Synthesis and characterization of porous WO_3–SnO_2 nanomaterials: An infrared study of adsorbed pyridine and dimethyl methylphosphonate

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ABSTRACT

High surface area porous W/Sn oxide nanomaterials were prepared via water/oil based (W/O) emulsion. Tungstic acid solution was generated by cation exchange of sodium tungstate in acidic Dowex resin. The acid was then mixed with a clear homogeneous aqueous N-cetyl trimethyl ammonium bromide (CTAB) solution followed by a slow addition of $0.2\,M$ $SnCl_4$ solution. The mixture was stirred for 24 h and then subjected to slow calcination at $500\,°C$. The prepared materials were characterized using SEM-EDX, BET surface area, and sorption of nitrogen and water. Fourier transform infrared spectroscopy (FTIR) was used to characterize the surface acidic properties using pyridine vapor as a probe. The materials were then tested toward the Dimethyl methylphosphonate (DMMP) adsorption at various temperatures using infrared spectroscopy. At elevated temperatures, the desorption of DMMP from WO_3 and SnO_2 surfaces results in forming methyl phosphonate that strongly bounds on the metal oxide surfaces. In contrast, the FTIR spectra showed that the adsorbed dimethyl methylphosphonate (DMMP) on the mixed W/Sn oxide powders can be molecularly desorbed without any decomposition.

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1. Introduction

Developing semiconducting metal oxide (SMO) based sensors has been a cornerstone of research activity for the last 20 years [1–15]. SMO sensors provide an inexpensive, compact, and rapid method for the detection of low concentrations (ppb) of gases [16–19]. They can either be deposited as thin films on the sensing element via ultrahigh vacuum (UHV) [20] or as thick films using screen printing process [21–23]. However, little is known about the mode of interactions, between the target gaseous molecules and the SMO surfaces, that leads to the change in the material's conductivity. Therefore, the lack of sufficient information about the available sites on the SMO detectors surface and their reactions with the target molecules results in the poor detection, selectivity and reproducibility of these sensors in several applications [24]. Few experimental approaches were investigated to achieve unique sensor array units include controlling variables such as the SMO composition, impregnation with metal catalysts and operational temperature [25–28]. Recent studies reported the development of various nano-sized metal oxides [29–32], mixed oxides

systems [33,34], and porous SMO components for similar applications [35,36]. It has been shown that the selectivity and the operational temperature problems have been vastly improved using various solid blending SMO materials [37,38].

WO_3 is one of the SMO based sensors that are known to provide sensitive detection for sarin, one of the most popular chemical warfare agents (CWA). Several issues limit the fabrication and commercializing of these sensors due to their low selectivity, high operational temperature, and its poor recovery. In previous studies, the fabrication of nano-sized WO_3 powders with high surface area were reported [36,39]. Our studies provided a better understanding of the mode of interaction between the simulant molecule, dimethyl methylphosphonate (DMMP), and the WO_3 surface sites using FTIR spectroscopy [39–42]. Therein, the DMMP adsorbed on the surface was shown to decompose and poison the surface via the methylphosphate group at temperatures above $300\,°C$. Therefore, there is a growing demands on developing selective and sensitive device for CWA materials but without changing the base of the detection. Several strategies are under investigation including pre-filtration techniques [43] and the use of size selective detection where two sensors, porous and nonporous ones, were put in use simultaneously [36].

In this work, we provide a synthetic protocol to fabricate W/Sn mixed metal oxide with porous structure to tune the surface

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features and change the DMMP adsorption/desorption profiles; hence, enhance the sensors' recovery. The proposed material is tempted to vary the H-bonded, Lewis, and Brønsted acid sites. Such variation is expected to change the mode of interaction between the mixed oxide and the simulant molecule.

2. Experimental

2.1. Materials

DMMP 99%, sodium tungstate (99%), $SnCl_4$ (~99%), methanol (HPLC grade) and ethanol (HPLC grade), DOWEX 50X2-200, and N-cetyl trimethyl ammonium bromide (CTAB) were purchased from Aldrich Chemical Company and were used without any further purification.

2.2. Synthesis of WO_3–SnO_2 nanomaterials

Two samples of mixed tungsten-tin oxide powders (labeled as W/Sn-1 and W/Sn-2) were made by the emulsion-based sol–gel synthesis. In this process, a condensation reaction occurs in the aqueous phase of the water-in-oil (W/O) emulsion. The emulsion is composed of a continuous phase containing solvent, micro-water-droplets, inverse micelles and free surfactant. The synthesis was done in multi-steps process. Initially, a CTAB solution was made by adding 1.0 g CTAB in 10 mL distilled deionized water (ddH$_2$O) solution and stirred until the solution was homogeneous and clear. Then 2.0 mL of NH$_4$OH (32 wt%) was added to the CTAB solution and the mixture was stirred for an additional 5 min. Tungstic acid (H$_2$WO$_4$) was then prepared by passing 0.12 M Na$_2$WO$_4$ solution through ion exchange resin packed, into a 50 mL buret, with 35.0 g of an acidic Dowex 50WX2-200. The resin was washed with water to adjust the solutions' pH to 5–6. The resin capacity was determined to be equivalent to exchange 40.0 mL of 0.12 M Na$_2$WO$_4$ solution. The eluted solution was collected in two aliquots of 20 mL each. The two eluted aliquots were used for the preparation of W/Sn-1 and W/Sn-2 samples, respectively. Each of the freshly eluted solutions of H$_2$WO$_4$ was then added to the CTAB solution along with a slow addition of 5.0 mL of 0.2 M SnCl$_4$ solution. The final mixture was stirred for 24 h at ambient temperature and then the sol–gel polymerization process was allowed to continue without stirring for an additional 48 h. The resulting yellowish green powder was filtered, then washed sequentially with ethanol and deionized water. The dried powders were calcinated at 500 °C for 5 h under slow heating rate of 1.0 °C/min. To understand the morphology and the surface properties of the prepared W/Sn mixed oxides, pure powders of SnO$_2$ and WO$_3$ were also prepared for comparative purposes. The pure powders were prepared using the procedure reported previously [39,44]. The tungsten and tin content in each sample were determined using SEM-EDX and ICP analysis.

2.3. FTIR spectra

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Bomem MB-Series spectrometer equipped with a liquid N$_2$ cooled mercury cadmium telluride (MCT) detector. Typically 200 scans were co-added at a resolution of 4 cm^{-1}. Transmission Spectra were recorded using a thin film technique. In brief, a thin film of the metal oxide powder was pasted on a CsI disk of 1.0 in. diameter. A reference spectrum was then recorded through the metal oxide thin film. The metal oxide film was evacuated and then exposed to an excess amount of adsorbate to be studied in their vapor form (i.e.: pyridine, water, and DMMP) for 5 min followed by evacuation at room temperature. All spectra were recorded at ambient temperature.

2.4. SEM-EDS analysis

The SEM images were taken on films that were obtained by slow drying of the metal oxides suspension in water. The images from the films were collected at 23 °C in a Tescan VEGA III LMU-Scanning Electron Microscope with EDS Oxford Instrument. The range of accelerating voltage was 0.2–30 kV.

2.5. Sorption of water

Sorption of water was done using "Autosorb iQ" from Quantachrome equipped with a vapor sorption kit. The temperature was controlled through "Thermo Cube 300" thermoelectric temperature control system. Bath water temperature was adjusted to 297 K at which the water adsorption isotherms were collected. Before the analysis, all samples were heated at 393 K and outgassed under vacuum of 10^{-6} Torr to constant pressure. The water used as an adsorbate was free of any ions or dissolved gases. It was prepared by distillation using "GFL 2004 Water Stills" followed by deionization using "Millipore® Simplicity® Deionization" system. The mass of the metal oxides samples used in this study ranged between 50 and 100 mg. The water uptake was measured, after achieving equilibrium, over a wide range of relative pressures (p/p^o) that ranged from 0.01 to 0.95 [45]. From the adsorption isotherms, pore size distribution and total pore volumes were calculated using Density Functional Theory (DFT) [45].

2.6. Sorption of nitrogen

Nitrogen adsorption and desorption isotherms were measured at 77 K using "Autosorb iQ" from Quantachrome. Prior to the experiment, the samples were outgassed at 393 K and under a vacuum of 10^{-6} Torr to constant pressure. The variation between the adsorption and desorption isotherms provide information about the adsorption hysteresis. Characterization of pore sizes and pore structure were accomplished using density functional theory (DFT) where the surface area (S_{DFT}), total pore volume (V_t), micropore volume (V_{mic}), and volume of pores less than 10 Å ($V_{<10Å}$) were calculated [46]. Moreover, Brunauer–Emmett–Teller (BET) theory was used to calculate the BET surface areas (S_{BET}) [46].

3. Results and discussion

The EDX analysis for the tungsten and tin content in each sample were determined. The results indicate that sample W/Sn-1 contains 16.5% Sn and 60.5% W whereas, the W/Sn-2 sample contains 21.4% Sn and 49.5% W. The SEM images (Fig. 1) also indicate that the prepared W/Sn samples are of well-defined porosities unlike the morphology appearing for both WO$_3$ and SnO$_2$ powders. The EDS analysis indicates the presence of higher tungsten content in W/Sn-1 which is expected since the first eluted amount of tungstic acid is with higher concentration than the second batch exiting the column.

The nitrogen adsorption and desorption isotherms were measured for all samples and the results are displayed in Fig. 2. As shown, the adsorption isotherms for all measured samples follow type II. The nitrogen uptakes for the pure SnO$_2$ and WO$_3$ samples are similar to each other at various relative pressures except at very high p/p_0 where the SnO$_2$ sample showed a significant increase in the nitrogen uptake. The observed isotherms for the synthesized samples, W/Sn-1 and W/Sn-2, are similar throughout the whole adsorption range with higher initial nitrogen uptake relative to SnO$_2$ and WO$_3$. The increase in the number of micropores for the mixed oxide powders is a clear indication of the difference in their surface structures relative to the initial oxides.