Catalytic applications of char from gasification: influence of composition and morphology on catalytic activity

Naomi B. Klinghoffer[1*], Marco J. Castaldi[1], Ange Nzihou[2]
[1]The City College of New York, New York, NY 11238 USA
[2]Université de Toulouse, Mines Albi, Albi, CEDEX 09, F-81013 France
**corresponding author:nbk2107@columbia.edu*

Introduction

Gasification is a thermo chemical conversion technology enabling the production of fuels or chemicals from solid fuel sources such as biomass or waste. The process typically yields a solid char residual and recent research has focused on finding useful applications for char. Char is a high surface area carbon material, containing highly dispersed inorganic elements and resembles catalysts currently being used. For example, carbon based catalysts have been used in a variety of applications, such as NO_x reduction, SO_x oxidation, and dehydrogenation reactions. In this research, the catalytic activity of char from biomass gasification is demonstrated and the influence of char composition and morphology on its catalytic activity is investigated. Hydrocarbon decomposition reactions were tested because one application for catalytic use of char is for decomposition of tars, which are produced in gasifiers. In these applications, where impurities (ex. sulfur or chlorine compounds) can lead to catalyst poisoning and tar cracking can cause coking, it is beneficial to use char, which is an inexpensive alternative to conventional catalysts.

Materials and Methods

Char was produced from gasification of poplar wood in a fluidized bed reactor under a steam or CO_2 atmosphere at temperatures from 550-920°C, with a heating rate of 20°C min^{-1}. The char was recovered from these reactions and the BET surface area, porosity, and composition were measured. The catalytic activity of the char was measured for decomposition of methane, propane and toluene, in a flow through fixed bed reactor. The sample was heated in nitrogen to a set point of 800°C and then a N_2/hydrocarbon mixture was introduced. Effluent gases were measured with an Inificon 3000 micro gas chromatograph. Char composition was measured with a ThermoQuest CHNS analyzer, and inorganics were analyzed in an Environmental Scanning Electron Microscope (FEI XL30) and by ICP (HORIBA Jobin Yvon Ultima 2).

Results and Discussion

The catalytic activity of char was demonstrated for decomposition of methane, propane, and toluene, which is a surrogate molecule for gasification tar. These tests indicated that char properties such as composition, surface area, and porosity, which depend on gasification conditions, influence the catalytic activity of the char. For example, Figure 1 shows hydrogen production from methane decomposition using char that was recovered from steam gasification. The reaction temperature was 750°C and residence was either 30 or 60 min, which influenced the surface area of the char. Longer residence time resulted in higher surface area, which improved catalytic performance.

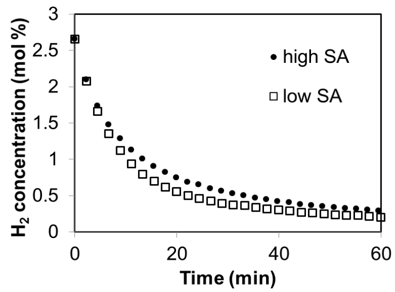

Figure 1. Hydrogen production from methane decomposition using char catalysts from gasification in steam. Surface area of high and low surface area chars were 621 m^2 g^{-1} and 429 m^2 g^{-1}, respsectively.

The char was primarily composed of carbon (85%) and also contained oxygen (7%) nitrogen (2%), hydrogen (2%), sulfur (0.5%), and trace amounts of many inorganic elements (ex. Ca, P, K, Na, Fe, Ni, Al, etc.). Removal of inorganic elements by acid washing (with 16% hydrochloric acid) reduced the catalytic performance of the char, indicating that the inorganics that are present in biomass and remain in the char play a role in its catalytic activity. In addition, even at gasification temperatures of 920°C, the inorganic elements were highly dispersed, which improved catalytic performance, as demonstrated by a decrease in activity when dispersion was reduced.
Gasification conditions influenced the surface area and micropore volume of the char. Surface area ranged from 429-687 m^{2}g^{-1}. Higher gasification temperature (up to 920°C) and longer residence time created chars with higher surface areas. In addition, the gasification environment influenced the porosity. Gasification in CO_2 produced char with more micropores (with diameter <1nm) compared to gasification with steam. As expected, the catalytic activity increased with increasing surface area. However, diffusion limitations were observed in the micropores, leading to lower catalytic activity for microporous chars, compared to non-microporous char with the same surface area. After the char was used as a catalyst the surface area was reduced by 20% and the pore volume was reduced by 30%, indicating that catalyst deactivation takes place via pore blocking.

Significance

Utilization of char as a catalyst for tar reforming presents an economical and convenient solution for the reforming of tars, which remains a significant issue with commercialization of gasification. The activity of the char is attributed to the high surface area of the char, which is dependent on gasification conditions. The porosity also influences catalytic activity, and diffusion limitations in micropores can reduce catalytic activity. The presence of inorgancis, and their high dispersion on the catalyst surface play an important role in catalytic activity of char.