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New methods of increasing the catalytic activity and selectivity in the oxidative conversion processes of methane and propylene

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Abstract

The methane and propylene oxidative conversion over Na_2O/ZnO systems – with ultrasonic treatment (UST) during preparation and without preparation – was studied. Methane oxidative coupling has been also studied over a number of oxide catalysts: Pb/aerosil, ZnO and 10%Na_2O/ZnO, with the mixtures of CH_4–O_2 and CH_4–O_2–H_2O_2. It has been shown that a pulse introduction of H_2O_2 vapours into the methane–oxygen mixture enables to increase the yield of C_2 hydrocarbons and to stabilize a state of surface. The positive influence of the UST on catalytic activity has been established too.

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1. Introduction

A change of catalytic activity is dependent on the preparation method, phase composition, morphology, as well as on modifier introduction. An increase of catalytic activity is achieved by the various chemical as well as mechanical and physical methods [1]. Naturally, those can cause the appearance of catalytically active centers. They can arise and during the heterogeneous decomposition of homogeneous additives introduced into reaction mixture, such as H_2O_2 and so on [2].

The purpose of this study is the elucidation of the UST during the 10% Na_2O/ZnO preparation on its activity and selectivity in the process of methane oxidative coupling and propylene oxidation, as well as the influence of H_2O_2 vapours introduction into methane–oxygen mixture on activity of the oxide catalyst for methane coupling.

2. Experimental

The impregnation of ZnO with a Na_2CO_3 solution with further drying and calcination in oxygen atmosphere was used. In order to study UST influence, another portion of the same catalyst was treated by US during the mixing of ZnO powder with the Na_2CO_3 solution. The duration of UST was selected experimentally [1]. The experiments on the sample activity testing were performed at atmospheric pressure in the flow U-shape reactor, $T = 750°C$. The mixture composition was $CH_4{:}O_2{:}N_2 = 6{:}1{:}7.5$ (42 vol.% of CH_4). The volume of catalyst was 3.5 cm^3. For C_3H_6 oxidation the mixture composition was $C_3H_6{:}O_2{:}N_2 = 1{:}2{:}5.5$ (11.8 vol.% of C_3H_6), $T = 570°C$ and contract time $\tau = 5.5$ s. The volume of catalyst was 1.1 cm^3.

The influence of H_2O_2 vapours was studied in flow U-shape reactor at atmospheric pressure and $T = 740°C$. There is the possibility to feed mixture

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into the reactor through ampul with concentrated H_2O_2 or by pass way [2].

3. Results and discussion

The kinetic data on C_2 hydrocarbons formation showed that conversion is equal 14% and selectivity; 40% without UST. When the reaction mixture is passed through the catalyst subjected to UST for 60 min. (optimum duration) the conversion increases to 18% and selectivity reaches 54% at $\tau = 6–7$ s. The increase of τ leads to the selectivity decreasing and to the increase of CO_2 content in the products.

When a sonicated catalyst is used instead of a nonsonicated one, the C_3H_6 conversion increases (by 4%). The composition of products is changed: the amount of diallyl increases and the amount of hydrogen and benzene diminishes.

Electron microscopy studies showed, that the sodium oxide located on a zinc oxide surface as agglomerates is dispersed over a zinc oxide surface in course of UST. Earlier it has been shown that the promoter (Na) increases the yield of radicals into the gas phase; therefore, the uniform distribution of Na ions achieved by UST seems to increase their generation by decreasing the probability of their capture by the ZnO surface. As a result, the yield of dimerization and disproportion products increases, in whose formation radicals participate.

It can be seen from data on the reaction products yield for mixtures $9CH_4 + 1O_2$ and $9CH_4 + 1O_2 + H_2O_2$ that H_2O_2 action on products amount and correlation depends on the catalyst nature. The influence of H_2O_2 vapours is more effective on $10\%Na_2O/ZnO$ [2]. With the time of influence of H_2O_2 became weaker. It may be connected with a possible action of H_2O, as product of H_2O_2 decay, which is accumulated and blockaded the surface active centers. The pulse H_2O_2 introduction enables to support the high yield of methane dimerization products during the time. It is possible that the catalyst is activated by ions-radicals forms, which arise during the H_2O_2 decay and reoxidize the catalyst. It was shown experimentally that H_2O_2 introduction removes the hardening products from the catalyst surface and enables to support it in stable active state.

4. References

[1] T.A. Garibyan, A.A. Muradyan, R.R. Grigoryan and N.S. Manukyan, Kinet. Katal., N3, 34 (1993) 742.
[2] L.A. Vartikyan, V.T. Minasyan and T.A. Garibyan, Arm. Khim., N6, 43 (1990) 357.