Journal of Thermal Analysis and Calorimetry, Vol. 65 (2001) 445–450

POTASSIUM FERRITES FORMATION IN PROMOTED HEMATITE CATALYSTS FOR DEHYDROGENATION
Thermal and structural analyses

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Abstract

K-promoted hematite catalysts for ethylbenzene dehydrogenation were studied by thermal analysis (TG/DTG) and high-temperature XRD. The formation of potassium ferrite ($K_2Fe_2O_4$), considered to be a catalytically active phase, was observed during calcination of the Ce-promoted catalysts. A linear correlation of the catalytic activity and the temperature of potassium ferrites formation was found.

Keywords: DTG, ethylbenzene dehydrogenation, hematite catalysts, potassium ferrites, XRD

Introduction

The commercial catalysts of ethylbenzene dehydrogenation to styrene are usually prepared from paste of powdered iron oxide (hematite) and promoters (K and Cr compounds). The well-mixed paste is pressed in cylinders then cut, dried and calcined (above 900°C). Although the obtained catalysts are stable, their catalytic performance (activity and selectivity) can vary within rather broad range, which constrains an adjustment of the catalytic process parameters to any new catalyst load.

Our studies have been focused on dependence of the catalytic performance upon details of the catalyst preparation. In a previous paper [1] a series of hematite catalysts of different compositions and preparation methods were reviewed. They were characterized in relation to surface and phase development during a particular preparation and compared with the catalytic performance in ethylbenzene dehydrogenation. No clear correlation has been found. Nevertheless, a strong influence of dispersion of the promoters and α-Fe_2O_3 has been noticed. Hence, the coprecipitation and incipient wetness impregnation methods should be preferred for the catalysts preparation. Additionally, such a way of synthesis leads to obtain the strongly defected

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1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

α-Fe_2O_3, which was recognized as an effective catalyst for ethylbenzene dehydrogenation [2].

Thermal analysis has been found to be a useful tool for the investigation of transformation of alkali doped Fe oxides systems occurring at elevated temperatures. Orewczyk [3] reported on influence of Ca and Mg oxides on reduction of magnetite. The reactions of potassium carbonate with several transition metals oxides were studied by Milic *et al.* [4]. It was shown that potassium carbonate reacts with iron(III) oxide in one stage, whereas the reactions with titanium, vanadium, chromium and manganese oxides are more complex. The present paper is devoted to thermal analyses of the differently promoted (K, Cr, Ce) hematite catalysts supported by high-temperature XRD. A correlation between DTG peaks of these catalysts and their catalytic performance in ethylbenzene dehydrogenation will be shown.

Experimental

A series of iron oxide-based precursors were prepared by the coprecipitation method from aqueous solutions of suitable metal nitrates, $Fe(NO_3)_3\cdot 9H_2O$ (POCh), $Cr(NO_3)_3\cdot 6H_2O$ (POCh), $Ce(NO_3)_3\cdot 4H_2O$ (Merck), and a precipitating agent, KOH (POCh) or K_2CO_3 (POCh). The details of preparation were reported in [1].

To compare the promoted catalysts with the simple oxide system, two samples were obtained by mixing of solid K_2CO_3 (POCh) or $KHCO_3$ (POCh) with Fe_2O_3 (Riedel) at molar ratio $K_2CO_3/Fe_2O_3=0.22:1$ and $KHCO_3/Fe_2O_3=0.45:1$, respectively. A part of each prepared mixture was moistened to prepare pastes. The comparative samples were dried in the same way as the catalysts.

The thermal analyses (TG/DTG) were performed in TG/SDTA 851^e Mettler Toledo apparatus. About 25 mg of samples were heated in an argon atmosphere (80 mL min^{-1}) at a heating rate 10°C min^{-1} over a temperature range from 30 to 1100°C in a Pt pan (150 μl). The catalysts were examined by polythermic X-ray powder diffraction (XRD) using a PW3710 PhilipsX'pert diffractometer with CuK_α radiation (λ=1.54056 Å). The diffractograms were collected in air atmosphere at room and elevated temperature (from 500 up to 1000°C in steps of 100°C).

The catalytic tests for ethylbenzene dehydrogenation were performed at 610°C in a flow quartz reactor using 60 mg of a catalyst. The carrier gas was helium (50 mL min^{-1}), saturated with ethylbenzene (0.3 vol%) and water (0.6 vol%) vapour. Reaction products (styrene, benzene, toluene) and unreacted ethylbenzene were analysed using a gas chromatograph CP-3800 (Varian) equipped with a capillary column CP-8 (Chrompack) and linked on line with a mass spectrometer Saturn 2000 (Varian).

Results and discussion

Thermal analyses of the calcined catalysts prepared by coprecipitation using K_2CO_3 solution are shown in Figs 1a–c. The small mass losses at about 100°C in case of the non-impregnated catalysts are related to evolution of water, confirmed by MS. How-

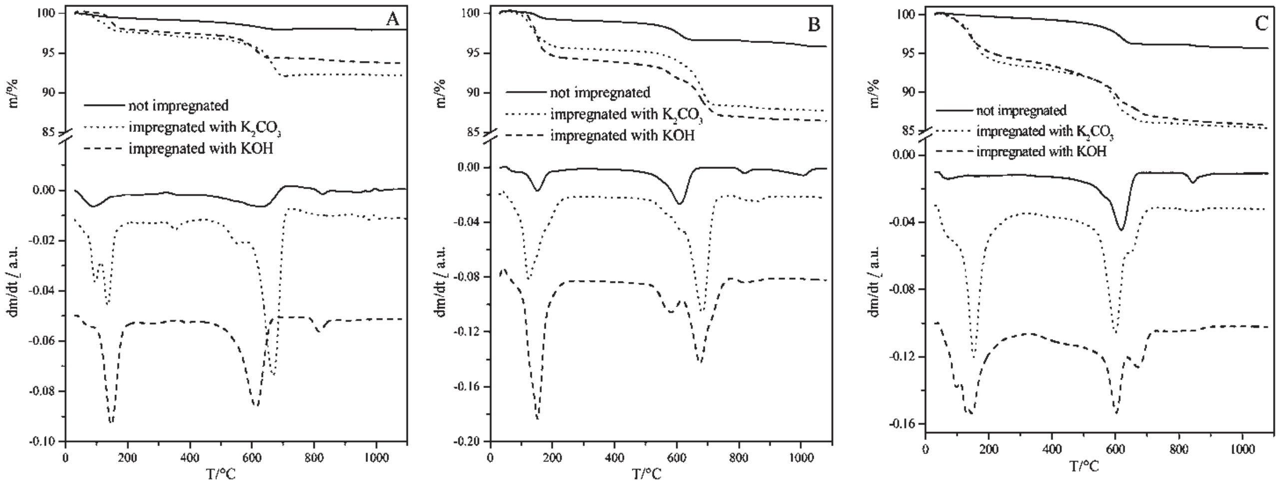

Fig. 1 TG and DTG curves for unpromoted (A), Cr-promoted (B) and Ce-promoted (C) hematite catalysts

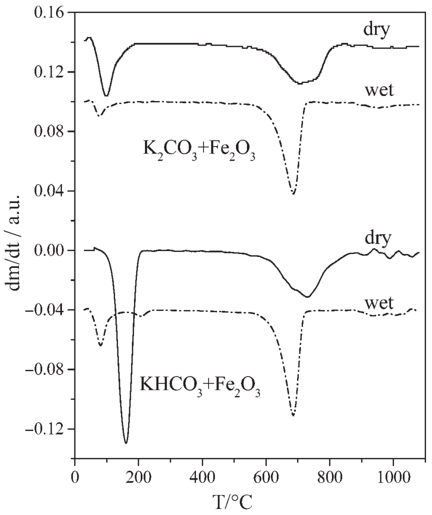

Fig. 2 DTG curves of Fe_2O_3 powder mixed with K_2CO_3 or $KHCO_3$

ever, the main mass losses of these samples take place above 500°C. The greatest effect is observed in case of the Ce-promoted catalyst.

The impregnation procedure, resulting in about 20 times increase of K_2O contents, causes serious enhancement of all the DTG peaks. A part of them divides into steps. The catalysts containing Cr or Ce show larger mass losses than the Fe–K–O catalysts. The DTG curves of the catalysts precipitated with KOH solution are very similar to those precipitated with K_2CO_3 solution. One may conclude that such a change of precipitating agent has no significant influence on the solid-state transformation of the promoted hematite catalysts.

The DTG curves of the comparative sample of mixed powders of Fe_2O_3 with K_2CO_3 or $KHCO_3$ are shown in Fig. 2. There is a significant difference between the samples obtained by mixing dry powders and those mixed together with water and then dried. The first samples show a strong mass loss above 100°C. In case of $Fe_2O_3/KHCO_3$ mixture the loss is equal to 6.5%. This value is close to the expected one based on the mixture composition and stoichiometry of the reaction:

$$2KHCO_3=K_2CO_3+H_2O+CO_2$$

The effect is much smaller for the samples mixed with water and dried because $KHCO_3$ has decomposed during the preliminary drying. All mixed powders loss the mass above 600°C with evolution of CO_2. However, it cannot be related to the simple thermal decomposition of K_2CO_3 because it happens above 890°C. Probably, potassium ferrites are formed with evolution of CO_2:

$$11Fe_2O_3+K_2CO_3=K_2Fe_{22}O_{34}+CO_2$$

$$Fe_2O_3+K_2CO_3=K_2Fe_2O_4+CO_2$$

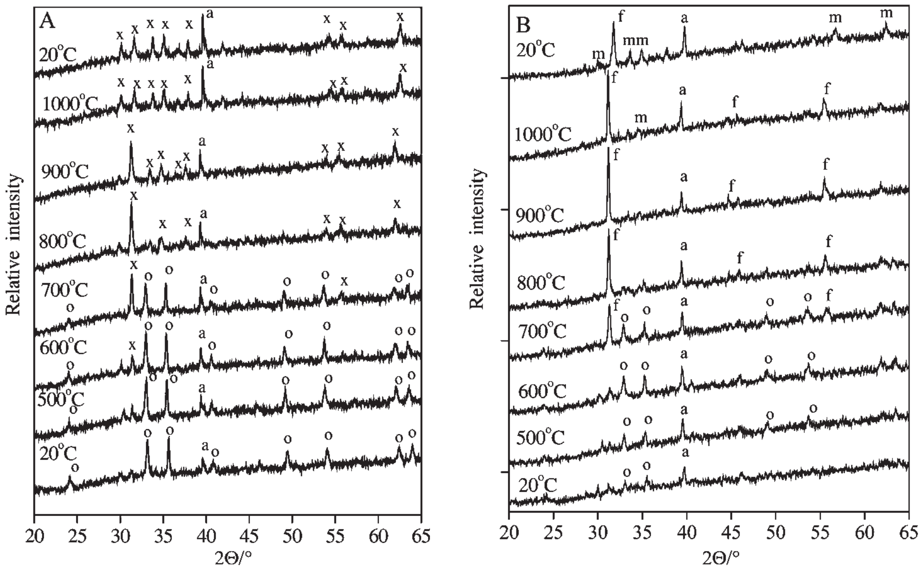

Fig. 3 XRD patterns of Cr- (A) and Ce-promoted (B) hematite catalysts measured at the elevated temperatures (up to 1000°C) and after cooling to the room temperature (o – hematite, m – magnetite, x – β-$K_2Fe_{22}O_{34}$, f – $K_2Fe_2O_4$, a – Pt holder)

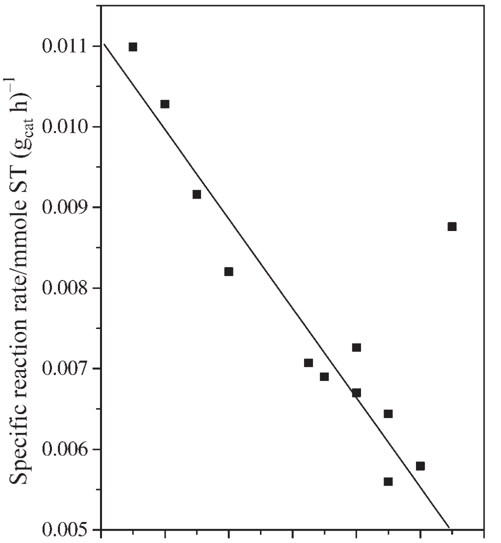

Fig. 4 Dependence of specific reaction rate *vs.* temperature of potassium ferrite formation for all the K-promoted catalysts

The results of TG analysis of the oxide mixture allow us to relate the low temperature effect observed in the impregnated catalysts case to dehydration and $KHCO_3$ decomposition. Similarly, the high temperature effects should be related to the formation of potassium ferrites.

XRD measurements confirm the above suppositions. The XRD patterns for Cr- and Ce-promoted catalysts are shown in Fig. 3. No doubts that with temperature increase the phase composition of the catalysts is changed. The peaks of α-Fe_2O_3 (hematite) vanish above 600°C. Instead of hematite peaks the ferrite ones appear. But, in case of Cr-promoted samples it is β-$K_2Fe_{22}O_{34}$, while in the Ce-promoted samples the peaks of $K_2Fe_2O_4$ are found. $K_2Fe_2O_4$, suggested as the active phase [5], is formed during the catalytic reaction according to Muhler *et al.* [6, 7]. This supposition should be modified at least in case of CeO_2 presence in the catalyst precursor. Overheating of such catalysts caused the decomposition of $K_2Fe_2O_4$, which overheated decomposes partially with evolution of Fe_3O_4, then a partial reduction of Fe(III) ions takes place. $K_2Fe_{22}O_{34}$ is much more stable and remains in the Cr-promoted catalysts even at 1000°C. After cooling to room temperature, both the ferrites – β-$K_2Fe_{22}O_{34}$ and $K_2Fe_2O_4$ – slowly decompose to α-Fe_2O_3 and a mixture of amorphous potassium compounds (carbonate, hydrocarbonate and hydroxide), undergoing further hydration.

Conclusions

The catalytic performance of the catalysts can be defined as the number of styrene mmole produced per 1 g of a catalyst during 1 h at the used reactor and reaction parameters. All the results obtained for the potassium impregnated catalysts (Fig. 4) lead to the conclusion that the specific reaction rate depends linearly on temperature of the maximum rate of the ferrite formation observed as the minima in the DTG spectra. CeO_2 doped hematite catalysts showed the best catalytic performance [1] and lower temperature of ferrite formation.

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