Synthesis and catalytic performances of K-OMS-2, Fe/K-OMS-2 and Fe-K-OMS-2 in post plasma-catalysis for dilute TCE abatement

Sharmin Sultana[a,*], Zhiping Ye[a,b], Savita K.P. Veerapandian[a], Axel Löfberg[b], Nathalie De Geyter[a], Rino Morent[a], Jean-Marc Giraudon[b,*], Jean-François Lamonier[b]

[a] Ghent University, Faculty of Engineering, Department of Applied Physics, Research Unit Plasma Technology, Sint-Pietersnieuwstraat 41, 9000 Ghent, Belgium
[b] Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 − UCCS − Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

ARTICLE INFO

ABSTRACT

Fe-doped manganese oxide octahedral molecular sieves (referred as OMS-2) of cryptomelane type structure were synthesized by co-precipitation and impregnation by refluxing at ambient pressure. The influence of Fe in the MnO_2 structure was assessed by several characterization techniques such as ICP-OES (inductively coupled plasma-optic emission spectroscopy), X-ray diffraction, Raman spectroscopy, N_2 adsorption analysis, H_2-TPR (hydrogen temperature programmed reduction), and TGA/DTA (Thermogravimetric analysis/Differential thermal analysis). The co-precipitated sample (Fe-K-OMS-2) shows better performances for TCE removal in moist air when used downstream from a NTP (non thermal plasma) generated in a DC multi-pin-to-plate corona/glow discharge in comparison to the iron free manganese oxide octahedral sieve (K-OMS-2). The enhanced performances towards TCE removal using Fe-K-OMS-2 downstream from the NTP are attributed to high surface oxygen mobility and to an increase of structural defects resulting from improved textural properties. These characteristics allow promoting O_3 decomposition and TCE catalytic total oxidation (CTO) efficiencies.

1. Introduction

A large and important group of air pollutants consists of Volatile Organic Compounds (VOCs) which particularly harm human health and our environment. Along with carcinogenic and mutagenic effects on human health [1], VOCs are also precursors to ground level ozone which is principally responsible for photochemical smog. The research of innovative technologies for VOC abatement is stimulated to accommodate the new stringent standards in terms of VOC emission. One emerging strategy is the coupling of 2 existing complementary technologies, namely here Non Thermal Plasma (NTP) and Catalytic Total Oxidation (CTO), to get a more efficient process for VOC removal in air. Indeed although NTP displays a high reactivity in air towards VOC removal at atmospheric pressure and ambient temperature, it has however a low CO_2 selectivity currently producing other VOC by-products, CO, and hazardous ozone. This lack of CO_2 selectivity can be overcome by the addition of a O_3 decomposition/VOC total oxidation catalyst downstream of the plasma discharge to form a post plasma-catalysis (PPC) system [2–4]. Here the catalyst takes advantage of its high efficiency towards the destruction of ozone to give active species able to oxidize the plasma processed hazardous by-products and the possibly remaining VOC into CO_2.

The performances of NTP in PPC have already been investigated in particular for trichloroethylene (TCE) removal which is a very reactive molecule towards cold plasma in dry/wet air [5–7]. Indeed TCE is recognized as a highly toxic chlorinated VOC widely used in industry as metal degreasing agent. The design of the catalyst has to be performed taking into account some basic requirements such as ozone decomposition ability, VOC total oxidation capacity, as well as hydrothermal stability and resistance to chlorine. Among the different catalysts already investigated MnO_2 appears to be very interesting, especially, due to its very high activity towards O_3 degradation [8]. However MnO_2 shows various crystallographic phases. Cryptomelane, an octahedral molecular sieve (OMS) is one allotropic form of MnO_2 having a (2×2) tunnel structure (OMS-2). The structure is made of the superposition of 4 units of 2 edged MnO_6 octahedra building blocks connected by corners along the c axis forming 1D microporous square tunnel of 0.46 nm in size. K^+ cations which are located inside the (2×2) tunnels provide charge balance and stabilize the structure (K-OMS-2; general formula $K_xMn_8O_{16}$ with an average manganese oxidation of about 3.8). The open structure of the channels, the easy cycling of Mn^{4+}/Mn^{3+} and the high mobility of lattice oxygen as well as more recently the morphology of the particles have been put forward as important characteristics to take into account for their activity in CTO of VOCs [9–18]. On purpose

* Corresponding authors.
   E-mail addresses: sharmin.sultana@UGent.be (S. Sultana), jean-marc.giraudon@univ-lille1.fr (J.-M. Giraudon).

MnO_2 oxides have been already shown interesting TCE abatement properties in PPC [6,7,19,20]. The TCE total oxidation performed in moist air in the presence of CO_2 was previously investigated as a function of energy density using an atmospheric pressure negative DC luminescent glow discharge combined with a cryptomelane catalyst positioned downstream from the plasma reactor [19,20]. The ability of the catalyst to decompose plasma generated ozone allows getting active oxygen species enabling the destruction of plasma generated poly-chlorinated hazards and the enhancement of TCE abatement. The main limitation is the side formation of some C1 chlorinated compounds believed to be in line with a partial chlorination of the catalyst when the temperature of the catalyst is to low [19,20]. In order to promote the efficiency of the PPC process towards VOC abatement a possible strategy is to improve the physical and catalytic properties of K-OMS-2 material by doping. Indeed doping of single–type, low or high-valent metal transition cations, has been previously showed to produce cryptomelane with novel morphologies [21] and improved catalytic properties [22]. Doping cryptomelane with various cations of different types can improve the textural properties [23,24], modify Mn average oxidation state (AOS) [9,25,26] and thermal stability [9,23,26,27], increase structural defects, e.g., vacancies [23,27], and also enhance the reactivity of cryptomelane towards the catalytic oxidation of various organic pollutants [24,28–30]. It follows from these considerations that the physico-chemical properties of the metal doped K-OMS-2 depend on the nature of the doping metal and of the synthesis conditions, such as among others, through the mode of incorporation and temperature of calcination of the oxide precursor material. As a result the doping cation can be incorporated into the channels, partially replacing K^+ ions and/or substitute M^{3+} or Mn^{4+} cations in MnO_6 octahedra and/or be present as dispersed transition metal oxides supported on the cryptomelane phase [23]. Among the possible transition metal dopants Fe has been chosen as it has been previously reported that Mn-Fe oxides may be promising catalysts for ozone decomposition [31]. Taking advantage of this property, Mn-Fe oxides dispersed on cordierite have been recently used successfully in a PPC process for the decomposition of diethylether [32]. Additionally Fe doped cryptomelane catalysts have been reported to enhance VOC total oxidation [33]. Reported Fe-doped cryptomelane synthesis methods include hydrothermal treatment of Fe-doped layered birnessite [9], redox precipitation under reflux [34], sol–gel assisted combustion methods [26], addition of iron precursor to cryptomelane and heating [33].

This present study focuses on the preparation, characterization and evaluation in TCE oxidation (in presence of moist air) of Fe-doped K-OMS-2 oxides placed downstream from a NTP reactor prepared by introduction of Fe either by co-precipitation [34] or by deposition of Fe $(OH)_x$ (x = 2-3) over the K-OMS-2 solid [35] prepared by the reflux method in order to modify the chemical/physical properties of the catalysts.

2. Materials and methods

2.1. Catalyst preparation

The introduction of iron to cryptomelane was performed by 2 different ways inspired by literature: (i) by co-precipitation followed by calcination at 450 °C (Fe-K-OMS-2) [34]; (ii) by deposition of Fe(OH)$_x$ (x = 2; 3) over K-OMS-2 followed by calcination at 450 °C (Fe/K-OMS-2) [35]. A reference cryptomelane (K-OMS-2) was also synthesized.

2.1.1. Synthesis of K-OMS-2

A $KMnO_4$ (Fluka, 99%; 6.385 g in 150 mL; $n_{Mn(II)} \approx 1.5 \ n_{Mn(VII)}$) solution was added dropwise to manganese (II) acetate (Mn $(CH_3CO_2)_2 \cdot 4H_2O$; Prolabo, 99%; 14.854 g in 50 mL) dissolved in a CH_3COOH/CH_3COOK buffer solution of pH 4.5 while stirring. A black brown precipitate was rapidly formed and the mixture was stirred 24 h at reflux. The precipitate was then washed thoroughly with distilled water and dried overnight at 100 °C. The resulting powder was calcinated at 450 °C for 4 h (1 °C/min) in air (0.3 L/min).

2.1.2. Synthesis of Fe-K-OMS-2

A $KMnO_4$ (Fluka, 99%; 6.98 g ≈ 0.044 mol in 80 mL) heated at 60 °C was added to an aqueous acidified solution (CH_3COOH; Alfa Aesar, 99%; 12 mL of a 2 mol/L solution into 90 mL of water) of Mn and Fe nitrate precursors (($Mn(NO_3)_2 \cdot 4H_2O$; Sigma-Aldrich, 97%; 11.76 g ≈ 0.045 mol) and Fe($Fe(NO_3)_3 \cdot 9H_2O$; Fisher Scientific, 98%; 1.9 g ≈ 0.00461 mol)) to get a precipitate. The suspension was stirred vigorously at reflux for 20 min. An additional amount (≈ 8 mL) of 2 mol/L acetic acid was added to retrieve the volatilized acetic acid during reaction. The precipitate was separated through centrifugation and washed with deionized water several times until neutral pH, followed by drying at 100 °C for 12 h. The resulting solid was calcined in air (0.3 L/min) at 450 °C for 4 h (1 °C/min).

2.1.3. Synthesis of Fe/K-OMS-2

0.41 g of $Fe(NO_3)_3 \cdot 9H_2O$ (Fisher Scientific, 98%; ≈ 0.001 mol) and 0.40 g of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (Sigma-Aldrich, 98%; ≈ 0.001 mol) ($n_{Fe(II) = } n_{Fe(III)}$) were dissolved in 50 mL of water (pH = 2.6). A KOH (Sigma-Aldrich-85%) solution of 1 mol/L was added dropwise to the initial solution, under constant stirring, to a final pH of 9.6 allowing the successive precipitation of Fe(OH)x (x = 2,3). At that stage K-OMS-2 ($n_{Fe}/n_{Mn} = 0.10$) was introduced above this pH as powder to the aqueous suspension and KOH was again added dropwise until a pH of 12. The resulting solid was intensively washed with distilled water and dried before to be calcined at 450 °C for 2 h.

2.2. Catalyst characterization

K, Mn and Fe elemental analyses were performed by inductively coupled plasma-optic emission spectroscopy (ICP-OES) at the REALCAT platform (Lille University). The sample preparation was made by dissolving 10 mg of dried and ground solid in 1.5 mL of concentrated aqua regia solution. Solutions were heat at 50 °C and stirred during 12 h. All sample solutions were stirred and the volume was adjusted up to 50 mL with ultrapure water before being analyzed by ICP-OES.

X-ray diffractograms were recorded using a Bruker AXS D8 Advance diffractometer. Data were collected using the Cu Kα line in the 10–70° 2-theta range with a 0.02° 2 θ step and a counting time of 3 s per step. Crystallite size was estimated from the FWHM of the peak located at 2 θ = 28.9° using the Scherrer equation, after correction of the FWHM to account for the instrumental broadening using the Diffrac. EVA-crystallite size determination.

The Raman spectra of the samples were recorded at room temperature using a Raman microprobe (Labram HR) equipped with a Peltier-cooled detector. The exciting light source was the 488 nm line of an Ar^+-ion laser and the spectral resolution was ± 1.5 cm^{-1}.

The morphology of the materials was observed using Scanning Electron Microscopy images recorded on a Hitachi S-4700 apparatus. The specific surface areas were determined using a conventional multipoint BET nitrogen adsorption method with a MicromeriticsTristar II apparatus. Prior to nitrogen adsorption, the samples were outgassed for 4 h at 150 °C under vacuum.

TGA analyses were performed on sample size of about 10 mg in air flow (50 mL/min) with a heating rate of 10 °C/min up to 800 °C *using a TA Instruments TGA-SDT 2960*.

Temperature programmed reduction (TPR) were carried out using a Micromeritics 2920 Autochem II Chemisorption Analyzer. 50 mg sample was put into a quartz U-shaped tubular quartz reactor. The samples were pre-treated in flowing Ar at 150 °C for 60 min followed by cooling down to room temperature. The reducing gas was a mixture of 5 vol.% H_2/Ar at a total flow rate of 50 mL/min. The temperature was allowed to increase from 25 °C to 800 °C with a heating rate of 10 °C/min.