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The role of crystallite size of iron oxide catalyst for soot combustion

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ABSTRACT

A series hematite structure iron oxide nanoparticles of various sizes was synthesized and tested in the soot combustion in oxygen rich conditions in the tight and loose contact modes. The catalysts were characterized by XRD, TEM, and Raman Spectroscopy, whereas the catalytic reactivity with model soot (Printex U) was evaluated by TGA/DTA method. It was found that the catalysts activity is size dependent for the particles dimensions in the range of 5–100 nm with the smallest one exhibiting the highest activity (lowest soot ignition temperature). The most active nanohematite particles, formed in situ in the laboratory and real process conditions of light fuel oil combustion with addition of fuel borne catalyst (FBC) precursors, exhibit the beneficial size range of 5–15 nm.

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1. Introduction

The particulate matter (PM) emission, especially soot, from combustion of diesel or heavy and light heating oils has gained an increased attention in the recent years. Soot inhalation can cause serious lung, cardiovascular and heart diseases as well as mutagenic changes, depending on its size and chemical composition [1]. Soot emission is also considered as an important factor influencing global warming [2]. For these reasons many technologies, such as diesel particulate filter for mobile sources, are being developed for soot emission abatement. Due to its efficiency and economic appeal the most promising abatement technology is the catalytic soot combustion [3]. Many catalytic materials have been investigated to decrease the ignition temperature of soot oxidation but so far the practical satisfactory solution has not been reached [4].

Among the soot combustion catalysts iron oxide based materials (Fe_xO_y) have received a great deal of attention owing to their low price, environmental friendliness, high reactivity and susceptibility for facile surface and/or structural modifications. Indeed, iron oxides in the form of hematite [5–7], potassium ferrites [8,9] or supported particles on alumina [10] are reported to be catalytically active in this reaction. One of the other promising ways of reducing the PM emission is the application of the so-called fuel borne catalysts (FBC) as a low concentration additives to liquid fuels [11,12]. These additives are most often based on iron oxo/hydroxo complexes stabilized by long-tail organic ligands. The inorganic, iron based content is in situ transformed during the combustion process into the iron nanooxide combustion catalyst (essentially hematite) of soot [13,14]. The main advantage of the FBC is an effective dynamic intermingling of the nascent nanoparticles of the catalyst and soot in a gas phase which is beneficial for increasing of the number of their mutual contact points. As a result, the oxygen transfer from the catalyst toward the soot particles is facilitated, enhancing the combustion process [12].

Due to the size dependent catalytic properties a range of different synthetic methods are developed to obtain desired types, shapes and sizes of various iron oxide materials [15,16]. Moreover, structural phase transformations of Fe_xO_y nanoparticles are also investigated in relation to their reactivity [17,18]. Recently, several iron oxide catalysts, either pure hematite or with γ-Fe_2O_3 and Fe_3O_4 impurities, as well as promoted with alkali, mainly potassium, were examined. These investigations were focused on the effect of catalyst composition and structure on the mechanism of the soot oxidation [5–8,10,19]. It has been found, inter alia, that both surface and bulk oxygen transport in the nanocrystals is crucial for effective spillover of reactive oxygen from the catalyst to the soot, beneficial for the combustion process. The surface oxygen diffusion is reported to be facilitated by the amorphous domains, whereas the latter with crystalline ones. Although the strong influence of chemical composition of iron-oxide catalysts on the soot

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oxidation activity is well documented, to our best knowledge the problem of the particle size impact has not been addressed as yet. This issue is of particular interest for designing appropriate FBC precursors for optimal catalytic performance by size control of the resultant iron oxide nanograins.

The aim of this work was to systematically investigate the soot oxidation activity of hematite catalyst of various crystallite dimensions in the nanometric range in oxygen rich conditions to establish an optimal size range for the catalytic activity enhancement. The comparison of catalyst reactivity in loose and tight contact modes was also investigated for evaluation of the catalytic performance in two conventional boundary conditions. Finally, the synthesized materials were compared with the nanohematite produced in situ from FBC precursor in laboratory and real engine conditions.

2. Material and methods

The series of hematite samples, α-Fe_2O_3, were synthesized with the use of several methods in order to obtain catalysts with crystallite sizes in the range of 5–100 nm. A commercial material, Merck, was used for comparison (Fe_2O_3-C).

The hydrothermal synthesis at 150–160 °C was performed with different pH and time periods. A solution of $Fe(NO_3)_3$ (0.03 M 150 mL) was alkalized with 6 M NaOH to obtain pH 10, with constant stirring. The slurry was transferred to a teflon lined autoclave and kept there at 150 °C for 12 h. The obtained precipitate was washed with deionized water and dried at 60 °C for 20 h (sample Fe_2O_3-H-B). In another assay a 1.687 g of $FeCl_3 \times 6H_2O$ was dissolved in 200 mL of deionized water. The obtained solution was stirred and 3.2×10^{-3} M HCl was added dropwise to obtain pH 2. The mixture was next transferred to a teflon lined autoclave and kept there at 160 °C for 36 h. The obtained precipitate was washed several times with deionized water and dried at room temperature overnight (sample Fe_2O_3-H-A).

Two precipitation methods were applied with different precursors ($FeCl_3$ and $Fe(NO_3)_3$), precipitating agents (KOH and NaOH) and final pH (7.1 and 11.4). A constantly stirred 0.01 M solution of $FeCl_3$ was alkalized dropwise with 0.5 M solution of KOH to obtain pH 7.1. Then, the solution was heated to a boiling point and stirred for another hour. The precipitate was washed six times with hot deionized water and centrifuged. The obtained powder was dried at room temperature overnight and calcined at 330 °C for 30 min (sample Fe_2O_3-P-K). For the other sample, a 3.637 g of $Fe(NO_3)_3$ was dissolved in 300 mL of deionized water. The solution was constantly stirred and portions of 6 M NaOH were added to obtain pH 11.4 and stirred for another 30 min. The obtained precipitate was washed four times with deionized water and dried at 60 °C for 20 h. Thus obtained material was characterized XRD and Raman spectroscopy and was found to have a ferrihydrite structure (sample Fe_2O_3-F), and was also used for catalytic testing. To obtain α-Fe_2O_3, the ferrihydrite powder was calcined at 330 °C for 30 min (sample Fe_2O_3-P-Na).

Beside the laboratory synthesized samples the hematite nanoparticles were also produced in situ in the laboratory and process conditions from FBC emulsions composed of oxohydroxy iron core stabilized by oleic acid ligands (Fe_2O_3-FBC). For the sake of clarity all the investigated samples are collected in Table 1 together with the corresponding labels.

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 rate 1.5° per minute in the range from 5° to 80°. Crystallite sizes were determined following the Scherrer equation. The micro-Raman spectra were recorded in ambient conditions using a Renishaw InVia spectrometer equipped with a Leica DMLM confocal microscope and a CCD detector, with an excitation wavelength of 785 nm. The laser power at the sample position was in the range of 0.1–3 mW (from 0.05 to 1% of the total power) with a 50× magnification. The Raman scattered light was collected in the spectral range of 100–1500 cm^{-1}. At least 4 scans, 10 s each, were accumulated to ensure a sufficient signal to noise ratio.

Table 1
The crystallite size obtained from XRD analysis of the hematite samples.

Method	Crystal size (XRD)/nm	Sample name
Precipitation with NaOH/ferrihydrite based	4	Fe_2O_3-F
Precipitation with KOH	17	Fe_2O_3-P-K
Precipitation with NaOH	19	Fe_2O_3-P-Na
Commercial Merck	56	Fe_2O_3-C
Hydrothermal in basic conditions	63	Fe_2O_3-H-B
Hydrothermal in acidic conditions	100	Fe_2O_3-H-A
Fuel borne hematite	5–15*	Fe_2O_3-FBC

* Based on TEM observations.

Temperature-programmed oxidation of model soot (Printex U, particle size 25 nm, specific surface area 100 $m^2\,g^{-1}$, additional characteristics can be found in [20]) was done on a Mettler Toledo TGA/DSC1 using thermogravimetric analyses (TGA) method. The experiments were conducted under air atmosphere (air 40 mL/min + purge Ar 20 mL/min) at a temperature ramp of 10 °C/min in the range from room temperature to 700 °C. As in a typical TGA/DTA module, the temperature was measured directly below the sample crucible and compared with the empty reference crucible. The reaction mixtures (catalyst-soot) were prepared by mixing the hematite nanoparticles and soot with mass ratio 8:1. Following the literature, two types of soot-catalyst contact modes were applied: a loose contact, where the catalyst and soot were mechanically mixed in a plastic vessel, and a tight contact, where the catalyst and soot particles were ground in an agate mortar for 10 min. In each measurement ~7 mg of the sample (soot and catalyst mixture) was put in the crucible. As a reference each catalyst without soot was also investigated for the mass loss in the reaction temperature range to ensure that the observed mass changes can be associated with the soot oxidation process exclusively. The characteristic temperature of the heat flow maximum due to soot oxidation (T_{HFmax}) was used as a descriptor of catalysts activity. Since the soot oxidation is highly exothermic the maximum of the heat flow curve ($W = J/s$) reflex in a better way the very nature of the combustion process than an arbitrary T50% or T10%. For the sake of comparison with other studies we have included the conversion curves as well.

High-resolution transmission electron microscope (FEI Tecnai Osiris) with X-FEG Schottky field emitter operated at accelerating voltage of 200 kV, equipped with Super-X windowless EDX was used to evaluate the fuel borne hematite particles. Powder samples were dispersed in ethanol, ultrasonicated, dropped into a lacey carbon-coated copper grid then dried at a room temperature. FBC emulsions were deposited directly onto the grid. A selected area electron diffraction (SAED) was collected/under broad parallel electron illumination with an aperture (in the image plane) selecting the diffracted region of the specimen in order to confirm the α-Fe_2O_3 phase of synthesized catalysts. The acquired SAED polycrystalline ring pattern was converted into an intensity distribution and then indexed using the ProcessDiffraction software [21]. The intensity in the measured SAED ring pattern was averaged over circles, and presented graphically as a function of the radius of the circle. A nonlinear background of electron diffractogram was removed in order to facilitate assessment of peak positions in terms of peak intensities and *d*-values.

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