

Promotion of iron-oxide with potassium as optimization of the soot combustion catalyst

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In this work the effect of potassium addition to iron oxides (FeO , Fe_3O_4 , Fe_2O_3) as catalysts for soot combustion was investigated. While the addition of potassium by impregnation had positive effect on all oxides the strength of this effect varied considerably. Comparison with potassium ferrites ($\text{K}_2\text{Fe}_{22}\text{O}_{34}$, KFeO_2), with potassium as a part of a crystal lattice, proved that they were more active than unpromoted oxides. The determined range of activity was as follows: $\text{FeO} < \text{Fe}_3\text{O}_4 < \text{Fe}_2\text{O}_3 < \text{K}/\text{Fe}_3\text{O}_4 \sim \text{K}_2\text{Fe}_{22}\text{O}_{34} < \text{K}/\text{Fe}_2\text{O}_3 < \text{K}/\text{FeO} \sim \text{KFeO}_2$.

Keywords and phrases: soot combustion, promotion, potassium, iron, ferrite, catalyst.

Introduction

In recent years, environmental awareness and need for improvement of life quality in metropolises increased considerably. In response to these issues, the European Commission has introduced very strict standards limiting the emission of harmful environmental agents, including particulate matter (PM). Currently used technologies, e.g. catching particles of soot filters (DPF), are not sufficient. The idea of increasing the effectiveness of filters by covering them with a layer of catalyst was introduced in the '80s [1], but only in the recent years the research in this field led to some important progress [2].

There are a lot of tested catalysts, for example perovskites [3], spinels [4] and noble metals [5] but catalytic system that satisfies simultaneously the conditions of activity, stability, affordability being in the same time environmentally friendly are still sought.

Iron is both cheap and environmentally friendly, so attempts to apply it in catalysis, also in soot combustion, is not surprising. Iron was investigated as a constituent of perovskite-type oxide $\text{La}_{1-x}\text{K}_x\text{FeO}_3$ in [6] and it was reported that its activity was comparable with $\text{Pt}/\text{Al}_2\text{O}_3$. Also iron was tested as dopant for known soot combustion catalyst — ceria [7] and a small positive effect was observed. Iron oxide Fe_2O_3 was also used as model catalyst in kinetic modeling of soot combustion in [8].

Experimental

Iron oxides were obtained from commercial suppliers: FeO (Aldrich), Fe_3O_4 (Aldrich), Fe_2O_3 (Merck). Potassium doping was realized by impregnation with potassium carbonate (POCh) solution (1.2 cm³ 0.2326 M solution to 1.6 g of oxide, 2.4 wt%_K). Afterwards, powder was dried (100°C, 1h) and calcinated (400°C, 4 h). Potassium monoferrite KFeO_2 was synthesized by the high-temperature reaction of stoichiometric amounts of K_2CO_3 and $\alpha\text{-Fe}_2\text{O}_3$ according to descriptions in [9]. Compounds was mixed in agate mortar, pressed under 8 MPa and sintered in air (7.5°C/min, 1 h in 800°C), again mixed in agate mortar and sintered in air (7.5°C/min, 20 h in 800°C). Potassium β -ferrite $\text{K}_2\text{Fe}_{22}\text{O}_{34}$ was synthesized by the high-temperature reaction of stoichiometric amounts of K_2CO_3 and $\alpha\text{-Fe}_2\text{O}_3$ according to descriptions in [9]. Compounds was mixed in agate mortar, pressed under 8 MPa and sintered in air (7.5°C/min, 1 h in 900°C), again mixed in agate mortar and sintered in air (7.5°C/min, 5 h in 1200°C).

Synthesized samples ($\text{K}_2\text{Fe}_{22}\text{O}_{34}$, KFeO_2) were examined by X-ray diffraction using a DRON3 powder diffractometer with $\text{Cu}_{K\alpha}$ radiation in the Bragg-Brentano geometry.

The Temperature Programmed Oxidation (TPO) measurements of soot combustion in the range of 20-

-900°C were performed in a quartz flow reactor using mixture of 100 mg of the catalyst and 13 mg of model soot (*Printex80* from Degussa). Before the test, catalyst and soot were mixed in agate mortar for 10 min (*tight contact*). The flow rate of gases (5% O₂ in He) was 60 ml/min, and the heating rate of 10°C/min was used. The progress of the combustion was monitored by a quadruple mass spectrometer (SRS RGA200). Mass/charge ratios 44 (CO₂), 32 (O₂), 28 (CO), 18 (H₂O), 16 (O) was examined as a function of temperature. Conversion was calculated as integral of CO₂ signal.

Results and discussion

Characterization by XRD

Diffraction patterns of potassium β -ferrite K₂Fe₂₂O₃₄ and potassium monoferrite KFeO₂ in Fig. 1. Diffraction data confirm that ferrite phases were synthesised as planned. Relatively narrow diffraction maxima indicate that obtained materials possess large crystals, as can be expected after prolonged high temperature treatment. No differences in diffraction patterns of ferrites before and after the reaction were observed.

Catalytic tests

Fig. 2. shows light-off profiles for mixtures of soot with investigated catalysts. For all iron oxide systems positive effect of potassium addition is observed. Potassium addition leads to increase activity of iron oxides and that changes were from 50°C (Fe₃O₄, Fe₂O₃) to 200°C (FeO). This effect is most pronounced for the least active FeO which after K promotion turns from the worst to the best catalyst in the group.

Activity of investigated samples is summarized in Fig. 3 which shows that the least active catalyst were undoped iron oxides: FeO, then was Fe₃O₄ and then Fe₂O₃. Reference potassium containing oxides show comparable reactivity to K-promoted iron oxides. β -ferrite K₂Fe₂₂O₃₄ had intermediate activity to K/Fe₃O₄ and K/Fe₂O₃, while the most active samples was potassium monoferrite. A possible explanation of the fact that potassium containing iron oxides show catalytic activity in soot combustion may be formation of surface KFeO_x phase. This phase, present in different concentration on the catalyst surface, would determine the reactivity of the material. The formation of KFeO_x phase could be the reason why least active FeO becomes very active after K doping.

Conclusions

In this study of catalytic soot combustion over surface K-promoted iron oxides was compared with potassium β -ferrite and monoferrite potassium containing phases. On the basis of reported results the following conclusions can be summarized:

- all investigated samples were active as catalysts for soot combustion;
- unpromoted iron oxides show moderate reactivity and among them FeO is least active;
- potassium addition leads to increase of activity of all iron oxides and K/FeO is most active among them;
- reference iron-potassium oxide phases show reactivity in the temperature window characteristic for surface K-promoted iron oxides and potassium monoferrite KFeO₂ was the most active catalyst.

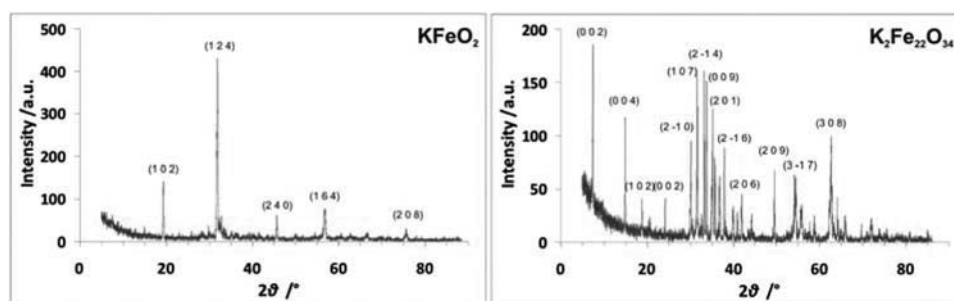


Fig. 1. Diffraction pattern of potassium monoferrite KFeO₂ and potassium β -ferrite K₂Fe₂₂O₃₄.

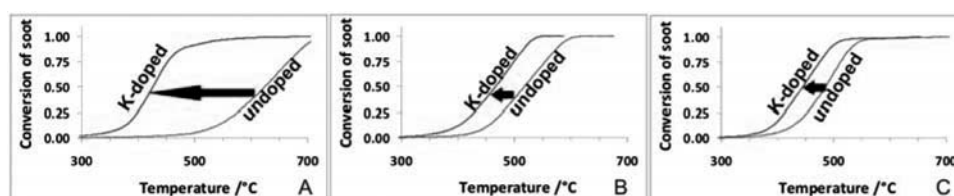


Fig. 2. Effect of potassium addition on FeO (A), Fe₃O₄ (B) and Fe₂O₃ (C) on its catalytic activity in soot combustion.

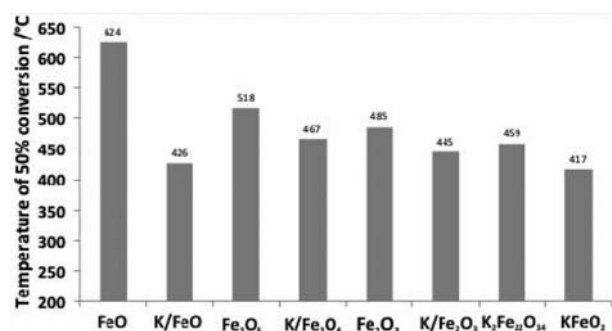


Fig. 3. Temperature of 50% conversions of soot for all investigated samples.

The inversion of activity sequence for iron oxides before and after K doping is assigned to the formation of KFeO_x phase responsible for reactivity towards soot combustion.

References

- [1] Goldenberg, E., and P. Degobert. *Revue de l'Institut Francais du Petrole* 41 (1986): 797.
- [2] Fino, D. *Science and Technology of Advanced Materials* 8 (2007): 93.
- [3] Ura, B., et al. *Applied Catalysis B: Environmental* 101 (2011): 169.
- [4] Fino, D., et al. *Powder Technology* 180 (2008): 74.
- [5] Azambre, B., et al. *Fuel Processing Technology* 92 (2011): 363.
- [6] Taniguchi, K., N. Okinaka and T. Akiyama. *Journal of Alloys and Compounds* 509 (2011): 4084.
- [7] Zhang, Z., et al. *Journal of Catalysis* 276 (2010): 16.
- [8] Reichert, D., et al. *Applied Catalysis B: Environmental* 84 (2008): 803.
- [9] Kotarba, A., et al. *Catalysis Letters* 67 (2000): 129.