Oxidative conversion of C_3-C_4 hydrocarbons to oxygenates over Mo-containing modified catalysts

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Abstract: Polyoxide supported catalysts on a basis of Mo and also natural clays during oxidative conversion of propane-butane mixture are investigated. The influence of reaction temperature, contact time, composition of the catalysts and content of oxygen in reaction gas mixture are determined.

Keywords: Propane, Butane, Oxidation.

1. Introduction

The problems of optimum selection of raw material and catalysts for different processes are very important for decision due to the rapid development of a petrochemical industry at the last decade in Kazakhstan and world. Under the forecasts for the nearest period C_1-C_4 saturated hydrocarbons not only will keep, but also will strengthen the positions as raw material for manufacture unsaturated hydrocarbons. In these conditions there is urgent problem the search of ways of effective processing of saturated light hydrocarbons into various oxygen-containing compounds. It is necessary to expect formation of unsaturated hydrocarbons, aldehydes, acids and alcohols at the partial oxidation of propane and butane as against of methane and ethane, which form compounds, giving less complex composition. Only optimum selection of catalysts can purposefully carry out the process with primary formation of one of the listed products. The heterogeneous catalysts investigated in reaction of partial oxidation of propane and butane, represent as individual oxide, polyoxide catalysts, and also supported on various carriers, including zeolites.

The purpose of the work is investigation of supported polyoxide catalysts on a base of Mo and natural clays in the process of oxidative conversion of propane-butane mixture, determination the influence of reaction temperature, space velocity and ratio of components in a reaction mixture.

2. Experimental

The investigations were carried out on installation of a flowing type at atmospheric pressure in tubular quartz reactor with the fixed layer of the catalyst. The catalysts were characterized by XRD. The determination of surface, porosity and element content of samples are carried out. The catalysts on the basis of elements - Mo, Bi, Ce, Ni, W, Sb, Mn, Fe, Ga, and Cr were synthesized. White and red clays are used as the carriers. The temperature range was 300-600°C at the space velocity 7,500-15,000 h^{-1}. Reactants and products were analyzed by chromatographic method.

3. Results and discussion

The influence of the reaction temperature on direction of oxidative conversion of propane-butane mixture on MoCrGa/white clay was investigated. The content of reaction mixture: hydrocarbons-60.0 %, O_2-8.4 %, N_2-31.6 %, W-7,500 h^{-1}.

Acetone, methanol, acetaldehyde and other oxygen containing products are the basic products. Besides ethylene is the basic product in a gas phase. 300-350^{o}C - the optimum temperature by methanol and acetaldehyde, 450-500^{o}C - by acetone, 500-600^{o}C - by acetic acid. Also it was shown that the content of ethylene in waste gas at 500-600^{o}C is increased from 5 up to 17 % during rise of temperature. The conversion did not exceed 50 %.

The results on oxidation of propane-butane mixture on granulated catalysts have shown that the homogeneous oxidation practically does not take place. The conversion of propane-butane mixture is higher on the clean carrier. Use of the catalyst sharply raises the conversion at all temperatures.

The investigation of natural clay by a XRD method have shown, that the basic phase of white clay is kaolin $Al_2(OH)_4Si_2O_5$ (ASTM-29-1488) and α-quartz SiO_2. Red clay is differed from white by the presence of hematite Fe_2O_3 and absence of α-quartz - less 1 %. The element analysis of the samples of sorbents of initial and processed by 10% HCl has shown, that oxide compounds of Si, Al, and also Ca, Mg, Fe, Na are present mainly at samples of clay. Ratio SiO_2/Al_2O_3 (the silicon module) was 5-0.4. The silicon module grows after acid processing. The phase composition of clay after processing by a hydrochloric acid practically did not vary. Specific surface and porosity of investigated samples of sorbents were determined by low-temperature adsorption of nitrogen by BET method. It was established that the surface of clay was 10-16 m^2/g. Change of optimum radius of pores were from 20 up to 50 Å. The processing of sorbents by 10 % HCl promoted development and increase of pore radius.

The influence of processing of the catalyst before experiment on the content of acetone in catalyzate was investigated too. The content of acetone grows at high-temperature processing by acid. The same behaviors were observed for others oxygen-containing compounds.

The influence of space velocity on the contents of oxygen-containing compounds in catalyzate was investigated at oxidation of propane-butane mixture on MoCrGa/clay. 7,500 h^{-1} is the optimal space velocity for acetone at 450-500^oC and for methanol at 300-350^oC, 7,500 h^{-1} and 9,000 h^{-1} is optimal for ethylene.

The influence of the content of oxygen in reaction mixture on the content of acetone and methanol in catalyzate over MoCrGa/clay is shown. The content of acetone in catalyzate is increased during raising the content of oxygen.

4. Conclusions

The analysis of composition of products of C_3-C_4 oxidative conversion has shown that the process carries out by complex mechanism including oxidation, oxidative dehydrogenation and cracking. Polyextreme character of change of catalytic properties in oxidation of propane-butane mixture and greatest activity of low-percentage supported catalysts are caused by existence in catalysts as crystal and amorphous phases over carriers and occurrence of strong interaction in system active phase-carrier.