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Short Communication

# Boosting the catalytic activity of magnetite in soot oxidation by surface alkali promotion ☆

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ABSTRACT

The effect of alkali promotion of a $Fe_3O_4$ catalyst in soot combustion was systematically investigated for a series of alkali elements (Li, Na, K and Cs) at various surface coverages. The correlation between catalyst performance and work function lowering was established and discussed in terms of the electron donor character of the alkali promotion. This effect was found to follow the sequence of the increasing ionic radii of the alkali promoters Li < Na < K < Cs. For each alkali promoter, the highest activity corresponds to a different optimal surface coverage.

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## 1. Introduction

Soot is a highly impure and complex material produced during the incomplete combustion of materials containing carbon. It mostly consists of amorphous carbon and some of its crystalline allotropes like graphite or fullerene, as well as unsaturated hydrocarbons. Due to its cancero- and mutagenic properties [1] together with the nanometric size of particles soot is considered as a very harmful pollutant. It is also claimed, that soot pollution is one of the main negative factors causing climate changes [2]. Therefore, a notable increase in the interest of soot abatement is observed in the scientific community [3].

Several approaches to eliminate soot residue or reduce its emission to atmosphere have been proposed so far. Among them, the engine and combustion reactor modifications are technically difficult and usually expensive. An approach employing fuel additives, which would prevent the formation of soot during the fuel combustion process or catalyze in-situ oxidation of already formed soot particles, was also presented [4]. Until now, the most effective solution is the usage of diesel particulate filters (DPF), with effectiveness reaching 90%. Unfortunately, such filters need periodic regeneration, which eventually affects engine efficiency [5]. Another solution intensively investigated and promising for after-treatment applications is the catalytic combustion of soot.

There are a number of reports on different catalytic systems tested for soot oxidation, recently reviewed in [6]. The noble metal-based catalysts [6–8] which include the classic $Pt/CeO_2–ZrO_2$ system [9], are among the most often reported. However, due to the high price of noble metals and their limited availability, cheaper substitutes are extensively explored [6]. Undoubtedly, the most investigated catalysts are ceria-based systems—bare and modified $CeO_{2-x}$: mixed with $ZrO_2$, doped by $CuO_x$, and even supported on $ZrO_2–TiO_2$ [6,10,11] reviewed recently elsewhere [6]. Other groups of investigated catalysts include perovskites [6,10,12,13], spinels [6,10,14,30], ferrites [6,10,15] or even simple oxides [6,10,16]. Catalytic soot combustion with alkali carbonates (Li, Na, K) was reported, with the best reactivity of $K_2CO_3$ [17]. Also, alkali promotion of some of the above mentioned systems was studied, namely $SrTiO_3$ perovskite [18] or different ceria systems [19,20].

Owing to their low price and environmental friendliness iron-based catalysts have attracted considerable attention as soot combustion catalytic materials [15,21]. However, the iron oxides themselves exhibit rather unexceptional activity in soot oxidation and research to improve their performance by engineering their structure [15,16] and surface properties [14,30] has been reported recently.

One of the most important factors in soot combustion in real conditions is the soot–catalyst contact, as emphasized in [22,23]. A very effective way to improve such contact is the use of alkali promoters [15,24,25]. There are several reports describing the strong effect of alkali promotion, most often potassium, on the catalytic activity of

☆ Dedicated to Professor Walerian Arabczyk on his 70th birthday.

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transition metal oxides in soot combustion [13–15,24,26,27,30]. The positive role of alkali doping on catalytic soot combustion has been discussed in terms of several effects, such as: an electron transfer effect (activation of molecular oxygen [3,15]), formation of low melting point compounds or eutectics (increase of soot–catalyst contact [6,28]), formation of a superficial carbonate intermediate [28,29], and transformation of the parent oxide into more active phases, nano-structuration [15].

In this paper the effect of alkali promotion of $Fe_3O_4$-based catalysts in soot combustion was systematically investigated for a series of alkali elements (Li, Na, K and Cs). The series of catalysts with various alkali surface coverages were obtained to determine their optimal loading. Alkali carbonates were chosen as the precursors due to their stability in soot oxidation conditions and as the most probable surface state of alkali due to the presence of $CO_2$ product [30]. The electronic character of the promotional effect was investigated by studying the correlation between catalyst work function and the catalytic performance.

## 2. Experimental

The catalysts were prepared by the wet impregnation of 1 g of iron spinel $Fe_3O_4$ (*Aldrich* 98 + %) with an alkali carbonate: lithium (*POCh* p.), sodium (*Chempur* p.a.), potassium (*POCh* p.a.) and cesium (*Merck* ultrapure), to achieve the desired alkali loading. The concentrations of alkali in the prepared catalysts varied in the range of 0.1–3.5 wt.% (Table 1). The theoretical 0.5 monolayer alkali loading level was chosen as the optimum for the promotion effect, as reported elsewhere [30,31]. After impregnation, the catalysts were dried at 100 °C for 1 h and subsequently calcined at 400 °C for 4 h. As a reference material the iron spinel was also subjected to similar treatment in order to eliminate the effects resulting from material preparation at elevated temperature. However, the addition of alkali in the investigated samples does not affect the surface area of the parent magnetite, since the calcination temperature was low enough to prevent an appreciable crystallites sintering.

The XRD patterns were recorded by a Rigaku MiniFlex powder diffractometer with Cu Kα radiation at 10 mA and 10 kV, 2θ step scans of 0.02° and a counting time of 1 s per step. Fourier transform infrared spectra (FTIR) were obtained using a Nicolet 6700, Thermo Scientific spectrometer. The measurements were performed in the transmission mode for which the powder samples were ground and pressed with a KBr (*Aldrich*). Work function measurements (contact potential difference) were performed with a Kelvin Probe (McAllister KP6500) in a vacuum of $10^{-6}$ mbar at 150 °C after heating the sample at 400 °C to remove the surface contaminants.

**Table 1**
Alkali concentrations in the investigated samples.

| Dopand | wt.% | $n_A$ per nm$^2$ | Monolayer |
|---|---|---|---|
| Li | 0.1 | 2.5 | 0.2 |
| | 0.2 | 5.0 | 0.4 |
| | 0.6 | 15.0 | 1.2 |
| | 1.0 | 25.0 | 1.9 |
| | 2.0 | 50.0 | 3.8 |
| Na | 0.3 | 2.5 | 0.2 |
| | 0.6 | 5.0 | 0.4 |
| | 0.8 | 6.7 | 0.6 |
| | 1.0 | 8.3 | 0.7 |
| | 2.0 | 16.7 | 1.4 |
| K | 0.4 | 2.0 | 0.2 |
| | 0.6 | 3.0 | 0.3 |
| | 0.8 | 4.0 | 0.4 |
| | 1.0 | 5.0 | 0.5 |
| | 2.0 | 10.0 | 1.0 |
| Cs | 0.5 | 0.7 | 0.1 |
| | 1.0 | 1.4 | 0.2 |
| | 2.0 | 2.9 | 0.4 |
| | 3.5 | 5.0 | 0.7 |

The activity of the prepared catalysts in soot combustion was measured by means of a temperature programmed oxidation method (TPO). A quartz fixed-bed reactor was heated (10 °C/min) from room temperature to 700 °C and a gas mixture of 5% $O_2$ in He at a 60 ml/min flow was used during the tests. The samples for the soot combustion in the *tight contact* regime were prepared by grinding c.a. 0.006 g of soot (Degussa—Printex80) and 0.050 g of the catalyst in an agate mortar for 10 min to achieve the 1:8 soot–catalyst ratio. The soot combustion was monitored by a quadrupole mass spectrometer (SRS RGA200) following the lines for $m/z = 44$ ($CO_2$), 32 ($O_2$), 28 (CO), 18 ($H_2O$). The conversion of soot was calculated by the integration of the QMS signal from $CO_2$, which was the only detectable gaseous carbon containing product of the soot oxidation.

## 3. Results and discussion

Typical XRD patterns of bare and alkali-doped magnetite are shown in Fig. 1. The $Fe_3O_4$ is the dominant phase in each catalyst. However, for samples with the highest alkali loading in the series, presented in the Fig. 1, small peaks from hematite can be found. This results from the calcination procedure, as observed previously in [14]. Only in the case of the Li-doped sample characteristic peaks for the carbonate phase can be noticed (filled circles in Fig 1). FTIR spectra confirm a stronger interaction of potassium carbonate with the magnetite surface (Fig. 2) than in the case of lithium carbonate. This is revealed by the shift of the $\nu_3$ bands of the carbonate species between 1300 and 1500 cm$^{-1}$ towards lower wavenumbers [32]. In the case of Li promotion, where the formation of crystalline $Li_2CO_3$ is shown by the X-ray diffraction, the FTIR spectrum remains characteristic for pure lithium carbonate. The segregation of $Li_2CO_3$ is visible in the FTIR spectra regardless of the lithium loading.

The electron donor nature of alkali doping of the $Fe_3O_4$ surface is shown in Fig. 3, where the work function changes ($\Delta\Phi$) are plotted against alkali coverage. The observed changes strongly depend on both the ionization potential of the alkali promoter and its loading. The addition of lithium does not change the work function of magnetite in the whole investigated concentration range. In the case of heavier alkali (Na, K, Cs), the changes in $\Delta\Phi$ are well pronounced and follow the classic Topping dependence with the doping level, discussed in detail elsewhere [31]. The characteristic minima in the work function profiles correspond to the strongest electron donor properties of the catalyst. The higher the alkali metal atomic number the deeper the work function minimum, $\Delta\Phi = 0.19$ eV (Na), 0.24 eV (K) 0.28 eV (Cs). Also with increasing alkali metal atomic number this minimum moves towards lower coverage (surface alkali concentration). This effect can be explained by surface ionization of alkali promoters (A) on the $Fe_3O_4$ surface. The electron density donation from the alkalis to the catalyst

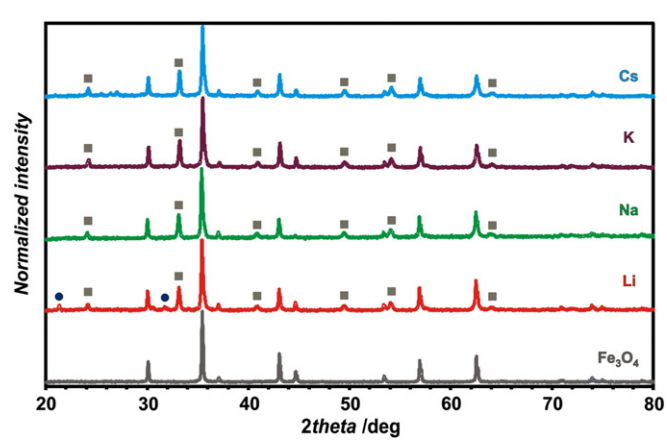


**Fig. 1.** XRD patterns of bare and alkali-doped magnetite (squares—hematite, circles—lithium carbonate) for the most concentrated samples as indicated in Table 1.

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