

Control of Effluent Gases from Solid Waste Processing using Impregnated Carbon Nanotubes

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ABSTRACT

One of the major problems associated with solid waste processing technologies is effluent contaminants that are released in gaseous forms from the processes. This is a concern in both biological as well as physicochemical solid waste processing. Carbon dioxide (CO_2), the major gas released, does not present a serious problem and there are currently in place a number of flight-qualified technologies for CO_2 removal. However, a number of other gases, in particular NO_x , SO_2 , NH_3 , and various hydrocarbons (e.g. CH_4) do present health hazards to the crew members in space habitats.

In the present configuration of solid waste processing in the International Space Station (ISS), some of these gases are removed by the Trace Contaminant Control System (TCCS), demands a major resupply. Reduction of the resupply can be effective by using catalyst impregnated carbon nanotubes. For example, NO decomposition to N_2 and O_2 is thermodynamically favored. Data showing decomposition of NO on metal impregnated carbon nanotubes is presented. Comparisons are made of the existing TCCS systems with the carbon nanotube based technology for removing NO_x based on mass/energy penalties.

INTRODUCTION

Processing of solid wastes invariably requires the use of thermal methods in order to destroy potentially harmful biological organisms and organic compounds. A major problem encountered during such processes is the release of decomposition products in the form of gases that can be harmful to humans. Other sources are off gases coming from structural materials of space vehicle, crew activities (e.g. exercise, food preparation etc), experimental payload operations, accidental releases, microbial metabolism and contingency events. An excellent compilation of the list

of chemicals released into the space cabin is provided in references [1, 2].

We present our recent investigation of using SWNTs as catalytic supporting materials to impregnate metals, such as rhodium (Rh), potassium (K) and other catalysts. A protocol has been developed to impregnate the Rh and K in aqueous metal chloride solution, according to unique surface properties of SWNTs. The Rh has been successfully impregnated in SWNTs. The SWNTs, Rh-SWNTs and K-SWNTs have been characterized by thermogravimetric analysis (TGA) and scanning electron microscope (SEM). The NO decomposition is characterized by a residual gas analyzer (RGA).

The project is funded by a NASA Research Announcement Grant to find applications of single walled carbon nanotubes in eliminating toxic gas contaminant in a life support system. This knowledge will be utilized in the development of a prototype SWNT NO_x gas purification system that would represent a significant step in the development of high efficiency systems capable of selectively removing specific gaseous for use in regenerative life support systems for human exploration missions.

THEORY OF NO REDUCTION

The theory of NO reduction on metals has been extensively studied. Rhodium metal appears to be one of the best catalyst for this purpose [3]. The key step of the NO reduction has long been thought to be the breaking of the O-bond upon chemisorption onto the metal. The bond energy and bond length are 149.9 Kcal/mol and 1.2 Å. NO is thermodynamically unstable ($\Delta G_{298}^0 = 86.32$ KJ/mol) but once formed it's decomposition at 1 Atmosphere is kinetically not-favored, though it can be broken down at higher pressures [4]. Rapid recombination of surface nitrogen

atoms to form N_2 follows rapidly. The remaining oxygen atom then is released as O_2 , CO or CO_2 depending on the conditions and the supporting matrix of the catalyst. Luo et al. [5] demonstrated the decomposition of NO on carbon nanotubes and rhodium impregnated carbon nanotubes. Since carbon nanotubes are relatively non-reactive, we believe that the atomic oxygen will be released as oxygen gas.

Alkali metals are known to act as catalysts in carbon gasification reactions. Kapteijn et al. [6] observed a large increase in NO reduction (and carbon reactivity) when K was added to the carbon. Okukara and Tananka [7] found that, upon potassium addition to activated carbon, both the NO adsorption capacity and carbon reactivity increased. Illan-Gomez et al. [8,9] studied NO reduction by K-loaded activated carbon in detail and found that the catalytic role of K was attributed to its effective participation in an oxidation-reduction (redox) cycle between K_xO_y and K_xO_{y+1} , in which the catalyst is oxidized by NO and reduced by carbon to produce N_2 and CO_2 .

MATERIALS AND METHODS

SOURCES OF CARBON NANOTUBES

The purified single walled carbon nanotubes containing less than 2% impurities in this study were purchased from Carbon Nanotechnologies Inc, Houston, TX. The method of producing the SWNTs is by the high-pressure carbon monoxide disproportionation (HiPCo) reaction [9]. This raw HiPCo SWNTs normally contains between 22-30% iron originating from the catalyst used for carbon nanotube growth. These samples obtained from Rice University are referred to as "Raw HiPCo" in the paper.

RHODIUM CATALYST PREPARATION

Rhodium impregnation was achieved by adding a known concentration of rhodium chloride solution to a pre-weighed sample of carbon nanotubes. The rhodium chloride solution is prepared so that when added to the carbon nanotubes, the percentage of metallic rhodium ranged from 1-20%. A mild vacuum was applied for 1 hour and the sample stirred overnight. The mixed solution was dried for 8-12 hours at 105°C in an atmosphere of N_2 . The dried sample was reduced in a stream of 10-20% H_2 in Argon with heating from room temperature to 200°C at a temperature ramp of 5°C per minute. When the temperature reached 200°C , the sample was maintained in the H_2/Ar atmosphere for a further 30 minutes. TGA analysis, SEM imaging was done on the samples prior to testing its catalytic activity.

POTASSIUM CATALYST PREPARATION

Potassium carbon nanotube catalysts were prepared by adding a known concentration of "Analytical Grade" potassium nitrate to a pre-weighed sample of carbon

nanotubes with the concentration being so designed to produce a 20% K carbon nanotube catalyst. The mixture was stirred for 24 hours and then dried at 105°C overnight. The sample was subjected to a 1-hour treatment in helium at 300°C to decompose any adsorbed nitrate. TGA analysis and SEM imaging was done on the samples before using it for catalytic activity.

CATALYTIC ACTIVITY MEASUREMENT

A concentration of 250 ppm NO in helium was used as the source of NO. The choice of the concentration was based on two major criterion namely the known concentrations of NO_x in typical flue gases and the sensitivity of analysis using the residual gas analyzer (RGA). The basic protocol involved placing an accurately weighed amount of the metal catalyst between 35-100 mg into the sample tube. Glass wool was placed on top and below the sample to ensure that the sample is held firmly in the tube during the experiment.

The catalyst was first treated with H_2 (99.9%) gas to ensure that the rhodium remained in the metallic form followed by a flow of He (99.999%) to flush out residual H_2 and measure the free space. Subsequently, the 250 ppm NO in He was passed through the catalyst-SWNTs in the sample tube at different temperatures – temperatures of 200, 250, 300°C for 20 minutes of each in the case of the Rh-SWNTs and temperatures of 150, 200, 250, 275 and 300°C for the K-SWNTs. A temperature of 400°C was used only once with the 20% rhodium-SWNTs and subsequently it was decided not to use this temperature as we noticed evolution of CO_2 that suggested that it was possible that some of carbon matrix was being oxidized. The gas flow of H_2 , He and NO was controlled by a MKS 640A Absolute Pressure Controller for closed-loop electronic pressure control. The pressure at the outlet of sample tube was accurately controlled at 761Torr to ensure a gas flow through the tube, see a flow chart in Figure 1.

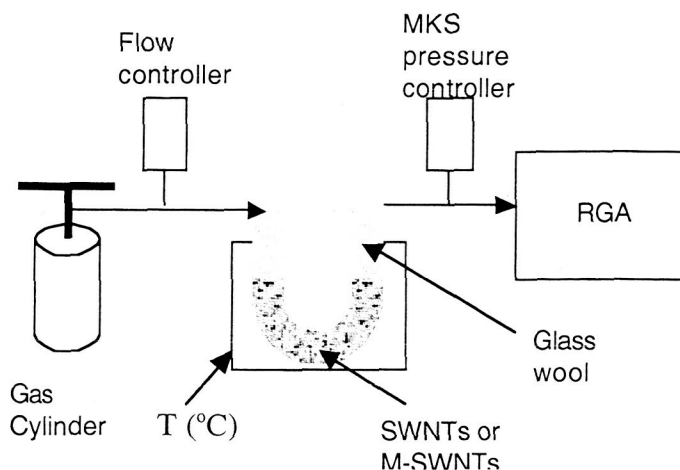


Figure 1 A flow diagram of the setup for NO conversion measurement.

The NO conversion measurement protocol is summarized in table 1 below. There are slightly difference in timing for the blank tube control experiment and Rh-SWNT, K-SWNTs samples.

Table 1: Protocol for gas flow, temperature and reaction time in Chemisorption studies.

PROCESS	TEMP (°C)	RAMP RATE(°C/min)	TIME (min)
Evacuate	150	10	20
Flow H ₂	150	10	20
Evacuate	150	10	20
Flow He	150	10	20
Evacuate	150	10	20
Flow NO or He	150	5	20-30
Evacuate	200	10	20
Flow NO or He	200	5	20-30
Evacuate	250	10	20
Flow NO or He	250	5	20-30
Evacuate	250	10	20
Flow NO or He	300	5	20-30
Evacuate	300	10	20

THERMOGRAVIMETRIC ANALYSIS

A Perkin Elmer thermogravimetric analyzer (TGA Pris 1) was used to measure the metal contents in the SWNTs, Rh-SWNTs and K-SWNTs samples by burning off all carbonaceous material and check the percentage of residues. The carrier gas was nitrogen with a flow rate of 20 cc/min. The temperature ramping rate was set at 10°C/min. The temperature range was set from 50°C to 1025°C.

SCANNING ELECTRON MICROSCOPE

The carbon nanotube impregnated with rhodium was dispersed in dimethylformamide (DMF). This solution was

drop deposited onto a silicon dioxide substrate. After the DMF evaporated the Rh-SWNTs lay on the silicon dioxide for SEM imaging.

RESULTS

SEM IMAGE OF RH-SWNTS

The SEM image of Rh-SWNTs sample is displayed in Figure 2. The rhodium forms a type of flower shape nestled with carbon nanotube bundles. The size of carbon nanotubes bundles is about 20-30 nm and the rhodium flower is in the diameter of 500nm. This flower shape of rhodium is reproducible from spot to spot with similar size. They may be formed during the drying of RhCl₃-SWNTs from water while the rhodium was still in the form of rhodium chloride salt. After the hydrogen reduction of rhodium in dry phase of Rh-SWNTs, the rhodium spots may stay in the shape as they were in the form of salt. The preference of Rh shaped in carbon nanotubes needs more exploitation and the size of Rh cluster will be studied for them to be controllable with correlation to the NO conversion efficiency.

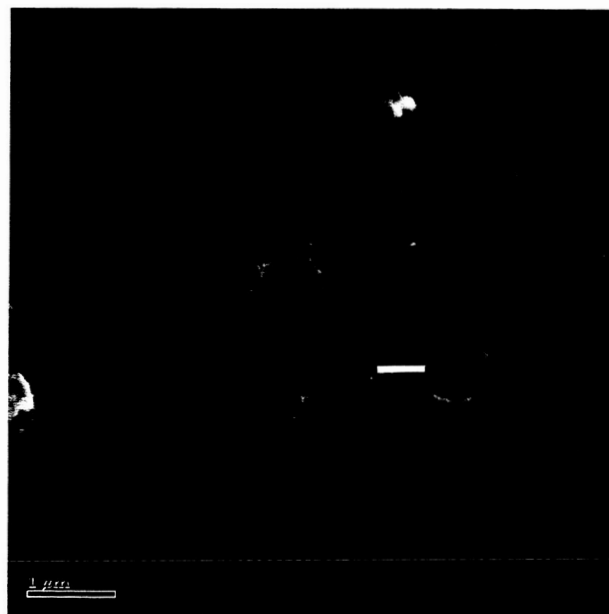


Figure 2 SEM image of rhodium impregnated single wall carbon nanotubes

THERMOGRAVIMETRIC ANALYSIS DATA

Figure 3 shows a thermogravimetric analysis of the different materials with nitrogen as a carrier gas. The non-impregnated SWNTs begins to decompose at temperatures between 375-400°C and plateaus at around 1.6% confirming that the carbon nanotubes do have less than 2% impurities as reported by the supplier. In the presence of rhodium, decomposition of the carbon nanotubes begins at a lower temperature around 325-350°C, while in the presence of potassium it begins at temperatures even lower below 300°C. The rhodium

content of one catalyst sample had 18% and the second 15% based on the TGA analysis. The potassium catalyst

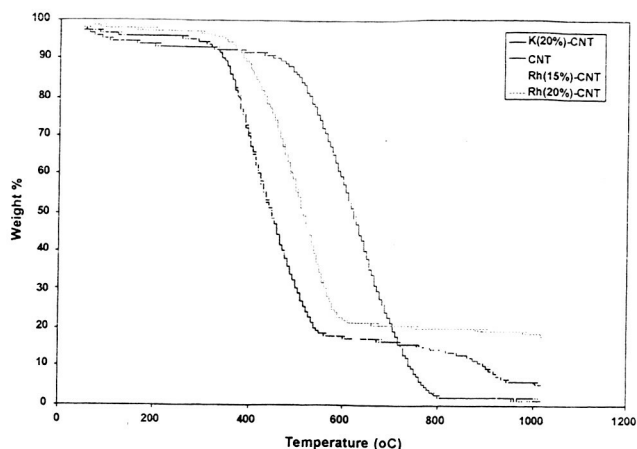


Figure 3 TGA plots of different materials: SWNTs, Rh(15%)-SWNTs, Rh(18%)-SWNTs, K(19%)-SWNTs

had a potassium content of around 19%. These results enabled us to make a decision on the temperature ranges that were considered suitable for performing catalytic studies without burning off the carbon nanotubes matrix.

EFFECT OF TEMPERATURE ON NO REDUCTION

Reduction of NO was carried out in the Micromeritics 2010 instrument using the chemisorption setup that the temperature can be ramped above room temperature.

A preliminary study with 20% Rhodium impregnated carbon nanotubes suggested that at temperatures around 350-400°C, the carbon in the catalyst was being oxidized as evidenced by the evolution of CO₂ detected by RGA. In order to eliminate the oxidation of carbon nanotubes by NO gas, the operating temperature for NO reduction was then setup equal or below 300°C for rest of the study in this paper.

Figure 4a shows a RGA scan data for 250ppm NO injection into a sample tube for a control (Blank tube). It is clear that the NO peak kept a constant value over the temperature of 200, 250, 300°C. There is no readout from CO₂ peak at these temperatures except a cosmos spike occurred when NO sample was first time injected. The control experiment tells the levels of NO peak and CO₂ peak without possible conversion taking place.

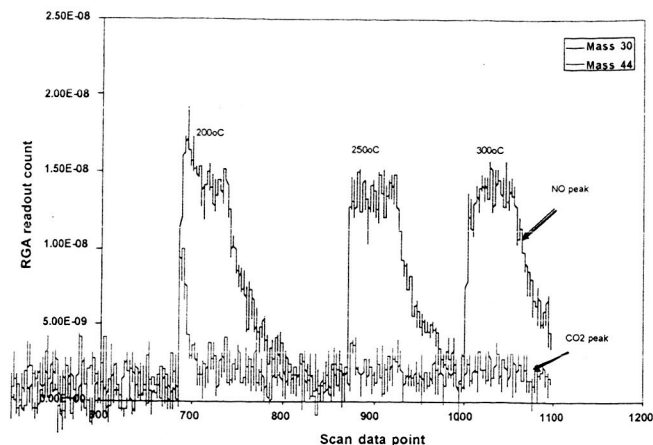


Figure 4a RGA scan data from the control experiment (blank sample tube).

Figure 4b shows a RGA scan data for 250ppm NO injection into a sample tube contained 15% rhodium impregnated SWNTs at temperatures of 200, 250 and 300°C. At the lower temperatures of 200 and 250°C, the RGA readout level of NO is not significantly smaller than that in the control experiment. This means very minimal conversion taking place at these temperatures (200 and 250 °C). However, NO decomposition occurred at 300°C virtually no NO was detected after the NO was passed through the catalyst. Compared with the results from the control experiment, it would suggest that the Rh-SWNTs driven NO reduction is almost 100% complete at 300°C. The cause of NO reduction can be considered in two possible ways; 1) NO decomposed on the surface of rhodium, 2) NO oxidized the carbon nanotubes to form CO₂. There are spikes showing in CO₂ peak in Figure 4b. However, the spikes are so sharp that could be the cosmos pulse or due the valve switch. And the CO₂ level is down towards the baseline after the spikes, which means the CO₂ was not formed in a significant amount, if there is any, to be maintained at a constant level. This may indicate that the NO reduction is mainly caused by catalysis of Rh in the SWNTs.

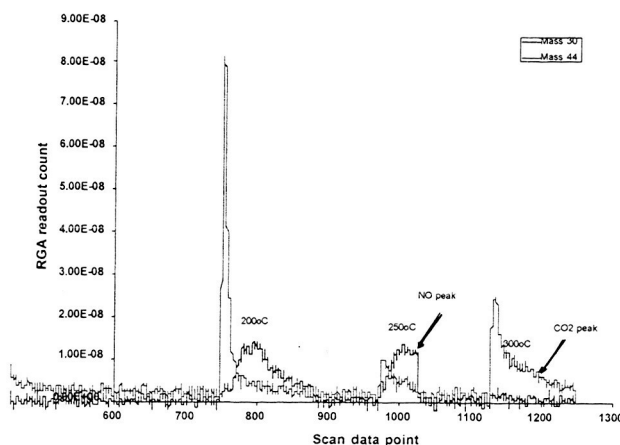


Figure 4b RGA scan data from Rh-SWNTs sample for NO conversion measurement

are currently in progress to determine the temperature optimum specifically between 250 and 300°C.

Further studies are also in progress to study the optimal metal concentration required for NO decomposition. Luo using 1% Rh-SWNTs reported only about about 10% NO decomposition at 300 °C. It is critical for NASA's application that the activity be expressed as a function of concentration of NO, since rates of generation of NO on ISS are well known and the permissible SMAC levels are established.

ACTIVITY OF POTASSIUM IMPREGNATED CARBON ANAOTUBES

Decomposition of NO at low temperatures has been reported by Ilan-Gomez et al (1995). We have measured the out gases after the NO passing through the K-SWNTs at 150, 200, 250, 275, and 300°C. There is no obvious reduction of NO observed. The NO peak level was maintained a constant at all these temperatures and similar to the level in the control experiment.

POWER/MASS PENALTIES & ESM

On the Russian Space Station, Mir, the trace contaminant control system was composed of 5 components – a fan, an expendable charcoal canister weighing 6 Kg and 2 regenerable charcoal canisters weighing 23.4 Kg each. The regenerable canisters were regenerated every 20 days by exposing to space vacuum for 60 minutes followed by heating to between 180 and 200°C for 1.5 hours. The system processes 20 m³ of air/h and handles a number of contaminants. The nitrogen oxide generation rate is around 13.5 mg/day and the trace control system maintains the nitrogen oxides within the SMAC value.0.3 mg/m³. This same system is in place on ISS but recently a thermal oxidation was added in which a Pd/Pt catalyst on Alumina was added. Unlike the United States TCCS system, the Russian system operates at a lower temperature (200-250°C) and this is achieved by flowing at a lower flow rate of 0.5 cm³/hour. Other major differences between the Russian and US TCCS system include (a) the Russian air handling capacity is greater and in the present configuration in ISS has been increased to handle 27 m³/hour vs 15.3 m³/hour (b) The Russian system purifies almost 37,000 Kg of air per 1.28 KW.hr, while the original US design was only capable processing 928 Kg of air per 7.63 KW.hr. Clearly, the Russian system was more efficient from an energy perspective. The Rh-carbon nanotube catalyst will operate at lower temperatures than the existing catalyts system (275-300 °C vs 400 °C). Preliminary estimate assumes a slow flow rate of 1.7m³/hr contaminated air flow through the catalyst. With this slow flow rate, it is estimated that 0.06 KW.hr energy will be

required to destroy the 13.5 mg of NO produced per day by a 6 person crew.

CONCLUSION

The 7-day Space Craft Maximum Allowable Contaminant (SMAC) level for NO, NO₂ and N₂O are in ppm 4.9, 0.5 and 491 and in mg/m³ 6.1, 0.94 and 900 respectively. In order to ensure the safety of the crew, it is essential that these standards be met.

TGA analysis of the prepared catalytic materials showed that rhodium metal and the potassium metal contents in the SWNTs matrix are within experimentally acceptable levels of the required metal/ion ratio.

SEM images of the Rh-SWNTs showed that the rhodium appeared to be in clusters nestled in the bulk of the carbon nanotubes bundle meshes.

We have provided evidence that 250 ppm NO can be completely decomposed with a 15% Rh-SWNTs at 300°C. There is no reduction of NO from the 19% K-SWNTs up to 300°C.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

CNT Carbon Nanotubes

HiPCo High Pressure Carbon monoxide disproportionation reaction

Rh-SWNTs Rhodium impregnated single wall carbon nanotubes

K-SWNTs Potassium impregnated single wall carbon nanotubes

SEM Scanning Electron Microscopy

SMAC Space Station Maximum Allowable Contaminant levels

TGA Thermogravimetric Analysis

RGA Residual gas analyzer