

Characterization of Ni-olivine materials as tar removal catalysts for biomass gasifiers

John N. Kuhn^{*1}, Zhongkui Zhao¹, Umit S. Ozkan¹, Larry G. Felix², and Rachid B. Slimane³

¹The Ohio State University, Columbus, Ohio 43210 (USA)

²Gas Technology Institute, Birmingham, Alabama 35211(USA)

³Gas Technology Institute, Des Plaines, Illinois 60018 (USA)

* kuhn.488@osu.edu

Introduction

Biomass is an attractive fuel source due to its domestic availability and renewable nature. Gasification is a common technique to convert biomass into a usable fuel. During gasification, aromatic hydrocarbons or tar compounds (MW > 78 or benzene) form and cause processing problems downstream. The addition of catalytic materials into the bed of a fluidized bed gasifier is an attractive way to reduce or to eliminate tar formation [1-3]. Dolomite catalysts decompose tar efficiently at the operating conditions usually employed in gasification processes (typically temperatures = 800 to 850°C), but attrit too easily for use in a fluidized bed gasifier. Olivine minerals, (Mg,Fe)₂SiO₄, can be used as erosion resistant catalysts, but exhibit lower activity for tar conversion than dolomite catalysts. The present work focuses on the characterization of Ni-olivine catalysts for tar removal in biomass gasifiers.

Materials and Methods

Ni-olivine catalysts are prepared by a submerged glass melting technique [4]. This technique allows for the preparation of robust and economic catalysts for use in a fluidized bed. Tar removal activity measurements are made by using naphthalene (5.3 mg/L) as a model feed molecule in synthetic syngas (30% N₂, 20% H₂, 10% CO, 15% CO₂, 5% CH₄, and 20% H₂O) between 750°C and 900°C. The operating conditions (GHSV = 1166) were selected to closely simulate those prevailing in practical gasification systems. Catalytic activity is also measured by temperature-programmed reactions using lower hydrocarbons and alcohols. A thorough catalyst characterization is performed to understand both the influence of the preparation variables and time-on-stream factors on the activity and to determine the nature of the active surface reaction sites. Evidence is provided by techniques such as BET surface area measurements, temperature-programmed reduction/oxidation/desorption studies, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and vibrational spectroscopy.

Results and Discussion

Steady-state reaction results show that activated olivine catalysts and Ni-doped olivine catalysts reach complete or near complete naphthalene conversion under conditions selected to simulate the fluidized bed gasifier. The activation process occurs through the dispersion of active Fe after the decomposition of a Fe-bearing serpentine phase. The serpentine phase is monitored in XRD and Raman Spectroscopy. Results for Raman Spectroscopy are displayed in Figure 1. The spectrum for the olivine mineral contains the serpentine phase. Treatment under oxidizing (10% O₂/He at 900°C for 2 hours) or reducing (10% H₂/Ar at 900°C for 2 hours) conditions leads to the decomposition of the serpentine phase. The olivine phase is also prominent in the spent sample (exposed to simulated syngas

for 30 hours). While the serpentine phase decomposes more readily under reducing conditions, Fe clustering occurs more easily and leads to less active surface.

The catalysts also exhibit activity for the steam reforming of smaller hydrocarbons and alcohols. During methane-steam reforming, activity increases with time-on-stream or following a reducing pre-treatment. The increase in activity is linked to the creation of free Fe species following the partial reduction of the olivine phase. The claim is supported by the identification of free Fe phases with *in-situ* XRD. Mechanistic data are also presented from results obtained through temperature-programmed desorption and *in-situ* vibrational spectroscopy.

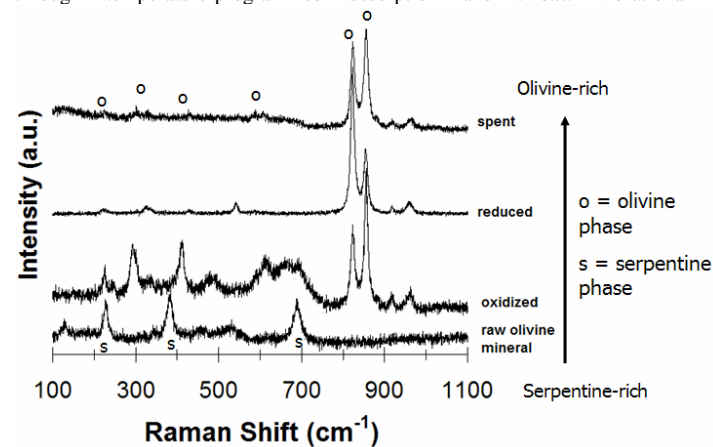


Figure 1. Raman Spectra for olivine catalysts.

Ni-olivine catalysts prepared by submerged glass melting have been demonstrated for tar conversion under conditions relevant to biomass gasifiers. The catalysts also display potential for steam reforming of lower hydrocarbons.

Significance

Effective, robust, and economic catalysts for eliminating tar formation would find widespread use in gas clean up applications.

References

1. Dayton, D., *A review of the literature of catalytic biomass tar destruction. U.S. DOE NREL Report, 2002. NREL/TP-510-32815.*
2. Devi, L., Ptasiński, K.J., and Janssen, F.J.J.G., *A review of the primary measures for tar elimination in biomass gasification processes. Biomass and Bioenergy, 2003. 24: p. 125.*
3. Milne, T.A., Abatzoglou, N., and Evans, R.J., *Biomass gasifier tars: Their Nature, Formation, and Conversion. U.S. DOE NREL Report, 1998. NREL/TP 570-25357.*
4. Rue, D., *Submerged combustion melting. American Ceramic Society Bulletin, 2004. 83: p. 18.*