Oxidative conversion of light alkanes on Mo containing catalysts

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Abstract: The reaction of oxidative conversion was investigated in the presence of 15-30% mas. PMo- and PVMo containing catalysts, supported on SiO_2. Interaction with O_2 (air) in the presence of water vapor, H_2, alkane in TPR regime, O_2 – in TPO regime (298-1273K), H_2O (298, 923K) was tested. The rank of reversible structural conversion of supported surface compounds was established under influence of temperature and medium.

Keywords: Oxidative conversion, Molybdenum, Structure.

1. Introduction

Oxidative conversion of alkanes to olefins instead of using crude oil represents practical interest, since ethylene and propylene are the basis for the production of approximately 50% of all organic products in chemical industry. Currently, their annual production is one of the main indicators of the potential for industrial development. The results of development the composition of supported catalysts for oxidative conversion are presented in report. Supported polyoxide catalysts were investigated in reaction of oxidative conversion of C_1-C_4 alkanes into oxygen-containing compounds and olefins[1-3]. It was established their high activity and thermal stability at 300-800°C and P = 1atm in reaction mixtures containing alkane, O_2, N_2 (Ar), water vapor. At the same time it is known, that compact polyoxide compounds undergo irreversible structural transformations on air with transferring into oxides at 400-500°C[4].

2. Experimental

Oxidative conversion of alkanes was carried out in reaction mixtures – hydrocarbons : oxidant : inert gas : steam at reaction temperatures 600-900°C and $P_{atm.}$ Experiments were performed in flow quartz reactor with the system of quick remove of products from reaction zone to cooling zone. The results of investigation of the structural transformations of PMo, $PVMoO_{40}$ supported on SiO_2 in conditions of action of oxidation-reduction reaction components (air, H_2, H_2O, and alkane) and temperatures by complex of physical and chemical methods: IR-spectroscopy, XRD, TPR, and TPO are represented.

3. Results and discussion

It was established, that supported Mo-HPC-catalysts are characterized by TPR peaks of structural oxygen, °C: I - 380-400, II $\geq$ 550, III - 670, IV> 800; by presence of absorption bands from the valent and deformation fluctuations of metal-oxygen connections in functional groups M-O-Mo (505, 590 cm^{-1}), Mo-O-Mo (780, 860 cm^{-1}), Mo=O (950 cm^{-1}), and P-O-Mo (1050 cm^{-1}) in IR-spectra; by occurrence of diffraction maximums on roentgenograms in the field of 2θ = 8-12° (12.22, 11.04, 9.93, 9.48) due to formation of Keggin type HPC crystallites on carrier.

Heating of catalyst on air at T $\geq$ 500°C results in destruction of supported HPC and formation of MoO_3. Disappearance the diffraction maximums 2θ = 8-12° from XRD spectra and occurrence of the new diffraction maximums from MoO_3 phase with a rhombic lattice (ASTM No5-0508) indicate on that fact. Characteristic absorption bands from HPC disappear in the IR-spectra and occur the new wide absorption bands at 460, 550, 840, 990 cm^{-1} which can be superposition of absorption bands from V_2O_5 (460, 580, 810, 1000 cm^{-1}) and MoO_3 (590, 860, 990 cm^{-1}) after heating on air at T $\geq$ 400°C.

Reduction of MoO_3 on the base of HPC with formation of MoO_2 which is reduced up to metal Mo° as a result of interaction with H_2 at 900-1000°C (TPR) is observed at increase interaction temperature of oxidized and supported HPC with H_2 in TPR regime up to 700-750°C. These reduction stages of catalysts are reflected in occurrence in TPR spectra of absorption peaks of H_2 at 300-500°C (reduction of HPC), 600-650°C (formation of MoO_3 on the base of Mo^{6+} cations of HPC), 700-750°C (reduction of MoO_3 into MoO_2), and 900-1000°C (reduction of MoO_2 into Mo°).

Re-oxidation process by oxygen in TPO regime of catalysts after preliminary reduction by hydrogen up to Mo° proceeds at 200-600°C with occurrence of three absorption peaks of O_2: 350-370, 430-450, 530-550°C. Re-oxidation process is on 100-200°C more low-temperature, than reduction process. A partial replacement of molybdenum on vanadium in HPC ($H_3PMo_{12}O_{40}$, $H_3PV_2Mo_{10}O_{40}$) increases reduction temperature of acid-forming cation $Mo^{6+} \rightarrow Mo°$, but reduces oxidation temperature of Mo° into Mo^{4+} and further into Mo^{6+}. The subsequent preservation in water for catalysts after TPR up to 700-750°C (from MoO_3 and MoO_2 phase) and TPO up to 600°C, or TPR up to 1000°C (Mo°) and TPO up to 850°C results in renewal of initial structure of supported Mo-HPC. Renewal of the diffraction maximums $2\theta = 8\text{-}12°$ in XRD spectra, absorption bands from Keggin type groups in IR-spectra, and initial TPR spectra indicate on that fact.

4. Conclusions

Comparative analysis of the reaction of oxidative conversion of propane-butane under optimal conditions, physical and chemical characteristics and structure of optimal catalysts indicates that the formation of C_3H_6 and C_2H_4 from propane-butane mixture at 700-800°C is carried out through a stage of thermal decomposition and the formation of finely dispersed oxides or mixed oxides at preserving of the fragments of supported HPA. As shown previously, this greatly facilitates the process of reduction ↔ reoxidation of oxides from fragments of supported salts of HPA under oxidative catalysis.

Thus, the convertible cycle of structural transformations of HPC under influence of medium and temperature was established by TPR, TPO, IR and XRD methods at oxidation-reduction-oxidation stages and processing by water. Determination such mechanism is very important for construction selective catalysts of oxidative conversion of C_1-C_4 alkanes.

References

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