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Real catalysis on single crystalline model catalysts with in-situ reactivity measurement

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The pressure and materials gap between reactivity studies in UHV and real catalysis can only be overcome by application of in-situ methods for catalyst characterization and/or activity measurements under realistic pressure and temperature conditions. As a model reaction we study the economically important catalytic dehydrogenation of ethylbenzene (EB) to styrene (St) [1]. The technical catalyst consists of potassium-promoted iron oxides. We use single crystalline epitaxial layers of Fe₂O₃, Fe₃O₄ and K-Fe-oxides, characterized by surface science methods (LEED, STM, UPS, TDS, AES) concerning surface structure and composition [2]. They are transferred under vacuum into a stagnation point micro flow-reactor [3] where the EB→St conversion is studied with the EB pressure in the mbar region without or with H₂O in excess as in the technical process. Also O₂ can be admitted in order to study the oxidative dehydrogenation. Conversion yields are measured gas chromatographically. After interruption of the reaction, the sample can be transferred back into the UHV chamber for post-reaction surface analysis.

The initial catalytic activity of Fe₂O₃ decreases after 20 to 40 min due to reduction to Fe₃O₄ [4]. A second activity decrease is related to coke deposition. This coke is still catalytically active and most likely responsible for the activity observed on unpromoted technical catalysts. Water limits coking and further reduction to metallic Fe. Reduction and coke deposition can be prevented by admission of a low partial pressure of O₂ so that the initial high conversion rate is conserved.

The activity of potassium promoted samples is similar to the initial high activity of unpromoted samples but the decrease by coking is much slower. Coke can be removed by stopping admission of EB while H₂O admission is continued but this causes also K depletion. K thus prevents extensive coking but a thin coke layer is also needed to limit K depletion. High activity appears to result from the dynamic equilibrium between coke production and removal. It cannot be ruled out that the “right” coke produced in this way actually represents the catalytically active phase

In conclusion, the combination of surface science for pre- and post-reaction analysis with studies of catalytic activity under realistic conditions demonstrates that the unpromoted iron oxide based catalysts for EB dehydrogenation can assume three different functional states. The initial high-yield state can be maintained by admission of oxygen. K on promoted catalysts prevents extensive coking. Yet, a thin coke layer is necessary to limit K depletion. Whether the thin coke layer is catalytically active has to be checked.

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