

OC-38: Ultrasound Intensification of Ethylbenzene Oxidation

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Processes of liquid-phase catalytic oxidation of hydrocarbons play significant role in industry. Their importance is characterized by economy in synthesis of wide row of oxygen containing products in comparison with other methods, by high selectivity and easy handling of chemical reactions.

Production of chemical and oil-chemical industries on 80% is related to catalytic processes. It also includes liquid-phase oxidation of hydrocarbons.

Despite there are a lot of scientific researches in this area, search of new catalytic systems that can improve technical and economical indicators of industrial homogeneous catalytic processes of oxidation will stay relevant for many more years.

Process of liquid-phase oxidation of ethylbenzene is not only valuable industrial process, main products of which are acetophenone (AP) and hydroperoxide of ethylbenzene (HPEB), but also a model process for oxidation of alkylaromatic compounds.

Along with chemical ways of improving productivity and selectivity of oxidation process we shouldn't forget about physical and chemo-physical methods as well. There are known researches of temperature influence on ethylbenzene oxidation process [1]. Also from previous researches we know that ultrasound have influence on cyclohexane oxidation improving technological indicators of the process. However we didn't find any research data on ultrasound influence at ethylbenzene oxidation.

Research were conducted in steel reactor under industrial temperature (403K) and pressure (4-4,5 atm). Catalytic systems consisted from most used industrial catalysts – naftenate of cobalt (NC) and acetate of cobalt (AC), and catalytic additives. As additives were used polyethylene glycol (PEG) and hromoksan. Ultrasound treatment was conducted during first hour of experiment with frequency. HPEB was identified titrimetrically AF and methylfenylcarbinol by chromatography.

Obtained results showed that usage of ultrasound treatment changes selectivity of the process in path of obtaining acetophenone (S~90%) suppressing obtaining of HPEB. Also, in case of usage AC as primary catalyst, ultrasound treatment allows to obtain highest value of conversion, up to 25% comparing with industrial 5%-7%. But arguably one of the most important achievements of conducted experiments was that ultrasound influence on oxidation process proved existence of complex between catalyst-catalytic additive and substrate. So, for example, without ultrasound process of ethylbenzene oxidation with AC as main catalyst and PG as catalytic additive shows very low conversion of ethylbenzene (2,5%-3%). But oxidation conducted with ultrasound treatment showed tremendous growth of conversion (up to 20%). This proves that AC forms low reactivity complex with PG and substrate, and ultrasound treatment destroys that complex allowing increasing productivity of reaction volume.

Another example of ultrasound influence on ethylbenzene oxidation is its influence on oxidation in presence of NC-PG and NC-H catalytic systems. Without ultrasounds this systems showed high selectivity on obtaining HPEB (up to 50%), and this results allowed us to suppose that NC forms an effective catalytic complex with additives leading to increase of HPEB concentration in the reaction mixture. However results obtained under ultrasound showed that this complex destroys leading to reduction of general conversion (to 1,5%) and HPEB selectivity (to 5%-6%)

References

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