Influence of surface-active additieves on processes of alkylaromatic catalytic oxidation

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Abstract – The process of ethylbenzene oxidation in the presence of catalytic systems, that consists fromsalt of variable valence metal and organic additives, was explored. Suggestion about the influence mechanism of additives on the ethylbenzene oxidation process were made.

Key words – oxidation, alkylaromatic, ethylbenzene, additieve, surface active matter, radical, catalysis, catalytic system.

I. Introduction

Over a past decade chemical industry was going through some tough challenges: such as high price of reagents (mainly oil), decrease of production and increase of production standards. But due to rapid decrease of oil prices today situation changed and many economic specialist are predicting new outburst of chemical production all over the world (mainly in large industrial economics (USA, China, Germany etc.) and traditionally oil-countries (Saudi Arabia, UAE etc.)). In such economical situation manufacturer needs to stay on the "edge" providing more quality products for lower price. This task can be achieved in several ways. One of them is search for new technology, creation of new technological schemes based on new data and researches. However this way needs major investments and often means building new production facilities "from the ground". Taking all this into account we can say that this way is more suitable for creation of new productions. However major "players" on the chemical market usually have not only long history but also long-time working factories and plants based on older technological schemes. Such facilities are still making money for their respective owners but in comparison with newer plants can lose parts of the markets leading to their shutdowns. This leads us to another way of improvement – "evolution" of existing technology. Such way of improvement needs much less investments. Basically you need to make changes in few most "crucial" and/or" control-able" points of process and this can lead to major changes in process productivity, quality and time of production. Also such changes can help to fit into new production regulations because often higher productivity means less sewage (and this makes even out-of-date process "greener"). Also it needs to be noted that usually for "speeding" of processes were used temperature and/or pressure, but despite the fact that such changes can increase productivity or change selectivity of the process , their applying will lead to increase in process cost and as a result will lower the possible income. In our opinion the best way to make "older" technological process more productive and relevant is search, development and improvement (some kind of "evolution") of catalytic systems used in such processes.

II. Problem statement

Radical oxidation processes are one of the best ways to show how improved catalytic systems can change outcome of "out-of-date" industrial chemical process. Every industrial radical process is a "two edged sword" situation. At one hand you have a process that needs just a "little push" at the start (creation of free radicals) and later it becomes self-catalyzing[1]. On other – the further you go in terms of conversion the poorer would be selectivity of aim products (basically in the end you will receive mixture of products further processing of which would be a nightmare). Therefore most of radical processes (and almost all radical oxidation processes) are characterized by low conversions and huge recycle of raw materials. For example conversion of cyclohexane (CH) during oxidation to cyclohexanole (CHL) and cyclohexanone (CHN) (processes of obtaining adipic acid and caprolactane) is from 2% to 4%[3]. 20% conversion of ethylbenzene (EB) during process of hydroperoxide of ethylbenzene (HPEB) obtaining is reached due to use of 4 connected oxidation reactors (therefore conversion in 1 reactor is about 4-5%)[4, 5]. Relatively high selectivity on aim products in those processes is achieved with help of catalysts which are organic salts of Cobalt (cobalt naphtenate(CN), cobalt acetate (CA), etc.). Our previous studies showed that during oxidation Cobalt in form of Co^{3+} forms an active catalytic complex with raw material and organic substrate. Further decomposition of this complex provides high selectivity for aim products[5]. However effect of catalyst is limited and "deeper" oxidation still causes shifts of selectivity. Search for other salts of variable valence metal (SVVM) that could be used as catalyst for these processes is not relevant due to relatively low price of cobalt salts, their proven efficiency and accessibility. More logic way of solving productivity problem would be improvement of catalytic system by additives of different nature. This would create new catalytic systems based on industrially used catalysts.

Oxidation of cyclohexane in the presence of catalytic systems, along with variablevalence metal salt containing organic additives of electron-donor or electron-acceptor nature, has shown high efficiency of their applyence. Using the above mentioned additives allowed to change the ratio between the target product, to improve selectivity for the target products and increase the conversion of cyclohexane [1, 2, 6]. However, for cyclohexane oxidation process it is difficult to determine impact of organic additives on the elementary stages of the process. For this purpose it is expedient to use a model substance, which is characterized by a smaller number of stages of oxidation and a smaller number of products formed by oxidation. Substance of such a model can be ethylbenzene.Investigation of the process of oxidation of ethylbenzene in the presence of catalytic systems of different nature allows to set the mechanism of influence of these systems at the elementary stage of oxidation.

III. Experimental

Research was carried out in a steel reactor at temperatures 130 C and pressure 0.4 Mpa. As a basic component of the catalyst was used naftenat of cobalt. As catalytic additives were used poliglikol (PG), chromoksane and tcianethyl ether (TCEE). The concentration of cobalt naftenate was 0.003 mol / liter. Molar ratio of cobalt naftenate /organic additive was 1 / 1. The concentration of ethylbenzene hydroperoxide (HPEB) was determined tytrymaticlly, concentration of atcetofenone - by gas-liquid chromatography.

IV. Results and discussion

Obtained results revealed that in the presence of catalytic system naftenat Co – PG HPEB formation rate increases, indicating that the presence of PG increases the amount of dissolved oxygen in the system. However, considering that the influence of catalytic systems for oxidation is smaller than the total impact of naftenate of Co and PG, you can assume that in the reaction mixture is present the reaction of complexation between Co naftenate and PG, and oxidation catalyst in this case is not an individual compound but the complex between variable valence metal salt and organic additive. The highest growth of rate of accumulation HPEB was observed when we used the catalytic system naftenat Co - hromoksan. We can assume that hromoksan affects the ratio of Co^{+2} / Co^{+3}, increasing amount of the last in the system. Results obtained by using the system naftenat Co - TCEE also responds to the literature data (Fig. 1), as TCEE contains triple connection, and by its structure is an inhibitor of oxidation process.

The results of oxidation of ethylbenzene in the presence of catalytic systems containing organic additives such as PG and chromoksan show results opposite to those obtained in oxidation of ethylbenzene in the presence of individual compounds [5].

These results and data on the impact of ethylbenzene oxidation ratio of oxidized and reduced forms of cobalt Co^{+2}/Co^{+3} shows that the impact of PG is related to its surface-active properties and the effect of X and E in complex with their participation and thus different effects on the ratio of Co^{+2}/Co^{+3} in the reaction system – electronaceptor chromoksan shifts ratio towards $Co^{+3,}$ and TCEE,that has electrondonor properties, forms more stable intermediate complexes and thereby has inhibiting effect on the process of oxidation. These results confirm that the effect of organic additives is largely due to the chelation of salt of variable valency metal.

Other aspect of obtained data is obvious existing of synergetic effect of organic additives on reaction mixture. In both cases – alkyl-aromatic oxidation and oxidation of CH – raw materials could be looked on as non-polar solvents and all studied organic additives are surface-active matters (SAM) of different nature (ionic and non-ionic). Such nature of additives and raw materials would most definitely influence changes in surface tension (leading to changes of oxygen consumption and solubility, which is one of the most crucial points in oxidation processes) and also changes in micelles creation in reaction mixture. Structure of those micelles would influence structure of created active catalytic complexes and next stage of research should be finding of dependences of complex structure from nature of used SAM. Also it is worth mentioning that concedering miccelous-creation in raction mixture allows us to research oxidation process from the point of view of nano-catalytic systems as well as "classic" homogeneous catalysis.

Conclusion

Thus, the researches found that the nature of additives significantly affects the efficiency of the catalytic system in the process of oxidation of ethylbenzene. However,for a more detailed understanding of the influence of the studied catalytic systems it is necessary to explore a wider range of organic additives of different nature.

References

[1] P. B. Johns, "A symmetrical condensed node for the TLM method," IEEE Trans. Microwave Theory Tech., vol. MTT-35, pp.370-377, Apr. 1997.

[2] Melnyk Y. R., Reutskyy V. V., Mokryj E. M., "The influence of crown ethers by catalytic oxidation of cyclohexane ", Reports of NAS of Ukraine. № 1, pp.154 - 157, 2001.

[3] Melnyk Y. R., Reutskyy V. V., Mokryj E. M. "Influence of polyglicols on catalytic oxidation of cyclohexane", Bulletin NU "Lviv. technologies. Chemistry, technology of materials and their applications., № 426, pp.91 – 94, 2001.

[4] Emanuel N. M., Gal D. "Oxidation of ethylbenzene. (Model Rection).", 376 p. Moscow: Nauka, 1984.

[5] Reutskyy V. V., Melnyk Yu. R., Starchevskyy V. L. "Influence of surface-active matters on ethylbenzene oxidation", Book of abstract 17 th International Symposium on Homogeneous Catalysis, P. 201, Poznan, Poland, 2010.

[6] Reutskyy V., Melnyk Y., Starchevskyy V., "Oxidation of ethylbenzene in the presence of catalytic systems containing organic additives of different nature", Advances in chemical and mechanical engineering., pp.208-212 ,Gdansk, 2011

[7] V. Reutskyy, Yu. Melnyk, S. Melnyk, V. Starchevs-kyy, Vol. Reutskyy., "Catalytic oxidation of organic compounds in the presence crown-ethers" // Chemical Engineering Transactions, vol.24, pp.163–168, 2011