

# Hydrogen and Syngas Generation from Biomass: Catalytic Removal of NH<sub>3</sub> and Tars

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## Introduction

As the interest in renewable energy sources to replace currently used fossil fuels has increased, biomass conversion to syngas and hydrogen has taken center stage. Syngas can be converted easily to liquid transportation fuels. Considering the alternatives (solar, wind or microorganism assisted water splitting), biomass gasification serves as one of the most economical means for the production of H<sub>2</sub>. A major barrier in commercializing biomass gasification is the presence of impurities such as tars, NH<sub>3</sub>, and H<sub>2</sub>S. Undesirable conversion of NH<sub>3</sub> to NO<sub>x</sub> (conversion level as high as 50%) occurs when the gasification gases are fed to turbines [1]. When H<sub>2</sub> from biomass gasification is used as a fuel source for proton exchange membrane fuel cells, NH<sub>3</sub> blocks the acid sites of the membrane resulting in poor performance of the fuel cells. Hence, it is very important to decompose NH<sub>3</sub> to N<sub>2</sub> and H<sub>2</sub>. Further, the catalyst for NH<sub>3</sub> decomposition must perform satisfactorily in the presence of other biomass gasification gases such as CO, H<sub>2</sub>, CO<sub>2</sub>, and tars.

In the present work, decomposition of NH<sub>3</sub> and tars was studied on tungsten-based catalysts, tungstated zirconia (WZ) and tungsten carbide (WC). Levy and Boudart [2] have shown that WC qualitatively behaves like Pt. WC has been recently shown to be active for NH<sub>3</sub> decomposition [3]. Tar removal requires cracking, thereby necessitating an acid catalyst. WZ has been shown to possess strong acid sites and to be active for a wide variety of acid catalyzed reactions. The main focus of the present work was on the kinetics of NH<sub>3</sub> decomposition and toluene (model compound for tars) cracking on WZ and the effect of the presence of other gasification gases.

## Materials and Methods

WZ was obtained from Magnesium Electron Inc. while WC was obtained from Alfa Aesar. The catalysts were characterized by BET, XRD, NH<sub>3</sub>-TPD, ion exchange titrations and temperature programmed reaction (TPRx). The NH<sub>3</sub> decomposition and toluene cracking reactions were carried out in a micro-plug flow reactor in the temperature range from 450-800°C at atmospheric pressure. The inlet concentration of NH<sub>3</sub> was 4000 ppm while that of toluene was 2500 ppm. Other gases present were 10% H<sub>2</sub> and 15% CO with balance He. The effluent from the reactor was analyzed by gas chromatography.

## Results and Discussion

For WC, complete decomposition of NH<sub>3</sub> was observed at 550°C for the reaction conditions used. WC showed an induction period which in general decreased in time with an increase in temperature [3]. Although, WC was an excellent catalyst for the decomposition of

NH<sub>3</sub>, no decomposition was observed at 550°C in the presence of 10% H<sub>2</sub> and 15% CO. An induction period was also observed for WZ for lower temperatures (~ 500°C) and complete decomposition of NH<sub>3</sub> was observed at 600°C. But unlike WC, WZ showed some activity in the presence of 10% H<sub>2</sub> and 15% CO at 600°C as shown in figure 1. In the presence of these gases, an induction period was observed followed by a steady-state conversion of ca. 20%. In the presence of toluene, WZ initially showed some conversion. But after 25 min TOS, the catalyst deactivated rapidly with no conversion after 65 min TOS as shown in figure 1. The reasons for this behavior of WZ as well as its kinetic behavior will be discussed. Decomposition of toluene on WZ showed mainly formation of benzene and CH<sub>4</sub>. The time-on-stream behavior of WZ for toluene decomposition and the effect of the presence of gasification gases will be presented.

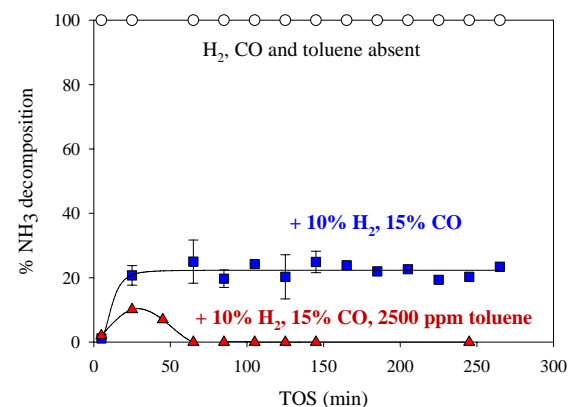


Figure 1. Effect of the presence of H<sub>2</sub>, CO, and toluene on the behavior of WZ at 600°C.

## Significance

Developing bi-functional catalysts that will remove NH<sub>3</sub> and tars from biomass gasification gas streams could have a huge impact on the potential commercialization of biomass gasification for production of H<sub>2</sub> as a renewable fuel.

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