

METHODS OF MODIFICATION OF HYDROCARBONS LIQUID

PHASE OXIDATION

S.P.Prokopchuk

**(S.P.Prokopchuk, 12, Kosmonavtov avenue, flat 30, Vinnytsa-21,
Ukraine, 21021)**

Abstract: it gives a short description of influence of the catalysts, polar solvents, reaction duration, temperature, pressure, hydrocarbons concentration in the reaction mixture, oxygen concentration in the oxidating gas, addition of water into the oxidation zone, removal of the reaction products out of the oxidation zone, step-by-step temperature change in the oxidation zone, step-by-step introduction of the oxygen containing gas into the oxidation zone on yield and selectivity of end products formation at hydrocarbons liquid phase oxidation.

Keywords: oxidation, modification, hydrocarbons, selectivity, yield, catalysts.

Introduction

Hydrocarbons liquid phase oxidation refers to one of the most available methods of oxygen containing substances obtaining. However, this method has not been widely adopted in industry. This can be explained by formation of a great number of by-products when end products are formed at liquid phase oxidation since the oxidation process goes by branch radical mechanism and it is difficult to regulate it. That is why selectivity of end products in many processes of hydrocarbons oxidation does not exceed 30-40 %. Development of science and industry enables complex approach to hydrocarbons liquid phase oxidation process regulation using both constructional formations of oxidation reactors and influence of different technological parameters in order to increase end products selectivity. In view of availability and cheapness of this process increase of end products selectivity over 50 % can make this method competitive with respect to other methods of obtaining of oxygen containing products.

There are different ways of increase of selectivity of end products formation at hydrocarbons liquid phase oxidation. They are: the use of catalytic systems, effect of technological parameters change and details of construction of oxidation reactors.

Discussion

Interaction of catalytic systems on modification of hydrocarbons liquid phase oxidation

The widespread catalytic system relates with the use of metals compounds of variable valence. As numerous investigations show the compounds of metals Co, Mn, Cr, Mo etc. are used at hydrocarbons liquid phase catalytic oxidation⁽¹⁾.

The role of these catalysts consists in their interaction with primary products of oxidation – hydro peroxides and peroxiradicals as well as with secondary products of oxidation- peroacids, alkyoxyradicals, acyloxyradicals. Interaction of catalysts with primary products of hydrocarbons oxidation, with hydroxyl peroxides in particular, exerts considerable influence on the end products yield.

Each of the catalysts reacts differently with hydroperoxides, thereby partially or completely changes the ways of conversion of hydrocarbons liquid phase oxidation intermediate products and influences their yield. Cobalt catalyst interacting with hydroperoxide passes from two-valence state to three-valence state and promotes hydrocarbon molecule cleavage with formation of aldehydes, alkyloxy – and acyloxyradicals which are basically converted to carbon acids.

Manganese catalyst (Mn - catalyst) interacting with hydroperoxide passes from two-valence state to unstable three-valence state⁽²⁾. Then this manganese ion absorbs oxygen molecule and passes to six or seven – valence state forming intermediate complex compounds with oxy hydrocarbon radical which is cleaved to aldehydes and acyl radicals.

Molybdenum catalyst (Mo – catalyst) partially stabilizes hydroperoxide owing to formation of intermediate complex compound^(3,4). This compound decomposes to oxyradicals which are converted to ketones or to alcohols without hydrocarbon molecule cleavage. Thus, cobalt catalyst promotes hydrocarbon molecule cleavage, manganese catalyst promotes deeper hydrocarbon oxidation, molybdenum catalyst promotes formation of oxygen containing compounds with hydrocarbon molecule keeping. That is why molybdenum catalyst is used for epoxide reactions of nonsaturated hydrocarbons by hydroperoxides. Cobalt and manganese catalyst is used to obtain carbon acids at hydrocarbons oxidation.

To increase control properties of catalysts it is possible to use complex catalysts which are composed of two, three or four compounds of different metals. The uses of such catalysts enable to increase their control properties. In particular, utilization of manganese catalysts during light hydrocarbons fractions oxidation increases considerably the yield of formic acid and decreases the yield of propionic acid. The use of two – complex

manganese – chromium (Mn – Cr – catalyst) catalyst at great yield of formic acid increases the yield of propionic acid, thereby increases the total selectivity of formation of lower carbon acids⁽⁵⁾. On the whole, complex catalysts activity differs slightly from simple catalysts, since each of catalysts shows its catalytic properties basically during interaction with hydro peroxides.

Some solvents are also of interest since they can be used as catalytic systems. Liquid substances the molecules of which have strongly polarized chemical bonds or active centers which consist of a polarized atom refer to them. Fluorcontaining compounds also refer to such solvents. They can be the carries of oxygen molecule or ligands in complex compounds formed at the expense of hydroperoxides or peroxiradicals, since fluor is the most electronegative element.

Such catalytic systems can be used as catalysts in some processes of hydrocarbons liquid phase oxidation, in particular, in the process of obtaining of propylene oxide by direct oxidation of propylene.

Interaction of basic technological parameters on modification of hydrocarbons liquid phase oxidation.

The process of hydrocarbons oxidation can be also controlled by changing the basic technological parameters: reaction duration, temperature, pressure,

hydrocarbons concentration in the reaction mixture and oxygen concentration in the oxidizing gas⁽⁶⁾. It is possible to influence the process of hydrocarbons liquid phase oxidation itself by changing the reaction duration only at the stage of initiation of the oxidation process during the induction period, since in 15-30 minutes after oxidation starting during induction period the rate of radical oxidation process increases considerably and only in 1-2 hours it begins to decrease gradually. Such decrease of reaction rate can apparently be explained by formation of radicals hydroxide in the process of oxidation which partly recombine the radicals formed in the process of hydrocarbone molecule cleavage. By changing the reaction duration it is possible to increase selectivity of formation of the reaction primary and secondary products. At the reaction duration 0.5-2 hours selectivity of formation of primary products increases: hydroperoxides, ketones and alcohols of the corresponding hydrocarbons. At the reaction duration more than 2 hours the yield of main products of oxidation and selectivity of formation of oxidation secondary products increase: carbon acids, alcohols, ketones and aldehydes formed at the expense of hydrocarbons oxidizing distruction. Practically, hydrocarbons oxidation reaction duration is determined by experiment depending on the process type, periodic or continuous, and oxidation conditions (temperature).

In the process of hydrocarbons liquid phase oxidation it is possible to control partly the yield of the reaction products by controlling the temperature change. At low temperature the induction period increases, oxidation rate decreases and the yield of primary products increases.

At high temperature the reaction rate increases and the yield of the oxidation secondary products which are formed at thermal decomposition of the hydrocarbon which is being oxidized increases. There is optimum temperature of oxidation reaction at which maximum yield of end products is achieved.

By changing the pressure in the process of hydrocarbons liquid phase oxidation it is possible to change insignificantly hydrocarbon concentration in the reaction mixture and the reaction rate. Practically, the pressure is chosen experimentally depending on the hydrocarbon to be oxidized and reaction temperature so as to keep hydrocarbon in liquid state during oxidation.

Hydrocarbon concentration in the reaction mixture influences, the process of the hydrocarbon liquid phase oxidation in the following way. Hydrocarbons oxidation in inert solvents at their concentration below 25 % leads to stopping of radical oxidation process since it becomes difficult to transfer radical to another molecule of hydrocarbon.

When hydrocarbon concentration in reaction mixture is 30-40 % the oxidation process takes place with less degree of branching and with greater selectivity of final products formation owing to oxidation cell effect. When hydrocarbon concentration is great in the reaction mixture or during pure hydrocarbons oxidation the branching process of hydrocarbons liquid phase oxidation with end products selectivity decrease prevails. Practically, the hydrocarbon concentration in the reaction mixture has its optimum value at which the greatest yield and the greatest selectivity of end products formation is achieved. By changing the oxygen concentration in oxidizing gas it is also possible to influence insignificantly the process of hydrocarbons liquid phase oxidation. When the oxygen concentration is up to 12 vol. % the yield of reaction primary and secondary products increases insignificantly, their molecules contain small quantity of oxygen (aldehydes, low-molecular alcohols and ketones). Under these conditions the reaction rate and hydrocarbon fractional conversion decrease. Increase of oxygen concentration up to 21 % increases the reaction rate and increases insignificantly the yield of reaction products containing maximum quantity of oxygen in the molecule (carbon acids, carbon dioxide). Further increase of oxygen concentration to 36 % at insignificant increase of hydrogens fractional conversion increases the yield of the carbon dioxide and decreases selectivity of end products formation.

Interaction of details construction of reactors on the modification of hydrocarbons liquid phase oxidation.

The yield and selectivity of end products formation at hydrocarbons liquid phase oxidation can be changed at the expense of water adding into the oxidation zone, by removing the reaction products from oxidation zone, by stage change of the reaction temperature and by stage introduction of oxygencontaining gas into the oxidation zone in the way of changing of construction of oxidation reactors. Addition of water (to 10 mass. %) into reaction mixture decreases insignificantly oxidation reaction rate and increases selectivity of forming of some reaction products, in particular, lower carbon acids. Further increase of water in reaction mixture decreases significantly hydrocarbons oxidation rate and when water is added over 50 mass % the oxidation reaction practically stops. While addition of water solutions of carbon acids up to 20-30 mass % increases selectivity of lower carbon acids formation at insignificant decrease of oxidation rate and hydrocarbons fractional conversion. The role of water additions into the reaction mixture is apparently explained by water absorption of active radicals, by transfer of some products of reaction into water layer. Since most of the products oxidize themselves in the reaction zone one of the ways to increase their yield and selectivity is removing of these products out of the oxidation zone. For that it is

necessary to carry out the oxidation process in the reactor of “Arlift” type in which the oxidant is recirculated by means of temperature difference in the reaction zone and in cooling system, followed by with a rawal of the oxidate lower water layer from the oxidation zone. Carrying out of such process also enables to increase the yield of primary products of the oxidation reaction.

Temperature change by stages enables to increase or to decrease the reaction rate of hydrocarbons thermal cleavage under different oxidation conditions, thus enabling to influence the yield and selectivity of end products. Step-by-step introduction of the oxygen containing gas into oxidation zone enables to introduce oxygen at different temperatures and influence oxidation cell effect simultaneously when hydrocarbons are oxidized more deeply, thereby to change partly the yield and selectivity of end products.

Conclusions

In some processes of hydrocarbons liquid phase oxidation it is not sufficient to use one of the above mentioned factors to influence the yield and selectivity of end products, this makes these methods less competitive with respect to other methods . Whereas combination of different path - ways of modification of hydrocarbons liquid phase oxidation enables to

influence sufficiently the yield and selectivity of end products formation, thus increasing competitiveness of these methods.

Reference

1. Prokopchuk S.P., Abadjev S.S., Shevchuk V.U. Catalytic oxidation n-pentane in the liquid phase. Ukr. Chem. Journ. Kyiv, 1983. Vol. 45, № 5, p.p.505-508.
2. Prokopchuk S.P., Abadjev S.S., Shevchuk V.U. The way of formation of n-pentane liquid phase oxidation. Ukr. Chem. Journ. Kyiv, 1985, Vol. 51, № 1, p.p. 89-93.
3. Prokopchuk S.P., Shevchuk V.U., Ivakht B.V. Catalytic conjugate oxidation n-pentane and propylene. Ukr. Chem. Journ. Kyiv, 1988, Vol. 54, № 5, p.p. 840-843.
4. Prokopchuk S.P., Abadjev S.S., Shevchuk V.U. Joint receiving of the propylene oxide and lower aliphatic carboxylic acids. Chem. Ind., Moscow, 1988, № 11, p.p.666-668.
5. Prokopchuk S.P., Morozova L.P. The complex catalysts influence on the n-pentane oxidation. Reports of Vinnitsia National Medical University, Vinnitsia, 2005. Vol. 9, №1, p.p. 52-54.
6. Prokopchuk S.P., Abadjev S.S., Shevchuk V.U., Makedonskyi O.O. The choice optimum conditions of the process of receiving carboxylic acids. Chem. Ind., Moscow, 1987, № 7, p.p. 399-401.