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EFFECT OF REACTION MIXTURE ON PHASE COMPOSITION AND MAGNETIC PROPERTIES OF MnNaW/SiO₂ CATALYST FOR OXIDATIVE CONVERSION OF METHANE

1. Introduction

Oxidative conversion of methane (OCM) is one of the promising ways for processing natural gas to C₂ hydrocarbons [1]. A tempting approach based on a combination of the OCM reaction to produce ethylene and carbon monoxide in the reaction products with the required CO/C₂H₄ ratio for hydroformylation reaction of this mixture to propylene is used in project C123 of the EU Horizon2020 program [2].

In this report the results of studies of the effect of reaction mixture on the structural features of MnNaW/SiO₂ oxide systems used as catalysts for the OCM reaction are presented.

2. Experimental part

The tetraethoxysilane (TEOS), cetyl-tri-methyl-ammonium bromide (CTAB), manganese Mn(CH₃COO)₂·4H₂O and tungsten Na₂WO₄·2H₂O were used as precursors for preparation of catalyst. The catalysts were characterized by scanning electron microscopy (SEM JSM-6610LV, JEOL) equipped with an energy-dispersive X-ray fluorescence spectrometer (EDX, Oxford), X-ray diffractometer XRD D2 Phaser, Bruker, Germany, EPR spectrometer EMX_micro, Bruker, Germany; the specific surface area and total pore volume of the samples was determined by low-temperature adsorption of nitrogen using Belsorp Mini II, BEL Japan Inc. instruments. Radical freezing system in combination with JES-PE-3X, Jeol EPR spectrometer and homemade quartz flow reactor for registration of hydrocarbon and peroxide radicals. The OCM reaction was carried out at 700 - 900 °C and atmospheric pressure. Gas-phase products of the reaction were analyzed using Agilent 7280A and Perkin Elmer Auto System XL (USA) chromatographs.

3. Results and Discussion

The SEM microphotographs of the samples were shown in fig.1.

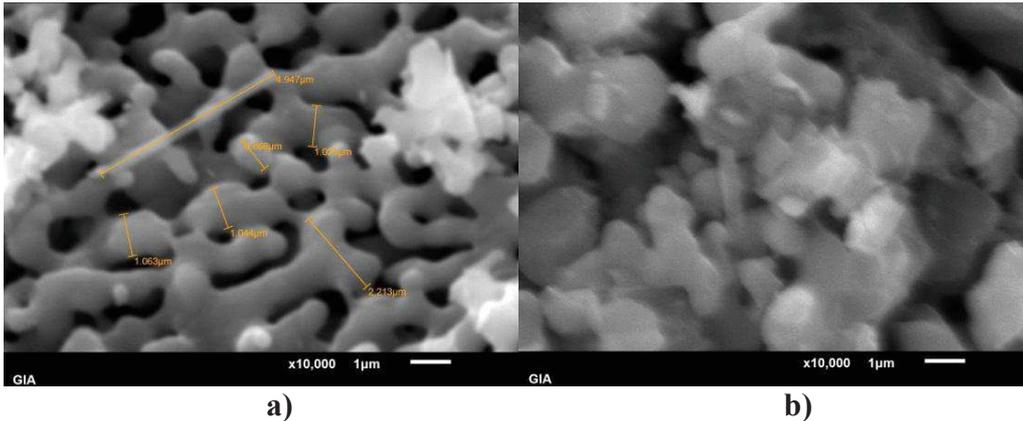


Fig. 1. SEM pictures of the samples $0.8\text{Na}3.2\text{W}2\text{Mn}/\text{SiO}_2$ at 850°C before (a) and after 2 hours of the reaction (b).

SEM pictures show the significant changes in surface structure of the samples after reaction. EDS data indicate the presence of manganese and tungsten and the effect of the reaction medium on their distribution in the catalyst samples.

Fig. 2 show the EPR spectra recorded at room temperature of the samples calcined at 850°C before (a) and after (b,c) the reaction.

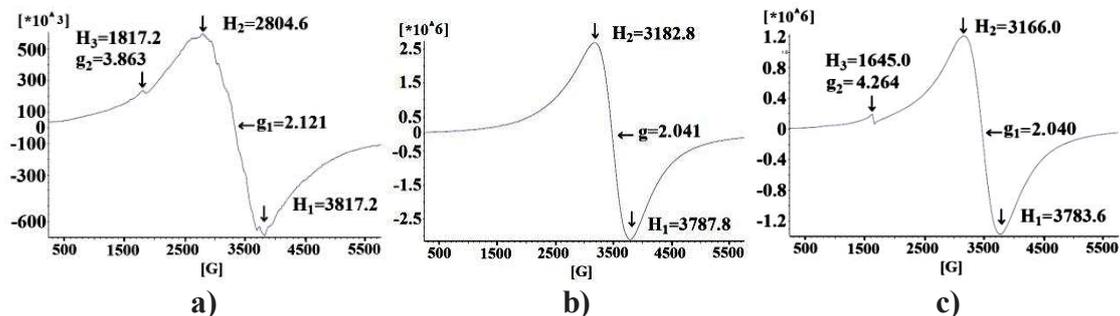


Fig. 2. EPR spectra of the sample $0.8\text{Na}3.2\text{W}2\text{Mn}/\text{SiO}_2$ calcined at 850°C before (a) and 2 (b), 10 (c) hours after reaction at 800°C .

Two set of EPR spectra for the samples with $g = 2.01\text{-}2.1$ and hyperfine constant of ~ 94 G (nuclear spin $I = 5/2$ for ^{55}Mn , six lines $(2I + 1 = 6)$) before and with unresolved hyperfine structure and $\Delta H \sim 600$ G after the reaction belongs to MnO_x , most likely to Mn_2O_3 nanoparticles are observed. The resonance signal at $g=2.0$ is attributed to the Mn^{2+} ions in an environment close to an octahedral symmetry. The signals at $g = 4.3$ have been attributed to the rhombic symmetry of the Mn^{2+} ions [3].

The significant changes of the values of specific surface area and pore volume of these samples 10 hours working in OCM reaction were observed ($116.8 \text{ m}^2/\text{g}$ and $0.590 \text{ cm}^3/\text{g}$ - before and $46.1 \text{ m}^2/\text{g}$ and $0.232 \text{ cm}^3/\text{g}$ - after). Methane conversion of up to 47.7 % and a selectivity of C_2

and C₃ hydrocarbons in the amount of up to 86.7 % and a yield of up to 27.4 % were observed. The ratio of C₂H₄ / (CO+CO₂) is approximately 1 for these samples with the same yield of C₂+C₃ hydrocarbons. An increase in temperature from 778 to 874 °C leads to an increase in ethylene selectivity and the yield of C₂+C₃ hydrocarbons. The experimental results show that after 10 hours of working in OCM reaction the activity, selectivity and yield of catalysts decrease approximately for 10-15%. Under the reaction conditions only CH₃O₂• radicals were detected and the changes of their concentration as a function of CH₄/O₂ ratio are observed. CH₃• radical is not detected because the liquid nitrogen temperature is high enough to detect the CH₃• radical.

X-ray diffractometric data show that the used MnNaW/SiO₂ catalyst is multicomponent and consists of the phases MnO_x, Na₂WO₄, and SiO₂. (with cristobalite and/or tridomite, quartz structure). At the reaction temperature OCM, i.e. 750-850 °C, one of these phases - Na₂WO₄ is in a melted state (the values of the melting and decomposition temperature of Na₂WO₄ are equal to 696 and 1200 °C, respectively). The phases MnO_x (MnO, Mn₂O₃, Mn₃O₄, MnO₂), MnWO₄ and SiO₂ have a melting point above 850 °C, i.e. under the reaction conditions Na₂WO₄, covering the surface of crystalline SiO₂ in the form of a film, and nanosized MnO_x particles contained in it, as shown by EMR data. It is supposed that at reaction conditions it is possible that the reaction between MnO_x (Mn₂O₃, and/or Mn₃O₄) and melted Na₂WO₄ with the formation of MnWO₄ takes place [4]. This example shows the peculiarities of high-temperature reactions catalyzed by multicomponent systems, the components of which are in different states of aggregation under the reaction conditions. We believe that the catalytically active particles of the OCM reaction are Na_{1-y}MnO_x, particles formed as a result of the interaction of the system components during the formation of the catalyst and characterized by the presence of lattice oxygen of the O-radical ion type (similar to the O-centers in the Li/MgO system [5]). For these catalysts, the specific surface area was 100-120 m²/g and after 10 hours of operation at a temperature of 800-850°C decreased significantly, but they average pore diameter is in the range of 2-50 nm still, so the behavior of these catalysts will be typical for mesoporous materials.

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REFERENCES

1. Kondratenko E.V. Methane Conversion into different hydrocarbons or oxygenates: current status and future perspectives in catalyst development and reactor operation / E.V. Kondratenko, T. Peppel, D. Seeburg, V.A. Kondratenko, N. Kalevaru, A. Martin, S. Wohlrab., // Catal. Sci. Technol. -2017. -Vol.7, Issue 2. -P. 366-381.
2. <https://cordis.europa.eu> › project H2020, C123.
3. Murzakhanov F. Conventional electron paramagnetic resonance of Mn^{2+} in synthetic hydroxyapatite at different concentrations of the doped manganese / F Murzakhanov, G Mamin, A Voloshin, E Klimashina, V Putlyaev, V. Doronin, S. Bakhteev, R. Yusupov, M Gafurov, and S Orlinskii. // IOP Conf. Series: Earth and Environmental Science, -2018. - Vol. 155, Issue 1. -P. 012006.
4. Werny M.J., Wang Y., Girgsdies F., Schlogl R., Trunschke A. Fluctuating Storage of the Active Phase in a $Mn-Na_2WO_4/SiO_2$ Catalyst for the Oxidative Coupling of Methane / M.J.Werny, Y.Wang, F. Girgsdies, R.Schlogl, A.Trunschke // Angew. Chem. Int. Ed., -2020. -Vol.59, Issue 35. -P. 14921–14926.
5. Wang D.J. Oxidative coupling of methane over oxide-supported sodium-manganese catalysts. /D.J. Wang, M.P. Rosynek, J.H Lunsford // J. Catal., -1995. -Vol.115, issue 2. -P.390-402.