

## Catalytic oxidative conversion of C<sub>1</sub>-C<sub>4</sub> alkanes over supported catalysts on the base of 12 series heteropoly compounds

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### Introduction

C<sub>1</sub>-C<sub>4</sub> alkanes of natural, oil casing-head gases and oil-refinery gases are used preferentially as household, engine fuel, reforming processes and cracking. Single-stage catalytic methods of oxidative processing of alkanes into products for needs of the industrial organic synthesis on the composite metal-oxide catalysts (olefins, oxygen-containing compounds, synthesis gas) are developed by researches [1-4].

Catalysts on a base of 12 series W and Mo heteropoly compounds (HPC) are investigated in reactions of oxidative conversion of C<sub>1</sub>-C<sub>4</sub> alkanes and their mixtures into oxygen-containing compounds, olefins, H<sub>2</sub>-containing compositions. They have a unique combination of acidic and red-ox properties and are applied in some commercial processes [5,6]. Their application are introduced in high-temperature gas-steam-oxidative catalysis [5,7-11].

### Materials and Methods

Experiments are carried out in flow type system at atmospheric pressure with removing of products in cooling zone. Catalysts were prepared from 12 series W or Mo HPC (1,5-15 mas. %) on carriers - synthetic aluminosilicates, silica gels, zeolites, and also Kazakhstan's natural zeolites and zeolite-like clay minerals. Experiments are carried out in the reaction mixtures containing alkane, oxidant, inert gas and overheated steam.

### Results and Discussion

The variation of HPC (acids, salts) composition, nature of carrier, reaction temperature, composition of reaction medium, nature of oxidant (O<sub>2</sub>, air, ± H<sub>2</sub>O, N<sub>2</sub>O, CO<sub>2</sub>), and also contact time of catalyst with reaction medium are investigated. Optimal catalysts and the priority methods for partial oxidative conversion of C<sub>1</sub>-C<sub>4</sub> alkanes were offered:

- CH<sub>4</sub> into CH<sub>2</sub>O. Catalyst (Ct): 2,3% H<sub>4</sub>(Ba, Mg, Li) SiMo<sub>12</sub>O<sub>40</sub>/aluminosilicate (natural clinoptilolite), 650°C. Productivity (P) - up to 14000g CH<sub>2</sub>O/kg HPC·h [7];
- CH<sub>4</sub> into CH<sub>3</sub>OH. Ct: 1,5-15% H<sub>4</sub>(K, Cu, Cr)Si(P)Mo(W)<sub>12</sub>O<sub>40</sub>/aluminosilicate (SiO<sub>2</sub>), 300-450°C, P - 840g CH<sub>3</sub>OH/kg HPC·h [8];
- CH<sub>4</sub> into C<sub>2</sub> hydrocarbons (C<sub>2</sub>H<sub>4</sub>). Ct: 5-15% H<sub>4</sub>(Ce, Na, Cs, Cu, Ca, Ba)Si(P)W(Mo)<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> (AlSi, MgO, pentasil). Yield of C<sub>2</sub> hydrocarbons - up to 25,0%, C<sub>2</sub>H<sub>4</sub> - 16-19%, C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> - 3,5-9,0. P - up to 7900g C<sub>2</sub>H<sub>4</sub>/kg HPC·h, 750-800°C [9];
- C<sub>2</sub>H<sub>6</sub> into C<sub>2</sub>H<sub>4</sub>. Ct: 1,5-15% Ca(Cs, Mg, Ba, Cr)Si(P)W<sub>12</sub>O<sub>40</sub>/aluminosilicate, 700-725°C, yield of C<sub>2</sub>H<sub>4</sub> - 46-51%, S<sub>C2H4</sub> - 88-94%, P - up to 537g C<sub>2</sub>H<sub>4</sub>/m<sup>3</sup> C<sub>2</sub>H<sub>6</sub>, 16000g C<sub>2</sub>H<sub>4</sub>/kg HPC·h [10];

- C<sub>3</sub>H<sub>8</sub>-C<sub>4</sub>H<sub>10</sub> mixture into C<sub>2</sub>-C<sub>4</sub> olefins. Ct: 1,5-15% H<sub>3</sub>(Cr, Cs, Ba, Na)PW<sub>12</sub>O<sub>40</sub>/aluminosilicate (natural clinoptilolite), 700-800°C, P - 2758g C<sub>2</sub>H<sub>4</sub>/l Ct·h, 1920g C<sub>3</sub>H<sub>6</sub>/l Ct·h, 840g C<sub>4</sub>H<sub>8</sub>/l Ct·h [11].

The offered catalysts show thermal stability at exploitation > 120h (T = 650-800°C) in developed methods. Considerable increase of HPC thermal stability on carriers in comparison with compact HPC was shown by parallel investigation of systems by complex of physical and chemical methods: a differential thermal analysis, XRD, IR-spectroscopy, TPR, TPO, and isotopic exchange [12,13]. It is caused by formation on carriers of bi-dispersed systems: finely divided crystallites and amorphous structures in states of interaction of HPC fragments with the carrier. Last results in a strengthening of the supported structure, bond strength of structural oxygen, considerable increase of start and final HPC destruction temperature with formation of non-phase oxides of unstated stoichiometry at conservation of separate fragments of initial HPC (IR-spectroscopy: a.b. of W-O-W, P-O-W) in investigated reactions.

Increase of activity and thermal stability at exploitation of catalysts is promoted by injection of water vapor in composition of reaction medium. It was shown by combination of isotopic and TPR methods, that water is a "mild" oxidant and participates in formation, for example, CH<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub>, and, on the other hand, promotes mild regeneration the structure of supported HPC in a state of half-decay in condition of high-temperature oxidative catalysis (650-800°C) especially at presence of O<sub>2</sub>.

Essential increase of activity, selectivity and productivity of developed catalytic systems in oxidative conversion of alkanes is promoted by using of some technological methods: application of amorphous supported HPC, system of reactors, and additional injection of overheated steam or hydrocarbons-modifying agents (C<sub>3</sub>, C<sub>4</sub>) in reaction mixture. Developed stabilization methods of activity for catalysts "HPC/carrier" and avoidance of deactivation in reactions of oxidative conversion of C<sub>1</sub>-C<sub>4</sub> alkanes can be used for other reactions on those catalytic systems.

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