



Short communication

Alkali tungsten bronzes as soot oxidation catalysts: The key role of electrodonor properties of catalytic surface



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ARTICLE INFO

Keywords:
Work function
Soot combustion
Alkali tungsten bronzes
Alkali promotion

ABSTRACT

The effect of bulk alkali (Li, Na, K, Cs) promotion on the tungsten(VI) oxide catalytic activity in soot oxidation was investigated. Catalyst oxidation and reduction susceptibility investigations have shown, that soot oxidation on the investigated catalysts operates through Mars van Krevelen mechanism. It has been also revealed, that increase in electrodonor properties (lowering the work function) of the A_xWO_3 ($A=Li, Na, K, Cs$) catalysts results in enhancing the catalytic activity in soot oxidation with the promotional effect increasing in order: $Cs < Na \ll K \approx Li$.

1. Introduction

Soot is usually described as a carbonaceous material formed during incomplete combustion of carbon-based materials, with varying composition and morphology strongly depending on the combustion conditions. It consists mostly of carbon (amorphous form, graphite, fullerene) and unsaturated aliphatic and aromatic hydrocarbons [1]. Due to the nanometric size of soot particles and cancer- and mutagenic properties [2], it is considered as one of the most harmful components of the PM (particulate matter). As a result of continuously increasing amount of PM being emitted, new regulations are being imposed by European Commission every few years with EURO6 being the most recent one [3].

One of the most significant soot emission mobile and stationary sources are diesel engines. Among many proposed soot emission reduction solutions so far, catalytic diesel particulate filter (CDPF) is the most effective one. In such system, the particulate matter is being deposited on the filter designed in a way enforcing the fumes to pass through its walls covered with soot oxidation catalyst. The active phase of the catalyst lowers the temperature of soot ignition, enabling the filter to be continuously regenerated in the standard exhaust system working conditions [4]. The catalysts that are used in commercial solutions for soot removal are usually based on rare elements like platinum, rhodium and palladium, but increasing price of noble metals creates demand for a cheaper substitute. It should be also mentioned, that soot oxidizing phases are also needed as a part of catalyst responsible for carbon deposit removal in reducing or inert conditions, which are usually present in hydrocarbon reforming processes [5–8]. Therefore, various classes of transition metal oxides, (like tungsten

bronzes investigated in [5,6] and in this manuscript) are tested to fulfill the demands of stability in specific process conditions.

There are two most common soot-catalyst contact regimes described in the open and patent literature – *tight contact* usually realized through grinding in agate mortar and *loose contact*, where soot and catalyst are just mechanically mixed without the pressure applied. Performing the experiments in both contact regimes is justified, since both deliver specific and different information concerning catalytic activity of the sample. The tight contact guarantees higher reproducibility and in this case the soot oxidation tests probe the surface chemical activity related to the formation of active surface oxygen species. Such species can be formed through activation of oxygen adsorbed on the surface in the form of O_2^- or O_2^{2-} (Langmuir-Hinshelwood or Eley-Rideal mechanism) or through Mars-van Krevelen vacancy mechanism involving O^{2-} . On the other hand, the loose contact conditions are more similar to the realistic ones with much lower soot-catalyst contact points. In such case other soot combustion mechanisms, like NO_2 -assisted oxidation or activation of soot with alkali, are investigated since when there is no direct soot-catalyst contact the remote soot activation mechanisms are necessary.

Wide spectrum of materials active in soot combustion has been reported so far. Ceria-based catalysts are the most intensively investigated ones due to exceptionally high oxygen mobility in CeO_2 lattice [9–12]. Lately the special attention has been drawn towards transition metal oxide-based materials due to the compromise of high catalytic activity, relatively low price and environmental friendliness [13–17]. One of the ways of enhancing the activity of the transition metal oxides catalysts is doping with alkali [18–24]. The promotion is discussed in terms of modification of the catalyst structure, enhancing the soot-

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catalyst contact, or stimulating surface electron transfer to the substrates (molecular oxygen and/or soot). It has been reported, that the amount of oxygen on the surface of some oxides (for example titanium and tungsten (VI) oxides) [25–27] is correlated with their work function.

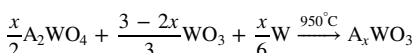
Tungsten bronzes are the non-stoichiometric materials of general formula of A_xWO_3 where A stands for an alkali cation located in the tunnels formed with WO_6 octahedra. Both structure and work function of the bronzes can be substantially modified by changing the constituting alkali cation. For example, with x value equal to 0.3, lithium tungsten bronze crystalize in regular, sodium in tetragonal, and potassium and cesium in hexagonal crystal systems. Since the large differences in ionic radius and ionization potential as well as the content of alkali cations influences the structure of tungsten bronzes strongly, the catalytic properties of tungsten bronzes could be improved significantly. Such structurally-doped transition metal oxides can both store and release alkali. Since the biomass-derived fuels usually contain sodium and potassium, “alkali breathing materials” may be used in the hydrocarbon processing systems retaining its activity and structure.

The main goal of the paper is the systematic investigation of the influence of structural doping of WO_3 with series of alkali cations on the electronic properties (gaged by work function changes) and catalytic activity in soot removal. The working hypothesis assumes work function-activity correlation which may be of more general notion providing the rational guidelines for designing the new oxidizing catalysts based on transition metal oxides.

2. Experimental

2.1. Materials

Alkali tungstate (A_2WO_4 , $A=Li, Na, K, Cs$) has been prepared by grinding equimolar quantities of A_2CO_3 (Li_2CO_3 from POCh, Na_2CO_3 and K_2CO_3 from Chempur and Cs_2CO_3 from Acros Organics) and WO_3 (Dor-chem) in a mortar and keeping in 500 °C for 2 h. Potassium tungsten bronzes were synthesized according to the following reaction:



Stoichiometric amounts of A_2WO_4 , WO_3 and W (Aldrich) corresponding to $x = 0.3$ (with 10% excess due to alkali volatilization) were ground for 30 min, pelletized under the pressure of 8 MPa, and calcined in 500 °C for 2 h. Afterwards substrates were grinded and pelletized under similar conditions again. Then the pellet was heated up to 950 °C for 4 h in the quartz tube that was constantly purged with Ar in order to keep inert reaction atmosphere. After the synthesis the samples were washed with water to remove the residual alkali from the surface and dried in 120 °C for 4 h.

Undoped tungsten(VI) oxide was chosen as a reference although it does not possess the similar structure as synthesized tungsten bronzes, since the tunnelled structure requires the stabilizing cations.

2.2. Methods

The diffractograms 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 calibra-

tion with a series of metallic standards and an UniQuant software were used.

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 800 °C and a gas mixture of 5% O_2 in He or pure He (for oxidation in an inert atmosphere) 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. 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 .

Contact potential difference (CPD) measurements were performed with a Kelvin Probe (McAllister KP6500). For each measurement, the 150 mg of the sample was pelletized ($d = 10$ mm) under the 8 MPa pressure. The measurements were performed in a vacuum of 10^{-7} mbar at 150 °C after annealing the sample at 400 °C in order to standardize the surface. The stainless steel electrode ($d = 3$ mm, $\phi_{reference} = 4.32$ eV) was used as a reference. Work function value is determined by simple equation: $\phi_{sample} = \phi_{reference} - CPD$.

3. Results and discussion

3.1. Material characterisation

The idea of nanostructurisation of WO_3 with alkali cations leading to formation of different structures has been graphically shown on Fig. 1. Typical XRD and Raman results for the synthesized bronzes (Li_xWO_3 , Na_xWO_3 , K_xWO_3 , Cs_xWO_3) as well as that of the reference tungsten(VI) oxide are presented in Fig. 2. The obtained diffractograms were similar to the references in the literature and all the maxima can be indexed in appropriate space groups. Tungsten(VI) oxide belongs to orthorhombic crystal system (*Pcnb*) [28]. The lithium tungsten bronze belongs to regular crystal system (*Im-3*) [29], sodium tungsten bronze crystalize in tetragonal system (*P4/mbm*) [30] while the potassium and cesium ones are of a similar hexagonal structure (*P6₃/mcm*) [31,32].

Although, as revealed by the XRD, the obtained bronzes were virtually monophasic, for additional conformation their Raman spectra were analysed, which are more sensitive for a short-range arrangement. All the samples exhibit characteristic peaks on the Raman spectra for the tungsten oxides. The peaks in the range of 600–850 cm^{-1} are usually assigned to the O–W–O stretching modes. The bands in the range of 850–950 cm^{-1} , which are characteristic for tungsten bronzes only, can be assigned to the stretching modes of the terminal W=O groups [33,34]. The shifts of the maxima characteristic for tungsten bronzes are associated with different WO_6 octahedra–alkali metal interactions.

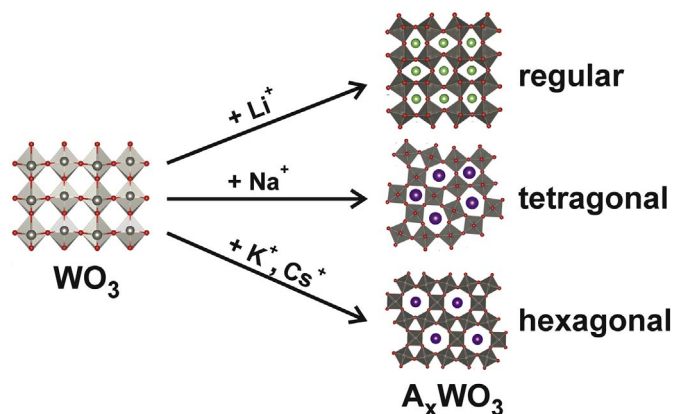


Fig. 1. WO_3 nanostructurisation with alkali cations leading to formation of A_xWO_3 ($A=Li, Na, K, Cs$) tungsten bronzes with various structures.

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