Dehydrogenation of ethylbenzene over unpromoted iron oxide model catalyst

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Introduction

The dehydrogenation of ethylbenzene (EB) to styrene (ST) is one of the ten most important catalytic reactions in industry. It is run at 870 K over iron oxide based catalysts in presence of steam. In several papers, the kinetics of the reaction [1] and the role of water and the deactivation process [2] were studied. All proposed models point to the importance of Fe^{+3} ions in the dehydrogenation process [3]. So far, most studies were carried out on powder oxide materials, which are not suitable for surface science investigations because of their insulating properties. In a first step, we present results on unpromoted model iron oxide catalysts which are prepared by epitaxial growth of thin iron oxide films on Pt(111) substrates. Surface science techniques and a single crystal micro flow-reactor are employed for the investigation of the surface chemical transformations during the reaction, of the activity for EB dehydrogenation and of the role of water.

Experimental

Well ordered epitaxial Fe_3O_4(111) and α-Fe_2O_3(0001) films are grown on a Pt(111) substrate by cycles of iron deposition and oxidation at different oxygen pressures. The oxide phase is identified from the electron diffraction (LEED) pattern and Auger (AES) spectrum. The stagnation point micro flow-reactor is located in a high pressure cell into which the sample can be transferred under vacuum from the ultrahigh vacuum (UHV) analysis chamber. Sample heating by two fiber coupled diode lasers from behind allows to work at 1 bar. The reactor is first vented with N_2. Then a He carrier gas flow is directed towards the sample which usually contains 3.3 mbar EB and 33 mbar H_2O at a total flow rate of 25 ml/min. In order to study the role of O_2 and H_2O in the reaction, O_2 can additionally be introduced or H_2O can be switched off. The product gas mixture is analyzed by GC/MS.

Results and Discussion

Fig(1) shows that Fe_2O_3 starts with a high yield of ~8% both with and without H_2O in the feed, only the length of this high activity period depends on the feed composition. After that, the yield drops quite to 3%: Post-reaction analysis in the 3% regime shows partial reduction to Fe_3O_4 with the degree of reduction increasing with time on stream. Since this yield is the same as the yield on Fe_3O_4 from the beginning, we believe that the drop in yield is related to the reduction of Fe_2O_3 in the surface layer to a depth determined by oxygen diffusion. If O_2 is added, the high yield is maintained since O_2 prevents the reduction. It also reduces carbon deposits as revealed from post-reaction analysis. The oxygen released by substrate reduction in the high yield regime is not sufficient for oxidation of the H_2 from the dehydrogenation reaction. The high yield is thus due to a catalytic and not to a stoichiometric reaction. Since the same high yield is observed without H_2O, the mechanism is not Mars-Van Krevelen. In the case of reaction without water the iron is almost reduced to Fe^0 at the end of 1% yield region. This could be due to a stoichiometric reaction. Since water prevents reduction to

Fe^0, the mechanism in the 3% regime may be Mars-Van Krevelen. The final drop of the yield to 1% is probably due to the deposition of significant amounts of carbon as seen in AES after reaction. We believe that this low yield 1% is characteristic for catalysis by carbon. Carbon deposits are much stronger without water in the feed.
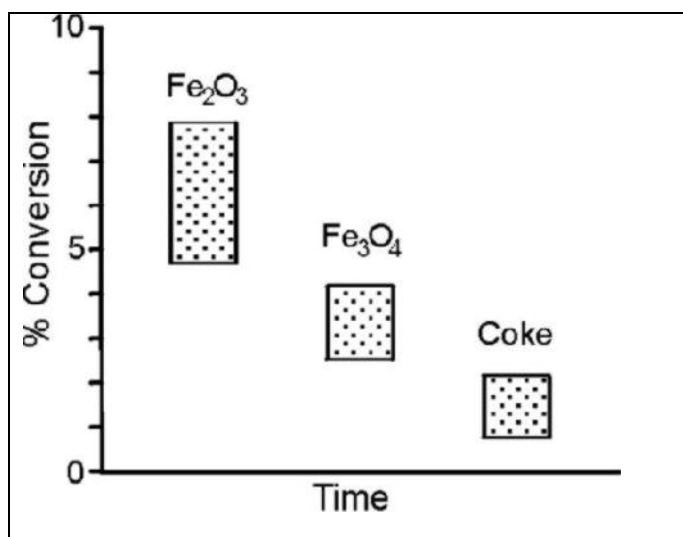
Conclusion

Clean Fe_2O_3 exhibits a high initial yield of ~ 6% and is deactivated by reduction to Fe_3O_4 and by carbon deposits. Presence of O_2 in the feed can help to maintain the high yield. The dehydrogenation in this range is a simple catalytic reaction. Water limits the carbon deposition and prevents reduction of the oxide to metallic Fe^0.

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