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Abstract

The economically important dehydrogenation of ethylbenzene (EB) to styrene (ST) is run at 870 K over potassium promoted iron oxide catalysts in the presence of steam. Here we present the continuation of model catalysis studies using thin epitaxial films (10-20 nm) of magnetite Fe_3O_4, hematite α-Fe_2O_3 and potassium ferrites KFe_xO_y of different composition. They allow the application of surface science methods for pre- and post-reaction surface characterization. The phases are identified from the LEED pattern and Auger (AES) spectrum. Catalytic conversions are measured using an in-situ stagnation point micro-flow reactor. The standard feed consists of EB: H_2O=1:10 (molar). The partial pressures of reactive gases (p(EB) and p(H_2O) are 3.3 and 33 respectively, the rest working pressure of 1 bar is He. The standard total flow rate is 25 ml/min. In addition, O_2 can be introduced or H_2O can be switched off. The low film thickness is an advantage; the whole "bulk" material is essentially in thermodynamic equilibrium at reaction conditions. The nature of the films also excludes pore diffusion effects.

When starting with Fe_2O_3 the high initial conversion drops within about 80 min by about an order of magnitude. Simultaneously, the film is reduced to Fe_3O_4 and covered by coke. Without water in the feed, the deactivation behaviour is similar but substrate reduction proceeds towards metallic iron and coking is heavier. This confirms that water is not involved in the catalytic reaction but it prevents substrate reduction beyond Fe_3O_4 and help in coke gasification. We conclude further that the final low activity is connected to coke. Addition of O_2 prevents both reduction and coking and the high initial conversion is maintained. The necessary amount of O_2 corresponds to that necessary to oxidize the produced H_2 and to gasify the coking products. Initial deactivation of the promoted catalyst is much slower and occurs mainly by coking which is counteracted by surface K, possibly as K_2CO_3. K accumulates at the surface but is in equilibrium with the bulk concentration. It is slowly but continuously removed during reaction which accounts for a slow irreversible deactivation. "Steaming" the catalyst by switching off EB but continuing the water admission causes removal of coke but also a fast removal or K. We conclude that in the presence of EB and its reaction- and decomposition-products, surface K is protected against removal, possibly because it forms carbonate. Substrate reduction is also prevented by K. Striking is the similarity of the initial conversion rates for unpromoted and promoted catalysts. Since Fe_3O_4 also contains Fe^{3+} but is much less active, we believe that the existence of Fe^{3+} is necessary but not sufficient. As proposed before, the adsorption strength for EB and St may be essential. Both are bound so tightly on Fe_3O_4 that they may block the active sites. Investigations over the promoted catalyst with different potassium loadings show that the potassium rich phase ($KFeO_2$) is not the active phase, the β–ferrite $K_xFe_{22}O_{34}$ is the active phase and the $KFeO_2$ is the potassium storage phase. The activation energy was found to be equal on the clean unpromoted and the promoted catalyst, which support that the active sites on both is the same. Unpromoted real catalysts in the form of pressed powder pellets were used for reactivity studies in the micro-flow reactor under the same conditions as for the model catalyst. The results show a good agreement but the conversion on real powder samples does not scale with the BET-surface, which means that there are diffusion limitations and not all the pores are accessible.

Zusammenfassung

Die wirtschaftlich bedeutende Dehydrierung von Ethylbenzol (EB) zu Styrol (St) wird bei 870 K über Kalium-promotierten Eisenoxid-Katalysatoren in Gegenwart von Dampf durchgeführt. Hier wird die Fortsetzung von Untersuchungen dargestellt, in denen dünne epitaktische Filme (10-20 nm) aus Magnetit Fe_3O_4, Hämatit Fe_2O_3 und Kaliumferriten KFe_xO_y unterschiedlicher Zusammensetzung als Modellkatalysatoren verwendet werden. Das erlaubt, Methoden der Oberflächenanalyse vor und nach der Reaktion anzuwenden. Die Phasen werden mit Hilfe der Beugung langsamer Elektronen (LEED) und der Auger-Elektronenspektroskopie (AES) identifiziert. Katalytische Umsätze werden in einem in-situ Prallplatten-Mikroreaktor gemessen. Die Standardzusammensetzung des Edukts is $EB:H_2O=1:10$ (molar). Die Partialdrucke der reaktiven Gase sind $p(EB)=3.3$ mbar, $p(H_2O)=33$ mbar, der Rest zum Arbeitsdruck von 1 bar besteht aus He. Der Standard-Gesamtfluss ist 25 ml/min. O_2 kann extra zugegeben und H_2O kann weggelassen werden. Die geringe Filmdicke ist ein Vorteil, da das gesamte Material im wesentlichen mit der Oberfläche im thermodynamischen Gleichgewicht ist. Der Film ist frei von Poren. Der anfänglich hohe Umsatz über Fe_2O_3 fällt innerhalb von etwa 80 min um fast eine Größenordnung ab. Gleichzeitig wird der Film zu Fe_3O_4 reduziert und mit Kohlenstoffablagerungen („Koks") bedeckt. Ohne Wasser im Edukt verläuft die Deaktivierung ähnlich, allerdings wird das Substrat bis zum metallischen Eisen reduziert und verkokt viel stärker. Wasser ist also nicht an der katalytischen Reaktion beteiligt, verhindert aber die Reduktion über das Fe_3O_4 hinaus und unterstützt die Vergasung des Koks. Wir schließen weiterhin, dass die niedrige Endaktivität dem Koks zuzuschreiben ist. Zugabe von O_2 verhindert sowohl Reduzierung wie Verkokung und erhält den hohen Anfangsumsatz. Die notwendige Menge O_2 entspricht der Menge, die nötig ist, um das erzeugte H_2 und den Koks zu oxidieren. Die anfängliche Deaktivierung des promotierten Katalysators verläuft viel langsamer und geschieht vor allem durch Verkokung, der durch Kalium an der Oberfläche entgegengewirkt wird, möglicherweise in Form von K_2CO_3. Im Gleichgewicht mit der Volumenkonzentration reichert sich K an der Oberfläche an. Es wird während der Reaktion kontinuierlich entfernt, was eine langsame irreversible Deaktivierung bewirkt. „Steaming" durch Abschalten des EB unter Aufrechterhaltung der Dampfzufuhr bewirkt die Entfernung des Koks aber auch eine rasche K-Verarmung. Daraus folgt, dass K in Anwesenheit von EB und seiner Reaktionsprodukte gegen Austrag geschützt ist, möglicherweise weil es Karbonat bildet. K verhindert auch die Reduzierung des Substrates. Auffallend ist die ähnliche Höhe des Anfangsumsatzes für unpromotierte und promotierte Katalysatoren. Da Fe^{3+} auch in Fe_3O_4 enthalten ist, das aber viel weniger aktiv ist, glauben wir, dass Fe^{3+} notwendig aber nicht ausreichend ist. Wie früher vorgeschlagen könnte die Adsorptionsstärke für EB und St wichtig sein. Beide werden auf Fe_3O_4 so fest gebunden, dass sie aktive Plätze blockieren könnten. Messungen an promotierten Katalysatoren mit unterschiedlichem K-Gehalt zeigen, dass nicht das K-reiche $KFeO_2$ sondern das β-Ferrit $K_xFe_{22}O_{34}$ die aktive Phase ist, während das $KFeO_2$ die K-Speicherphase darstellt. Die Aktivierungsenergie auf dem sauberen unpromotierten und promotierten Katalysator ist gleich, was die Annahme stützt, dass die aktiven Plätze auf beiden dieselben sind. Unpromotierte Realkatalysatoren in Form von Pulverpresslingen wurden unter denselben Bedingungen untersucht, wie die Modellkatalysatoren. Die Ergebnisse stimmen gut überein, aber der Umsatz skaliert nicht mit der BET-Oberfläche. Das deutet darauf, dass es Diffusionsbegrenzungen gibt und dass nicht alle Poren zugänglich sind.

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