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Deactivation of styrene catalysts: A microkinetic modelling approach to technical catalysts

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Introduction

The dehydrogenation of ethylbenzene (EB) to styrene (St) is a technically important reaction, catalyzed by K-promoted iron oxides with steam in excess in the feed [1]. Despite a large number of investigations [1-3], many basic questions concerning the active phase(s), the role of K as promotor, the role of structural promotors and the deactivation behaviour are still under discussion. Aiming at a microkinetic modelling of the process, we have collected basic adsorption-desorption data for the interaction of EB, St and water on unpromoted and K-promoted iron oxides using surface science methods in ultrahigh vacuum (UHV). Samples were prepared in UHV as ~10nm thick films of single crystalline quality, grown epitaxially on a Pt(111) substrate [2,4]. The starting phases include hematite α -Fe₂O₃(0001), magnetite Fe₃O₄(111), K- β -ferrite-like phases K_xFe₂₂O₃₄(0001) ($x \leq 2$) and K-ferrite KFeO₂ (polycrystalline). After characterization of the thin films in UHV, they were transferred under vacuum into a stagnation point microflow reactor [5] where reactivity and deactivation behaviour was studied quasi *in-situ* under realistic conditions ($p_{EB}=3.3$ mbar, $p_{H_2O}=33$ mbar, $T=870$ K). Also the influence of the addition of O₂ ($p_{O_2} \leq 1.9$ mbar) for the prevention of catalyst reduction was studied. After reaction, the films were transferred back into UHV for post-analysis of surface composition, order and phase composition [6].

Unpromoted model catalysts

Both the experimental results on reactivity and deactivation and their microkinetic modelling were presented and discussed in detail in [6,7]. Fig. 1 summarizes the results on unpromoted model catalyst films. Before the reaction experiment and at the positions marked by arrows, the samples were characterized in UHV concerning the amount of carbonaceous deposits (Auger electron spectroscopy, AES) and the phase of the substrate (low energy electron diffraction, LEED after oxidative removal of coke). These data were used in microkinetic modelling (see below). Qualitatively, fig. 1 shows that Fe₂O₃ is initially more active than Fe₃O₄, but both deactivate to the same final state where both are covered by coke. The activity of coke is thus low but not zero. In the final state, Fe₂O₃ is completely reduced to Fe₃O₄. Addition of O₂ (here $p_{O_2}/p_{EB}=0.55$) prevents deactivation. The final phase is predominantly Fe₂O₃ and the coke coverage is low. The lower initial activity of Fe₃O₄ may be explained by a stronger adsorption bond, especially for the product St which causes self-poisoning of the surface [8].

In order to model the observed behaviour, an elementary step kinetics was set up [7]. Fig. 2 shows all included partial reaction steps. From the altogether 30 reaction parameters, 18 were known from adsorption-desorption studies in UHV [2,9,10]. The remaining 12 parameters were sequentially fitted to the reactivity measurements in fig. 1. Since Fe₃O₄

does not undergo reduction, the initial conversion can be ascribed to pure Fe_3O_4 and the final activity to coke. 5 parameters were fitted to this reactivity measurement. Further 4 parameters were then fitted to the Fe_2O_3 measurement and the final 3 parameters related to the influence of O_2 to the third reactivity measurement in fig. 1. The phase composition of the samples resulting from simulation is presented in fig. 3, together with the experimental data corresponding to the analysis at the positions of the arrows in fig. 1.

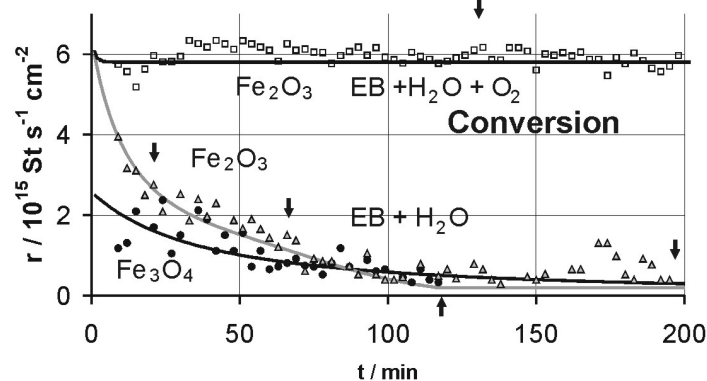


Fig. 1. Time dependence of the conversion rate of EB to St in the microflow reactor over single crystalline Fe_2O_3 and Fe_3O_4 films with and without addition of O_2 . Arrows indicate positions where the sample was analysed after transfer into UHV. Lines represent the kinetics based on the mechanistic model (fig. 2).

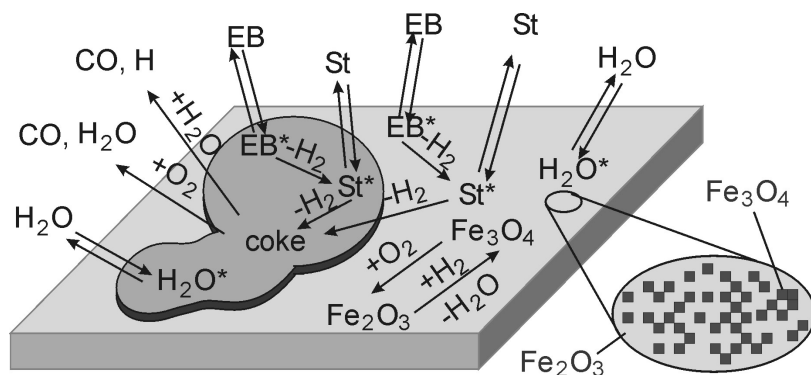


Fig. 2. Mechanistic catalyst model indicating all involved phases and all considered reactions. For the oxide Fe_2O_3 and Fe_3O_4 domains (reflecting the phase composition) are assumed. Coke is assumed to form islands.

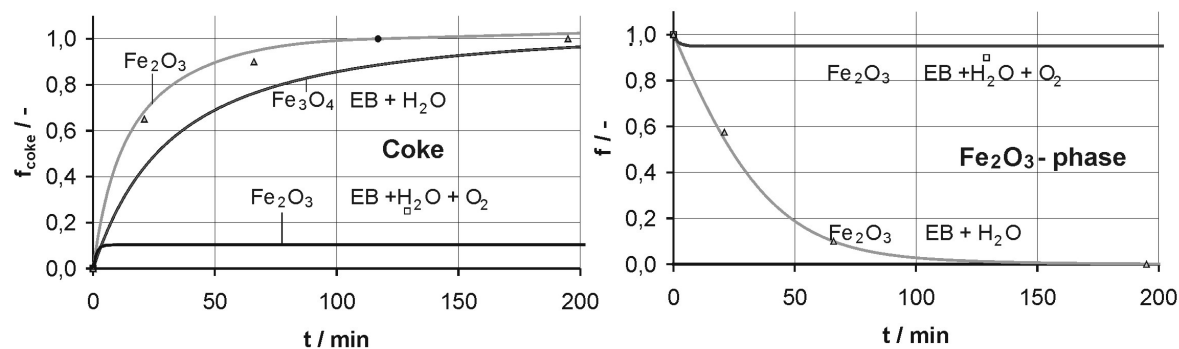


Fig. 3. Fraction of the surface covered by coke (left) and fraction of the oxide consisting of Fe_2O_3 (right, rest to 100% is Fe_3O_4) from simulation. The squares and triangles are the experimental values measured after transfer of the sample to the UHV chamber (arrows in fig. 1).

The derived kinetics was applied to the dynamic response of the conversion upon switching O_2 off and on. The excellent agreement shown in Fig. 4 proves the high quality of the modelling.

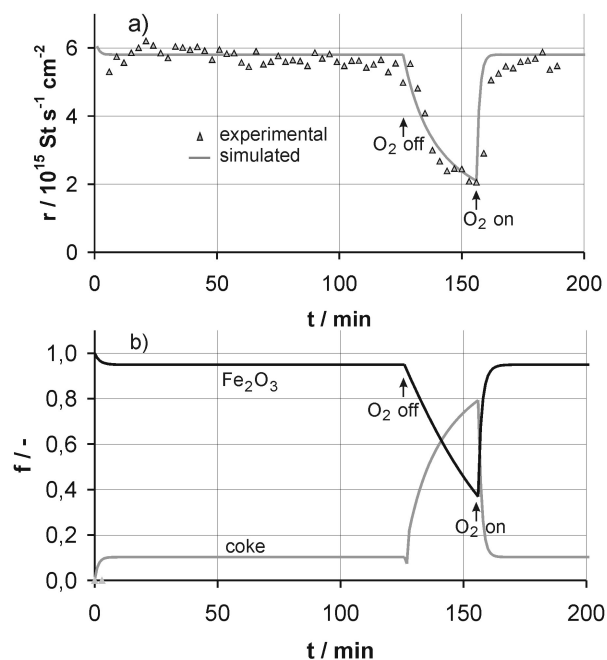


Fig. 4: Evaluation of microkinetics for EB to St conversion with addition of O_2 to the feed ($\text{EB:H}_2\text{O:O}_2=1:10:0.55$). (a) Dynamic response for O_2 off-on, triangles: experiment, line: modelling. (b) Surface composition from modelling.

K-promoted model catalysts

The role of promotion by K was tested in a number of reactivity measurements in the microflow reactor using epitaxial films with varying K-content. The samples were prepared in UHV by deposition of K on Fe_2O_3 or Fe_3O_4 , followed by annealing. For low K-content, the films are well ordered, corresponding to $\text{K}_x\text{Fe}_{22}\text{O}_{34}$ ($x \leq 2$) [11]. For high K-content, the films are not long-range ordered. Their composition may reach that of KFeO_2 which cannot grow homoepitaxially on the used Pt(111) substrate or on one of the iron oxides [11].

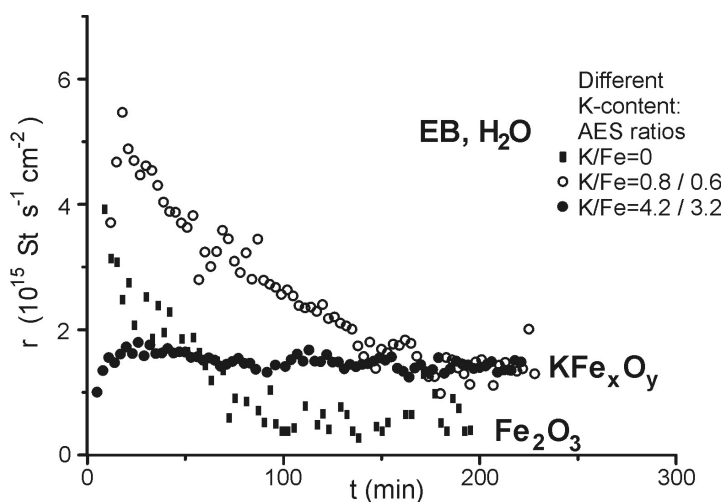


Fig. 5. Time dependence of the experimentally determined conversion rate of EB to St over K-promoted single crystalline samples. The K content is expressed as height ratios of the main Auger peaks of K and Fe, measured before and after the reaction experiment.

Fig. 5 shows the reactivity behaviour for films with different K-content and compares it to the unpromoted case. Deactivation is clearly slower after K-promotion and the deactivation time constant increases with K-content. However, the initial conversion drops with increasing K-content of the surface. Fig. 6 summarizes this behaviour. The decrease of the initial conversion with increasing K-content shows immediately that K has no catalytic activity. The decreases may be due to competition for surface sites. However, K is important for the prevention of deactivation. Both the build-up of coke and the reduction of the oxide are slower on K-promoted samples as checked by separate experiments [6].

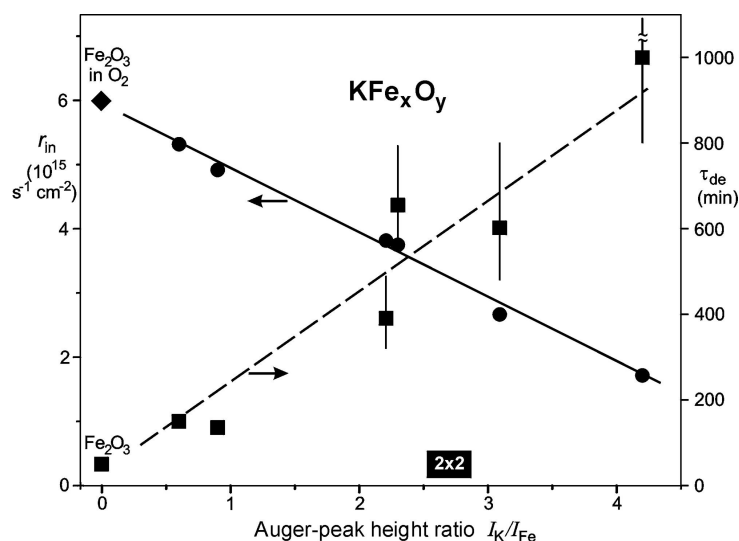


Fig. 6. Initial St conversion rate r_{in} and time constant for deactivation τ_{de} for samples with different initial K-content in terms of the Auger peak height ratio I_K/I_{Fe} . '2x2' marks the composition where an ordered pattern is observed in LEED. This corresponds to the composition $K_xFe_{22}O_{34}$ ($x \approx 2$). At higher K-content, the sample consists partially of $KFeO_2$.

Also "steaming", the removal of coke by running the reactor with steam alone (without EB in the feed), was tried. It turned out that H_2O induces removal of K (probably in form of KOH which is volatile at 870K). Without EB, K-removal is much faster than with EB in the feed. This indicates a stabilization of K as carbonate as intermediate in the coke removal process. Two conclusions can be drawn from this observation: (i) K prevents deactivation and the K-containing phases are only reservoirs for K, and (ii) steaming should be avoided. Oxidative coke removal is an alternative.

Concerning the catalytic mechanism, the results can be summarized as follows [6,7,12]:

- Most active is Fe^{3+} in Fe_2O_3 or KFe_xO_y .
- Fe_3O_4 is less active, due to self-poisoning by strongly bound EB and St.
- Deactivation of unpromoted catalysts occurs by reduction to Fe_3O_4 and by coking.
- Both can be prevented by admixture of some oxygen to the feed.
- K itself is not active but suppresses reduction and catalyses carbon removal.
- The stable phases $K_2Fe_{22}O_{34}$ and especially $KFeO_2$ are K-reservoirs.
- "Steaming" (reaction in steam without EB) exhausts the K-reservoirs.
- Even coke has a non-negligible catalytic activity.

Extension to pressed powder samples

In order to extend the modelling by inclusion of pore effects, experiments with pressed powder samples (Fe_2O_3 , BET surface $2.2 \text{ m}^2 \text{ g}^{-1}$, mean grain size 300nm, monomodal pore size distribution, mean diameter 240nm) were performed. TGA measurements in 4% H_2 at 770K in N_2 and oxidation of Fe_3O_4 in air show that the phase transformation between Fe_2O_3 and Fe_3O_4 are fast (few minutes for complete reaction of a several mm thick sample). Pore diffusion will therefore not limit the reduction-oxidation behaviour in the catalytic reaction. Oxidation of Fe_3O_4 in H_2O at 870K is much slower (some hours).

Fig. 7 shows the deactivation behaviour of a pressed powder sample in the microflow reactor under the same conditions as on the single crystalline films. Before the experiment, the powder sample was cleaned in the reactor by oxidation (30 min in 1 mbar O_2 at 1000 K). The initial conversion of the powder is about 2.5 times higher and the deactivation is slower. However, the activity scales not at all with the BET surface (powder: 2200 cm^2 , single crystal 0.5 cm^2). It rather scales with a roughness-related increase of the geometric surface area. Diffusion of H_2O and EB (in N_2 at 493 K) in the pressed powder material is quite fast and suggests that the reactivity should not be limited by pore diffusion. It seems thus clear that the blocking or deactivation of the inner pore surface is caused by coke formation from St. St, formed within the pores would thus mainly contribute to coke formation and not to the wanted product.

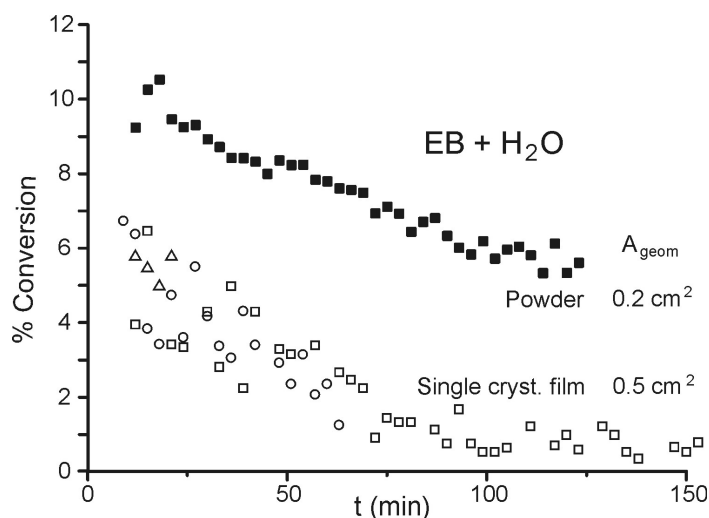


Fig. 7. Time dependence of the experimentally determined conversion rate of EB to St over Fe_2O_3 . Comparison of a single crystalline and a pressed powder sample. In order to refer the activity to equal geometric surface, the powder data have to be scaled up by a factor 2.5.

Modelling the deactivation behaviour of the pressed powder sample, based on these ideas will be the next step on the way to a complete understanding of the styrene catalysis process.

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