The absorption band at 340-350 nm is characteristic for the charge transfer band $Mn^{3+} + O^{2-} \rightarrow Mn^{2+} + O^{-}$ in oxide clusters. The absorption increase in the 240-320 nm region occurs after heating at 1,173 K and position of the maximum shifts to 320 nm, spectrum 2. Consequently, Mn^{4+} ions appear in the heated Mn/Al_2O_3 catalyst at 1,173 K without additives, along with Mn_2O_3. Additions of Ba and Sr oxides (spectrum 3) after heating at 873 K practically do not change the spectrum of the Mn/Al_2O_3 sample (spectrum 1). Additions of REE reduce the intensity of absorption in the visible part of the spectrum in the region above 550 nm (spectrum 4). A further decrease in the absorption intensity in the region above 500 nm, corresponding to a significant decrease in the oxide phase of Mn_2O_3, occurs after heating the $MnREE/Al_2O_3$ catalyst at 1,173 K. There are no characteristic changes in the spectrum indicating the formation of Mn^{4+} ions. The spectra of a mixed Mn catalyst with REE and AEE (spectrum 6), heated at 1,173 K, practically do not differ from the $MnREE/Al_2O_3$ spectra (spectrum 7). Hence, it follows that the introduction of REE has a determining effect on the state of Mn on Al_2O_3. They prevent the formation of Mn^{4+} ions due to the stabilization of their ions in the structure of the carrier. At the same time, the content of the dispersed phase of Mn_2O_3 decreases. The last and absence of a maximum absorption at 320 nm in the 240 - 320 nm region and absorption bands in the 400 - 500 nm (Mn^{4+}) region for samples heated at 1,173 K can be a consequence of the dispersion of Mn_2O_3 phase up to the ions and their partial interaction with REE with the formation of perovskite.

The process temperature, space velocity, concentration of reaction components and their ratio affect the efficiency of deep oxidation of CH_4 to CO_2 in order to generate heat, for cleaning the ventilation gases of coal mines from CH_4, to create an atmosphere for storage of agricultural products, and to use CO_2 for plant nutrition. 7 % MnREEAEE/2 % Ce/θ-Al_2O_3 catalyst was studied during the deep oxidation of CH_4 to CO_2 by varying the concentrations of initial reaction components at GHSV = 10×10^3 h^{-1}. Implementation of oxidation process in the methane concentration range from 0.5 % to 4 % and oxygen concentrations from 2 % to 20 % at 973 K results in 90 - 92 % methane conversion. Varying the concentration of CH_4 in initial mixture from 0.5 to 4% affects insignificantly the depth oxidation of CH_4 to carbon dioxide at 873 - 973 K. The degree of CH_4 conversion varies from 4 to 7 % under these conditions, whereas at 823 K it varies from 5 to 12 %.

Comparison of data on the activity of granulated Mn catalyst on θ-Al_2O_3 in oxidation of CH_4 (Table 2) and propane-butane mixtures (Table 3) indicates on a lighter oxidation of propane-butane in comparison with methane. Reduction of temperatures of the beginning of oxidation and α = 90 % on 160 and (180) - 270 (300) K are observed.

Table 2: Oxidation of methane in air

Catalyst	Degree of conversion, %	Temperature, K
MnREEAEE/2 % Ce/θ-Al_2O_3	20 - 30	733
	90	943
MnREEAEE/2 % Ce/θ-Al_2O_3 + Pt (0.1%)	20 - 30	753
	90	973

Table 3: Oxidation of propane-butane mixture in air

Catalyst	Degree of conversion, %	Temperature, K
MnREEAEE/2 % Ce/θ-Al_2O_3	20 - 30	573
	90	673
MnREEAEE/2 % Ce/θ-Al_2O_3 + Pt (0.1 %)	20 - 30	573
	90	673

To carry out additional fertilization of plants with carbon dioxide, a heat generator test was carried out in the experimental compartment of the greenhouse using different plant species. Heat generator represents the cylindrical stainless-steel tube with an inner diameter of 0.07 m and a length of 0.15 m. The combustion chamber was equipped with connections for gas sampling for analysis and measuring the temperature at the inlet and outlet of catalyst. Beneficial influence on the grown plants had an increase in the content of carbon dioxide in atmosphere of greenhouse. Roots were weightier in the experimental compartment of greenhouse. In this case the plants, forming roots (carrots and radishes), were the most receptive to the carbon dioxide fertilizing. Exceeding of the weight of roots reached 30.7 - 35.6 %.

Thus, the catalytic heat generator can be used in greenhouses for providing heat and carbon dioxide simultaneously. Using of heat generator to feed plants with carbon dioxide in greenhouses promotes increase their productivity, increasing the yield of different crops to 5 – 7 %.

4. Conclusions

Optimal conditions for deep oxidation of light hydrocarbons to CO_2 were determined as a result of study of the effect of process parameters on the combustion process of CH_4 and C_3H_8-C_4H_{10} mixture. Physicochemical methods (XRD, TEM, BET, ESDR) showed that the MnREEAEE/2 % Ce/θ-Al_2O_3 catalyst undergoes significant phase transformations as heating up to 1,473 K. The nanoparticles of Mn_2O_3 (d = 30-40 Å), available at 873 K, are partially converted to perovskites of $LaMnO_3$ after heating at 1,173 K, and then to hexaaluminates $LaMnAl_{11}O_{19}$ (d = 70-100 Å) at a temperature above 1,273 K. Analysis of results on thermal stability of catalysts in deep oxidation has shown that the degree of oxidation of CH_4 is decreased on the Ni-Cu-Cr catalyst after heating at 1,473 K unlike the MnREEAEE catalyst. Such reduction occurs apparently due to the decrease of catalyst surface as a result of sintering and formation of large Cu and Ni aluminates, in which the active elements are in tetrahedral coordination in contrast to octahedral coordination in the initial oxides, which are more active in oxidative reactions. The results indicate the real possibility of practical use of thermally stable up to 1,473 K MnREEAEE/2 % Ce/θ-Al_2O_3 catalyst for utilization of lean mixtures of CH_4 in catalytic heat generators. The developed catalyst does not concede to known analogues both in activity and thermal stability, where perovskites and manganese hexaaluminates were used.

References

Asampora L., Marra F.S., 2017, Investigation by Thermodynamic Properties of Methane Combustion Mechanisms Under Harmonic Oscillations in Perfectly Stirred Reactor, Chemical Engineering Transactions, 57, 1459-1464.

Barmina I., Valdmanis R., Zake M., 2016, Wheat Straw Combustion and Co-firing for Clean Heat Energy Production, Chemical Engineering Transactions, 52, 919-924.

Goryunov A.G., Goryunova N.N., Ogunlana A.O., Manenti F., 2016, Production of Energy from Biomass: near or Distant Future Prospects? Chemical Engineering Transactions, 52, 1219-1224.

Knoke T., Kenig E.Y., Kronberg A., Glushenkov M., 2017, Model-Based Analysis of Novel Heat Engines for Low-Temperature Heat Conversion, Chemical Engineering Transactions, 57, 499-504.

Kukulka D.J., Smith R., 2016, Comparison of Heat Exchanger Designs Using Vipertex 1EHT Enhanced Heat Transfer Tubes, Chemical Engineering Transactions, 52, 115-120.

Kushairi B.S., Nordin S., Kun S.S., 2018, Investigation the Relationship on CO_2, Energy Consumption and Economic Growth: A Panel Data Approach, Chemical Engineering Transactions, 63, 715-720.

Popova N.M., Dosumov K., Zheksenbaeva Z.T., Komashko L.V., Grigoriyeva V.P., Sass A.S., 2003, Mn-Containing Thermostable Multicomponent Oxide Catalyst of Low Concentration Methane Mixture Oxidation in Air, In: Jackson S.D., Hargreaves J.S.J., Lennon D. (Ed.), Catalysis in Application, Cambridge, UK, 210-215.

Schumm G., Philipp M., Schlosser F., Hesselbach J., Waimsley T.G., Atkins M.J., 2016, Hybrid-Heating-Systems for Optimized Integration of Low-Temperature-Heat and Renewable Energy, Chemical Engineering Transactions, 52, 1087-1092.

Tippawan P., Arpornwichanop A., 2016, Maximizing the Efficiency of a Heat Recovery Steam Generator for Solid Oxide Fuel Cell-based Trigeneration Systems, Chemical Engineering Transactions, 52, 1051-1056.

Tsyryul'nikov P.G., 1996, Thermally Stable Catalysts for Deep Oxidation on the Basis of Oxide Aluminum-Manganese and Modified Aluminum-Platinum Systems. PhD Thesis, Institute of Catalysis SB RAS, Novosibirsk, Russian Federation (in Russian).

Vereshchagin S.N., Solov’ev L.A., Rabchevskii E.V., Dudnikov V.A., Ovchinnikov S.G., Anshits A.G., 2015, New Method for Regulating the Activity of ABO_3 Perovskite Catalysts. Kinetics and Catalysis, 56, 640-645.