CHISA 2016 PRAGUE PRES 2016

22nd International Congress of Chemical and Process Engineering CHISA 2016

19th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction PRES 2016

organized by

ČSCHI ČESKÁ SPOLEČNOST CHEMICKÉHO INŽENÝRSTVÍ CZECH SOCIETY OF CHEMICAL ENGINEERING

Prague, Czech Republic, 27 August - 31 August 2016

P.3.25

Oxidative conversion of light alkanes to oxygenates

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The huge hydrocarbon reserves in Kazakhstan are consumed mainly in the form of domestic, industrial and motor fuel. The remaining gas is burnt in torches or pumped into the reservoir (petroleum gases). Therefore, processing of alkanes (the main component of natural gas and oil) to generate oxygen-containing organic compounds is one of the most urgent environmental problems in Kazakhstan. Preparation of these compounds by direct synthesis from alkanes is economically more expedient than by multistep processes. .

It should be expected the formation of unsaturated hydrocarbons, aldehydes, acids and alcohols at partial oxidation of methane, ethane, propane and butane. Only the optimal selection of catalysts may be specifically carry out the process with the preferential formation of one of the listed products.

The oxidation of hydrocarbons relates to important large-capacity industrial processes. Alcohols, aldehydes, ketones and carboxylic acids, which are the main products of oxidation of light hydrocarbons, are widely used [1].

Research of activity of the developed catalysts in the oxidation of C_1 - C_4 mixture into oxygenates is the aim of the present work.

Mono-, bi- and three-component catalyst systems for the oxidation of linear hydrocarbons have been developed. Their pre-treatment was carried out for the preparation of catalysts on natural carrier. Natural carriers were dried at T = 473 K for 2 h and calcined at T = 773 K for 2 h, and then treated with 10% HCl and calcined again at T = 773 K for 2 h.

Catalysts based on Mo, Cr and Ga were prepared by incipient wetness capillary impregnation using a mixed aqueous solution of nitrate salts of metals. Active phase was supported on natural carriers and alumina. Then the catalysts were dried at T = 473 K for 2 hours and calcined at T = 773 K for 2 hours in air to decompose the nitrate from the catalyst surface. Research the activities of the developed catalysts were carried out at a flow installation at atmospheric pressure in a quartz tubular reactor with a fixed catalyst bed.

Analysis of the initial mixture and reaction products was performed using a "Chromos GC-1000" chromatograph with the "Chromos" software. The chromatograph is equipped with packed and capillary columns. A packed column was used for the analysis of H_2, O_2, N_2, CH_4, C_2H_6, C_2H_4, C_3 - C_4 hydrocarbons, CO and CO_2. The capillary column was used for analysis of organic liquids such as alcohols, acids, aldehydes, ketones and aromatic hydrocarbons. The temperature of thermal conductivity detector - 473 K, the temperature of evaporator – 553 K, the column temperature - 313 K, the rate of carrier gas (Ar) - 10 ml/min.

Calculation of chromatographic peaks was carried out on calibration curves, which were built for the corresponding products using the "Chromos" software by pure substances. Exactly measured quantities of pure component or mixture of substances containing known concentrations were injected using microsyringe into the chromatograph. Calibration curve V = f (S), where V - amount of substance in ml, S - area of the peak, expressed in cm^2, was constructed based on measured peak areas corresponding to the number of injected substances. The concentrations of the resulting products were determined on the basis of the calibration curves.

Catalytic oxidation of methane of the natural gas into oxygen-containing compounds has been studied. The developed 5% Mo - 4% Cr - 1% Ga catalyst supported on the natural

Kazakhstan's clay with the structure of clinoptilolite, was investigated in oxidation of methane in flow quartz reactor under the conditions: $CH_4 : O_2 = 2 : 1$ (67% : 33%) T = 400 - 900°C and a space velocity W = 7500 h^{-1}. It was found that both liquid and gaseous products are formed during the reaction. The formation of oxygen-containing products: methanol, ethanol, propanol and acetaldehyde is observed at lower temperatures. The formation of H_2, CO and CO_2 were found in the gaseous phase.

Experimental studies of activity of the developed catalysts in the oxidation of propane-butane mixture to the oxygen-containing compounds have been conducted. Thus, the effect of varying the composition of catalyst (1% MoCrGa/TWC (Torgai white clay), 5% MoCrGa/TWC and 10% MoCrGa/TWC) on the yield of desired partial oxidation products depending on reaction temperature changes in conditions: temperature range 673-823 K, C_3 - C_4 = 60.0%; O_2 = 8.4%; N_2 = 31.6%; τ = 0.5s and W = 7500 h^{-1} has been shown.

Yield of acetaldehyde on the 1% MoCrGa/TWC catalyst is increased from 29.7 to 37.3% with increasing of reaction temperature from 673 to 823 K, respectively. Yield of acetone at 673 K is 10.9% and increases with growth of temperature up to 29% at 773 K and then reduced to 21.6% at T = 823 K. Yield of the MEK (methyl ethyl ketone) decreases from 33.6 to 10.9% with increasing of reaction temperature. The ethanol yield varied from 12.4 to 17.9%. The formation of small amounts of propanol, crotonaldehyde, iso-butanol, n-butanol, acetic acid and propionic acid are observed. A similar dependence of the yield of main reaction products (acetaldehyde, acetone, MEK and ethanol) on the 5% MoCrGa/TWC and 10% MoCrGa/TWC catalysts is retained. It should be noted that the formation of methanol is observed only on the catalyst of 10% MoCrGa/TWC. Methanol yield decreases from 19.2% to 10.6% with increasing temperature from 673 to 823 K, respectively. Up to 33% acetaldehyde, 50.9% acetone and 38% methyl ethyl ketone were obtained in the test interval.

Thus, it was studied the effect of changing the catalyst composition on yield and quantitative ratio of the major products of process.

References

1 Baizhumanova T.S., Tungatarova S.A., Zheksenbaeva Z.T., Kassymkan K., Zhumabek M. Synthesis of oxygenates by oxidation of light alkanes on modified catalysts // Chemical Engineering Transactions. – 2015. – Vol.45. – P. 1063-1068.

The work was supported by the Ministry of Education and Science of the Republic of Kazakhstan (Grant No 0330/GF4).