

# Catalytic Tar Reduction for Assistance in Thermal Conversion of Space Waste for Energy Production

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The Trash to Gas (TtG) project investigates technologies for converting waste generated during spaceflight into various resources. One of these technologies was gasification, which employed a downdraft reactor designed and manufactured at NASA's Kennedy Space Center (KSC) for the conversion of simulated space trash to carbon dioxide. The carbon dioxide would then be converted to methane for propulsion and water for life support systems. A minor byproduct of gasification includes large hydrocarbons, also known as tars. Tars are unwanted byproducts that add contamination to the product stream, clog the reactor and cause complications in analysis instrumentation. The objective of this research was to perform reduction studies of a mock tar using select catalysts and choose the most effective for primary treatment within the KSC downdraft gasification reactor. Because the KSC reactor is operated at temperatures below typical gasification reactors, this study evaluates catalyst performance below recommended catalytic operating temperatures. The tar reduction experimentation was observed by passing a model tar vapor stream over the catalysts at similar conditions to that of the KSC reactor. Reduction in tar was determined using gas chromatography. Tar reduction efficiency and catalyst performances were evaluated at different temperatures.

## Nomenclature

<i>AES</i>	=	Advanced Exploration Systems
$C_7H_8$	=	Toluene
$CH_4$	=	Methane
$CO$	=	Carbon monoxide
$CO_2$	=	Carbon dioxide
<i>GC</i>	=	Gas chromatography
<i>HMC</i>	=	Heat Melt Compactor
<i>HFWS</i>	=	High fidelity waste simulant
<i>ISS</i>	=	International Space Station
<i>ISRU</i>	=	<i>In-situ</i> resource utilization
<i>KSC</i>	=	Kennedy Space Center
<i>LRR</i>	=	Logistics Reduction and Repurposing
<i>LPM</i>	=	Liters per minute
$N_2$	=	Nitrogen
<i>NASA</i>	=	National Aeronautics and Space Administration
$O_2$	=	Oxygen
<i>ppm</i>	=	Parts per million
<i>Rh</i>	=	Rhodium
<i>TtG</i>	=	Trash to Gas

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## I. Introduction

THE Trash-to-Gas (TtG) project is a collaborative effort under NASA's Logistical Reduction and Repurposing (LRR) project designed to reduce total logistical mass through reduction, reuse and recycling of various wastes and components of long duration space missions and habitats. LRR is focusing on four distinct advanced areas of study: Advanced Clothing System, Logistics-to-Living, Heat Melt Compactor and TtG.<sup>1</sup>

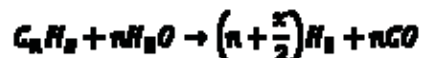
These four areas look to reduce volume and reuse items that would typically end up as logistical waste and instead convert the items into useful commodities. LRR models its research on long duration missions that would occur beyond low earth orbit.<sup>2</sup> TtG high-value products include life support oxygen and water, rocket fuels, raw material production feedstocks, and other energy sources. All technologies studied under TtG processed similar waste simulants such as food, food packaging, Maximum Absorbent Garments (MAGs), human waste simulants, and cotton washcloths. A gasification reactor was designed and manufactured in house at Kennedy Space Center (KSC) with the primary purpose of generating carbon dioxide (CO<sub>2</sub>).<sup>3,4</sup> CO<sub>2</sub> production was maximized so that it could be fed into a Sabatier reactor with the addition of hydrogen to produce methane and water.<sup>5</sup>

During gasification, large hydrocarbons (also known as tars), dust, and ash were generated as byproducts. Tars are potentially harmful to humans and cause considerable damage to processing equipment as they form and condense within a system. Tars contain energy that can be transferred to fuel such as hydrogen (H<sub>2</sub>), carbon monoxide (CO) and methane (CH<sub>4</sub>). Tar production is often a function of temperature. The first step in reducing tar formation typically resides in optimizing the gasifier design. Studies have also used char beds above the primary air inlet to minimize tar production. Another optimization technique includes operating the reactor at the optimal equivalence ratio of the gasification system. Tar concentration often decreases as the equivalence ratio increases since more oxygen is available to react with volatiles in the pyrolysis region when reacting. Literature also suggests that the equivalence ratio is more significant at higher temperatures. After the gasifier reactor has been optimized, a catalyst is introduced into the system for further optimization in tar reduction or for assistance in reactor kinetics.<sup>6,7,8</sup>

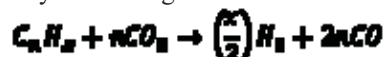
Many research studies have shown 98% tar reduction using calcined rocks, iron ores, dolomite, synthetic alkali metal-based catalysts, fluid catalytic cracking catalysts, Ni-based, ash and char in reactors operating well above 700°C.<sup>7</sup> Some catalysts create useful products like CO and H<sub>2</sub> from the breakdown of higher molecular weight hydrocarbons. Common criteria for picking catalysts in a system include resistance to deactivation, minimal fouling, easy regeneration, high attrition resistance, low cost, and effective tar removal.<sup>5,6</sup> Deactivation of a catalyst can be caused by coke formation, which is a major drawback to using catalysts. It is therefore important to select a catalyst with low attrition to avoid coking and clogging of a system. Tar reduction reactions typically occur on the catalyst surface. Common reduction reactions occurring during gasification and catalysis processes are displayed in the following equations.<sup>2,3,4</sup>

### Chemical Reactions

Steam Gasification



Dry Reforming



Thermal Cracking



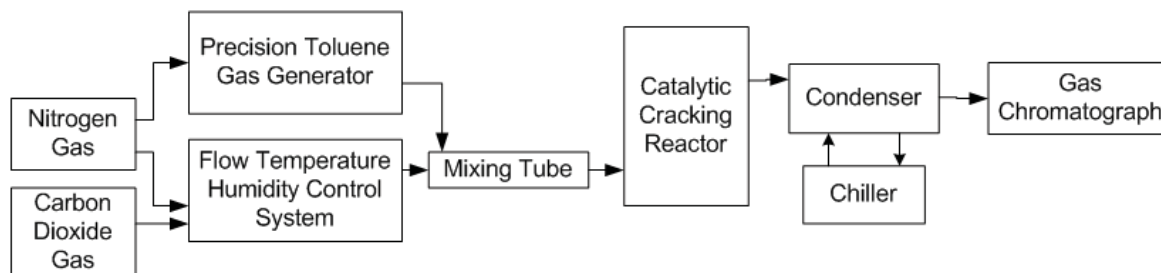
Primary tar treatment methods use a catalysis bed within the main reaction chamber. When primary additives of Ni-based, calcined dolomite and magnesite, zeolite, olivine, or iron catalysts are used, the changes of the product gas composition reduced tar yield but also promote coking of the bed. Secondary tar treatment methods include those downstream of the reactor system. Such treatment methods include catalytic and thermal cracking, various filtration methods (i.e. baffle, ceramic, electrostatic), scrubbers, rotating particle separators and external catalytic beds downstream from the reactor. Secondary methods often have economical disadvantages but can be very effective at removing tar. In some studies, the most effective secondary catalytic treatment for tar reduction included the use of guard bed catalysts such as dolomite to increase the life of a second catalyst. It is challenging to find comparable literature for primary catalysis treatment for this specific TtG gasification reaction, since each gasification system

has different operating conditions.<sup>3,9,10</sup>

Materials such as minerals, synthetics and metallics have been used as catalysts for tar reduction. The typical operating temperature for successful tar reduction catalysts have been at operating temperatures between 700°C and 900°C. The order of activity of catalysts is generally metallics>dolomite>char>olivine>sand. Calcined rocks contain calcium oxide and magnesium oxide (CaO/MgO). These minerals often have large pore sites and high alkalinity which are favorable conditions for catalytic activity. Calcined rocks are inexpensive, effective for tar removal and abundant. However, CaO/MgO minerals such as dolomite often deactivate due to coke formation and deteriorate to fine particulates. Minerals such as olivine consist primarily of silicate minerals with iron and magnesium cations embedded in the structures. Olivine is often stronger than dolomite, but the literature claims it is less effective in reducing tars than dolomite. Synthetic catalysts often include char (often a byproduct of pyrolysis) due to its large pore size and high mineral content. Metallic based catalysts often include transition metals, such as nickel and platinum, for effective tar removal and have a supporter material to provide strength against attrition and a promoter material to increase the activity of the catalyst.<sup>6</sup>

## II. Materials and Methods

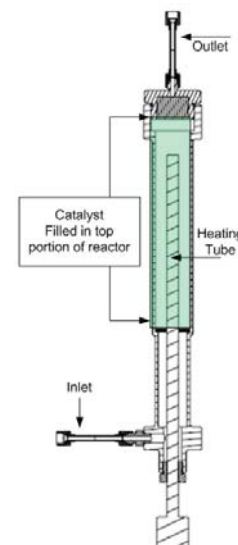
Reduction of a model tar using six different catalysts, for use as primary treatment within the KSC TtG downdraft gasifier reactor, were investigated in a test-bed thermal degradation reactor. The model tar was toluene (C<sub>7</sub>H<sub>8</sub>) and was selected as the model tar due to its availability, low hazard levels, easy handling, and use in previous studies. The catalysts selected in this investigation were obtained from the results of an internal KSC literature review. Of the catalysts that were available at KSC, those thought best for thermal cracking of tars under gasification conditions were selected and included: dolomag (Charles B. Chrystal Co.), olivine (Essix Resources, Inc.), dolomite (Charles B. Chrystal Co.), a three-step automobile type catalytic converter containing platinum, a



**Figure 1. Experimental Set-Up.** Mixed gases similar to the composition of the KSC TtG gasification reactor syngas were sent to the catalytic cracking reactor for tar reduction.

developmental rhodium (Rh) catalyst (Johnson Matthey), and ash byproduct from the gasification reactor that had processed trash.

A schematic of the experimental setup is shown in Figure 1. The feed gases into the reactor were similar to that of the TtG gasification product gases and included nitrogen (N<sub>2</sub>), water vapor, model tar and CO<sub>2</sub>. N<sub>2</sub> and CO<sub>2</sub> were conditioned via a Miller-Nelson HCS401 humidity control system to create a moist gaseous stream between 30-50% relative humidity at ambient temperature. A KinTek 491M Precision Gas Generator was used to produce a controlled concentration of toluene at 137 ppm using N<sub>2</sub> as the diluent gas. The total flow rate of the vapor stream was ~1.14 LPM at 70°C. Mixed feed gases were sent to the catalytic cracking reactor which was designed and manufactured at Johnson Space Center (Figure 2). The thermal reactor is a 1.5 inch internal diameter Inconel tube reactor with a Watlow multi-cell tube heater. The catalyst was pre-loaded into the reactor bed, which surrounded the tube heater. The heated zone of the reactor was approximately 9 inches tall with the tube heater at 8 inches tall. The void space of the reactor bed allowed 0.28 liters of catalyst to surround a tube heater. Approximately 133 grams of unused catalysts in its solid form were added to each experimental run. A new unused amount of catalyst was added prior to each experimental run that lasted eight hours at the designated temperature. LabVIEW data collection program was used to monitor temperatures and pressure of the system during runs. The downstream gas was cooled in a condenser with an ethylene glycol chiller and



**Figure 2. Catalytic Cracking Reactor.** This thermal degradation reactor was used to hold the catalyst bed for catalytic cracking.

sent to a gas chromatograph (GC) with a flame ionization detector for determining the apparent concentration of toluene for reduction calculations.

The TtG downdraft gasification reactor operated at a temperature range between 500°C and 700°C, therefore, testing of catalysts was performed at 25°C, 500°C and 700°C. An Agilent 7890A gas chromatograph was used to quantify toluene in the gas stream. Only toluene was measured in this study, no other byproduct formation was detected during this investigation.

The apparent percent reduction of toluene was calculated according to the following equation:

$$\%Reduction = \left( \frac{C_{toluene,in} - C_{toluene,out}}{C_{toluene,in}} \right) \times 100$$

(1)

Where,

$C_{toluene,in}$  = Apparent concentration of toluene into system, ppm

$C_{toluene,out}$  = Apparent concentration of toluene out of system, ppm

The operating conditions of various experiments are displayed in Table 1. Each run was performed with the reactor at a steady temperature for eight hours in order to observe the catalyst behavior for long durations to investigate

Catalyst				Reactor		Feed Stream		
Type	Physical State	Approximate Size [mm]	Mass [g]	Run Time [min]	Temp. [C]	RH, %	Feed Gas	Combined Flow, LPM
Empty	-	-	0	480	25	30-56		
Empty	-	-	0	480	500	31-51		
Empty	-	-	0	480	700	32-36		
Char/Ash	Ash	-	NA	480	500	30-34		
Dolomag	Solid, granular	2.0-6.4	133	480	25	33		
Dolomag	Solid, granular	2.0-6.4	133	480	500	33		
Dolomag	Solid, granular	2.0-6.4	133	480	700	41		
Olivine	Solid, granular	2.5-6.4	133	480	25	37	Gaseous	2.0-2.4
Olivine	Solid, granular	2.5-6.4	133	480	500	34-37	N <sub>2</sub> /CO <sub>2</sub> /	
Olivine	Solid, granular	2.5-6.4	133	480	700	36	C <sub>7</sub> H <sub>8</sub> / H <sub>2</sub> O	
Develop w/Rh	Solid, honeycomb pellet	12.7	133	480	25	37		
Develop w/Rh	Solid, honeycomb pellet	12.7	133	480	500	36		
Develop w/Rh	Solid, honeycomb pellet	12.7	133	480	700	35		
Dolomite	Solid, granular	3.2-12.7	133	480	25	36		
Dolomite	Solid, granular	3.2-12.7	133	480	500	36		
Dolomite	Solid, granular	3.2-12.7	133	480	700	37		
Catalytic Converter	Solid, cylindrical block	-	NA	480	500	58		

**Table 1. Experimental Operating Conditions**

catalyst activity and attrition. Empty runs were performed to baseline the concentration of toluene as well as any absorption or thermal cracking based on temperature and absorption alone. The majority of catalysts were in solid granular form.

### III. Results and Discussion

The average percent tar reduction with varying catalysts at 25°C, 500°C and 700°C is displayed in Figure 3. The stream of toluene was not emitted from the vapor generator until the reactor was at the designated experimental operating temperature. Triplicates of each run were performed and averaged to discuss experimental results. According to literature, at higher temperatures (above 25°C), dolomag is a very effective catalyst for tar reduction. In this study, dolomag exhibited the lowest reduction of toluene at 700°C compared to that at 500°C as shown in Figure 3. Dolomag was the first catalyst that was tested in this study, at which troubleshooting of the GC method was still occurring. The Dolomag data for 25°C is not reported due to instrumentation calibration issues early on in testing. The point at which the GC instrument was stable for reliable catalyst data collection, the supply of dolomag

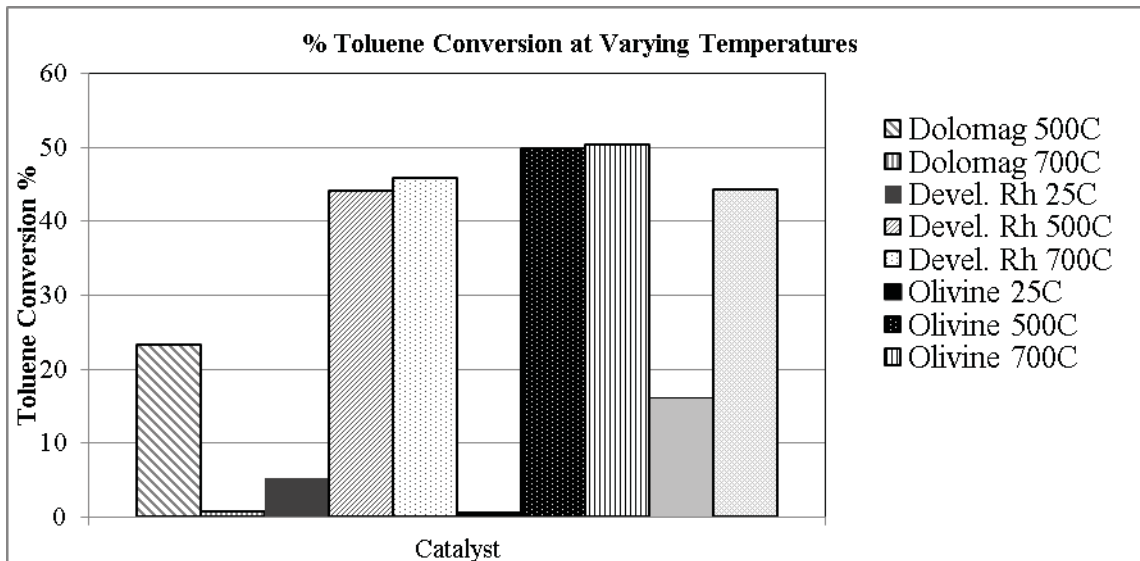


Figure 3. Average % Toluene Reduction at Varying Temperatures.

at KSC was used up since only a limited supply was available for testing. However, dolomag was implemented into the bed of the TtG reactor and the data correlates with the results show in this small-scale study.

The developmental rhodium catalyst was a honeycomb shape with high surface area of the metal on a supportive substrate. Percent toluene reduction increased as temperature increased and was highest at 500°C and 700°C as shown in Figure 3. The rhodium catalyst can be seen at the bottom right of Figure 4, resting on the sides of the reactor heater and the top portion above the tube heater. After testing at 700°C, the rhodium catalyst had visible discoloration and turned a darker shade of brown. In the concentration versus time plots of Figure 5, there is no evidence of attrition of the catalyst during the eight hour cycles, so the discoloration did not affect the performance of catalyst in this study.

The olivine catalyst had a dramatic increase in toluene reduction from 25°C to 500°C and almost no change as the temperature increased to 700°C. Olivine had a slightly higher percent reduction of toluene than the developmental rhodium catalyst. This is useful information for cost analysis of considering catalyst implementation. Olivine is much more abundant and naturally occurring than the manufactured developmental rhodium catalyst.

Dolomite had higher reduction of toluene at 700°C than 500°C. But at 500°C the dolomite was not nearly as effective at converting toluene as the olivine and developmental rhodium catalyst.

Only enough catalytic converter material was present for 500°C testing in the reactor. The percent reduction of toluene for the catalytic converter as a catalyst is not shown in Figure 3 no detectable toluene was observed and therefore a 100% reduction of the toluene occurred.

The ash used in this experiment was black with the appearance similar to that of activated carbon. The theory was the ash would have a high surface area for adsorption of the toluene and reduction of harmful tars. The ash was placed in the bed of the reactor and heated to 500°C. At the start of the temperature increase from 25°C to 500°C, the reactor quickly became clogged with a yellow wax-like material. Most of the components downstream to the reactor filled with the wax material and the testing was ceased. After this occurrence it was assumed the ash contained residual unreacted waste (i.e. polymer) which continued reacting via gasification and the ash was no longer used for further experimentation. If ash were to be utilized from the gasification reactor for future studies, it would have to be post processed at higher temperatures to ensure complete reaction and activation of the carbon. In this study, the TtG gasification ash byproduct was not useful as a tar reducing catalyst.

At 500°C and 700°C thermal and absorption activity does increase percent toluene reduction by approximately 28% and 38%, respectively. Overall, the performance of catalyst of those tested in order of highest reduction of toluene at 700°C include olivine>developmental Rh=dolomite>dolomag. At 500°C the performance of catalyst in order of higher percent reduction of toluene include catalytic converter>>olivine>developmental Rh>dolomite>dolomag. The reactor core of the gasification system typically remains between 400°C and 500°C, therefore the most

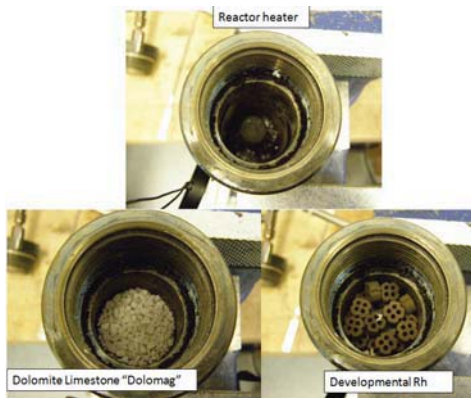


Figure 4. Catalytic Cracking Reactor. Open top view of the catalyst bed. Catalyst rests on the sides and top of the tube heater.

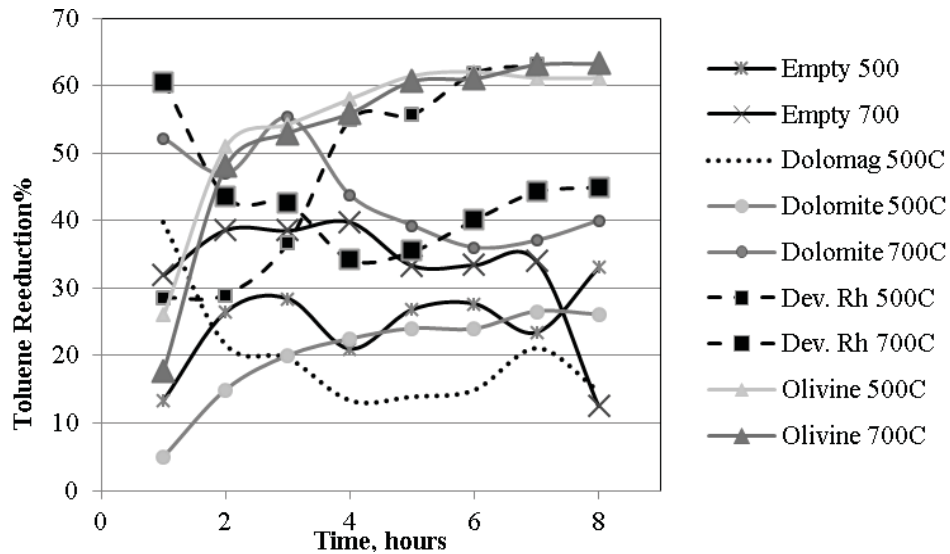


Figure 5. Average Toluene Reduction % vs. Time

effective and economical consideration for the gasifier for reducing tar would appear to be the catalytic converter for manufactured catalysts and olivine for natural catalysts.

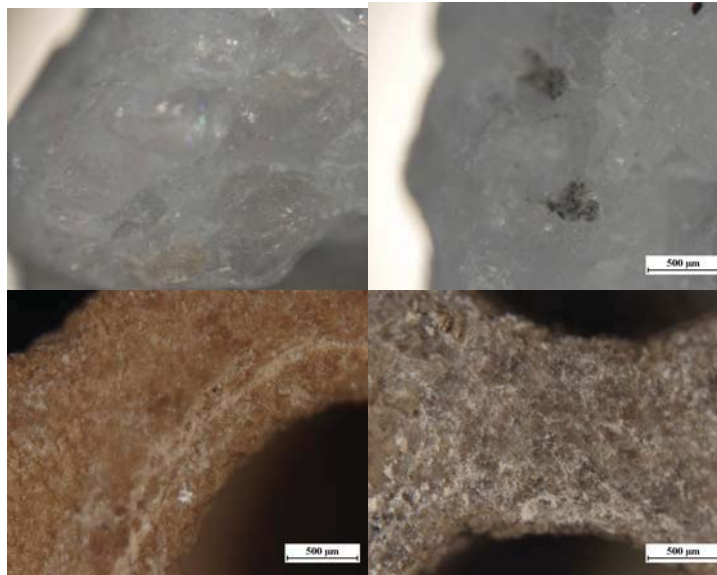
The percent reduction of toluene versus time plot is shown in Figure 5. The testing of catalytic activity over an eight hour time span was performed to investigate attrition of the catalyst. In general, the catalytic activity increases with time, except that of the catalytic converter which had no detectable toluene throughout its eight hour run cycle. In the case of dolomite at 700°C, and dolomag at 500°C that a clear decreasing trend exists in the percent toluene reduction. Dolomite and dolomag are both mineral compounds which can incur physical degradation and breakdown of minerals into fine particulates. Thermal degradation may have caused weakening in catalytic activity for the dolomite at the higher temperature of 700°C or 500°C, however no major physical decay was observed. Coking may have also cause the decreased performance in the catalyst. More testing would have to be performed to confirm this assumption. Overall, the catalysts show a general activation period within the first hour, before the percent reduction of toluene spikes and then remains fairly steady over the course of eight hours.

Some microscopy was performed on the catalysts both before and after exposure to the toluene system. The color of the developmental rhodium catalyst changed from light brown to dark brown during the 700°C runs and small black spots on the dolomite were found. These images are displayed in Figure 6.

The developmental rhodium catalyst and dolomag catalyst were tested in the TtG gasification reactor.<sup>3</sup> Both dolomag and the developmental rhodium catalyst were tested because the supply of the other catalysts had been depleted during the toluene testing. The compounds detected by the GC/MS in the gasification reactor for a run with and without catalysts while burning simulated space trash are displayed in Table 2. The developmental rhodium catalyst showed a significant reduction in the number of hydrocarbons detected by GC/MS. There is no isobutylene,

GC/MS	No Catalyst	Dolomag	Dev. Rh
1,3-Butadiene	X	X	X
1-Butene			X
1-Butyne	X	X	
Isobutylene	X	X	
2-Butene	X	X	
Acetaldehyde	X	X	
Ammonia	X	X	X
Carbon Dioxide	X	X	X
Cyclobutanol		X	
Cyclobutene	X	X	
Cyclopropane	X	X	
Ethane	X	X	
Ethyne	X		X
Nitrous Oxide	X	X	X

Table 2. GC/MS Detection in TtG Gasification Reactor



**Figure 6. Microscopy of Catalyst at 75x Before and After Toluene Exposure.** *Top left: Dolomite before butane, cyclobutene, cyclopropane or ethylene. Dolomag was less effective in that little change occurred in the number of hydrocarbons present in the outlet gas.*

#### IV. Conclusion

After determining candidate catalysts for the reduction of tars produced in the gasification of simulated spacecraft trash based on literature reviews and availability, we evaluated their performance using toluene as a model tar. The results indicate that automobile catalytic converter material (~100% reduction), olivine, and a developmental rhodium catalyst had the best performance at 500°C. Olivine, and the developmental rhodium catalyst had the best performance at 700°C. Due to limited supply, the catalytic converter material was not evaluated at 700°C. Testing of dolomag and the rhodium catalyst in our gasification reactor with high fidelity waste simulants showed that the rhodium catalyst was effective in removing several long chain hydrocarbons and, presumably, much of the tar present.

#### Acknowledgments

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