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Kinetic Investigations of the Oxydehydrogenation of Ethylbenzene

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The reaction mechanism and kinetics of the oxydehydrogenation of ethylbenzene to styrene have been investigated. It has been shown that the actual catalyst is an active coke deposited on a carrier, zirconium phosphate. The active coke is a C/H/O compound, which acts as an organic redox system. The reaction system can be described by five reaction equations. The main reaction is of a Mars–van-Krevelen type and the side reactions are described by power laws. © 1988 Academic Press, Inc.

INTRODUCTION

Until now, styrene has mainly been produced via a catalytic dehydrogenation of ethylbenzene. Recently, however, the oxydehydrogenation of ethylbenzene has been reported as a promising alternative (1–12),

$$\text{ethylbenzene(EB)} + \tfrac{1}{2}O_2 \rightarrow \text{styrene(STY)} + H_2O \quad -\Delta H_R = 120\ \text{kJ/mol}.$$

In the cases of zirconium phosphate, γ-alumina, nickel phosphate, etc., as catalytic material, a black carbonaceous deposit is formed, which certainly participates during the course of the reaction. How this occurs is discussed in the literature given above. In comparison with earlier publications (*1*, *2*), the present paper gives a more detailed investigation of the mechanism of coke formation and its action as a catalyst, as well as quantitative kinetic data.

EXPERIMENTAL

The reaction was carried out in a nearly isothermal electrically heated microintegral reactor (Fig. 1). The height of the catalytic bed was approximately 80 mm and varied according to the operation conditions. As base material for the catalyst, crystalline zirconium phosphate, $Zr(HPO_4)_2 \cdot xH_2O$ (ZrP′), was prepared according to Ref. (*1*) with a BET surface area of circa 30 m^2/g. Liquid ethylbenzene fed via a metering pump (Ismatec type PMP 10), and gases (nitrogen and oxygen) introduced using mass flow meters (Brooks type 5835, 5810) were mixed and preheated in an evaporator (see Fig. 2). The reactants and products (unconverted ethylbenzene, O_2, styrene, CO_2, CO, and H_2O) were analyzed automatically using a microprocessor-controlled gas chromatograph (Packard Type GC 429) in combination with a two-channel integrator (Spectraphysics 4200). For details of the analysis, see Ref. (*13*). Only those experiments in which the mass flows of C, H, and O in the inlet varied no more than ±5% from those at the outlet have been further analyzed. Using the respective criteria in Ref. (*13*), mass- and energy-transport limitations could be excluded. Preliminary experiments without a catalyst have shown that a homogeneous reaction and catalytic wall effects can both be excluded. The temperature was varied between 623 and 723 K, modified residence time was between 0.3 and 3.14 g ZrP′/(g EB/h), molar ratio N_2/EB was between 7 and 15, and

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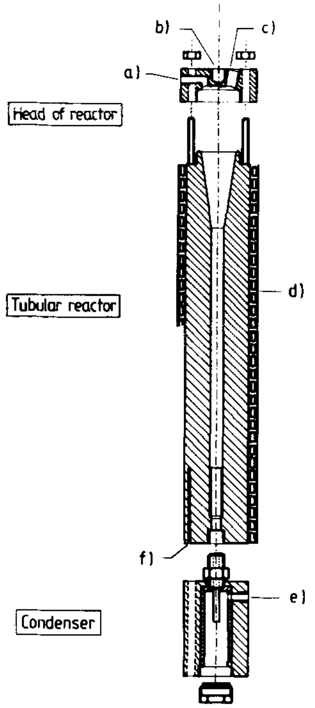

FIG. 1. Scheme of laboratory reactor (inner tube diameter, 10 mm; tube length, 300 mm). (a) Reactant inlet; (b) thermocouple fitting; (c) catalyst inlet; (d) heating jacket; (e) product outlet; (f) thermocouple bore hole.

molar ratio N_2/O_2 was between 6.66 and 22.5.

Conversion X and selectivities S_i used in this article are defined as

$$X = \frac{[EB]_0 - [EB]}{[EB]_0} \times 100\%$$

$$S_{STY} = \frac{[STY]}{[EB]_0 - [EB]} \times 100\%$$

$$S_{CO_2} = \frac{[CO_2]/8}{[EB]_0 - [EB]} \times 100\%$$

$$S_{CO} = \frac{[CO]/8}{[EB]_0 - [EB]} \times 100\%.$$

Yields Y_i are obtained by multiplication of X with the respective S_i.

RESULTS AND DISCUSSION

Catalyst Formation

The catalytic activity of freshly prepared ZrP′ was practically zero. As shown in Fig. 3, the conversion of ethylbenzene during 3 h of time on stream increased up to a stationary value of about 50% and the selectivity of styrene to approximately 90%. Simultaneously, crystal water evaporated which converted ZrP′ into ZrP and increased coke deposits. The coke could be burned off totally by air, leaving water-free white ZrP carrier. A new start-up of the reaction on this carrier (compare curve 2 in Fig. 4) showed characteristics similar to those of a fresh catalyst (curve 1 in Fig. 4, which is the same as that in Fig. 3). Repeated total burn-off under the same condi-

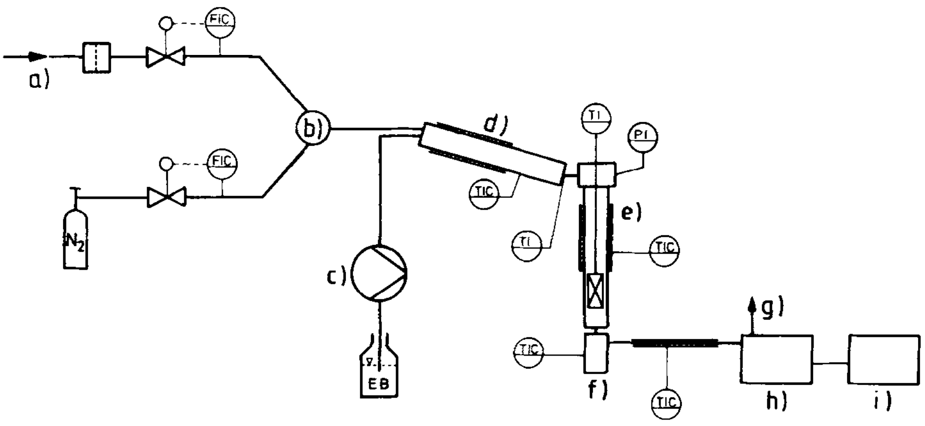

FIG. 2. Scheme of experimental apparatus. (a) Pressurized air; (b) mixer; (c) metering pump; (d) evaporator; (e) tubular reactor; (f) condenser; (g) vent; (h) gas chromatograph; (i) integrator.

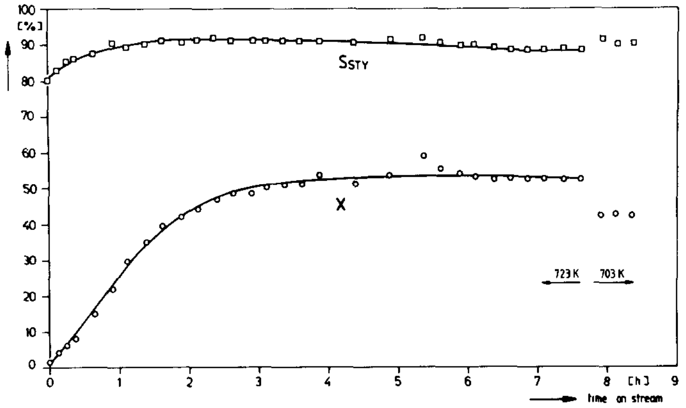

FIG. 3. Ethylbenzene conversion (X) and styrene selectivity (S_{STY}) versus time on stream for fresh ZrP′ (T = 723 K; modified residence time: 3 g ZrP′/(g EB/h); molar feed composition, EB/N_2/O_2 = 1/10/1).

tions always resulted in the same start-up activity as that in curve 2. Coked ZrP showed the stationary plateau activity and selectivity almost instantly (compare curve 4 in Fig. 4), whereas a partially burned off ZrP showed behavior between these two extremes (compare curve 3 in Fig. 4).

These results clearly show the active coke to be the true catalyst. This was supported by the observation that without oxygen in the feed no active coke was formed and consequently, at temperatures up to 723 K, no styrene was formed. Therefore, ZrP itself does not catalyze the dehydrogenation of ethylbenzene under these conditions. The dark black active coke was formed only in the presence of oxygen according to an "oxidative" condensation. An oxygen-free feed of styrene produced a gray polymer layer, which had a totally different structure compared to that of active coke. The increase in activity with time on stream was obviously dependent on the suitability of the surface to promote the formation of this active coke. Freshly prepared, thermally untreated ZrP′ seemed to

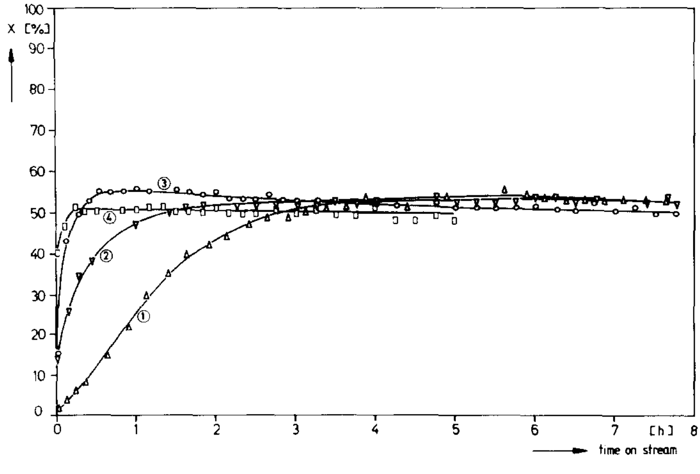

FIG. 4. Ethlybenzene conversion as function of time on stream for different situations: (1) fresh ZrP′; (2) ZrP after a total burn-off of coke; (3) ZrP after a partial burn-off of coke; (4) coked ZrP.

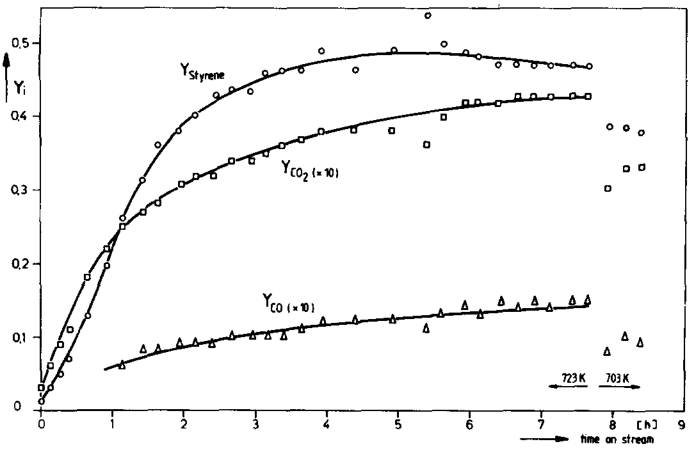

FIG. 5. Yield of products versus time on stream for fresh ZrP′ (conditions as in Fig. 3).

hinder the coke formation, possibly due to the simultaneous evaporation of crystal water, which resulted in a slower increase of activity (curve 1 in Fig. 4). This is in accordance with the results in Ref. (*14*), where the change in the surface properties of ZrP′ from heating it up to reaction conditions was analyzed by TPD measurements. It was also shown that the initial acidity of fresh ZrP′ disappeared totally at the prevailing reaction temperatures. Surface acidity was, therefore, a precondition neither for the formation of active coke on ZrP nor for the reaction itself.

Product Yield

Figure 5 shows that the increasing yields of styrene, CO, and CO_2 with time on stream run parallel to the increasing amount of active coke. The fact that the yield of carbon oxides reached an asymptotic stationary value with the absence of any aromatic oxidation products suggests that the carbon oxides are formed in a consecutive reaction from the active coke layer by oxidation. Similar results have been reported for γ-alumina used as a carrier (*9–11*).

Reaction Scheme

As the experimental results in Figs. 3–5 clearly show, the initial activity of the coke-free catalytic system is practically zero. This fact excludes zirconium phosphate from being the catalytically active species when combined with the observation that the partial oxidation with air or reduction with ethylbenzene affects the catalytic activity of the coked catalyst. The slow decrease in styrene formation after cutting off the oxygen in the feed gas shows the presence of oxidizing groups in the active coke. These can be reoxidized, i.e., reactivated, by reintroducing oxygen into the feed. The catalytic activity must therefore come from reactive, oxygen-containing groups in the active coke, which forms during the induction period on the zirconium phosphate carrier.

In Refs. (*13, 15*) it was shown, using several surface-analyzing techniques, that the active coke was a C,H,O-containing structure whose composition changed slowly with time on stream into a structure with a higher carbon content. The C/H ratio increased steadily from values of approximately 1.4 after 7 h to circa 4.9 after 30 h on stream. Studies by SIMS, ESCA and ESR indicated that the active coke contained CO groups of the aroxyl/phenol type (*15*). In additional experiments in which the catalytic system had been pretreated with an $N_2 : O_2$ mixture (10 : 1 at 723 K) for 10 min, an increase in ethylbenzene

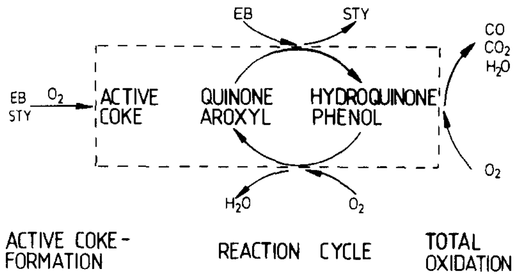

FIG. 6. Reaction scheme for the oxydehydrogenation of ethylbenzene on ZrP covered with active coke.

conversion was observed (after 5 min $X_{EB} = 58\%$; 19 min $X_{EB} = 52\%$; and 26 min $X_{EB} = 46\%$, which was the degree of conversion before the treatment). After treating the catalytic system with an N_2 : EB mixture (10 : 1 at 723 K) for several hours, a greatly decreased activity was observed under the normal operation conditions (with an N_2/O_2/EB mixture).

The EB/STY molar ratio during normal reaction conditions was 1.5, but after treatment with an N_2/EB mixture, styrene was still produced (e.g., a ratio of 32 after 2 h). This indicated that styrene was formed via surface oxygen groups in the active coke, which acted as a redox system. Similar results, supported by IR measurements (*16*), have been reported in Refs. (*13, 17*) for a polynaphthoquinone catalyst. By the addition of oxygen to the feed mixture of N_2/EB, the activity of the catalyst increased again within 10 min to a constant, but lower, steady-state conversion (X_{EB} = 39%). This decay of activity induced by long-lasting reducing conditions was irreversible. Only by a new, total burn-off of the coke could the original activity be restored.

On the basis of all the above results, the reaction scheme shown in Fig. 6 for the oxydehydrogenation of the ethylbenzene is proposed. It is an organic redox cycle. Aromatic compounds react with oxygen in an oxycondensation to form the active coke, whose level remains constant, if a certain surface coverage is reached (see Ref. (*1*)). From this point on, the total oxidation of the coke to CO_x and H_2O is in equilibrium with its new formation from EB and O_2. EB is dehydrogenated at the active sites in their oxygenated form, thereby reducing these sites simultaneously. In a second step, the reduced sites are reoxidized by oxygen and form H_2O simultaneously. A change of the reactant feed to a pure N_2 purge stream gives long-lasting EB (and STY) tailing in the outlet stream. This indicates strongly that EB is adsorbed at the active coke surface.

Kinetics

On the basis of the above results, the following detailed redox mechanism for the main reaction can be formulated,

$$\mathrm{EB} + l_{\mathrm{ox}} \underset{k_{1-}}{\overset{k_1}{\rightleftharpoons}} \mathrm{EB} \cdot l_{\mathrm{ox}}; \quad K_1 = k_1/k_{1-} \tag{1}$$

$$\mathrm{EB} \cdot l_{\mathrm{ox}} \xrightarrow{k_2} \mathrm{STY} \cdot l_{\mathrm{red}} \tag{2}$$

$$\mathrm{STY} \cdot l_{\mathrm{red}} \underset{k_{3-}}{\overset{k_3}{\rightleftharpoons}} \mathrm{STY} + l_{\mathrm{red}}; \quad K_3 = k_3/k_{3-} \tag{3}$$

$$l_{\mathrm{red}} + \tfrac{1}{2}\mathrm{O}_2 \underset{k_{4-}}{\overset{k_4}{\rightleftharpoons}} l_{\mathrm{ox}} + \mathrm{H_2O}; \quad K_4 = k_4/k_{4-}. \tag{4}$$

In this scheme, the hydrogen abstraction (step (2)) is regarded as the rate-determining step, in agreement with other authors (*11, 17*). Although the carbon oxides are formed through the active coke according to Fig. 6, the stationary stoichiometry for the oxidation reactions must be based on

$$\mathrm{EB} + 6.5\mathrm{O_2} \xrightarrow{k_5} 8\mathrm{CO} + 5\mathrm{H_2O} \tag{5}$$

$$\mathrm{EB} + 10.5\mathrm{O_2} \xrightarrow{k_6} 8\mathrm{CO_2} + 5\mathrm{H_2O} \tag{6}$$

$$\mathrm{STY} + 6\mathrm{O_2} \xrightarrow{k_7} 8\mathrm{CO} + 4\mathrm{H_2O} \tag{7}$$

$$\mathrm{STY} + 10\mathrm{O_2} \xrightarrow{k_8} 8\mathrm{CO_2} + 4\mathrm{H_2O} \tag{8}$$

For the surface reactions (1) through (4) the following rate equations can be formulated:

$$r_1 = k_1 c_{\mathrm{EB}} \theta_{\mathrm{ox}} - k_{1-} \theta_{\mathrm{EB}} \tag{9}$$

$$r_2 = k_2 \theta_{\mathrm{EB}} \tag{10}$$

$$r_3 = k_3 \theta_{\mathrm{STY}} - k_{3-} c_{\mathrm{STY}} \theta_{\mathrm{red}} \tag{11}$$

$$r_4 = k_4 \sqrt{c_{\mathrm{O_2}}}\, \theta_{\mathrm{red}} - k_{4-} c_{\mathrm{H_2O}} \theta_{\mathrm{ox}}. \tag{12}$$

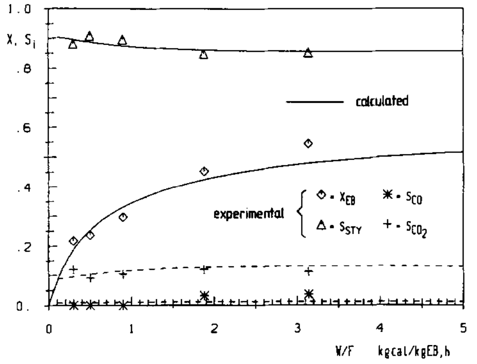

FIG. 7. Experimental results and calculated conversion (X) and selectivity (S_i) curves for oxydehydrogenation of ethylbenzene (T = 727 K; P = 1.1 bar; N_2/EB = 10; N_2/O_2 = 10).

Under the assumption that the total number of active sites is constant

$$\theta_{ox} + \theta_{EB} + \theta_{red} + \theta_{STY} = 1 \quad (13)$$

the global rate of styrene formation can be written as

$$r_2 = \frac{k_2 K_1 c_{EB} \sqrt{c_{O_2}}}{\sqrt{c_{O_2}} + K_1 c_{EB} \sqrt{c_{O_2}} + c_{H_2O}/K_4 + c_{H_2O} c_{STY}/K_3 K_4}. \quad (14)$$

According to Fig. 6 the total oxidation to carbon oxides occurs via a consecutive reaction EB → active coke → CO, CO_2. Due to the amount of active coke remaining constant in the stationary state, the active coke is viewed as an intermediate unimportant for the derivation of the kinetic equations. The formation of the carbon oxides is therefore formally described by a reaction between ethylbenzene and oxygen. Simple power law equations have been utilized, because for reactions (5)–(8) no details of the very complex actual reaction mechanism are known. Because of the low yields of carbon oxides (cf. Fig. 5) the resulting error should be small,

$$r_5 = k_5 c_{EB} c_{O_2} \quad (15)$$

$$r_6 = k_6 c_{EB} c_{O_2} \quad (16)$$

$$r_7 = k_7 c_{STY} c_{O_2} \quad (17)$$

$$r_8 = k_8 c_{STY} c_{O_2}. \quad (18)$$

The temperature dependence of rate constants, as well as equilibrium constants, is assumed according to

$$k_j = k_{0j} \exp(-E_i/RT), \qquad j = 2, 5, 6, 7, 8 \quad (19)$$

$$K_4 = K_{04} \exp(-\Delta G_4^\circ/RT) \quad (20)$$

$$K_j = K_{0j} \exp(-\Delta H^\circ_{sorpt j}/RT), \qquad j = 1, 3 \quad (21)$$

A preliminary, physically meaningful estimate of ΔG_4°, K_{0j}, and $\Delta H^\circ_{sorpt j}$ could be made independently via an incremental method (*18*), using the oxidation of hydroquinone to quinone as a model reaction and the standard sorption entropy and enthalpy according to the results in Ref. (*19*).

A first estimate for the activation energies E_5 through E_8 was made using values for the total oxidation of carbon, as given in Ref. (*20*). As a reactor model, a pseudo-

TABLE 1

Kinetic Parameters for the Oxydehydrogenation of Ethylbenzene (*22*)

$K_{01} = 0.153 \times 10^{-4}$ m^3/kmol	$\Delta H^\circ_{ad1} = -0.675 \times 10^2$ kJ/mol
$k_{02} = 0.406 \times 10^{14}$ kmol/kg cat, h	$E_2 = 0.180 \times 10^3$ kJ/mol
$K_{03} = 0.450 \times 10^3$ kmol/m^3	$\Delta H^\circ_{des3} = 0.142 \times 10^3$ kJ/mol
$K_{04} = 0.642 \times 10^{-3}$ (kmol/m^3)$^{1/2}$	$\Delta G_4^\circ = -0.750 \times 10^2$ kJ/mol
$k_{05} = 0.217 \times 10^{13}$ m^6/kg cat, kmol, h	$E_5 = 0.150 \times 10^3$ kJ/mol
$k_{06} = 0.111 \times 10^{14}$ m^6/kg cat, kmol, h	$E_6 = 0.146 \times 10^3$ kJ/mol
$k_{07} = 0.258 \times 10^{12}$ m^6/kg cat, kmol, h	$E_7 = 0.150 \times 10^3$ kJ/mol
$k_{08} = 0.167 \times 10^{13}$ m^6/kg cat, kmol, h	$E_8 = 0.147 \times 10^3$ kJ/mol

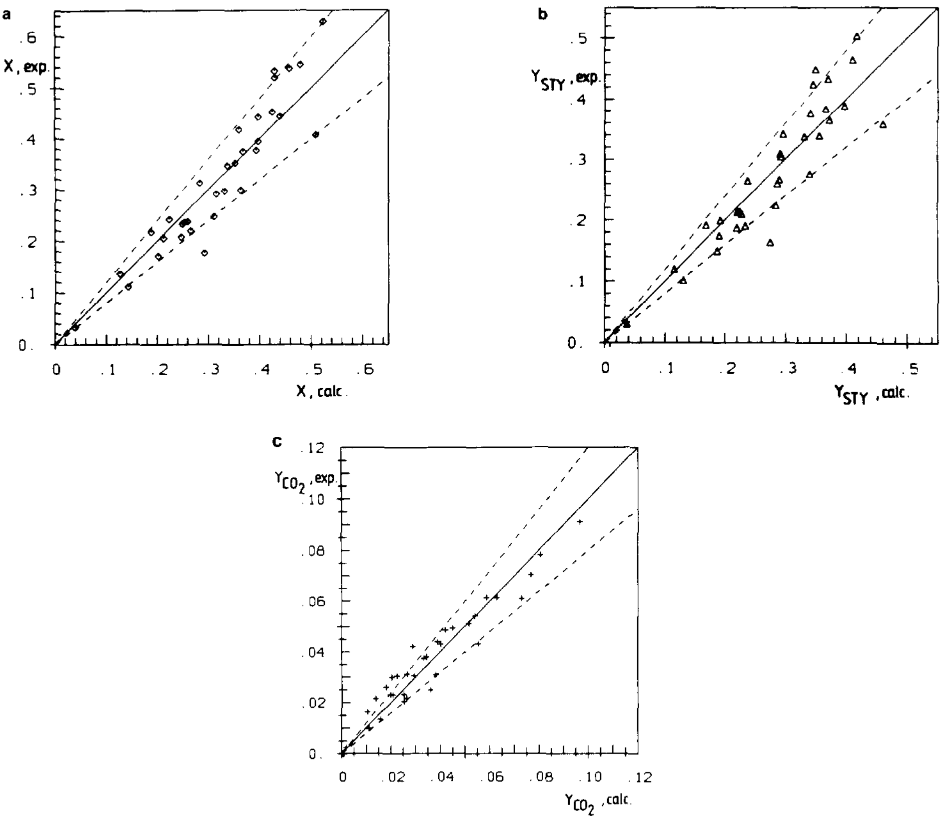

FIG. 8. Parity charts for the oxydehydrogenation of ethylbenzene. (a) Ethylbenzene conversion; (b) styrene yield; (c) CO_2 yield.

homogeneous plug–flow model was applied.

All experimental data have been used in a nonlinear regression with the COMPLEX routine (*21*) and a weighted least-squares objective function to finally arrive at the kinetic parameters given in Table 1.

A typical fit of experimental data with these model parameters is depicted in Fig. 7. The parity charts in Fig. 8 give an idea of the goodness of fit for all experiments.

CONCLUSIONS

It has been shown that the oxydehydrogenation of ethylbenzene on zirconium phosphate can be described by a redox mechanism with a carbonaceous structure deposited on the inorganic carrier containing quinoid or other oxygen-containing groups. Mechanistic rate equations can then be formulated with physically meaningful parameters. The increase in styrene yield is obviously limited by sorption equilibria of the reaction products, as demonstrated by Eq. (14). Only by promoting styrene desorption from the catalyst surface can higher yields be expected.

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