



Short communication

Surface versus bulk alkali promotion of cobalt-oxide catalyst in soot oxidation



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ABSTRACT

The effect of surface and bulk alkali (Na, K) promotions on the cobalt-oxide catalyst activity in soot oxidation was investigated. While surface promotion does not alter the cobalt spinel structure, the introduction of alkali into the bulk leads to the formation of layered cobaltates (revealed by XRD, Raman spectroscopy and XPS). The catalytic activity was determined using the temperature programmed oxidation of model soot (Printex 80), both in *tight* and *loose contact* conditions. The alkali bulk promotion is much more effective than surface promotion in soot oxidation, lowering the soot ignition temperature by 340 °C for the most active catalyst $K_{0.25}CoO_2$.

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1. Introduction

Due to their high efficiency and long lifetime, diesel engines are becoming much more popular than standard petrol ones. One of their main drawbacks is the inevitable formation of soot, which is proven to be harmful for human health. The most efficient way to decrease soot emission is by catalytic combustion. Catalytic materials that may be successful substitutes for the ones currently applied, which are based on noble metals (Pt, Rh), should be not only active, but also environmentally friendly and relatively cheap. The most promising materials in terms of these criteria are based on transition metal oxides, mostly those of Fe, Mn, Co, Cr and Cu. Among them perovskites and spinels draw particular attention [1–5]. The addition of alkali often leads to strong enhancement of their catalytic activity [6–9]. Likewise, alkali promotion of catalysts for soot oxidation is reported to have a strong effect as shown in [3,10–15]. It is worth mentioning that the alkali cations may be located on the surface of the oxide material or intercalated into its structure. In the first case, the activity enhancement is linked with changes in electron donor properties (activation of molecular oxygen [12]), the formation of low melting point compounds or eutectics (increase of soot-catalyst contact [16,17]) or the formation of a superficial carbonate intermediates [17,18], while the latter, intercalation of alkali into the crystal structure, leads to the formation of new phases with tunneled or layered [12,19] structures. Such nanostructures often exhibit

very high alkali cation mobility within the conduction tunnels or layers. Lithium and sodium cobaltates have garnered a lot of attention from the scientific community due to their unusual electronic and electrochemical properties and high potential for energy storage applications [20]. These properties are due to the structure of the materials, comprised of layers of edge sharing CoO_6 octahedra between which the Li^+ and Na^+ ions are located.

We have previously reported the enhancement of the soot oxidation catalytic activity of iron and manganese spinels by surface and bulk alkali doping [3,9,21]. Among the investigated catalysts the cryptomelane (KMn_8O_{16}) and birnessite (KMn_4O_8) phases were the most active with the reaction temperature window of 250–450 °C, comparable with the typical reference material – ceria [16]. On the other hand, although Co_3O_4 has been reported as a catalytically active phase in various vital reactions, such as N_2O decomposition [22], ethanol reforming [23] or methane oxidation [24], little is known about the stimulation of its soot oxidation activity by alkali bulk promotion. The aim of this work was to investigate the effect of surface and bulk alkali (Na and K) doping on the catalytic activity of the cobalt spinel in the soot combustion reaction.

2. Experimental

2.1. Materials

The surface doped catalysts were prepared by wet impregnation of 1 g of the cobalt spinel (Fluka) with a carbonate solution, either sodium or potassium (further designated as Na/ Co_3O_4 and K/ Co_3O_4 respectively), to achieve the optimal alkali loading corresponding to the theoretical 0.5

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monolayer, as described in [11]. The impregnated spinel was dried at 100 °C for 1 h, and subsequently calcined at 400 °C for 4 h. The temperature was optimal for alkali cations to disperse equally on the surface, and low enough not to change the structure or surface area of the investigated cobalt spinel. To obtain the sodium and potassium bulk promoted samples the solid state synthesis of the appropriate cobaltates ($\text{Na}_{0.6}\text{CoO}_2$, $\text{K}_{0.25}\text{CoO}_2$) was carried out. The sodium nanostructured cobalt oxide ($\text{Na}_{0.6}\text{CoO}_2$) was prepared by grinding 0.76 g of sodium carbonate (Chempur) with 1 g of cobalt(II) oxide (Aldrich). The produced powder was placed in a preheated oven and calcined at 800 °C for 11 h. The cobalt oxide nanostructured by potassium ($\text{K}_{0.25}\text{CoO}_2$) was prepared by grinding 2.13 g of the cobalt spinel with 1.1 g of potassium hydroxide (POCh). The produced powder was placed in a preheated oven and calcined at 700 °C for 12 h. The pre-calcined bulk materials were placed in preheated ovens to avoid alkali loss due to thermal desorption, further compensated by the use of excessive amounts of alkali substrate (2 times greater amount of sodium carbonate than the stoichiometric amount, 3 times excess of potassium hydroxide). The synthesized bulk doped samples were thoroughly washed with distilled water to remove excess alkali and ground in an agate mortar into a fine powder for further studies.

2.2. Methods

The XRD patterns were recorded by a Rigaku MiniFlex powder diffractometer with Cu K α radiation at 10 mA and 10 kV, 2 θ step scans of 0.02° and a counting time of 2 s per step.

The Raman spectra were recorded at room temperature in the range of 150–800 cm^{-1} with 1 cm^{-1} resolution (Renishaw InVia spectrometer, confocal microscope Leica DMLM, CCD detector with a wavelength excitation of 785 nm). Nine scans for each sample were accumulated in order to provide a sufficient signal to noise ratio.

The elemental analysis was performed with an Energy-Dispersive XRF spectrometer (Thermo Scientific, ARL QUANT'X). The X-rays of 4–50 kV (1 kV step) with the beam size of 1 mm were generated with the Rh anode. The detector used was a 3.5 mm Si(Li) drifted crystal with a Peltier cooling (~185 K). For quantitative analysis, the calibration with a series of metallic standards and a UniQuant software were used.

The X-ray photoelectron spectra (XPS) of the catalyst samples were measured with a Prevac photoelectron spectrometer equipped with a hemispherical VG SCIENTA R3000 analyzer. The photoelectron spectra were measured using a monochromatized aluminium AlK α source ($E = 1486.6$ eV). The base pressure in the analysis chamber during the measurements was 5×10^{-9} mbar. Spectra were recorded with constant pass energy of 100 eV for the survey and narrow scan spectra. The binding energy scale was aligned with the main C 1 s band set to 295 eV.

The temperature programmed oxidation method (TPO) was used to compare the activity of the prepared catalysts in soot combustion. 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 reaction mixture, weighing 50 mg, was prepared by grinding a catalyst sample with soot (Degussa–Printex80) in an 8:1 ratio. The mixture was ground for 10 min in the *tight contact* regime in an agate mortar or shaken in a plastic container for 5 s (*loose contact*). As a reference a portion of soot without the added catalyst (~5.5 mg) was oxidized using the aforementioned conditions. 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 $_2$ O). Since the conversion calculated from the CO $_2$ and CO signals gives essentially the same results, the conversion of soot was calculated by the integration of the much more pronounced QMS signal from CO $_2$. The reproducibility of the TPO experiments was confirmed by at least three independent experimental runs ($\Delta T_{50\%} < 10$ °C).

3. Results

Typical XRD patterns of the synthesized catalysts (Na/Co $_3$ O $_4$, K/Co $_3$ O $_4$, Na $_{0.6}$ CoO $_2$, K $_{0.25}$ CoO $_2$) as well as that of the reference cobalt spinel are presented in Fig. 1. The obtained diffractograms were compared to the appropriate ICSD database entries and indexed (9362 – cobalt spinel, 163249 – Na $_{0.6}$ CoO $_2$, 89454 – K $_{0.25}$ CoO $_2$). The sodium cobaltate belongs to hexagonal crystal system (P 6_3 /mmc), the potassium cobaltate the trigonal (R3m) while the cobalt spinel has a cubic structure (Fd $\bar{3}m$). There is no noticeable change in the cobalt structure in both of the surface doped samples. On the other hand, the intercalation of alkali cations into the cobalt oxide structure leads to significant structural changes – the formation of layers of cobalt oxide blocks between which the Na $^+$ and K $^+$ ions are located. The change in structure is apparent in the diffraction patterns of both bulk-doped phases. Thus, the synthetic procedure led to a formation of the sodium and potassium cobaltates of the stoichiometric formulas of Na $_{0.6}$ CoO $_2$ and K $_{0.25}$ CoO $_2$.

Typical Raman spectra of the investigated materials are shown in Fig. 2. Similarly to the XRD results, the surface-doped catalysts exhibit peaks characteristic of the cobalt spinel (195, 478, 517, 617, 685 cm^{-1}). For the alkali nanostructured catalysts, two different broad peaks are observed located at 469 and 581 cm^{-1} that may be assigned to the Raman-active out-of-plane A $_{1g}$ and in-plane E $_{1g}$ vibrations, respectively, of oxygen atoms in the CoO $_6$ octahedra. Since these groups of atoms are present in the cobalt oxide layers of Na $_{0.6}$ CoO $_2$ and K $_{0.25}$ CoO $_2$, both spectra may exhibit quite similar features [25]. Minor phase impurities, originating from the cobalt spinel or an orthorhombic cobaltate phase, were observed, which were not shown on the bulk Raman spectra.

Semi-quantitative analysis of the samples elemental composition verified with X-ray fluorescence spectroscopy confirmed the desired amounts of potassium in both surface (K/Co $_3$ O $_4$) and bulk (K $_{0.25}$ CoO $_2$) promoted catalysts. Sodium in expected amounts was detected in the bulk promoted sample (Na $_{0.6}$ CoO $_2$). In the case of the cobalt spinel surface-promoted with sodium its detected concentration was much lower than intended, probably due to a low atomic number and superficial occurrence. The XPS analysis, however, confirmed the presence of the sodium on the surface promoted cobalt spinel catalyst (Na/Co $_3$ O $_4$).

The Co 2p energy range exhibits the typical features of Co $_3$ O $_4$ for unpromoted and alkali modified samples (Fig. 3). However, a slight shift towards the higher energies of the Co 2p 3/2 band indicates changes of the mean cobalt oxidation state in the case of Na/Co $_3$ O $_4$ and both bulk alkali promoted samples (Na $_{0.6}$ CoO $_2$, K $_{0.25}$ CoO $_2$). This shift may be brought about by an increase of the Co $^{4+}$ content [26,27], but an overlap with a band due to Co $^{2+}$ [28,29] prevents an unambiguous interpretation in these circumstances. In either case, a change of the mean

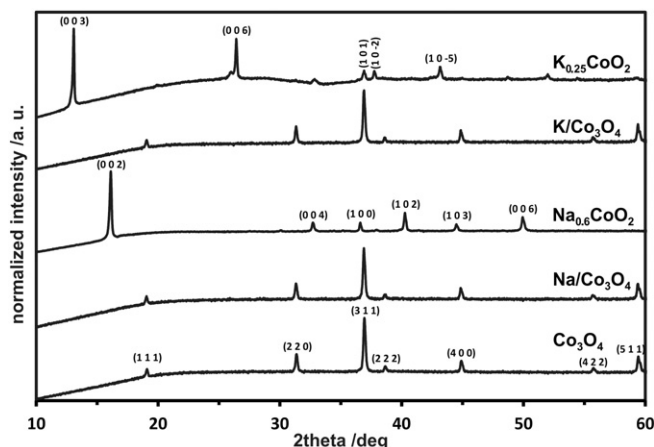


Fig. 1. XRD patterns of the undoped and alkali promoted (Na, K) cobalt catalysts.

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