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Research Note

How the iron oxide catalyst for EBDH is stabilized via Mn addition

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Abstract

The stability effect of Mn dopand on the potassium loss from β-ferrite, the active phase of a styrene catalyst, has been quantified for the first time in succinct measurements by means of a species-resolved (K and K^+) thermal alkali desorption technique. Upon introduction of 2 wt% of Mn the desorption energies increased by 1.06 eV for ions, whereas the atomic barrier, which is crucial for the potassium volatilization, was enhanced by 1.52 eV. As a result, both K desorption fluxes are significantly extinguished.

Keywords: Styrene catalyst; Alkali promoter; Potassium ferrites; Potassium desorption; Manganese addition

1. Introduction

The catalytic ethylbenzene dehydrogenation (EBDH) to styrene is one of the most important industrial processes, with the current world production level of 20×10^6 ton/year. In industrial practice iron oxide catalysts are exclusively used. The activity of bare iron oxides is very low, but the addition of alkali can readily enhance it by an order of magnitude [1]. However, the catalyst deactivates steadily and needs to be replaced every 1–2 years. Thus extensive research has been dedicated not only to an understanding of the nature of the catalyst and the active state of its surface but also to the deterioration process. The latter one consists in two main concurrent routs: deposition of excessive carbon and the loss of potassium promoter [2]. The activity decay is associated with potassium removal from the surface during the time-on-stream operation and both can be described by a first-order rate law [1]. In order to prolong the catalyst activity steam is cofed to the reactant stream for coke removal, whereas various attempts to improve potassium stability involve solid state doping with alien metal ions. Typical stabilizers include Cr, Ce, V, Al, and Mo [1]. Recently, spectacular results have been reported with Mn. The EBDH screening tests have revealed that manganese ferrite is the best catalyst among the five transition metals examined (Mn, Co, Ni, Cu, Zn), increasing the number of active sites and preventing the deterioration of the catalyst as well [3,4].

A newly developed species-resolved thermal alkali desorption (SR-TAD) method was applied to monitor the loss of K and K^+ from the model phases present in the EBDH catalyst. The life cycle of the catalyst elucidated by Muhler and co-workers [5,6] and Schlögl and co-workers [7] entails the following transformation steps

$$K\text{–}Fe_2O_3 \rightarrow KFeO_2 \leftrightarrows K_2Fe_{22}O_{34} \rightarrow K\text{–}Fe_3O_4.$$

The catalytic activity was found to be related to the equilibrium between the ferrite components, and the $K_2Fe_{22}O_{34}$ phase was explicitly identified as that responsible for potassium volatilization from the catalyst [8].

The aim of this work is to quantify the beneficial effect of Mn addition on the potassium volatility from the active β-ferrite phase in terms of desorption energetics

2. Experimental

Samples of undoped and Mn-doped $K_2Fe_{22}O_{34}$ were prepared by solid-state reaction of stoichiometric mixtures of K_2CO_3 with α-Fe_2O_3 in 1470 K according to the procedure given elsewhere [9,10]. For 0.25–2 wt% Mn-doped samples the apposite part of α-Fe_2O_3 was replaced by MnO_2. The phase identity was verified after each synthesis by X-ray diffraction using an X'pert Pro Philips powder diffractometer with Cu-K_α radiation in a Bragg–Brentano geometry. The diffraction pattern of the synthesized ferrites, indexed

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within the P6_3/mmc space group, revealed that the samples were essentially monophasic. The surface morphology was examined with a Philips scanning electron microscope Model XL 30 at magnification of ×5000 and ×10,000. The well-developed plate crystallites of hexagonal shape (0.5–2 μm in diameter and thickness of ∼ 0.2 μm) resembled that of a single K^+–β-ferrite with stoichiometric composition [9], regardless of the manganese content. The EDS (LINK-ISIS) elemental mapping showed a fairly uniform distribution of the constituents (K, Fe) and the Mn dopant. Thus, it can be concluded that the sample morphology and phase integrity were preserved upon Mn doping and the resulting materials exhibited good homogeneity.

The surface stability of potassium was investigated by the species-resolved thermal alkali desorption method [8]. The experiments were carried out in a vacuum apparatus with a background pressure of 10^{-7} mbar. The samples in the form of wafers of 10-mm diameter and mass of 100 mg were heated from room temperature to 900 K in the intermittent mode at the rate of 5 K/min. Since the previous desorption studies of potassium from styrene catalysts [11–15] and related ferite phases [8,16] have revieled that the K loss occurs in the form of atoms (in the ground and excited states) and ions to obtain an integral picture of the promoter stability we followed both K and K^+ desorption fluxes. The desorption flux of potassium atoms was determined by means of a surface ionization detector [17], while the flux of K^+ ions simply by the ion collector. Since ferrites are efficient electron emitters during the measurements the samples were biased with a positive potential (+10 and +60 V for K and K^+, respectively) to quench the thermal emission of electrons and additionally in the case of K^+ to accelerate them toward the collector. In this way the possibility of reneutralization of K^+ ions by thermal electrons outside the surface is effectively eliminated. In all measurements the resultant positive current was measured directly with a Keithley 6512 digital electrometer.

3. Results and discussion

The comparison of the K and K^+ desorption fluxes from undoped and Mn doped β-ferrite is shown in Fig. 1. For both samples the atomic flux overwhelmed the ionic one, which means that the main channel of potassium loss from the catalyst is due to atoms. The statistical probability of the ratio of ionic and neutral fluxes (j_+/j_0) from the surface is given by the Saha–Langmuir equation [18]

$$\frac{j_+}{j_0} = \frac{g_0}{g_+} \exp\left[-\frac{e(V-\varphi)}{k_B T}\right],$$

where g_+/g_0 is the ratio of the statistical weights of the ionic and atomic states (for potassium equal to $\frac{1}{2}$) and e, V, φ, k_B, and T denote elementary charge, ionization potential of desorbing atom (for potassium 4.3 eV), work function of the surface, Boltzmann constant, and temperature, respectively.

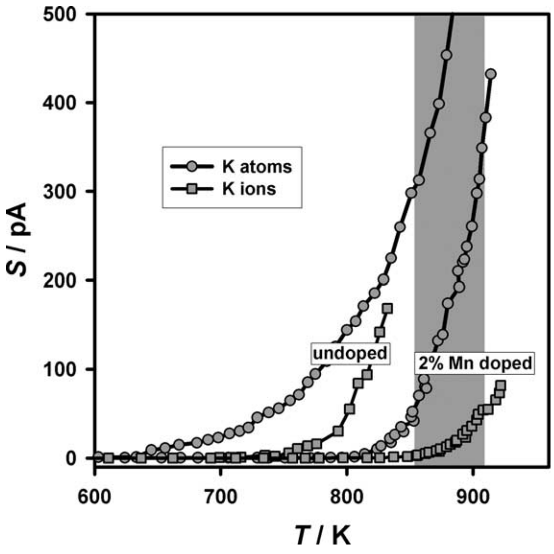

Fig. 1. Suppression of atomic and ionic desorption fluxes from the $K_2Fe_{22}O_{34}$ phase upon 2 wt% addition of Mn. The ionic signal from undoped sample is multiplied by 100. The gray rectangle represents the temperature range of industrial styrene synthesis.

The extent of surface ionization of potassium is relatively small, indicating that the work function of the samples is lower than its ionization potential. Indeed, the work function for the $K_2Fe_{22}O_{34}$ ferrite determined in a parallel experiment of electron thermionic emission was 2.2 eV, as assessed from the Richardson–Dushman formula,

$$j_{e-} = (1-r)AT^2 \exp\left(\frac{e\varphi}{k_B T}\right),$$

where j_{e-} is the thermionic electron current, r is the reflection coefficient (usually close to 0), and the preexponential factor $A = 4\pi emk_B/h^3$. The loss of potassium can grosso modo be regarded as a volatilization process.

For the undoped β-ferrite the beginning of the appreciable K desorption was observed at a temperature of about 650 K, whereas for Mn-substituted it was shifted above 800 K. The monotonous exponential changes of the signal with temperature indicate that in each case the potassium leaves the surface through a single potential barrier. Therefore the corresponding desorption energies were determined from the linear part of the Arrhenius-like plots ($\ln S$ versus $1/T$). Their values are collected in Table 1.

For desorption of potassium atoms the energy barriers varied from 0.83 ($K_2Fe_{22}O_{34}$) to 2.84 eV ($KFeO_2$). For ionic

Table 1
Activation energies for K and K^+ desorption from Mn-doped and undoped potassium ferrites[a]

Sample	E_d(K) (eV)	E_d(K^+) (eV)
$K_2Fe_{22}O_{34}$	0.83 ± 0.01	2.33 ± 0.03
$KFeO_2$	2.84 ± 0.06	2.95 ± 0.01
2% Mn–$K_2Fe_{22}O_{34}$	2.35 ± 0.03	3.39 ± 0.04

[a] The energies were calculated for the correlation coefficient higher than 0.98 and the errors correspond to a 95% confidence limit.

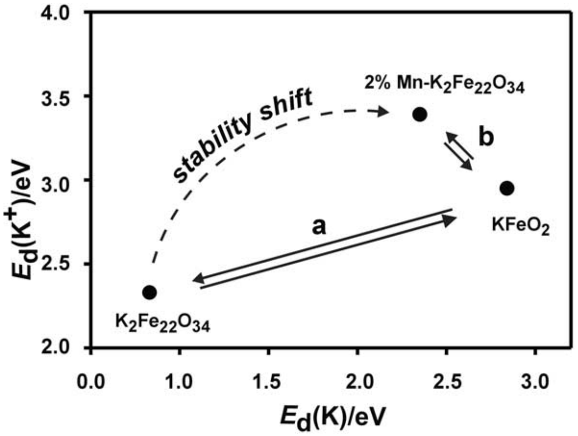

Fig. 2. Energetic of potassium loss ($E_d(K^+)$ vs $E_d(K)$) from active phases of EBDH catalysts and the desorption energy shifts caused by the 2% Mn additive. The equilibrium between potassium ferrites representing the active state of the undoped (a) and Mn-doped (b) catalyst surface.

desorption the energies are respectively higher ranging from 2.33 ($K_2Fe_{22}O_{34}$) to 3.39 eV (2% Mn–$K_2Fe_{22}O_{34}$). The lower desorption energies for atoms and the resulting domination of the atomic fluxes are characteristic for oxide surfaces in the measured temperature range [19]. The obtained activation energies can be accounted for by the desorption of potassium from the catalyst surface along several energetic pathways, leading to ionic and atomic potassium in different final states (4s, 4p, 3d, etc.) outside the surface [15].

From the previous desorption experiments [8] it has been inferred that the stability of K atoms varies as

$$K\text{–}Fe_2O_3 \gg KFeO_2 > K\text{–}Fe_3O_4 \gg K_2Fe_{22}O_{34},$$

while for K^+ ions the corresponding series is

$$K\text{–}Fe_2O_3 > K\text{–}Fe_3O_4 \gg KFeO_2 > K_2Fe_{22}O_{34}.$$

The energy diagram for the active state equilibrium between potassium ferrites shown in Fig. 2a points clearly at the β-ferrite as the most relevant phase for potassium loss from the catalyst. Therefore, the appearance of this phase opens an efficient channel for potassium desorption mainly in the form of atoms as the corresponding barrier is the lowest from the observed ones. Unavoidably, the catalyst activity is related to the extensive depletion of the promoter.

Introduction of 2 wt% of Mn led to drastic changes of the potassium stability. The desorption energies increased by 1.06 eV for ions and, even more important, the atomic barrier, crucial for the potassium loss, was enhanced by 1.52 eV. As a result, both K desorption fluxes (atomic and ionic) are significantly quenched and the catalytically vital equilibrium between ferrites (Fig. 2b) in the stability plane ($E_d(K^+)$ vs $E_d(K)$) occurs in the preferable region of high desorption energies. Interestingly, the noteworthy stabilization shift conferred by Mn was already observed at a loading as low as 0.25 wt%.

The beneficial role of manganese consists in stabilization of potassium in the β-ferrite phase; thus, it is important that in the course of catalyst formation the Mn dopand is incorporated into this component of the active catalyst. The thermal desorption method used in this study allows for a quick characterization of the potassium stability and can be therefore used as a time shortening alternative for the screening test of potassium volatilization from the styrene catalysts.

4. Conclusions

This study has demonstrated the applicability of the SR-TAD technique for characterization of the potassium surface stability in the EBDH iron oxide catalyst. For the first time the desorption fluxes and energies were quantified in a single concise experiment and used to account for the effect of Mn doping on extinguishing the loss of the K promoter from the $K_2Fe_{22}O_{34}$ key phase of the active catalyst.

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