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Carbon deposits on the surface of CaO/SiO_2 as active catalysts for the oxidative dehydrogenation of ethylbenzene

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Abstract

The oxidative dehydrogenation (OD) of ethylbenzene (EB) has been investigated over different catalysts of xCaO/SiO_2 and yP/xCaO/SiO_2 composition. It has been shown that the texture characteristics of initial SiO_2 exert an important influence on the activity of catalysts obtained on their basis. Higher conversion of ethylbenzene and selectivity on styrene are observed in the case of macroporous silica gels. The yield of styrene and quantity of carbon deposits (CD) in the initial reaction period are increased symbately. In the stationary reaction period achievable in 1–6 h after beginning of reaction, depending on texture characteristics of catalysts, maximal conversion of EB and minimal rate of accumulation of carbon deposits are observed over catalyst surface. In this period of process catalytically active system represents carbon deposits formed over catalyst surface and inclusive various carbonyl-containing groups. Catalysts are not passive carriers on which carbon deposits are formed; on the contrary, structure and catalytic activity of carbon deposits strongly depend on composition, texture characteristics and acid–base properties of used catalysts.

Keywords: Carbonaceous deposits; Oxidative dehydrogenation; Ethylbenzene

1. Introduction

Styrene is one of the most important base chemicals in the petrochemical industry [1]. Styrene is industrially manufactured by the dehydrogenation process of ethylbenzene (EB) over iron-based catalysts. Process is operated by adding excess steam to EB in an adiabatic reactor under pressurized condition with the reaction temperatures of about 873 K. The problems associated with the dehydrogenation process of EB are follows: thermodynamic limitation, low conversion rate, high endothermic energy and deactivation of catalysts by coke formation [2]. Developments are going on to increase the concentration level by removal of the reaction product hydrogen and thereby shifting the thermodynamic equilibrium towards higher conversions. As an alternative way the oxidative dehydrogenation (OD) of EB has been proposed to be free from thermodynamic limitations regarding conversion, operating at lower temperatures with an exothermic reaction [3–5].

It is known that in most of catalytic reactions the coke formation leads to catalysts deactivation. However, in the OD of EB over aluminum oxide [6,7], silicon and alkali-earth oxides obtained by the precipitation method [8], styrene yield increases in the process of carbon deposits (CD) accumulation.

2. Experimental

All the chemicals were analytically pure and used without additional purification. Narrow-pored, medium-pored and macroporous silica gels distinguished by the texture characteristics are used as starting silica gels (Table 1). Catalysts were prepared with impregnation of silica gels by aqueous solutions of calcium nitrate and/or phosphoric acid. In order to vary content of calcium nitrate and phosphorus in the process of catalysts preparation concentrations of solutions are varied taking into account silica gels moisture capacity, duration and ratio of impregnation. The samples denoted as xCaO/SiO_2 and yP/xCaO/SiO_2 (where $x = 0.5-4.5$

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Table 1
The texture characteristics and catalytic properties of silica gels at OD of ethylbenzene[a]

Samples of silica gel	Average radius of pores (nm)	Specific surface (cm^2/g)	Total volume of pores (cm^3/g)	Conversion of ethylbenzene (%)	Yields (%)		CD[b] (%)
					Styrene	CO_2	
SiO_2-I	1.1	527	0.29	23.2	18.5	2.3	5.0
SiO_2-II	1.6	715	0.57	31.4	23.0	4.5	8.5
SiO_2-III	3.5	522	0.92	39.1	30.0	5.5	13.0
SiO_2-IV	5.2	376	0.97	42.7	33.0	6.9	16.0
SiO_2-V	7.0	333	1.19	47.0	36.3	7.0	17.5
SiO_2-VI	8.5	300	1.10	39.9	32.0	6.8	16.5

[a] Temperature = 773 K, P_{EB} = 0.14 atm, P_{O_2} = 0.17 atm, space velocity = 0.5 h^{-1}.

[b] CD in steady state (wt.%) (after six working hours).

and y = 1.0–8.0 wt.%) were dried at 373–383 K and calcined at 773–823 K for 5–6 h. The texture characteristics of samples were determined according to isotherms of methanol adsorption and by chroma-tographic method according to heat desorption of nitrogen.

The thermal analysis of fresh and carbonized catalysts has been carried out on the apparatus Q-1500D in the interval from room temperature up to 1273 K with 10°/min heating rate. The quantities of carbon, hydrogen and oxygen in CD were determined by elemental analysis. With the purpose of removal of reversibly adsorbed reaction products, unreacted feedstock material and water formed in the process, first, the samples were kept in vacuum at 373–393 K up to the fixed weight, then blown by helium on the apparatus for microanalysis. The concentration of paramagnetic centers in CD was determined according to EPR-spectra taken on microwave spectrometer IES-pE-3x. Diphenylpicrylhydrazin was the standard with concentration of spins 6.11×10^{15} spin g^{-1}.

IR-spectra of surface hydroxyl and functional groups in CD extracted by alcohol–benzene solution were taken on spectrophotometer UR-20 in the range from 400 to 3800 cm^{-1}. The catalytic reactions have been carried out on flow installation with the fixed bed of catalyst at atmospheric pressure. Catalysts were activated before the tests in air current at 773 K. Catalysts regeneration has been carried out in the same conditions. The reaction conditions were varied in the following intervals: temperature 723–823 K, ratio EB:air = 1:(4–8) mol/mol, space velocity on EB 0.5–1 h^{-1}. The results given in the article are related to the optimal conditions: temperature 760 K, space velocity 0.5 h^{-1}, ratio EB:air = 1:6 (mol).

In order to appreciate the acid–base properties of catalysts in the conditions close to catalytic reactions their activity in the reactions of dehydration and dehydrogenation of isopropanol at 523 K has been investigated [9]. The reaction products were analyzed by chromatographic method.

3. Results

The investigation of commercial silica gels of different type distinguished by values of specific surface, average radius and pores volume showed that these samples display various activity in OD of EB (Table 1). Thus, with increasing of average pores radius (from 1.1 up to 7.0 nm) the initial reaction period, in the course of which EB conversion rises up to constant value, CD quantity and styrene yield are increased. The initial period of reaction for narrow-pored silica gels is 1–2 h and for macroporous ones 5–6 h. CD are intensively formed in the initial period of reaction, however, the rate of CD accumulation on the catalyst surface (mg g^{-1} h^{-1}) is decreased gradually with time. In stationary reaction period maximal conversion of EB for the given catalyst is observed. The simultaneous increase of EB conversion, duration of initial reaction period and quantity of CD may testify that the formation and accumulation of CD on the catalyst surface result in formation of a more active catalytic system.

It should be noted that in the presence of air CD is formed in the more quantity than in its absence. At the same time the higher concentration of paramagnetic centers in CD discovered by EPR method (1.7×10^{17} spin g^{-1}) is observed in comparison with CD formed without oxygen in the analogous conditions (1.3×10^{16} spin g^{-1}).

In comparison with γ-Al_2O_3 silica gels have less activity in EB OD [6,7]. However, the activity of silica gels slightly grows after their modification by CaO. The values of EB conversion, selectivity on styrene and CD quantity in steady state over catalysts xCaO/SiO_2 prepared on the base of macroporous SiO_2-V are presented in Table 2. As seen from the table, with increasing of CaO quantity up to 1%, EB

Table 2
The influence of CaO quantity (wt.%) in xCaO/SiO_2 composition on OD of ethylbenzene[a]

Catalysts	Conversion of ethylbenzene (%)	Selectivity on styrene (%)	CD[b] (%)
SiO_2-V	47.4	76	17.5
0.5% CaO/SiO_2	52.2	80	10.0
1.0% CaO/SiO_2	59.6	83	8.5
1.9% CaO/SiO_2	42.8	80	5.5
2.9% CaO/SiO_2	35.4	64	3.0
4.5% CaO/SiO_2	25.2	55	1.0

[a] Temperature = 760 K, P_{EB} = 0.14 atm, P_{O_2} = 0.17 atm, space velocity = 0.5 h^{-1}.

[b] CD in steady state (wt.%).

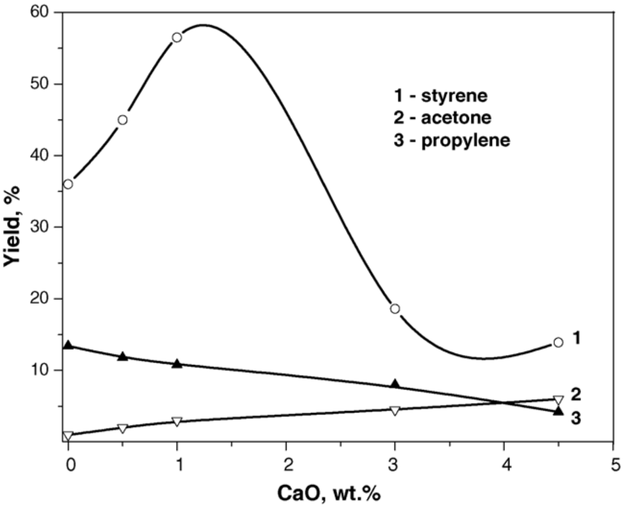


Fig. 1. The dependence of styrene (1), acetone (2) and propylene (3) yields from quantity.

conversion rises from 47.4 up to 59.6%. At further increasing of CaO quantity up to 4.5%, EB conversion and CD quantity are sharply decreased.

Investigations of dependence of reaction rate from oxygen and EB partial pressures in the range of 0.05–0.3 atm (helium was as a diluent) have shown that in the series of catalysts SiO_2-V–1% CaO/SiO_2–4.5% CaO/SiO_2 the change of reaction order with respect to oxygen is observed. Thus, if reaction order with respect to oxygen over SiO_2-V is equal to 1, then, in the case of 4.5% CaO/SiO_2, reaction order approaches to zero. The change of CaO quantity varies reaction order with regard to EB less. It may be supposed that CaO quantity exerts a more essential influence on activation of oxygen than on activation of ethylbenzene. It has been discovered by EPR method that at modification of silica gels by small quantities of CaO formation of anion vacancies is observed. Intensity of EPR signal practically is not changed at further growth of CaO quantity from 1.0 up to 4.5%.

With increasing CaO quantity from 0.5 up to 4.5% activity of catalysts in dehydration of isopropanol (as a measure of acidity) is decreased but in dehydrogenation of isopropanol into acetone (as a measure of basicity), vice versa, it is increased (Fig. 1). It is interesting to note that practically only reaction of isopropanol dehydration proceeds over SiO_2. treated by hydrochloric acid and 7% P/SiO_2. The extreme dependence of styrene yield (also selectivity) from calcium oxide concentration may be connected with presence of optimal ratio of acid and base centers taking part in activation of EB and oxygen which results in formation of catalytically active CD.

As has been already mentioned, with increasing average pore radius of silica gel from 1.1 up to 7.0 nm styrene conversion rises (Table 1). The analogous dependence is observed also for 1% CaO/SiO_2, prepared on the basis of different silica gels. It is seen from Fig. 2 that the bigger average pores radius, the stronger influence of calcium oxide is exerted on EB conversion. The character of dependence of stationary reaction period duration from average pores radius also remains, i.e. it is the smallest for 1% CaO/SiO_2-I (1 h) and is increased in case of 1% CaO/SiO_2-V up to 4–5 h (Fig. 3).

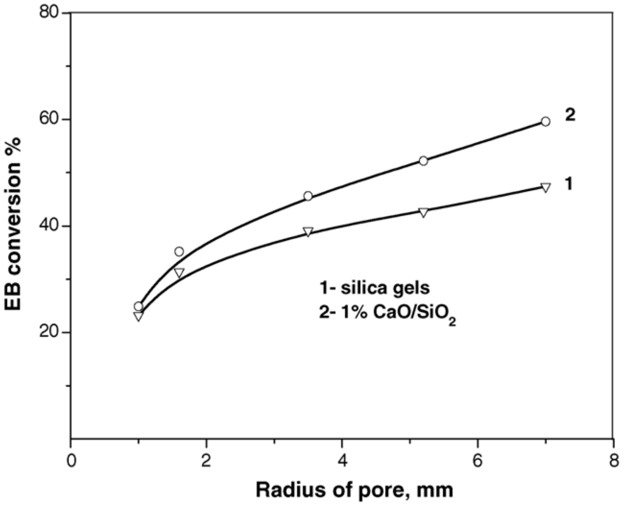


Fig. 2. The dependence of EB conversion from average radius of silica gels (1) and 1% CaO/SiO_2 pores (2) (temperature = 760 K, space velocity = 0.5 h^{-1}).

The thermal analysis of samples with CD shows that burn-out curves of CD formed over different catalysts in the same conditions are varied. At the treatment of initial silica gel $S1O_2$-V by EB in helium current CD are formed in the small quantity. The weak exothermic peak with maximum at 763 K points to it. Carrying out analogous treatment in the presence of air results in drastic increase of CD quantity and, also, DTA allows to observe a wide exothermic peak with maximums at 773 and 983 K, which point to complicated

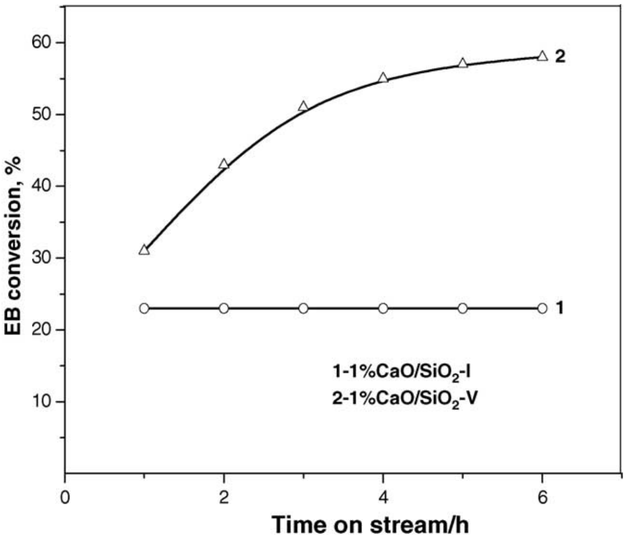


Fig. 3. The dependence of EB conversion from time on stream (temperature = 760 K, space velocity = 0.5 h^{-1}).

Table 3
OD of ethylbenzene over silica gel (sample V) modified by calcium and/or phosphorus (conditions are the same as in Table 2)

Catalyst	Conversion of ethyl-benzene (%)	Selectivity on styrene (%)	CD (%)
SiO_2-V	47.4	76	17.5
6% P/SiO_2	55.8	82	19.5
1% CaO/SiO_2	59.6	83	8.5
3% P/1% CaO/SiO_2	72.1	91	17.0
6% P/4.5% CaO/SiO_2	64.0	92	14.0

structure of CD formation. In the case of 1% CaO/SiO_2 the only exothermic peak with maximum at 773 K is observed. Increasing test duration from 6 up to 20 h results in just a little widening of the peak, which indicates formation of CD of a more homogenous composition than in the case of starting silica gel.

The treatment of SiO_2 and xCaO/SiO_2 by phosphoric acid results in increase of conversion of EB and selectivity on styrene (Table 3). However, the achievement of time of stationary state for phosphorus-containing catalysts is decreased down to 2 h. The dependence of styrene yield from content of phosphorus in yP/SiO_2 samples passes through a weakly marked maximum corresponding to 6–7% of phosphorus. Thermal analysis shows that CD quantity in the case of 7% P/SiO_2 is more than in SiO_2. Moreover, the temperature displacement of maximum of exothermic peak respective to CD burning-out in air medium up to 800–850 K is observed. It may be connected with a more condensed character of CD in the case of yP/SiO_2.

High conversion of EB is observed in the case of yP/xCaO/SiO_2 catalysts. The introduction of phosphorus into xCaO/SiO_2 composition decreases yield of CO_2, time of stationary state achievement and increases selectivity on styrene. The optimal quantity of phosphorus for this series of catalysts depends on content of CaO in the composition of xCaO/SiO_2 (Fig. 4). Maximum conversion of EB is observed for 1% CaO/SiO_2 and 4.5% CaO/SiO_2 at 3 and 6% contents of phosphorus, accordingly.

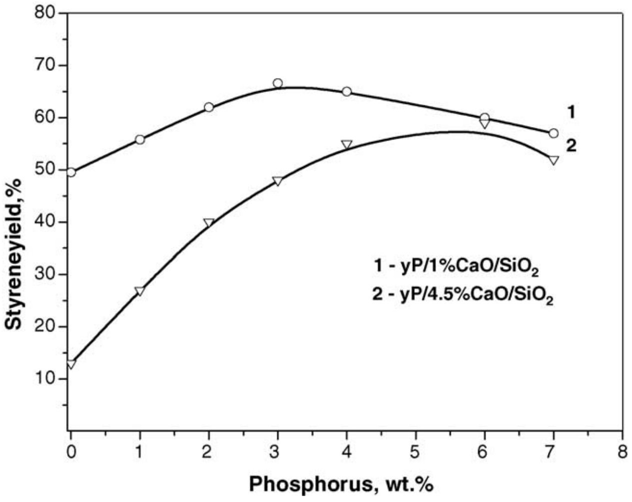
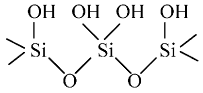


Fig. 4. The dependence of styrene yield from quantity of phosphorus in catalysts yP/1% CaO/SiO_2 (1) and yP/4.5% CaO/SiO_2 (2) (temperature = 760 K, space velocity = 0.5 h^{-1}).

4. Discussion

The possibility of carrying out OD of EB over silicates of alkaline-earth metals prepared by co-precipitation method was shown first in [8]. At the same time the high activity of beryllium- and magnesium-silicates has been marked. The next investigations showed that a more simple method of impregnation with following thermal decomposition of magnesium nitrate may be used for preparation of such a type of catalysts [10]. The same method of preparation has been used for catalysts of xCaO/SiO_2 series.

Hydroxylated surface of silicagel may be sketched out in the following way:



The chemical and adsorption properties of silica gel depend on number and reactivity of the surfaced silanol groups. Two forms of adsorption centers may exist over the surface of silica gel: (i) hydroxyl groups; (ii) coordinated-unsaturated atoms of silicon and surfaced electronegative atoms of oxygen nascent at dehydration of silica gel. The surface of dehydrated silica gel begins slightly to chernisorb oxygen, most likely, on the centers of $\not>$Si· type. The samples with super-stochiometric oxygen have expressed, pronounced oxidation power, which rises with increasing temperature up to the defined value at which irreversible change of framework structure begins. The comparative thermogravimetric analysis of SiO_2 and xCaO/SiO_2 does not reveal a significant difference in the thermal behavior of these samples excepting the change of concentrations of surfaced hydroxyl groups. The desolvation process of silica gel impregnated by calcium nitrate is completed at 573–773 K and the adsorption of cations is started over surface. The nature of calcium cations interaction with the surface of silica gel is complicated enough and leads to a change of pore structure and concentration of hydroxylic groups over the modified sample. The surface of silica gel has a weak acidity and many ions are rather strongly and even irreversibly held by forces, which arise, in addition, to the ion gravitation. Incomplete tetrahedrons $[SiO_3]^+$ at temperatures higher than 473 K vary its orientation and go out from framework leaving the volumetric defects over surface. As a result, the surface of silica gel becomes more opened for aciivation of reacting molecules.

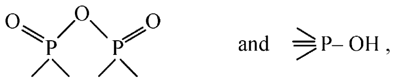
The characteristic feature of the given series of catalysts is a presence of non-stationary period in the beginning of reaction stipulated by the formation and accumulation of CD that is accompanied by increase of EB conversion up to maximum and a relatively constant value. Catalysts entirely regenerated by air at 773 K as well as fresh samples possess low starting activity, however, in some hours of work conversion of EB reaches the maximal value.

The role of CD in the reaction of EB OD is discussed in papers [2,6,7,11]. It has been shown that activated carbons display high selectivity at low temperatures as well [11–13]. However, very fast decline of activity with time is characteristic for them but at regeneration the gasification of coal starts to proceed [14]. From this point of view, creation of catalysts promoting formation of catalytically active CD over its surface is a more convenient way of formation of catalytically active system for OD of EB. At the same time catalyst itself is not an inert carrier for CD but it exerts a direct influence on the formation of active CD from EB and oxygen. In the absence of oxygen much less CD are formed from EB in identical conditions and they are not active enough in the formation of styrene. At the passing of mixture EB + helium via layer of 3% P/l% CaO/SiO_2 catalyst for 3–4 h (yield of styrene is insignificant) and then change of helium by air, the increase of EB conversion is observed for 3 h. After achievement of stationary reaction period conversion of EB is less than in the case of carrying out the reaction from the very outset in the presence of air. Quite likely, styrene—the OD product of EB rather than EB itself takes part at the formation of catalyticalJy active CD. If instead of EB at the beginning of reaction isopropylbenzene, *o*-xylene. toluene or benzene are taken, CD resulting from them in the presence of oxygen possess much less activity in OD of EB into styrene. Moreover, an addition of the small quantities (2–10%) of styrene to the initial EB does not exert a braking effect on the reaction rate and slightly decreases the duration of the reaction induction period. Thus, over the catalyst surface having the necessary properties the evolution of EB and oxygen molecules takes place with formation of defined structures of CD at the beginning, which further begin to operate as a real catalyst.

From various types of SiO_2 (quartz glasses, aerosils) only the rnacroporous silica gels show good activity in the EB OD reaction. After treatment by acid activity of silica gel is increased, however it is accompanied by excessive accumulation of CD leading to further reduction of styrene yield. EPR-spectra show that concentration of the paramagnetic centers in CD is increased with the rise of CD quantity and continues to grow after establishing of stationary reaction period. The concentration of the paramagnetic centers after 2 h of catalyst work is 1.7×10^{17} spin g^{-1}, but after 20 h goes up to 3.4×10^{19} spin g^{-1}. The accumulation process of excessive CD quantity may be slowed down by modification of SiO_2 with different oxides. In fact, the introduction of 0.5–1% CaO into the silica gel composition changes the acid–base properties and texture characteristics of the latter. Conversion of EB over 1% CaO/SiO_2 catalyst is higher than over SiO_2 at the less rate of CD accumulation in the stationary reaction period. Calcium atoms appear to influence favorably on the formation of anionic vacancies, which make the surface ofSiCh more open for activation of EB molecules with participation of coorditiately unsaturated Si^{4+} ions, which are electron-acceptor centers [15]. In the activation of EB the surfaced hydroxyl groups may participate as well. The activation of oxygen can be carried oui on the electron-donor centers representing anions of the lattice oxygen, anionic vacancies, concentrations of which, according to EPR-spectra, increase when CaO is introduced into silica gel composition.

Still higher increase of EB conversion and selectivity on slyrene in the case of *y*P/*x*CaO/SiO_2 is likely to be connected with some factors. So, at the impregnation of phosphoric acid on silica gel the new hydroxyl groups appear $\rangle\mathrm{Si{-}}\overset{|}{\underset{\|}{\mathrm{P}}}\mathrm{{-}OH}$, characterized by a higher electron-acceptor ability than $\rangle\mathrm{Si{-}OH}$ groups [16].

The thermal treatment leads to formation of surface groups:



which are reversibly rehydroxylatcd into acid groups partly covering the surface [17]. The electron-acceptor properties of catalysts are increased because of a bigger electronegativity of phosphorus in comparison with silicon (2.1 and 1.8, accordingly). The investigation of texture characteristics of phosphorus-containing silica gels shows that at the introduction of phosphoric acid the specific surface is decreased but the total pores volume is not changed at increasing their average pores radius. On the other hand, phosphoric acid, neutralizing a part of strongly basic centers, reduces yield of CO_2 and thereby increases selectivity on styrene. The presence of maxima in dependences of styrene yield on phosphorus content in *y*P/*x*CaO/SiO_2 samples is likely to be connected with the optimal ratio of the concentrations of the centers activating EB and oxygen. On their basis catalytically active structure of CD is formed.

The elemental analysis of CD, extracted by alcohol–benzene solution from active OD catalyst, which is in stationary state, indicates the following CD composition (in wt.%): carbon 76–81, oxygen 16–19 and hydrogen 3–5. IR-spectra of the obtained extract reveal a number of absorption bands typical for carbonyl-containing groups. It may be supposed that these groups take an immediate part in the formation of styrene from EB. Duration of stable work of catalytic system is determined by the ratio of consumption and resumption rates of oxygen-containing groups in the CD composition. In contrast to activated coals which are deactivated very fast [11–13], in the case of 3% P/l% CaO/SiO_2 catalyst a slow decrease of styrene yield is observed only in 8–10 work hours. However, cessation of EB supply and catalyst aeration for 30–40 min practically restore maximal conversion of EB. Furthermore, calcium- and phosphorus-containing catalysts are characterized by high accumulation rate of CD in the initial reaction period (63–

68 mg g^{-1} h^{-1}) and drastic decrease of this value in stationary reaction period.

Thus, promoting influence of optimal quantities of CaO and phosphorus on the activity of silica gels appears to be connected with creating and balancing of acid and base centers of definite force activating EB and oxygen molecules that further results in formation of catalytically active CD in the optimal quantity. CD extreme accumulation on the catalyst surface and its excessively condensed character promotes deactivation of catalytic system in EB OD.

5. Conclusion

OD of EB over silica gels and their forms modified by calcium and/or phosphorus is accompanied in the initial reaction period by the formation and accumulation of CD over catalysts surface. In the stationary reaction period a catalytically active system is CD/catalyst in which the catalyst is not an inert carrier. On the contrary, the composition, acid–base properties and texture characteristics of the catalyst exert an important influence on the structure and activity of CD, containing in its composition carbonyl and other oxygen-containing groups. Sometimes, EB conversion and selectivity on styrene at 760 K are higher than 70 and 90%, accordingly. The decrease of EB conversion at the continuous work of catalytic system may be connected with reduction of concentration of oxygen-containing groups restored by partial regeneration with air.

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