Tar and Light Hydrocarbon Steam Reforming using Ir, Rh, and IrNi MgAl₂O₄ Supported Catalysts: A Combined Theoretical and Experimental Study
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Introduction
Biomass-derived syngas must be treated to remove a number of impurities, which would otherwise poison the processing catalysts. The objective of this work is to assist in the development of catalysts that can effectively remove tars and reform methane in raw gas from a biomass gasifier. This research is examining the performance of alternative catalysts that have the potential to provide improved performance over commercial nickel-based reforming catalysts. The product gas from a biomass gasifier is mainly composed of CO, H₂O, 19.7% H₂, 9.9% CO₂, CH₄, and H₂O. It also contains small quantities of hydrocarbon gases such as ethane, organic compounds broadly classified as tars, and inorganic impurities, such as H₂S, HCl, NH₃, and alkali metals. These tars (e.g., aromatic hydrocarbons) are notorious for condensing and subsequently polymerizing on downstream equipment such as compressor and gas turbine surfaces, if the gas is cooled sufficiently. Tars also accelerate carbon deposition on catalyst surfaces leading to deactivation.

In this study, comparative activity and stability measurements were made for the steam reforming of methane (SMR) and for SMR in the presence of tars (i.e., benzene and naphthalene) over noble metals (i.e., Pd, Pt, Ru, Rh and Ir) and for a series of IrNi bimetallic catalysts supported on MgAl₂O₄.

Materials and Methods
Pd, Pt, Ru, Rh, Ir, Ni, and a series of bimetallic IrNi catalysts were prepared by incipient wetness impregnation of nitrate solutions with MgAl₂O₄. After impregnation, the catalysts were dried at 110°C for 8 hrs and calcined under static air at 500°C for 4 hrs. Catalytic activity and stability tests using model biogas were measured over the temperature range 700-850°C, P = 1 atm, and GHSV=114,000 hr⁻¹, and using a premixed feed gas containing 52.6% H₂O, 19.7% H₂, 9.9% CO₂, 9.9% CO, 5.6% CH₄, 0.95% C₂H₆, 0.95% He, 0.34% Benzene, and 0.06% Naphthalene. Theoretical simulations were performed using Density Functional Theory (DFT) based Ab Initio Molecular Dynamics with the CP2K software package. A total of 3 model systems consisting of 50-atom metal nanoparticles (Ni50, Ir50, and Ir50Ni50) on the MgAl₂O₄ (111) spinel surfaces at 700°C. Binding energies of water, naphthalene and selected intermediates in the reforming process were computed and compare with bulk surfaces in order to assess reactivity and coke resistance of both small and large metal particles.

Results and Discussion
Noble metals (i.e., Pd, Pt, Ru, Rh, and Ir) supported on MgAl₂O₄ were evaluated for methane and tar reforming under high temperature (e.g., 850°C) conditions typically required for tar conversion. Although higher methane turnover rates are obtained over supported Pd and Pt catalysts, their rapid deactivation due to coking and sintering make them unsuitable for SMR. Supported Ir and Rh catalysts are significantly more stable than other precious metals (i.e., Pd, Pt and Ru) for SMR. For the steam reforming of methane in the presence of tars (i.e., benzene and naphthalene) a 5%Ir/MgAl₂O₄ catalyst is not only more active than a commercial Ni catalyst but its conversion is also ~60% higher than the one for a 5% Rh/MgAl₂O₄ catalyst. A major finding from this study is that bimetallic IrNi/MgAl₂O₄ catalysts (15%Ni, 0.5% < Ir loading ≤ 5%) present higher stability during steam reforming of methane and tars as compared to monometallic Ni and Ir catalysts. Addition of Ir to a Ni/MgAl₂O₄ diminishes greatly the sintering of Nickel during reaction partly responsible for catalyst deactivation. Minimal loss of activity for steam reforming of methane and tars is shown for a bimetallic catalyst with 2.5%Ir and 15% Ni. Theoretical analysis offers rationalization for the coke resistance offered by this bimetallic structure.

Significance
Comparative catalytic performance for precious metal and bimetallic catalysts under model gasifier-derived syngas conditions offers fundamental understanding for the influence of metal and metal particle size, and provides insight into the structure and function relationship critical for the design of improved catalysts.

References