Oxidation of alkanes into olefins on the polyoxide catalysts

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ABSTRACT

Catalysts based on Si-Mo heteropoly compounds (HPC) supported on carriers were investigated in oxidative dehydrogenation of ethane (ODE) to ethylene. Determination of the effect of reaction parameters and the nature of catalyst on composition and distribution of products was carried out. The optimal reaction conditions: C_2H_6 – 20.0%, O_2 – 2.5%, N_2 – 57.5%, H_2O – 20.0%, space velocity – 8000 h^{-1}, contact time – 0.45 s were installed. Ethylene yields exceeding 42% with selectivity above 87% were obtained over novel Pb-Si-Mo heteropoly compound catalysts under oxidative dehydrogenation of ethane at 1023 K. Water vapor in the composition of reaction mixture increases the yield and selectivity of ODE products. Supporting of Si-Mo HPC on aluminosilicate does not destroy the Keggin molecular structure and increases its thermal stability. Reduction of heteropoly acid (HPA) molecule in methane atmosphere is different from the reduction in hydrogen atmosphere.

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1. Introduction

Natural and oil gases are an important alternative source of raw materials that can compete with oil in the future. Activation of light alkanes for targeted one-step obtaining of intermediates of organic synthesis and fuel compositions using the nano-cluster polyoxide catalysts is one of the major problems in the field of organic catalysis. Highly active, thermally stable nanostructured catalysts can be used for the processing of natural gas to olefins.

The decrease of export of primary raw materials and replacement of export by deep processing of it may give a powerful impetus to the development of the national economy [1]. It is known that the main economic results is achieved at realization of the final product which usually get countries that have technologies of the final stages of its production, but not the owners of resources. For example, the cost of ethane as component of natural gas is about $80–90/t, ethylene – $600/t, the cost of low-density polyethylene is above the cost of ethane to 20 times, and the cost of finished products made of polyethylene (plastic pipe) reaches $2500–3700/t [2]. Therefore, finding the ways of activation of light alkanes and their involvement in chemical reaction for targeted production of

olefins based on nano-cluster catalysts is important task of organic catalysis.

It is known that the petrochemical potential of many countries is assessed by production volume of lower olefins – ethylene and propylene, which are the basic chemical raw materials for the production of polyethylene, polypropylene, plastics, styrene and other products. World consumption of ethylene in the next 10 years will increase from 100 to 160 million tons per year according to the forecast of Nexant Inc. consulting company. Demand for polyethylene will increase from 60 to 100 million tons, and the polypropylene from 40 to 60 million tons per year. Thus, the average annual growth rate of ethylene (basic petrochemicals) are expected to be 5–5.5%, while the rate of growth in demand for oil, according to the Energy Information Administration (EIA), will be only 1.7% per year (including in developed countries – about 1% per year).

Taking into account the large reserves of alkanes in Kazakhstan, their inefficient use, lack of industrial processing methods, intensive research on the development of catalysts and processes for production of olefins from alkanes has theoretical and practical interest [3]. Development of new technology oxidative conversion of alkanes to olefins may enter into a complex of petrochemical manufacture, organic synthesis at processing of hydrocarbons as provided in strategy of fuel and energy complex of the Republic of Kazakhstan. At present, the problem of rational utilization of natural and associated gases and termination of their burning in the "torch" is one of the most pressing and unresolved environmental issues. Both natural and associated gases can be considered

as an alternative source to obtain oxygenates [4–8], synthesis gas [9–14], and olefins [15–18]. The oxidative coupling of methane (OCM) to C_2H_6 or C_2H_4 is a reaction, which has received a lot of attention since the fundamental works of Keller et al. [19,20] and Hinsen et al. [21]. A large number of catalyst systems have been studied extensively. Multicomponent oxide systems demonstrate relatively high activity and selectivity. Generally, highly active catalysts for OCM have C_2 (ethane + ethylene) selectivity less than 70% at a methane conversion of 20–28% with the maximum C_2 yield being in the 20% range [22–24]. Several catalysts have been investigated in detail for their use in OCM especially in the 90s of the 20th century and the first decade of the 21st century. The various heterogeneous catalysts, for example, supported metal oxide catalysts containing oxides of alkali, alkali earth metals [25–27], transition metal and rare-earth oxides [17,28–31], especially samarium oxide [32,24,33] catalyzed the OCM reaction via the activation of the CH_4 molecules to methyl radicals. The recombination of free methyl radicals results in the formation of ethane [34,35], which is converted into ethylene as a result of oxidative dehydrogenation. Ethane together with methane is the main component of natural and associated gas. Researchers from different countries actively search ways of the utilization of ethane too. Various types of catalysts are used in the oxidative dehydrogenation of ethane: on the base of noble metals (Rh, Pt) including honeycomb catalysts with the addition of sulphur to the feed [36–38], Ni-containing catalysts [39,40], perovskites [41], NaWMn where $C_2H_4/CO/H_2 = 1/1/1$ can be obtained as a reaction products [42]. High yields to ethylene of ca. 75% were obtained by using MoVNbTe catalysts [43,44]. Polyoxometalate catalysts based on heteropoly compounds are used in oxidative dehydrogenation too [45].

Heteropoly compounds are unique substances which are strong Brönsted acids and many[46,47] electron oxidants. Redox and acidic properties of HPC can be varied within wide limits by changing their composition. Recently it has been proposed to use a more general their name – metal-oxygen clusters. Therefore, a study of this type of compounds in oxidative conversion of alkanes is interesting. In recent years, the development and implementation of various processes using HPC have been conducted. However, their use in the oxidative coupling of methane and dehydrogenation of ethane is still limited. The results on oxidative conversion of ethane to ethylene on supported silica-molybdenum heteropoly acid and heteropoly compounds, as well as the results of physical–chemical studies of catalysts are presented in the paper.

2. Experimental

2.1. Catalysts preparation

Catalysts based on Mo 12th series heteropoly acids (HPA) were used in the process of oxidative conversion. Silicomolybdic acid $H_4SiMo_{12}O_{40} \times 6H_2O$ (with the purity of 96–97%) was purchased from LLP ANT, Russia; metal nitrate salts (97–99%) from Reachim, Russia and high-purity aluminosilicate (AlSi) from Angarsk Factory of Chemical Reactants, Russia. All reactants were used without further purification. Heteropoly compounds were synthesized from heteropoly acids with the salts of corresponding metals by known methods [48]. The catalysts were prepared by the incipient wetness impregnation of AlSi (particle size 1.5–2.0 mm) with aqueous solutions containing appropriate amount of salts. Then samples were evaporated to dryness and dried in air at 150 °C for 5 h. The concentration of active phase on carrier was varied from 0.1% to 20.0%.

2.2. Catalysts characterization

Morphology and particle sizes were performed on transmission electron microscope TEM-125_K operated with enlargement up to

Table 1
Textural properties of samples.

Sample	BET ($m^2 g^{-1}$)	Pore volume (m^3g^{-1})	d (Å)
AlSi	392.6	0.30	30–120 Max 50–60
2.3% Si-Mo/AlSi	416.0	0.28	30–125 Max 40–60
10% Si-Mo/AlSi	412.4	0.38	30–100 Max 55–60

120,000 times by replica method with extraction and micro diffraction. Carbonic replicas were sputtered in vacuum universal station, and carrier of catalysts was dissolved in HF. Identification of micro diffraction patterns were carried out by means of ASTM cart index (1986). The crystalline phases were evaluated by X-ray diffraction (XRD) using the powder method and Fe anode operating at 28 kV and 28 mA. The diffraction patterns were recorded on a DRON-4-7 diffractometer. The diffractograms were recorded in the range 10–80°. Infrared (IR) spectroscopy research of the Si-Mo HPC and catalysts based on them were carried out on UR-20 and Specord-80 spectrometers. An Agilent 6890 N (Agilent Technologies, United States) gas chromatograph with computer software equipped with flame ionization and thermal conductivity detectors was employed for on-line analysis of initial substances and reaction products. The feed components and the reaction products were analyzed on copper capillary column HP-PLOT Q with 30 m long and 0.53 mm in diameter, filled with polystyrene-divinylbenzene. The conversion of ethane was calculated from the inlet and outlet concentration of C_2H_6. The product selectivities were calculated on the product basis. The BET specific surface area and the pore size distribution of the catalysts were determined by adsorption method using an Accusorb instrument (Micromeritics, United States) at the low temperature adsorption of N_2. The samples were degassed for 5 h under vacuum at 250 °C prior to the analysis. Table 1 presents the specific surface area, pore volume and pore sizes of these samples.

2.3. Catalytic reaction

Experiments on the oxidative dehydrogenation were carried out on flow type installation at atmospheric pressure in a tubular quartz reactor with a fixed catalyst bed. Catalyst was placed in the central part of reactor and quartz wool placed above and below the catalyst bed. The free space of the reactor below the catalyst bed was filled with quartz wool to reduce the free volume and gas phase zone of catalyst bed as well as to minimize the further reaction of the desired product in post-catalytic volume. Gas mixture containing ethane (99.9%) and oxygen (99.8%) diluted with an inert gas (Ar, 99.5%) in the presence or absence of water vapor was used for oxidation. Temperature was measured by a thermocouple inserted in a jacket of the reactor. A cold trap was placed at the outlet of the reactor to separate any condensed water vapor from the reaction products. The ratio of components of reaction mixture is widely varied. Oxidation of ethane was carried out in a mixture with an excess or shortage of hydrocarbon (C_2H_6 – 20.0%, O_2 – 2.5%, (Ar $\pm H_2O$) – 77.5%; C_2H_6 – 5.0%, O_2 – 10.0%, (Ar $\pm H_2O$) – 85.0%).

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. IR-spectroscopy

IR spectroscopy method was used to determine the physical and chemical characteristics of catalysts based on Si-Mo HPA during operation and regeneration. Unsupported $H_4SiMo_{12}O_{40}$ HPA was initially investigated due to the fact that the intensive absorption bands (a.b.) from the carrier (AlSi) may interfere for observation