

The n-pentane partial oxidation and catalysts for its realization.

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It is known that n-C₅H₁₂ oxidation over VPO catalysts leads to maleic anhydride (MA), citraconic anhydride (CA) and phthalic anhydride (PhA) obtaining. The formation of PhA which contain eighth carbon atoms from C₅-alkane attracts the scientific as well as commercial interest. Today the industrial production of PhA is base on the reaction of o-xylene oxidation. The perspective of new process for PhA manufacture connects with difference of raw materials price (the n-pentane is 5 times more cheap than o-xylene). First studies of the n-C₅H₁₂ oxidation shown a perspective of alternative method use for the PhA production. However, subsequent development these results did not receive and catalytic parameters did not improve. In our opinion the reason of this situation is insufficient study of the n-C₅H₁₂ oxidation mechanism and the factors determined catalytic properties. In present work we realized the investigation of peculiarities of the n-C₅H₁₂ selective oxidation and the modification of VPO catalysts by different additives such as Bi, Te, Mo, Zr, La, W, Fe.

Mechanism of the n-pentane activation and the pathways of the partial oxidation product formation were studied in detail on VPO and VPMeO catalysts. The results obtained at introduction of olefins (1-, 2-butene, 1,3-butadiene) in reaction mixture (n-C₅H₁₂ in air) shown the increase of PhA yield. Experiments carried out in a specially constructed installation with two consecutive flow type reactor confirmed the possibility of the PhA formation by reaction between MA and 1,3-butadiene. The scheme of mechanism of the n-C₅H₁₂ oxidation with its activation at C¹ and C⁴ atoms was proposed. The possibility of the paraffin isomerization with the increase of the catalyst surface acidity was predicted and the oxidation of formed intermediate to CA was proposed. It was established that the selectivity to CA increases with the growth of a acidic centre concentration. An abstraction of the methyl group from n-C₅H₁₂ molecule leads to radical-like particles formation which fast oxidize to C₄-olefins. The oxidation of the 1,3-butadiene formed results to MA. The formation of PhA proceeds by the Diels-Alder reaction between MA and 1,3-butadiene and the low stationary concentration of diolefin limits this process.

The modification of VPO catalyst surface properties was realized by introduction of additives, which differ by their electronegativity. It was established that introduction of elements, which decrease the values of O 1S-electrons binding energies leads to the increase of the catalyst activity. Last case could be explain on the base of the proposed mechanism, which supposes the protons abstraction in the reaction limiting step and as results the increase of a specific rate oxidation with the rise of effective negative charge on surface oxygen atoms. Thus the introduction of additives, which change the value of O 1S-electron binding energy is the way for regulation of the alkane oxidation rate.

It was determined the influence of the additive nature on the surface acidity of catalysts and on relative content of the Brønsted and Lewis centres. In accordance with the proposed mechanism of n-C₅H₁₂ oxidation the stabilization of 1,3-butadiene molecule on Lewis acidic centres must increase a probability of the diolefin participation in the Diels-Alder reaction, which results to the PhA formation. This fact was confirmed experimentally. It was established that the PhA selectivity rises with the increase of Lewis acidity of VPO catalysts after the introduction of additives while the MA selectivity naturally reduces. It was shown that the additives introduction allows to increase the selectivity to PhA up to 55 mol. % without reduction of the catalytic activity.

Thus in the work the mechanism of the n-C₅H₁₂ oxidation and the formation of partial oxidation products was proposed. The obtained experimental results confirm this scheme. The possible pathways for the regulation of the activity of catalysts and the selectivity to each anhydrides were defined.