Nanostructure Formation of Platinum (Pt) Clusters on K-OMS-2 Manganese Oxide Paper by Reactive Spray Deposition Technique (RSDT) - CO Oxidation and Conductivity Measurements

H.F. Garces[‡§], J. Roller[ξ§], C. K. King'ondu[†], S. Dhamarathna[†], R. Marik[ξ], and S.L. Suib[‡†]

[‡]Institute of Materials Science, 97 N. Eagleville Rd, Storrs CT 06269-3136, University of Connecticut.
[§]Center for Clean Energy and Engineering, 44 Weaver Rd, Storrs CT 06269-5233, University of Connecticut.
[†]Department of Chemistry, 55 North Eagleville Rd, Unit 3060, Storrs CT 06269-3060, University of Connecticut.
[ξ]Chemical, Materials and Biomolecular Engineering Department, 191 Auditorium Rd, Storrs CT 06269-3222, University of Connecticut.

ABSTRACT

Nano-cluster formation of Platinum (Pt) on a modified K-OMS-2 manganese oxide inorganic paper by reactive spray deposition technology (RSDT) is presented. RSDT was employed to produce a film of controllable thickness on the inorganic K-OMS-2 paper material. The resultant Pt/K-OMS-2 composite material was fully characterized by X- ray diffraction (XRD), scanning electron microscopy, X-ray energy dispersive spectroscopy (EDX), transmission electron microscopy (TEM), X-ray 3D micro-tomography, and high temperature scanning electron microscopy (HTSEM). The non-destructive characterization technique (X-ray tomography) resolved the coating layer and the nature of the K-OMS-2 inorganic modified paper; layers of K-OMS-2 fibers superimposed to form a stack. The nanostructured coating on the inorganic paper type material is evaluated for carbon monoxide (CO) oxidation and conductivity measurements. Carbon monoxide (CO) oxidation with the Pt/K-OMS-2 modified inorganic paper presented 100 % conversion to CO_2 at temperatures as low as 200°C. A simple, fast, and new deposition technique has been employed for the formation of highly homogeneous coating of Pt on an inorganic K-OMS-2 modified paper.

Keywords: X-ray tomography; Manganese Oxide; K-OMS-2 Paper; Reactive Spray Deposition Technique (RSDT); Films Deposition.

INTRODUCTION

Cryptomelane manganese oxide is a type of octahedral molecular sieve with a 2x2 tunnel structure that has been synthesized via different methods including reflux, microwave, sol-gel, solid state reactions, and hydrothermal treatments to produce different morphologies such as nanofibers, nanorods, nanowires and dendritic cluster with applications in catalysis, electrochemistry, and as semiconductor.

RSDT is a method of depositing films through combustion of metal-organic or metal-inorganic compounds dissolved in a solvent, and it has emerged as an alternative to other deposition techniques such as atomic layer deposition (ALD), chemical vapor deposition (CVD), pulse laser deposition (PLD), and physical vapor deposition (PVD). RSDT is an open atmosphere deposition, exceptional for direct film formation and cost efficiency; does not require post deposition thermal treatment, vacuum, drying or annealing.

EXPERIMENTAL SECTION

Synthesis: The inorganic K-OMS-2 paper like material was prepared as previously reported.[1] After the synthesis, about 0.4 g of the material was dispersed in DDW and formed as free standing inorganic paper.

Deposition of Pt on K-OMS-2 Paper: Platinum was deposited on modified K-OMS-2 by reactive spray deposition technology (RSDT). Briefly, the method involved pumping platinum acetyl acetonate (PtAcac) dissolved in toluene through an atomizing nozzle and combusting the atomized spray. Deposition onto a 4 mm x 4 mm K-OMS-2 modified inorganic paper like material occurred by impinging the flame on the substrate.

Characterization: X-ray diffraction analysis performed in an Ultima IV Rigaku X-ray diffractometer (Cu Kα radiation). Diffraction patterns were obtained in the range of 5-75 2θ degrees at a scan rate of 2° min^{-1}. Transmission electron microscopy (TEM) micrographs were obtained using a FEI Tecnai T12 S/TEM and JEOL JEM 2010 FasTEM operating at 200 kV. The specimens were loaded onto a carbon-coated gold grid. Scanning electron microscopy (SEM) was performed in a FEI Quanta ESEM 250 scanning electron microscopy. The sample was cut into a square piece of about 5 mm and placed in a carbon tape. Cross section of the inorganic Pt/K-OMS-2 modified paper- like material after deposition was performed by immersing the paper-like material in an epoxide, polishing with different grits, alumina, and silica dispersions. Elemenental mapping of the samples was done by energy dispersive X-ray analysis (EDX) in an FEI Quanta ESEM 250 operated at 20.0 kV with X-ray spectra acquired and processed with an Ametek Genesis Apex 4. High temperature scanning electron microscopy (HTSEM) was performed in a FEI Quanta ESEM 250 scanning electron microscopy. Paper-like Pt/K-OMS-2 material was heated to the analysis temperature at 50 °C min^{-1}, and stabilized for 30 minutes before and SEM image was taken. High resolution X-ray 3D tomography was performed in a MicroXCT-400. The specifications for the tomography employed are 40 keV accelerating voltage and power of 4 watts. Projections were collected from -90 to 90 theta with a exposure time of 14 seconds per image. Reconstruction and visualization was performed afterwards.

Catalytic studies: CO oxidation in a temperature range from 200 to 400 °C was done employing a vertical fixed-bed tubular reactor made of quartz with an internal diameter of 2 mm. In each experiment, the membrane was cut in square pieces of about 2 mm, packed in the quartz reactor, and held by quartz wool in both ends. The catalyst was heated to the analysis temperature with an Ar down flow of 40 SCCM and held for 1 h before the beginning of the CO oxidation. Afterwards, three consecutive automatic injections were sampled at each evaluation temperature. The analytical system comprised an Agilent 3000 Micro GC equipped with two thermal conductivity detectors. A Molecular Sieve and a Plot Q capillary was used for the separation. Tubing and fittings were stainless steel throughout. In each experiment, about 0.06 g of K-OMS-2 and Pt/K-OMS-2 catalyst was placed in the reactor. A furnace with PID control held the temperature constant in the reactor. The thermocouple was placed at the top of the catalyst bed. Mass flow controllers (MFC) were used to control flow rates, feed, and composition. A certified gas mixture (Airgas: 10% CO in N_2), pure O_2, and Ar as balance were used for the CO oxidation. Stability test for CO oxidation was performed at 200 °C.

RESULTS

The diffraction peaks correspond to the hexagonal manganese oxide K-OMS-2 cryptomelane phase (JCPDS No. 29-1020). Diffraction peaks for platinum phase deposited are also observed (JCPDS No. 01-089-7382). No additional phases were detected.

Scanning electron microscopy (SEM) images for the modified and coated Pt/K-OMS-2 paper-like materials showed that surface fibers are completely covered after deposition of Pt by RSDT.

X-ray spectroscopy mapping and cross section SEM images showed a layer of Pt on K-OMS-2 membrane. The FIB/SEM showed that the coated Pt layer is ~ 50 nm.

X-ray 3D tomography also resolved the layer of platinum deposited on the membrane. It is also observed that the membrane is composed of layer of K-OMS-2 fibers superimposed to form a stack. The contrast between the high (Pt) and the low absorption material (inorganic membrane) was well resolved.

Catalytic activity of K-OMS-2 and Pt/K-OMS-2 paper type material for CO oxidation as a function of reaction temperature is presented. A low temperature is required to achieve 100% conversion for CO oxidation with the modified Pt/K-OMS-2. Both materials present equal conversion at 300 and 400 °C.

DISSCUSION

Xray diffraction analysis for the initial K-OMS-2 modified paper-like and the Pt coated K-OMS-2 paper-like material resolved the two crystalline phases. Reflections for the initial precursor was not detected after the deposition, which suggest completed decomposition of the platinum acetyl acetonate precursor. This is needed in catalysis where small amounts of carbon deposits left after incomplete decomposition of organic by-products block paths and posion the catalyst active sites, reducing the activity.

SEM images shows a complete coverage of the K-OMS-2 fibers after the depsotion by RSDT. The thickness of the coating is about ~ 50 nm for the individual fibers but the active coated layer can be of the orders of microns depending on how the individual fibers that form the cloth paper superimpose on each other forming the stack.

The Pt/K-OMS-2 paper-like presented 100% for CO oxidation at 200°C compared to about 70% conversion when the material is not coated. However, the coated Pt/K-OMS-2 is expected to maintain a high conversion at low temperature in presence of humidity

CONCLUSIONS

A simple and fast deposition technique has been employed for the formation of a highly homogeneous thick coating of Pt on an inorganic K-OMS-2 paper-like material. The uniform Pt coating wrapped K-OMS-2 fibers completely. No agglomeration of the coating or covered empty spaces were observed. The materials presented 100% conversion for CO oxidation at 200°C.

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