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Study of the deactivation of a commercial catalyst for ethylbenzene dehydrogenation to styrene

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Abstract

The catalytic performance and characteristics of an industrial catalyst, fresh and spent, i.e. downloaded from an industrial reactor after a normal lifetime cycle, were compared. Some different causes of catalyst deactivation, such as loss or redistribution of promoters, active phase modification, Fe^{3+} reduction, coke deposition on catalyst surface and physical modifications, were evidenced by means of several techniques. All the mentioned causes of deactivation showed strictly interconnected and concurred to the decrease of conversion. However, the key factors leading to irreversible deactivation showed potassium migration towards the inner part of the extrudate particle, its agglomeration into concentrated spots and its volatilisation from the surface, together with the progressive Fe^{3+} reduction to Fe^{2+}. These modifications led to the enhancement of coking activity and to the loss of mechanical properties, so making deactivation irreversible.

Keywords: Ethylbenzene dehydrogenation; Catalyst deactivation

1. Introduction

Styrene is one of the most important intermediates of the chemical industry, with a production exceeding 20 million tons/year. Besides that co-produced in the propylene oxide process, up to 80% of styrene is commercially produced through the catalytic dehydrogenation of ethylbenzene. The reaction is limited by equilibrium, heavily endothermic and it is carried out in either adiabatic or isothermal mode in fixed bed reactors, over promoted Fe-based catalyst. Temperature is usually around 600 °C and steam is co-fed with the reactant in order to supply heat, to help maintaining the active phase in the correct oxidation state and to prevent or limit catalyst deactivation by coking.

An extensive body of work has been published, aiming at clarifying the nature of the active phase and the role of promoters [1]. Indeed, the catalyst precursor is Fe_2O_3 (hematite), which however is not believed to be the real active phase for the present reaction. Many promoters are usually added to confer specific properties, such as Cr_2O_3, MoO_3, V_2O_5, CeO_2 [2–4]. Other promoters, such as alkali-earth oxides or even Portland cement act as structural agents to improve mechanical strength [5–7]. However, an increase of catalytic activity up to one order of magnitude can be attained only by adding a consistent amount of K (10–30 wt%), mainly as K_2CO_3 [2,8]. The effect of K on catalytic activity has been deeply studied, and it was demonstrated that it has a multifunctional role. The most important finding is that K is involved in the formation of $KFeO_2$, through reaction with the Fe-precursor, leading to what is believed to be the real active phase for the reaction. This hypothesis was first addressed by Hirano [5,8], later confirmed and modelled by Muhler et al. [9], who invoked also the presence of an additional $K_2Fe_{22}O_{34}$ phase, acting as K-supplier for the active $KFeO_2$ species. More recently, inverted roles for these two phases were hypothesised [10,11].

Besides its effect on catalytic activity, the role of K is fundamental also to prevent or limit catalyst deactivation [1]. The latter is usually attributed to four causes, often interacting with each other: (a) coke formation, (b) promoters' loss or redistribution, (c) Fe^{3+} reduction and (d) physical degradation.

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Among these, coking can be strongly limited by K addition, KOH and K_2CO_3 being active for the gasification of carbonaceous deposit [5,12–14], and Fe^{3+} reduction can be prevented as long as K can be supplied from $K_2Fe_{22}O_{34}$ to the active $KFeO_2$ phase or vice versa [9,10,11,15]. Hence, the loss or uneven distribution of K (cause (b)) seems the main cause of irreversible deactivation of the catalyst.

In the present work we compared the main physical-chemical properties and catalytic activity of a fresh industrial catalyst with those of a sample of the same catalyst (Süd Chemie AG), downloaded in 1999 from an industrial reactor after a normal lifetime cycle, aiming at analysing and comparing the role of the four previously mentioned possible causes of catalyst decay. To the best of our knowledge, some comparison of this kind have always been published on specially prepared samples or even in monocrystalline samples only, after relatively short accelerated decay tests in laboratory or in pilot reactor. By contrast, the aim of the present work was to analyse the transformations undergone by a real industrial catalyst during its normal whole lifetime.

2. Experimental

2.1. Catalyst characterisation

Crystalline phase identification on both the fresh and spent catalyst was done by X-ray diffraction analysis (powder method), by means of a Philips (mod. 1025) diffractometer, comparing the patterns obtained with literature data [16].

Specific surface area (SSA_{BET}) of the samples were measured by nitrogen adsorption/desorption on a Micromeritics ASAP 2010 instrument. Hg porosimetry was employed to determine meso- and macro-porosity, by means of a Micromeritics Autopore3 instrument.

Elemental analysis was carried out by means of a Jordan Valley (mod. EX 310) X-ray spectrofluorimeter. In order to obtain the average composition of the sample, several extrudates were finely ground and the powder pressed to homogeneous pellets (diameter 20 mm). To distinguish between shell and core composition of the spent catalyst some extrudates were carefully erased, in order to recover 10 wt% of external layer. Both the erased powder and the ground internal core were then pelletized as described.

The topographic distribution of the elements in the fresh and spent catalyst extrudates (mainly focusing on K) was obtained through SEM-EPMA analysis, on a Jeol, mod. JSM-5500LV scanning electron microscope, equipped with a Jeol IXRF EDS2000 electron probe micro-analyser. Sample preparation was carried out by embedding the extrudates in a thermo-hardening resin and erasing the embedded particles either axially or radially with progressively finer and finer diamond-powder-covered paper.

The concentration of Fe^{2+} was determined by titration with aq. $K_2Cr_2O_7$ of a solution obtained by dissolving a known amount of the spent catalyst with aq. HCl under inert atmosphere.

Coke content was determined by temperature programmed oxidation (TPO), carried out on a previously described apparatus [17]. Ca. 0.2 g of spent catalyst powder were loaded into a quartz microreactor and heated by 10 °C/min up to 800 °C in a stream of 10 vol% O_2 (SIAD, purity 99.999 vol%) in He (SIAD, purity 99.9999 vol%). Qualitative analysis of the species evolved during the TPO experiment was done by a MKS PPT-C200-MZY quadropolar mass spectrometric (QMS) detector. The amount of oxygen consumed was determined by a HWD detector, after careful calibration. The amount of C on the spent catalyst was calculated by taking into account the oxygen consumption due to oxidation of Fe^{2+}, determined as described (vide supra).

The radial crushing strength was determined by means of a Crush-BK by MA.TEK. dynamometer.

2.2. Apparatus and procedure for catalytic activity testing

Activity tests have been carried out by means of a continuous, downflow, Incoloy 800 tubular reactor, 9 mm i.d., fitted with a 1.6 mm o.d. axial thermowell. Oven temperature was regulated by means of a temperature programmer (Eurotherm, mod. 2408). Water and ethylbenzene (Aldrich, purity 99.5 wt%, further purified by distillation) were fed through two independent pumps (Saphirwerk, mod. MDP2000) and the reactant partial pressure was lowered by co-feeding N_2 (SIAD, purity 99.995 vol%) through a mass flowmeter (Brooks, mod. 5811-N), regulated by a Brooks 5874 control unit. The reaction products were trapped at −40 °C at the reactor outlet, by using a Neslab Endocal ULT-80 DD cryogenic unit. The collected organic phase was analysed by means of a Hewlett-Packard, mod 5890 gaschromatograph, equipped with flame ionization detector and a capillary HP Ultra PONA column.

Ca. 2 g of catalyst, obtained by grinding and sieving to 0.25–0.42 mm particle size the original estrudates, were loaded in the isothermal middle part of the reactor. The reactor void space over and below the catalyst bed were filled with quartz beads (0.7–1.7 mm in size). Catalyst activation was carried out in flowing N_2 by heating (3.17 °C/min) up to 350 °C. Water was added to the feed at 350 °C. Temperature was then further increased (1.75 °C/min) up to 610 °C and ethylbenzene (EB) was added at 550 °C. Reactant/inert flow rates were set so to obtain $(EB + H_2O)/(EB + H_2O + N_2) = 0.5$ (vol/vol in the gas phase), $LHSV = 0.5\ h^{-1}$ and steam/oil (S/O) weight ratio = 2.

3. Results and discussion

Activity data (Table 1) showed the expected remarkable (more than 15%) drop of activity for the spent catalyst with