http://www.moderntechno.de/index.php/meit/article/view/ge3-024
DOI: 10.30890/2567-5273.2018-03-01-024

УДК 661.7

ROLE OF SURFACE-ACTIVE COMPOUNDS IN HOMOGENEOUS CATALYTIC OXIDATION PROCESSES

РОЛЬ ПОВЕРХНОСТННО-АКТИВНЫХ СОЕДЕНЕНИЯ В ГОМОГЕННО-КАТАЛИТИЧЕСКОМ ОКИСЛЕНИИ

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Abstract. *Article is devoted to research of catalytic activity of surface-active compounds in processes of homogeneous catalytic oxidation.*

Catalytic processes play significant role in chemical industry. Due to ease of use and high adaptivness of homogeneous catalytic systems they are more preferable. Our previous works have proven effectiveness of surface-active compounds as additives to industrial catalysts of ethylbenzene and cyclohexane oxidation. Based on received data we came to a conclusion that additive forms an active catalytic complex with main catalyst and substrate. However, identification of such complexes remains a very hard task. In order to find more proves of our hypothesis and to clarify role of surface-active compounds in oxidation process we needed to research catalytic activity of individual surface-active compounds without main catalyst of oxidation. For identification of role of additives in oxidation mechanism we've conducted series of experiments using surface-active compounds of different nature as individual catalysts.

For identification of change of surface properties of reaction mixture, we've conducted experiments under mild conditions –relatively low temperature 363 K and atmospheric pressure. For identification of possible complex creation, we've conducted experiments under conditions close to industrial. Obtained results were compared of performance traditional ethylbenzene oxidation catalysts.

Obtained results showed that all researched compounds have catalytic influence on oxidation of ethylbenzene. This impact is connected not only with changes of surface properties of reaction mixture – solubility of oxygen – but also with formation of catalytic complexes between surface-active compound and substrate, resulting in improvement of direct oxidation into secondary oxidation products – ketone and alcohol.

Key words: *oxidation, surface-active compounds, ethylbenzene, catalyst, catalytic system, complex, variable valency metal, ion-genic*

Introduction.

It is common knowledge that production of chemical and petro-chemical industries more than on 80% is connected with catalytic processes [1]. This numbers are also valid for liquid-phase oxidation of hydrocarbons.

When we talk about industrial use heterogeneous catalysts can be more selective and active compared to homogeneous. However lower price, easier installation and ease of control make homogeneous catalytic processes more preferable. Usually as homogeneous catalysts in industry are used organic salts of metals with variable valency (SMVV). Despite numerous researches in this area problem of creation of highly effective and selective catalytic systems remains very important.

Use of different catalytic additives that are able to form active catalytic complexes, increase effectiveness of catalyst performance and impact selectivity of oxidation is one of main research areas.

For example – one of the most perspective ways of cyclohexane (CH) oxidation intensification is creation of complex catalytic systems on basis of SMVV with different specific additives of different nature, in particular surface-active compounds (SAC) [2-4]. Use of systems that as co-catalyst doesn't use ions of heavy metals but organic ligands is better choice not only from ecological point of view but also for more directional impact on oxidation process [5].

It is known that binary catalytic systems based on SMVV with electronic-acceptive salts of perfluoric sulfoacids (SPFSA) shows major activity in CH oxidation process [5]. Their presence in reaction system allows increasing of oxidation speed and selectivity for aim products. Impact of SPFSA additives is explained by catalytic intensification of stages of chain creation and transfer, and by its catalytic presence in parallel routes of cyclohexanole (COL) and cyclohexanone (CON) formation [6, 7].

Major improvement of quality and quantity indexes of oxidation process can be achieved by use of bi-component catalytic systems, that contain SMVV and electronic-donor additives that are able to form active catalytic complexes in specific reactional conditions [8,9].

However, despite literature data and previous researches [8,10] exact mechanism of influence of complex catalytic systems remains unclear. It is so due to few reasons. First of all, due to the fact that assumption of formation of catalytic complexes [catalyst-additive-substrate] is very hard to prove instrumentally.

Secondly additives of SAC are involved not only in formation of catalytic complexes, but also their presence changes properties of entire reaction environment and they can have their one catalytic activity as well.

Experimental.

Our previous works showed that SAC combined with industrial catalysts for oxidation form active binary catalytic systems that allow not only to increase productivity but also control and change selectivity for aim products [10].

For our previous research of influence of SAC additives of different nature on processes of homogeneous catalytic oxidation of hydrocarbons we used process of ethylbenzene [EB] oxidation. Mechanism of EB oxidation is well-known and described because it is a model reaction for oxidation of alkyl-aromatic compounds.

Our next step was identification and research of catalytic activity of single SAC without industrial catalyst.

First of all, we needed to exclude surface-active aspect of researched compounds. As researched SAC we used nonion-genic – polyethylene glycol with molecular mass 200 (PEG200), and ion-genic – chromoxane (Ch). Behavior of SAC in EB oxidation process was studied under temperature of 363K and atmospheric pressure. Such conditions are not enough for formation of catalytic complexes, but can show influence of surface-active properties. Obtained results were compared to performance of industrial catalysts of EB oxidation – naphtenate of cobalt (NC) and acetate of cobalt (AC), and to thermal autoxidation. Concentration of catalyst was $1{,}0\cdot10^{-2}$ mol/l.

While experiments were conducted under mild conditions main product of oxidation was hydroperoxide of ethylbenzene (HPEB). Quantity of HPEB was determined by method of iodometric titrimetry.

Results and discussion.

Obtained results are presented in Table 1.

Table 1.

Influence of individual SAC on EB oxidation process. T = 363 K, P = 0,1 MPa

Catalyst	Time, min	C(HPEB), mol\l	Conversion of EB, %
Thermal	30	0,003	0,036
	60	0,006	0,073
	100	0,01	0,122
	130	0,013	0,153
	160	0,015	0,184
PEG200	30	0,013	0,159
	60	0,025	0,307
	100	0,036	0,442
	130	0,037	0,442
	160	0,039	0,473
Ch	30	0,005	0,061
	60	0,007	0,092
	100	0,008	0,104
	130	0,012	0,153
	160	0,016	0,196
NC	30	0,017	0,208
	60	0,021	0,258
	100	0,030	0,368
	130	0,037	0,461
	160	0,041	0,504
AC	30	0,007	0,092
	60	0,014	0,178
	100	0,020	0,245
	130	0,025	0,301
	160	0,036	0,442

As we can see form presented data all researched compounds have influence on EB oxidation process.

Influence of PEG200 is comparable with impact of industrial catalysts (NC and AC). Such influence is explained by surface-active properties of PEG200. PEG200 increases solubility of oxygen in reaction mixture providing increase of reactions of creation and transfer of radical chain leading to increase of reaction speed mainly on early stages of oxidation. This is proven by decrease of HPEB accumulation speed after 100 minutes of experiment

Influence of Ch on liquid-phase oxidation process are first of all related with possible formation of active catalytic complexes with main catalyst and organic substrate. Individual catalytic activity of Ch is very low and obtained results are almost same as in the case of thermal autoxidation of EB.

Next logical step was research of individual SAC catalyzed EB oxidation under conditions close to industrial (Temperature 403 K, pressure 0,45 MPa). Obtained results were compared to performance of industrial oxidation catalysts (NC and AC).

Obtained results are presented in Table 2.

Table 2.

Influence of individual SAC on EB oxidation process. T = 363 K, P = 0,45 MPa.

Cat.	Time, min	C (HPEB), mol/l	C (AP), mol/l	C (MPC), mol/l	Conv. EB, %	S (AP), %	S (MPC), %	S (HPEB), %
T.	10	0.0065	traces	traces	0.08	-	-	100
	60	0.007	traces	traces	0.09	-	-	100
	180	0.014	traces	traces	0.17	-	-	100
	240	0.015	traces	traces	0.18	-	-	100
PEG200	10	0,01795	0,007	0,001	0,32	26,97	3,85	69,17
	60	0,03295	0,0013	0,001	0,43	3,69	2,84	93,48
	180	0,04995	0,0025	0,002	0,67	4,59	3,67	91,74
	240	0,05265	0,0063	0,002	0,75	10,34	3,28	86,38
Ch	10	0,006	0,0014	0,00184	0,11	15,15	19,91	64,94
	60	0,0095	0,0025	0,0017	0,17	18,25	12,41	69,34
	180	0,019	0,0089	0,0026	0,38	29,18	8,52	62,30
	240	0,019	0,0107	0,0024	0,39	33,33	7,48	59,19
NC	10	0,006	0,011	0,003	0,24	54,93	16,84	28,23
	60	0,028	0,03	0,011	0,85	43,12	16,50	40,38
	180	0,068	0,089	0,018	2,15	50,87	10,42	38,71
	240	0,067	0,131	0,026	2,75	58,47	11,56	29,97
AC	10	0,007	0,015	0,002	0,29	62,29	7,85	29,86
	60	0,009	0,603	0,191	9,87	75,1	23,78	1,12
	180	0,017	0,875	0,124	12,49	86,15	12,18	1,67
	240	0,019	1,275	0,149	17,75	88,34	10,34	1,32

As we can see from presented data tendencies of thermal (T.) oxidation under industrial conditions are similar to general tendencies of autoxidation process. Oxidation goes slowly with creation of HPEB on first stage of reaction with further transformation into secondary oxidation products – acetophenone (AP) and methyl phenyl carbinol (MPC). Increase of reactional conditions leads to appearance of traces of secondary oxidational products in reaction mixture. However due to low speed of oxidation quantities of those products are insignificant.

Influence of PEG200 on EB oxidation process remains similar to oxidation under milder conditions. This results tell us that main influence of PEG200 presence is increase of soluble oxygen in reaction mixture. But it also is worth mentioning that appearance of secondary oxidation products (mainly AP) can indicate possible formation of complex with substrate leading to conversion of HPEB and creation of ketone instead of alcohol.

Presented data shows that influence of Ch on EB oxidation is more significant compared to low-temperature oxidation. Conversion of EB increases more than two times with significant increase of secondary oxidation products quantities. As in the case of PEG200 mainly increases selectivity for AP. Such results and previous research of Ch influence allows to assume formation of catalytic complex [Ch-substrate] that promotes secondary oxidation processes and direct oxidation of EB into AP and MPC.

Presence of PEG200 as oxidation catalyst leads to higher reaction speed compared with use of Ch. Also it is worth mentioning that presence of PEG200 leads to increase of HPEB formation, while presence of Ch – to formation of secondary oxidation products (mainly AP) due to increase of direct EB oxidation into AP.

However catalytic activity of researched SAC is significantly lower compared to industrial catalysts (NC and AC). Mainly due to lack of variable valency metal ion that is needed for effective complex creation. Therefore, we can assume that SAC plays role of ligand surrounding in creation of highly active catalytic complexes.

Conclusions.

Obtained results allow as to make following conclusions:

1. SAC have catalytic influence on EB oxidation process.
2. Main influence of SAC on oxidation is related with changes of reaction mixtures surface properties – increase of oxygen solubility. But also results showed that SAC are able to form complexes with substrate and catalytically improve oxidation process.
3. Catalytical impact of PEG200 under mild reactional conditions is quite comparable to industrial catalysts of EB oxidation (NC and AC).

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Аннотація. *Стаття присвячена дослідженню каталітичної активності поверхнево активних сполук у процесах гомогенно-каталітичного окиснення вуглеводнів.*

Каталітичні процеси відіграють значну роль у хімічній промисловості. Завдяки легкості використання та високій адаптивності гомогенні каталітичні системи є пріоритетними. Наші попередні роботи показали ефективність поверхнево-активних сполук у якості добавок до промислових каталізаторів окиснення етилбензолу та циклогексану. Основуючись на одержаних результатах ми прийшли до висновку, що добавка створює активний каталітичний комплекс з основним каталізатором та субстратом. Однак точне визначення складу таких комплексів є надзвичайно важким завданням. Для підтвердження нашої гіпотези і для прояснення ролі поверхнево-активних сполук у процесах окиснення було необхідно дослідити каталітичну активність поверхнево-активних сполук при відсутності основного каталізатора окиснення. Для визначення ролі поверхнево-активних сполук ми провели серію дослідів з використанням цих сполук у якості індивідуальних каталізаторів окиснення етилбензолу.

Для визначення впливу зміни поверхневих властивостей реакційної суміші ми провели експеримент при м’яких умовах – відносно низький температурі 363 К та атмосферному тиску. Для визначення можливого комплексоутворення ми провели експерименти при умовах близьких до промислових .Одержані результати порівнювались з результатами традиційних промислових каталізаторів окиснення..

Одержані результати свідчать що усі досліджувані сполуки володіють каталітичним впливом на процес окиснення етилбензолу. Цей вплив пов'язаний не тільки зі змінами поверхневих властивостей реакційної суміші – розчинністю кисню – але і з утворенням активних каталітичних комплексів між поверхнево-активною сполукою та субстратом, що призводить до зростання швидкості прямого окиснення етилбензолу у вторинні продукти – кетон та спирт.