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THE NATURE OF THE ACTIVE PHASE OF THE Fe/K-CATALYST FOR DEHYDROGENATION OF ETHYLBENZENE

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The industrial catalyst for high temperature dehydrogenation of ethylbenzene based on iron and potassium oxides undergoes, under reaction conditions, essentially a transformation into magnetite, Fe_3O_4, and a mixture of ternary oxides containing trivalent iron, viz. $K_2Fe_{22}O_{34}$ and $KFeO_2$. The latter compound constitutes the outside of the catalyst particles and is indeed the catalytically active phase.

1. Introduction

Dehydrogenation of ethylbenzene to styrene is carried out industrially over an iron oxide based catalyst containing about 14 mol% potassium oxide as well as several other oxides with concentrations around 1% which serves as promoters [1]. Typical reaction conditions are 873 K and a 6 : 1 molar ratio of water vapour and ethylbenzene at atmospheric pressure. With short contact times the conversion reaches about 95% of the thermodynamic limit with a selectivity around 90%, the main byproducts being benzene, toluene and carbon dioxide.

It was found [2] that the catalytic activity is essentially due to the combination between iron and potassium oxides, and several models about the actual nature of the catalyst under working conditions were suggested in the past. These include proposals of potassium ions being embedded in a matrix of iron oxides [3,4], as well as the concept of a supported liquid phase (SLP) catalyst [5]. The latter considers the catalyst as a two-phase mixture of solid magnetite (Fe_3O_4) and a supported liquid film of KOH. This film is believed to be predominantly located within the pore system of the solid which acts in a dual way as transport and storage medium. This model was supported by the fact that under reaction conditions iron oxides are transformed into magnetite which does not form a ternary phase with potassium because of the unfavourable size of the K^+ ion. The ternary Fe-K oxides known so far [6] are exclusively based on *trivalent* iron and form non-closely packed structures which were found to be incompatible with the

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crystallographic phases identified in *post mortem* studies of the catalyst. Little attention had been paid to the possibility of subsequent chemical transformations of the active phase.

Recent X-ray diffraction studies with quenched samples, however, brought evidence that the active phase might not consist exclusively of magnetite. Hirano [4] found the existence of $KFeO_2$ and suggested that the active phase might comprise some kind of ternary oxide. Koppe et al. [7] demonstrated that the phase which is commonly ascribed to the spinel structure of Fe_3O_4 may contain a considerable excess of Fe^{3+} ions. They proposed Fe_2O_3 in the form of maghemite as active phase, but rejected an explanation in terms of the presence of a substantial amount of ternary potassium-iron oxides.

The present short paper will describe the essential conclusions about the actual nature of the active phase of the catalyst under consideration which were obtained in an extended study in which a large variety of techniques were applied. These included *in-situ* X-ray diffraction, surface spectroscopies (XPS, UPS and ISS), electron microscopy, Mössbauer spectroscopy, catalytic testing and thermal analysis. A full account of the results obtained will be given later.

2. Experimental

The experiments were performed with samples of industrial catalysts provided by BASF, Ludwigshafen. Powders of 1 mm sieve fraction were prepared by crushing pellets. Catalytic testing was carried out with a microreactor containing 8 ml of the catalyst, as well as during X-ray analysis (see below) under typical reaction conditions of 873 K, 0.5 LHSV of 1 : 1 volume mixtures of ethylbenzene and water. Product analysis was either performed off line by gas chromatography (quantitative) or on line by mass spectrometry (qualitative). The UHV system containing – among other techniques – facilities for X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) as well as ion scattering spectroscopy (ISS), to which the microreactor was coupled via a transfer mechanism is described elsewhere [8].

In-situ X-ray diffraction studies under the stated reaction conditions were performed by use of an Anton Paar high temperature camera. A Jeol CX 200 instrument served for the electron microscopy resp. diffraction experiments.

3. Results and discussion

All active catalysts exhibit a typical morphology showing a uniform porous structure with average pore diameters around 1 μ, giving rise to a N_2 BET surface area of about 2.5 m^2/g. Electron microscopy demonstrates that the pore walls are formed by stacks of hexagonal platelets with dimensions of about 50×10 nm.

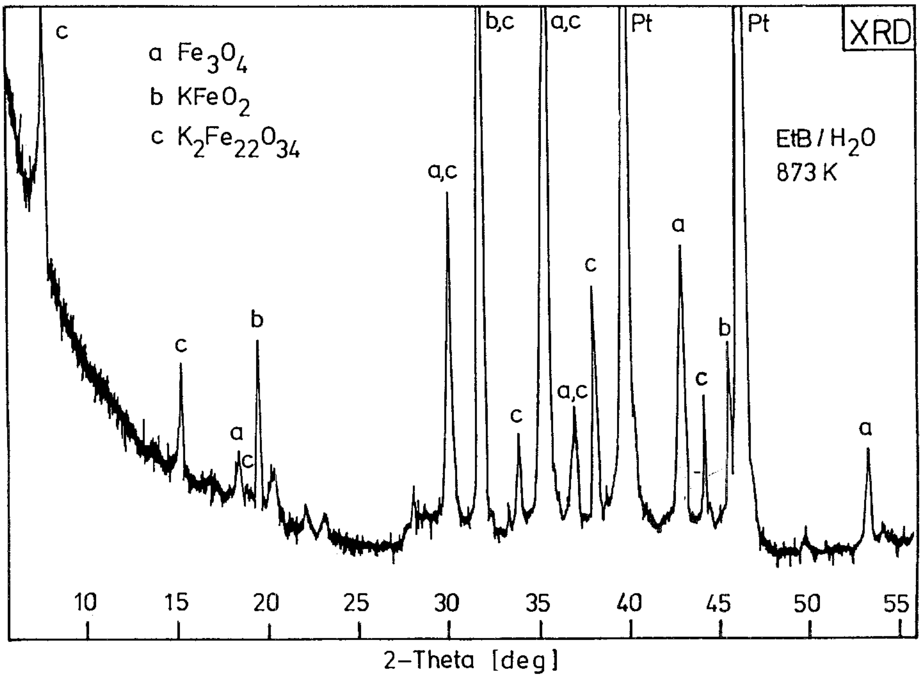

Fig. 1. In-situ X-ray diffraction pattern (post-monochromated CuK_α radiation) of an industrial catalyst under reaction conditions. The lines from the Pt sample holder serve as internal reference. The background intensity at $2\theta < 15°$ arises from the X-ray scattering of the reaction atmosphere.

There is no indication for the formation of a liquid film in the inner parts of the catalyst [9], while the outer surface of a used catalyst becomes – after storage in air – covered by precipitated basic potassium carbonates. There are, however, substantial amounts of potassium also present in the inner parts of the catalyst as evidenced by EDX. Catalysts which had been in use for several months and were therefore already subject to irreversible long-term desactivation exhibited, however, the appearance of solidified droplets within their core region [9]. This phenomenon is clearly not characteristic for the active state of the catalyst and will not be discussed further in the present context.

Figure 1 shows an in-situ wide scan X-ray diffraction pattern of a catalyst sample being on stream for 24 hours. Analysis of the inelastic scattering part in comparison with the pattern from molten KOH revealed no evidence for the existence of a liquid phase containing potassium. There was also no indication for the presence of crystalline K_2CO_3 which would be a solid compound under reaction conditions. The data of fig. 1 demonstrate, on the other hand, besides magnetite clearly the existence of the ternary K-Fe oxides $KFeO_2$ and $K_2Fe_{22}O_{34}$, which contain iron as Fe^{3+} as mentioned above. The diffraction intensities from these compounds varied considerably with different types of catalyst samples, suggesting that substantial amounts may also be present in a non-crystalline

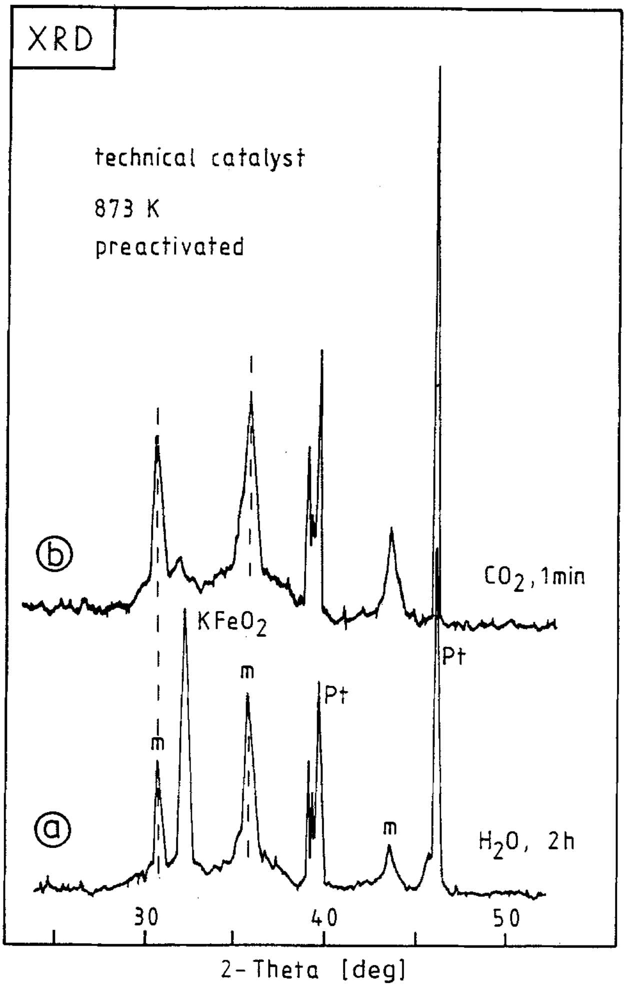

Fig. 2. In-situ X-ray diffraction pattern of another catalyst exhibiting peaks from magnetite (m) and from $KFeO_2$. a) After activation with water vapour at 873 K. b) After poisoning with CO_2 has the intense peak from $KFeO_2$ disappeared.

form. This active state of the catalyst is metastable: If samples are cooled in air or moist nitrogen, these ternary oxides disappear and transform into Fe_2O_3, non-stoichiometric magnetite and basic iron oxides, as well as into complex mixtures of potassium hydroxide-carbonate phases. This is the reason why the quoted ternary oxides escaped identification in previous post mortem structural investigations.

Figure 2, curve a, shows a section of the diffraction pattern of another active catalyst sample which in this case exhibits, besides Fe_3O_4, only the presence of crystalline $KFeO_2$. (Note the absence of the $K_2Fe_{22}O_{34}$ peaks which were marked by c in fig. 1). This sample was prepared by treating a preactivated catalyst with water vapour. In this stage the sample was briefly exposed to CO_2 which is known to very efficiently cause poisoning [2,4]. The resulting diffraction pattern (trace b) demonstrates that this procedure causes the disappearance of the $KFeO_2$ phase. This experiment therefore strongly suggests that this compound is indeed the catalytically active phase.

This conclusion is corroborated by further experimental findings:

(i) The surface of a catalyst which was rapidly quenched from its active state and then transferred to the UHV chamber was analysed by ion scattering spectroscopy (ISS), which technique probes the elemental composition of the outermost layer of a solid [10]. The resulting K : Fe ratio of about 1 : 1 indicates strong surface enrichment of potassium and is fully consistent with the stoichiometry of $KFeO_2$. After mild sputtering with Ar ions this ratio dropped to about 1 : 10, indicating that a potassium-rich phase does not exist as a thick overlayer. XPS measurements of the K 2p and Fe 2p core level intensities revealed a surface stoichiometry of 1 : 1 for the active catalysts, again in strong support of the proposed model.

(ii) $KFeO_2$ contains only trivalent iron ions. While the distinction between Fe^{2+} and Fe^{3+} by means of XPS is not easy because of the complex satellite structure of the spectra, this is more straightforward by the use of UPS ($h\nu = 21.2$ eV). The A 1g transition of Fe^{2+} shows up in the valence spectrum as a feature centered at about 1 eV below the Fermi level, and is, on the other hand, not existent for the Fe^{3+} ion with d^5 configuration. Figure 3, curve a, reproduces the UP spectrum of a poor catalyst exhibiting the spectral feature of Fe^{2+} just mentioned, which disappears after subsequent oxidation (curve b). The spectrum from an active catalyst (curve c) is again characteristic for the absence of any noticeable concentrations of Fe^{2+} within a depth of a few atomic layers are probed by this technique.

(iii) XPS measurements from the K 2p core level region were performed with a series of reference compounds and revealed – in agreement with literature data [11] – a binding energy of 294.0 eV for K coordinated to hydroxyl groups, and of 293.3 for K coordinated to oxide anions. With highly active catalysts only the latter species was found, while less active samples revealed also the presence of potassium ions attached to hydroxyl groups.

These pieces of evidence are believed to be conclusive to identify the catalytically active surface as a phase consisting of a high concentration of K^+ in a matrix of trivalent iron oxide such as $KFeO_2$. Inspection of fig. 1 reveals, however, the existence of another ternary oxide, $K_2Fe_{22}O_{34}$, which sometimes may even be identified in the precursor state of the catalyst prior to its activation. This phase may form continuous mixtures with Fe_3O_4 yielding the nominal overall composition of the catalyst, and is considered as a storage medium for both Fe^{3+} and K^+. These structural relations could be clarified by using selected area electron diffraction and lattice imaging techniques in transmission electron microscopy.

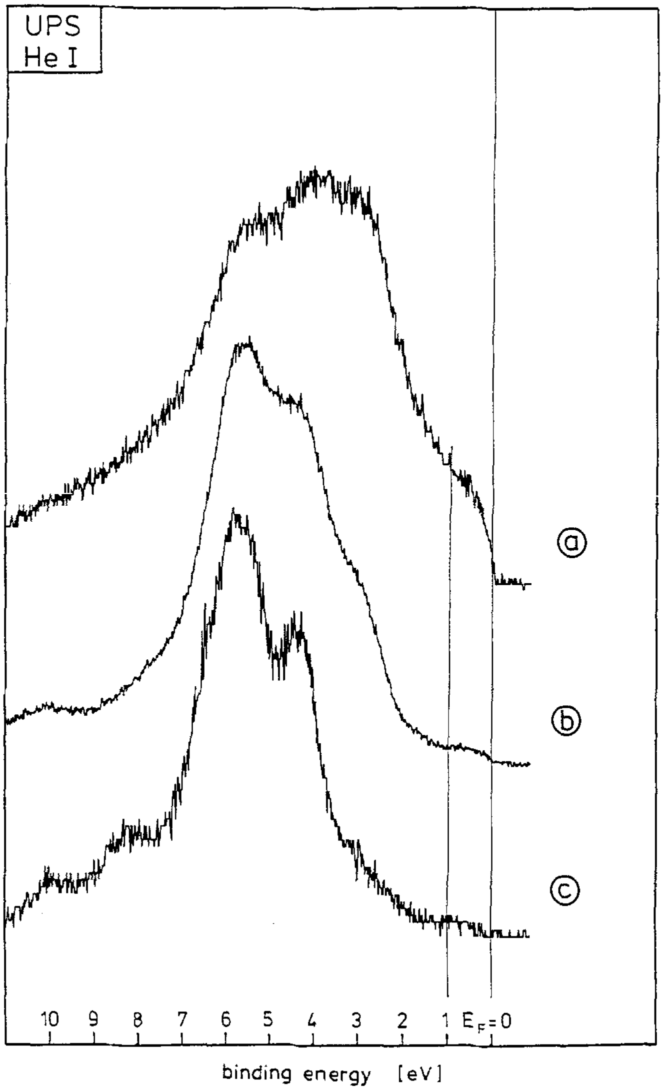

Fig. 3. HeI ultraviolet photoelectron spectra from the valence band region of technical catalysts. The energy scale is referred to the Fermi level E_F. a) Spectrum from a poor catalyst after transfer of the sample from the reactor to the UHV system. b) The same sample after oxidation in air. c) Spectrum from an active catalyst.

Figure 4 shows a series of electron diffraction patterns recorded from $K_2Fe_{22}O_{34}$ (a) and from two different spots of the same catalyst platelet (b and c). The more intense spots in the latter two images correspond to diffraction at the lattice of Fe_3O_4 which *apparently* exhibits a 2 × 2 superstructure. The assignment of a true superlattice cannot, however, be correct, as becomes immediately evident from the different intensity ratios of the two spot systems in both images. The weaker spots are in fact due to $K_2Fe_{22}O_{34}$, as becomes evident by comparison with fig.

4a, and the differing intensity ratios in figs. 4b and c simply reflect varying relative proportions of both places within the two regions analysed. More specifically, the indexing of the diffraction spots reproduced in fig. 4d demon-

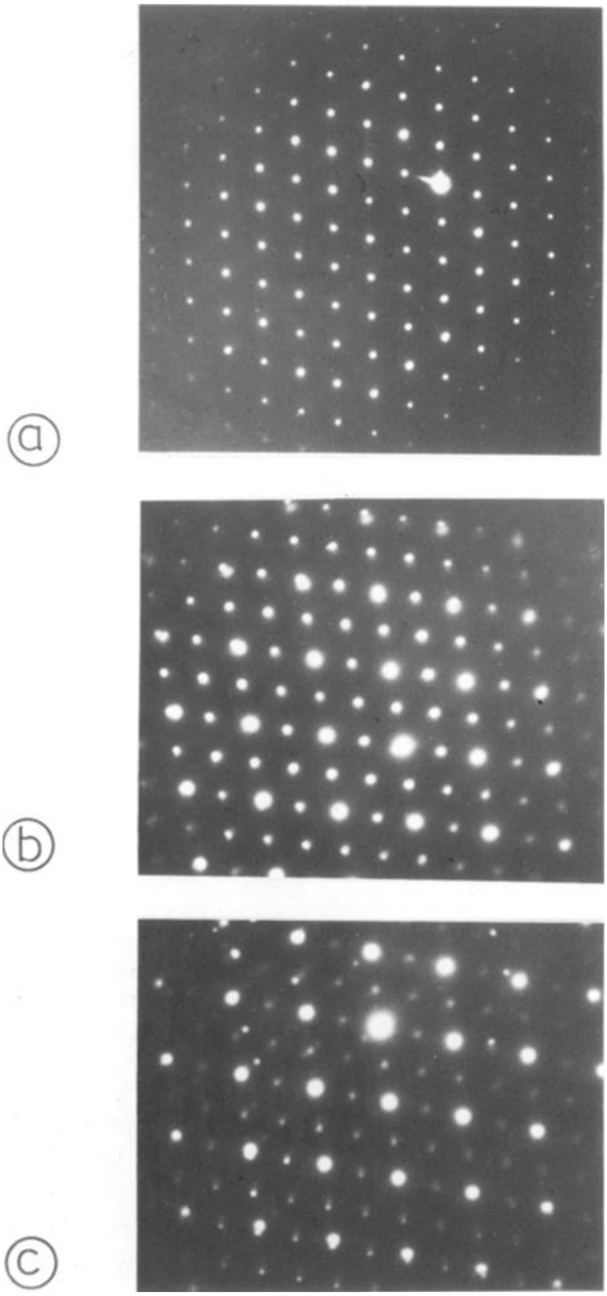

Fig. 4. Electron diffraction patterns (200 kV) a) from a $K_2Fe_{22}O_{34}$ reference sample; b) and c) from two different regions of the same platelet of a preactivated catalyst.

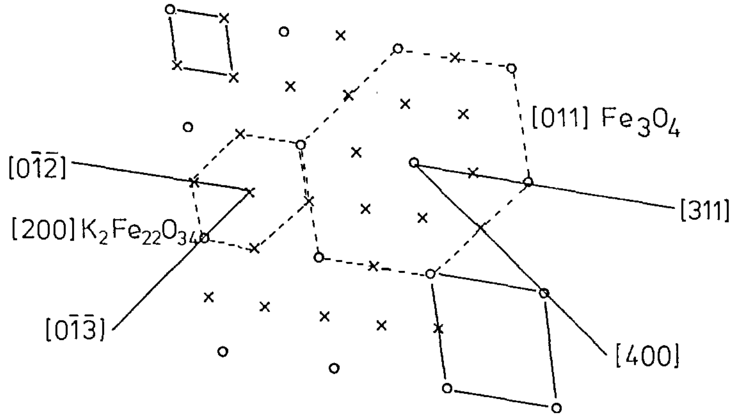

Fig. 4 (continued). d) Analysis of the patterns: Directions of projections as well as indexing of the two sub-patterns from Fe_3O_4 (O) and $K_2Fe_{22}O_{34}$ (×).

strates how the apparent superlattice is formed as the (200) projection of $K_2Fe_{22}O_{34}$ over the (011) projection of Fe_3O_4, with the (311) lattice spacing of the latter compound being just half as large as the (010) spacing of the ternary oxide. This perfect epitaxial matching permits continuous intergrowth of $K_2Fe_{22}O_{34}$ into the magnetite matrix without the formation of grain boundaries or the build-up of mechanical strain.

The structural uniformity of the $Fe_3O_4 + K_2Fe_{22}O_{34}$ mixture is also reflected in the lattice image reproduced in fig. 5. Distinction between $K_2Fe_{22}O_{34}$ and Fe_3O_4 is hard with this image, but corresponding evidence will be presented in a forthcoming more extended report about these investigations. Apart from the mixed phase under discussion, the image of fig. 5 exhibits, in addition, at the

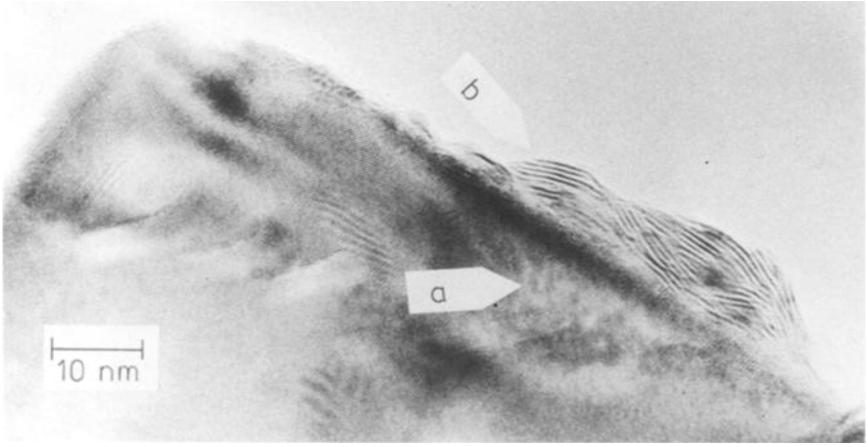

Fig. 5. TEM-lattice image from a preactivated catalyst particle exhibiting regions with the $Fe_3O_4/K_2Fe_{22}O_{34}$ mixture (a) and of the $KFeO_2$ shell forming the catalytically active phase (b).

Table 1
Comparison of kinetic data obtained with an industrial catalyst and with a $KFeO_2$ sample. Reaction conditions as indicated in the text.

	Catalyst	$KFeO_2$
Conversion [%]	43	42
Yield of toluene [%]	1.8	1.7

outside of the catalyst particle a shell with different lattice spacings and poor crystallinity. On the basis of its structural parameter this part can be identified as $KFeO_2$, so that the proposed model for the catalytically active phase is nicely confirmed in this way.

A test of catalytic activity was performed as final check of the validity of the presented conclusions. $KFeO_2$ was synthesized from hematite and potassium carbonate and characterized by X-ray diffraction. This green material (which was unstable in air) was loaded in chip form into the microreactor and subjected to the ordinary reaction conditions. The degrees of conversion as well as yields of the main byproduct, toluene, measured after about two days on stream are listed in table 1 in comparison with the corresponding data obtained with an industrial catalyst. The agreement is very remarkable and is considered as final proof for identifying $KFeO_2$ as the catalytically active phase.

4. Conclusions

The complex solid state chemistry of the iron oxide based catalyst for dehydrogenation of ethylbenzene to styrene can now be summarized in a simplified manner as follows:

The inactive precursor consists of Fe_2O_3 and unspecified K compounds (partly $K_2F_{22}O_{34}$). Under the conditions of the reaction (ethylbenzene + water vapour) conversion into Fe_3O_4 and $K_2Fe_{22}O_{34}$ takes place which two compounds are forming continuous mixtures by practically perfect epitaxy. This reduction process during the start-up period causes the release of mobile K^+ ions which in turn react with remaining trivalent iron oxides to the active phase $KFeO_2$. Under steady state conditions the latter compound forms a thin layer at the outsides of the hexagonal catalyst platelets. Desactivation of the catalyst may take place along two routes, either reversibly by the formation of carbon deposits which can be gasified by water vapour, or – on a longterm scale – irreversibly by complete reduction:

$$3\ KFeO_2 + \tfrac{1}{2}H_2 + H_2O \rightarrow Fe_3O_4 + 3\ KOH.$$

It is only this desactivation process which causes the formation of a liquid phase (KOH), so that the term SLP denotes indeed the 'dead' state of the catalyst. The role of the additional promoters consists essentially in stabilising the (metastable) active state of the catalyst against this further reduction step as will be outlined in more detail elsewhere.

Acknowledgements

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