THE EFFECTS OF PREPARATION AND SOME PHYSICO-CHEMICAL PARAMETERS ON THE PROPERTIES OF STYRENE CATALYSTS — BASED ON IRON(III) OXIDE

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Hydrated iron(III) oxides were obtained by discontinuous precipitation of an iron(II) sulfate solution with aqueous ammonium — saturated with carbon dioxide to different CO_2/NH_3 ratios. An additional thermal treatment of these oxides, under different conditions, provided genetic sequences of intermediates and their final products — catalysts on a Fe_2O_3/K_2O basis, with different promoters. The catalysts were studied by means of the microstructural analysis, thermogravimetry, DTA, IR spectroscopy and further tested by the dehydrogenation of ethylbenzene to styrene. It was observed that by changing the CO_2/NH_3 ratio in the precipitation of the initial solutions one can influence some of the properties, as well as, the morphology and thermal stability of the initial intermediates of the preparation of the catalysts. The above mentioned properties become practically unified with the increasing number of the heat treatment operations, with all the investigated catalysts — with the exception of the catalysts' behaviour during their reduction with hydrogen. The presence of iron oxides in various valency states and the different phase composition of the catalysts during their reduction affect the final activity and selectivity of the catalyst in the reaction under the study.

The present industrial production of styrene is based on the gas phase catalytical dehydrogenation of ethylbenzene, which is carried out in the presence of overheated water vapour — reducing the partial pressures of the reaction components, supplying the necessary heat to the system and shifting the equilibrium in favour of the higher styrene concentrations among the other reaction products. In addition to the standard catalysts of dehydrogenation — *e.g.* Al_2O_3; Cr_2O_3/Al_2O_3 (ref.[1]), and to other types of catalysts tested in the past few years predominantly on a laboratory scale[2], in the industry mainly the catalysts based on Fe_2O_3 — using different promoters, are applied. The use of self-regenerative alkaline promoters[3] enabled a continuous removal of carbonization products by the carbon combustion to CO_2 or CO. The occurrence of other side processes in the system increases the demands not only on the activity but also on the selectivity of the used catalysts. For this reason, great attention has been paid to the conditions of preparation and activation of the catalysts[4], their composition and to the selection of the promoters[5]. So far, only single attempts have been made[6] to correlate the physico-chemical parameters with the activity and selectivity of the styrene catalysts based on Fe_2O_3.

This paper is a study of the physico-chemical parameters of several catalysts which were prepared in different ways, as well as, of their genetic intermediates — with special concern to the catalytic properties of these catalysts for ethylbenzene dehydrogenation.

EXPERIMENTAL

Preparation of the Samples

Two initial samples of hydrated iron(III) oxides were prepared by discontinuous precipitation of a 20% ammonium bicarbonate solution (sample A) or a 12·5% ammonium solution (sample B), with the 30% solution of iron(II) sulfate. In the first case, the ammonium bicarbonate solution was obtained by the saturation of aqueous ammonium with carbon dioxide up to a mass ratio $CO_2/NH_3 = 2{\cdot}58$. The precipitation proceeded under permanent stirring at 50°C, for 15 minutes, until the pH values 7·2—7·5 (sample A) and 8·5 (sample B) were reached. After a repeated decantation and rinsing with distilled water, the precipitate was filtered and dried in the air — at first for 5 hours, at the temperature 60°C, and after for 2 hours, at 115°C. The genetic products were prepared from the both hydrated oxides in the following way: A1: the dried precipitate A was calcinated in the air for 1 hour, at 520°C. A2: the washed-out precipitate A was calcinated directly, without preliminary drying, in the atmosphere of its own decomposition products — for 1 hour, at 450°C and then for 1 hour, at 520°C. A3: sample A2 was further heated in the air for 1 hour, at 700°C. In an analogous way — samples B1, B2 and B3 were obtained from the precipitate B. In the next step, the corresponding final catalysts were prepared from the iron(III) oxides A1—A3 and B1—B3.

The oxides were mixed in a laboratory mixer with a potassium solution containing also TiO_2 CrO_3 and KVO_3. The quantities of these components were selected in such a way that the resulting catalyst contained 15% K_2O, 2% Cr_2O_3, 2% TiO_2 and 2% V_2O_5. The formed paste was shaped by means of an extruder into small rods which were dried for 2 hours at 110°C and then calcinated for 1 hour at 750°C in the air. In this way, samples K1—K3 and K4—K6 of the final catalysts were obtained from the corresponding oxides A1—A3 and B1—B3.

Testing of the Catalysts

The catalytic properties were tested by the dehydrogenation of ethylbenzene in an isothermal integral flow reactor. Inside an aluminium bronze block, heated by two automatically controlled heating elements, six stainless steel tubes of 22 mm i.d. and 1 700 mm length were inserted. In this way it was possible to test simultaneously six samples under comparable conditions. 50 ml of a catalyst were placed on each of the supports located in the centres of the tubes. To make sure that the reaction will proceed in a kinetic region, the catalyst was crushed and the fraction with the grain size between 1·0—1·4 mm has been separated by sieving. Water and ethylbenzene (99·87%) were dosed by means of micropumps (with the rates 65 ml/hour of water and 25 ml/hour of ethylbenzene), then mixed and finally heated up to a reaction temperature — on a layer of steatite beads placed in the tube above the catalyst. The temperature was measured by means of a thermocouple probe, with the accuracy ±2°C along the entire length of a catalytic bed. The reaction products leaving the reactor were cooled down in a water condenser. After separation of the water layer, the hydrocarbon layer was weighed and analyzed using a gas-chromatograph with a thermal conductivity detector. The amount of the uncondensed gas was also measured and analyzed. The dehydrogenation reaction was measured at 540, 560 and 585°C. After stabilizing the reaction conditions (for 24 hours), the catalysts were tested for 10 hours at each of the above temperatures. The activity and selectivity were calculated from the mass balance of all the reaction products. After the end of testing, the catalysts were gradually cooled down in an inert nitrogen atmosphere to the laboratory temperature and finally removed from the reactor. In this way, two new sets of samples — catalysts after the process (*i.e.* spent catalysts) KA1—KA3 were obtained from the catalysts K1—K3 (similarly KB1—KB3 from K4—K6).

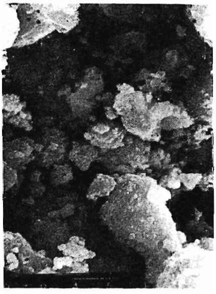

FIG. 1

Morphology of sample A. A micrograph taken by electron scanning microscope; magnification $10^4\times$; line segment above the number equals 2 μm

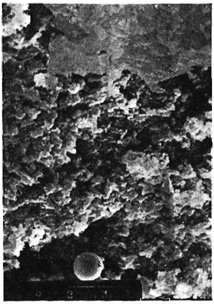

FIG. 2

Morphology of sample B. A micrograph taken by electron scanning microscope; $10^4\times$; line segment above the number equals 2 μm

Measurement of the Physico-chemical Parameters

The qualitative phase composition was determined from the X-ray diffraction patterns, obtained in focusation chambers of a 57·3 mm diameter, using the CrK$_\alpha$ line. The mixture of phases in the final catalysts K1—K6 was evaluated also quantitatively. In order to determine the size of the coherent regions, selected reflections were analyzed on a Dron diffractograph with direct registration, using the FeK$_\alpha$ line. The specific surfaces of all samples were measured applying the dynamic method of selective nitrogen adsorption from a binary mixture N_2/H_2 at liquid nitrogen temperature.

The morphology of the intermediates, as well as of the fresh and spent catalysts was studied by means of the electron scanning microscope JSM A (JEOL). The powder samples were analyzed after the previous vacuum deposition of a carbon and a Pd-Au layer.

The kinetics of the reduction with hydrogen and the dehydration of intermediates A and B in an inert argon atmosphere was investigated by means of thermogravimetry on the earlier described apparatus[7]. The isothermal reduction was measured at 520°C and 470°C, using hydrogen flow rates 56 ml/min and a standard sample weigth 50 mg. The thermal treatment in dry argon flow was carried out in the temperature range 20—520°C, applying linear heating rate 60°C/min. The DTA-diagrams were registered on a simultaneous thermoanalyzer (Netzsch), for a temperature range 20—1 000°C, in the air. The samples with the standard weight of about 200 mg, in a powder-form, were placed in a platinum crucible and heated up at the rate 10°C/min.

RESULTS AND DISCUSSION

As can be seen from the data in Table I, the initial oxides of both genetic sequences A and B consist of the majority phase — *ortho*-rhombic goethite α-$Fe_2O_3 . xH_2O$, which after the first heating is transformed into dehydrated iron oxides — present in different relative amounts (samples A1 and B1). The minority phase in the first genetic sequence is formed by the γ-modification of Fe_2O_3 — while in the second sequence it consists mainly of magnetite Fe_3O_4 and to a lesser extent also of γ-Fe_2O_3. The presence of the last form was proved by the DTA method only. A high temperature calcination in the air (yielding samples A3 and B3), in both sequences results in unification of the structure of all the studied oxides — giving a stable rhombohedric α-Fe_2O_3 (haematite). In general, in both sequences the dispersity of the given phase decreases — with the increasing temperature of heat treatment and with the number of such heat treatment operations. In these operations, after the primary dehydration — the crystallites are gradually sintered, which consequently results in the decrease of the surface area. For both hydrated oxides, the surface area values can be very well correlated with the dispersity of the majority phase. The initial hydrates differ in both of the mentioned parameters. Unlike the first sequence, the first heating of the precipitate prepared with pure ammonium (sample B1) is not connected with a change of the specific surface.

The final catalysts of both sequences contain large excess of α-Fe_2O_3 — with the exception of samples K2 and K5 — which were both prepared without preliminary drying, by direct heating of the precipitation products in the atmosphere of their own decomposition products. Both catalysts show higher contents of γ-Fe_2O_3. The increase in size of the coherent regions of the majority phase – observed with the increasing temperature of the heat treatment – is also found for the group of the final catalysts, only the differences between the sizes of the specific surfaces of both sequences are smaller. In the course of the dehydrogenation, all catalysts are partially reduced. The average size of microcrystallites of the majority phase of the spent catalysts – the magnetite – varies within a very narrow range between 54·8 to 61·2 nm. Also the crystallochemical transformation $Fe_2O_3 \rightarrow Fe_3O_4$ during the reaction does not lead to any surface changes. Different morphology is found especially in the two initial hydrated oxides. As follows from Fig. 1*, sample A consists of larger, relatively well separated aggregates with a porous structure, which explains its large surface. On the other hand, sample B (obtained by precipitation with the ammonium solution) forms well developed flat agglomerates in close interaction (Fig. 2*). In both genetic sequences it is possible to see clear substantial morphological changes resulting from the heat treatment. The higher resistivity of the oxides derived from sample B, to sintering, is probably connected with the existence of two opposite processes during the heat treatment: the disintegration of macroaggregates and surface sintering of microaggregates. With the oxides of the first sequence – only the aggregation, connected with continuous decrease of the surface size, was observed. With the final and the spent catalysts, the morphological differences which are due

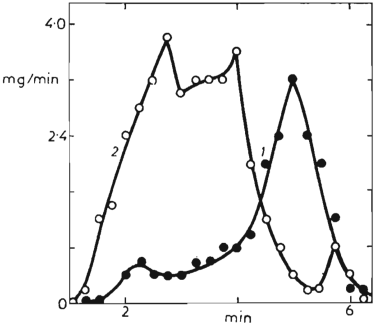

FIG. 3

Kinetics of dehydration of the hydrated iron oxides: *1* sample B, *2* sample A

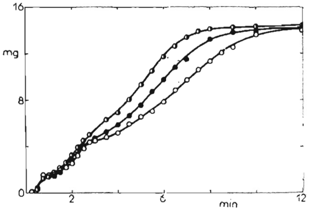

FIG. 4

Time courses of the reduction of oxides A1–A3, at 520°C, A_1 ○, A_2 ●, A_3 ◑

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* See insert opposite p. 422.

to their different genetic origin disappear. On the basis of the thermogravimetry measurements, the sample A can be characterized as $Fe_2O_3 . 1·9 H_2O$ (a dihydrate), while the corresponding initial sample of the second sequence as a monohydrate ($Fe_2O_3 . 0·95 H_2O$). The kinetics of the dehydration of both samples is shown in Fig. 3. In both cases, the dehydration of the constitutionally bonded water is practically completed at 410 °C. The remaining genetic samples contain only the physically sorbed water — with the average amount 0·2–1·4 weight % in the oxides of both sequences and 0·2–5% in the final catalysts K1–K6 and all the spent catalysts.

TABLE I

Phase composition, size of coherent regions *L* and specific surfaces *S* of styrene catalysts and of the intermediate products of their preparation

Sample	Phase composition (for K1–K6 catalysts in %)	*L* nm	*S* m^2/g
A	diffuse line α-$Fe_2O_3 . H_2O$	<20	92
A1	α-Fe_2O_3	37·7	36·7
A2	majority α-Fe_2O_3	167·7	13·0
	minority γ-Fe_2O_3	102·5	
A3	α-Fe_2O_3	182·4	9·8
B	majority α-$Fe_2O_3 . H_2O$	54·8	24·4
	minority Fe_3O_4	72·8	
B1	majority α-Fe_2O_3	30	27·8
	minority $Fe_3O_4 + \gamma$-Fe_2O_3	—	
B2	majority α-Fe_2O_3	116·3	14·6
	minority $Fe_3O_4 + \gamma$-Fe_2O_3	96·6	
B3	α-Fe_2O_3	118·3	9·5
K1	α-Fe_2O_3 (91·1), γ-Fe_2O_3 (8·9)	63·1 (α), 111·3 (γ)	3·6
K2	α-Fe_2O_3 (62·7), γ-Fe_2O_3 (37·3)	89·5 (α), 49·5 (γ)	5·7
K3	α-Fe_2O_3 (90·2), γ-Fe_2O_3 (9·8)	153·0 (α), 71·6 (γ)	3·3
K4	α-Fe_2O_3 (80·1), γ-Fe_2O_3 (19·9)	56·9 (α), 53·0 (γ)	7·0
K5	α-Fe_2O_3 (72·0), γ-Fe_2O_3 (28·0)	108·0 (α), 57·8 (γ)	4·8
K6	α-Fe_2O_3 (82·1), γ-Fe_2O_3 (17·9)	119·5 (α), 50·8 (γ)	3·4
KA1	Fe_3O_4	60·4	6·5
KA2	Fe_3O_4	56·3	6·0
KA3	Fe_3O_4	61·2	3·8
KB1	Fe_3O_4	55·2	6·1
KB2	Fe_3O_4	54·9	4·8
KB3	Fe_3O_4	54·8	4·1

From Fig. 4 and Fig. 5 one can say that the course of isothermal reduction of the oxides of both series, at 520°C is different. On the samples A1 – A3 – which are reduced at the initial and medium stages at a lower rate than their corresponding counterparts – one can see the effect of the preceding thermal activation. The sample heated at 700°C (the surface of which is rather low due to the sintering processes – Table I) is reduced at the highest rate (Fig. 4). The reduction rate of the intermediates derived from the oxide B, on the other hand, decreases with the increasing temperature of calcination. The maximum reduction degree of the oxides of both sequences is practically identical and corresponds – under given conditions – to the gradual reduction of the oxides to metallic iron. Similarly, differences were observed in the kinetics of reduction of the both initial oxides A and B (after their previous dehydration) – as well as – differences in the rate and degree of reduction of the final – and especially of the spent catalysts. It is evident from the integral kinetic curves that the catalysts K4 – K6 (derived from the B1 – B3 intermediates) are reduced, under comparable conditions, at a higher rate and to a higher reduction degree than the corresponding samples of the first sequence. The reduction kinetics of the final catalysts of both sequences is affected by the presence of other components, which under given conditions, are not reduced for thermodynamic reasons (Cr_2O_3, TiO_2) or, they are reduced to lower oxidation states only (V_2O_5). From the DTA diagrams of

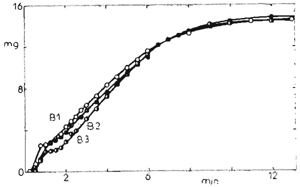

FIG. 5

Time courses of the reduction of oxides B1 – B3, at 520°C

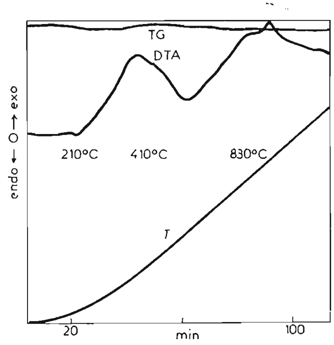

FIG. 6

DTA-diagram of a spent catalyst – sample KB1 the spent catalysts (Fig. 6) it follows – in agreement with X-ray analysis – that the majority component of the system is formed by the Fe_3O_4 phase (magnetite) and that its content differs in the samples of both sequences. Two exothermic effects registered at temperatures 410 and 830°C correspond to the transformations $Fe_3O_4 \rightarrow \gamma\text{-}Fe_2O_3$ and $\gamma\text{-}Fe_2O_3 \rightarrow \alpha\text{-}Fe_2O_3$ (haematite). An endoeffect at 200°C and weight deficit due to dehydration of the catalyst were also observed. The differences in the kinetics and in the degree of reduction of the spent catalysts of both sequences are similar to those described for the genetically preceding fresh catalysts.

The results of testing of the catalysts of both sequences by the dehydrogenation with ethylbenzene are summarized in Table II. The catalysts of the first sequence exhibit higher activity – but lower selectivity in comparison with the catalysts derived from the B1 – B3 oxides. The properties of the final catalysts can be therefore modified by the change of the CO_2/NH_3 ratio in precipitation of the initial intermediates. Since in the course of the dehydrogenation process the catalyst is always partially reduced[3], it can be assumed that the differences observed in the activity and selectivity can be connected with different reducibility of the catalysts of both genetic groups. In agreement with the above assumption, the higher activity of the catalysts of the first group can be attributed to the presence of iron oxides in various valency states – facilitating the electron transfer in the gas/solid interface. The higher selectivity of the catalysts of the second group is then connected with the reduction of these oxides to higher reduction degree. Similar conclusions were presented in paper[8], according to which a slight prereduction of the catalyst increased its selectivity in the following reaction. The long term testing showed a gradual increase in the selectivity of the catalyst, depending on the increasing reduction degree of the catalyst during the dehydrogenation[3].

TABLE II

Activity *A* (mol s^{-1} g^{-1} 10^8 of styrene) and selectivity *Y* (mol per cent of styrene) of the styrene catalysts K1–K6 for dehydrogenation of ethylbenzene, at different temperatures

Catalyst	540°C		560°C		585°C	
	A	*Y*	*A*	*Y*	*A*	*Y*
K1	31·0	94·2	42·6	93·6	54·6	91·3
K2	29·2	92·6	39·2	91·4	48·3	88·7
K3	25·9	93·7	37·0	93·9	49·9	92·2
K4	28·1	94·7	40·3	94·9	54·1	92·8
K5	27·3	95·3	39·2	95·0	53·8	93·4
K6	25·8	95·6	38·1	95·3	53·6	94·0

In addition to the majority component Fe_3O_4 in the spent catalysts, the X-ray analysis showed some additional reflections, which could not have been identified because of their small number and low intensity.

With respect to this fact – and in order to check the assumption according to which the course of the reaction is influenced both by the extent of reduction of the catalyst and by the crystallographic changes occurring during the reaction – two pure oxides differing in the CO_2/NH_3 ratio of precipitation were prepared independently by the standard procedure. From these oxides, two simple catalysts on a Fe_2O_3/K_2O basis were prepared – without any additional promoters. In the former oxide, the CO_2/NH_3 ratio equalled 2·58 – which corresponds to the solution of ammonium bicarbonate (analogue of sample A); in the latter oxide, the above ratio equalled 1 – which corresponds to the solution of ammonium carbonate with a 30% excess of NH_3. The oxides consisted in both cases of α-Fe_2O_3. The infrared spectra of the two oxides, as well as, of the derived freshly prepared catalysts showed no differences. The isothermal reduction with hydrogen was measured at 470°C. The reduction of the first oxide and of the related final catalyst proceeded at a lower rate and to the lower reduction degree. In the corresponding spent catalyst, the X-ray analysis and IR spectroscopy showed a presence of Fe_3O_4 and a small amount of unreduced α-Fe_2O_3.

The second oxide was, under comparable conditions, reduced at a higher rate through the following oxidation states, totally to metallic iron

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe_xO \rightarrow Fe\,.$$

The reduction of the corresponding final catalyst (showing lower activity but higher selectivity in the dehydrogenation) proceeded in a similar way. Differences in the reduction behaviour (*i.e.* in the rate and extent of reduction) were observed also with the spent catalysts obtained from both initial oxides. The spent catalyst derived from the second oxide is formed by the magnetite phase only.

On the basis of the results obtained from the model reduction it may be assumed that the catalysts which were prepared in different ways will be reduced with different kinetics and to different reduction degrees also in the dehydrogenation process itself. This fact, together with the phase transformation of the main component occurring during the reaction, affects the final activity and selectivity of the catalyst.

REFERENCES

1. Lisovskii A. E., Alkharov T. G., Safarov M. G.: Kinet. Katal. *13*, 1504 (1972).
2. Heynen H. W. G., Van der Baan H. S.: J. Catal. *34*, 167 (1974).
3. Lee E. H.: Catal. Rev. *8*, 285 (1973).
4. Skibata K., Kiyoura T.: J. Catal. *13*, 103 (1969).
5. Lee E. H., Holmes L. H.: J. Phys. Chem. *67*, 947 (1963).

6. Świeczerwska M., Berak J., Matecka B., Soszyńska H., Eysymontt J.: Przem. Chem. *51*, 669 (1972).
7. Pospíšil M., Cabicar J., Rejholec V.: This Journal *35*, 1319 (1970).
8. Pitzner E. W.: U.S. 3, 306 942 (1963).

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