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Steam reforming of hydrocarbons from biomass-derived syngas over $MgAl_2O_4$-supported transition metals and bimetallic IrNi catalysts

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ABSTRACT

This study presents an investigation into the steam reforming of hydrocarbons from biomass gasifier-derived syngas over $MgAl_2O_4$-supported transition metals (Ni, Rh, Ir, Ru, Pt, and Pd) and novel bimetallic IrNi catalysts. Using a model syngas consisting of H_2, CO, CO_2, CH_4, C_2H_4, and H_2O, Ir and Rh catalysts were found to be the most stable catalysts (at 850 °C, 1 bar, 114,000 h^{-1}). When benzene and naphthalene are added to the feed (as a tar simulant) stability is affected by both tar concentration and type of tar. Catalytic deactivation, caused primarily by coking can be minimized by operating at a high reaction temperature (e.g., 850 °C). In addition, promoting Ni catalyst with Ir significantly enhances stability. By using bimetallic formulations of Ir and Ni (0.5–5.0% Ir, 15%Ni), nickel sintering during the reaction is reduced. Surprisingly, IrNi catalysts also offer more stability than catalysts with Ir particles alone. In agreement with theoretical calculations, small Ir° clusters ($\sim$2–3 atoms) supported on large Ni° particles ($\geq$5 nm) present more resistance to coking than either small Ir° clusters or Ni° particles alone. Hence, superior stability of the bimetallic catalysts results from both resistance to coking and a decrease in nickel sintering. Minimal loss of activity of 12% for TOS = 80 h is demonstrated for a bimetallic catalyst with optimal concentrations of 2.5% Ir and 15% Ni. Both monometallic Ir and Ni catalysts suffer substantial loss of activity (i.e., $\geq$40% loss, TOS = 80 h) under comparable conditions.

1. Introduction

Biomass-derived synthesis gas (syngas) for catalytic conversion to fuels and chemicals has been the focus of much research [1]. Biomass-derived syngas must be treated to remove a number of impurities that would otherwise poison the processing catalysts. The product gas from a biomass gasifier is mainly composed of H_2, CO, CO_2, CH_4, H_2O, and small quantities of higher hydrocarbon gases such as ethane, organic compounds broadly classified as tars, and inorganic impurities, such as H_2S, HCl, NH_3, and alkali metals [2]. Many of these inorganic constituents must be removed to part per billion levels because they strongly interact with downstream water-gas-shift and/or synthesis catalysts [3]. Tars are notorious for condensing and subsequently polymerizing on downstream equipment such as compressor and gas turbine surfaces [4]. Tars and other hydrocarbons also contribute to significant carbon deposition on downstream synthesis catalyst surfaces. Catalytic reforming of the tars and hydrocarbons provides additional syngas and offers higher carbon utilization of the biomass feedstock.

The objective of this study is to evaluate the effectiveness of transition metal catalysts for the steam reforming of tars and higher hydrocarbons found in gasifier-derived syngas. Catalyst poisoning by the inorganic constituents (e.g., H_2S) and catalyst coking are generally the two main reasons for the deterioration of the catalyst performance during steam reforming of biomass-derived syngas. In a previous report we demonstrated proof-of-concept for a warm syngas clean-up process that is efficient for removing the inorganic constituents (to ppb level) from the biomass-derived syngas prior to the steam reforming unit [3]. Upon sulfur removal catalyst deactivation due to coking can still be problematic. Thus, in this

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study we evaluate the steam reforming of tars and other hydrocarbons present in sulfur-free syngas. Tar removing catalysts are grouped into mineral (e.g., dolomite, calcite and magnesite) and synthetic catalysts (e.g., alkali metal-based and transition metal-based catalysts). Mineral catalysts are generally not efficient for secondary tar removal since the polycyclic aromatic hydrocarbons remain in the flue gas [5]. Currently, commercial Ni-based catalysts are widely used for steam reforming of biomass-derived tars [2,5,6]. Most studies pertaining to tar removal have focused on Ni-based catalysts primarily because precious metals typically are too expensive to be used in conventional tubular reactors [7]. However, nickel is well known to be prone to deactivation from coke [2,8]. Very few studies have evaluated Group VIII precious metals specifically for tar removal. Tomishige et al. suggested the following activity order for steam reforming of biomass-derived tars when using a CeO_2-SiO_2 support: Rh > Pt > Ni > Pd > Ru [9]. Rh-based catalysts were found to be less susceptible to coking in comparison with other Group VIII metals. Steele et al. also reported a Rh-based catalyst to offer significantly improved catalyst performance when compared to a Ni-based catalyst [10]. Group VIII precious metals are generally well known for their resistance to carbon formation in other steam reforming processes [7,11]. Precious metal catalysts have thus been evaluated for this project specifically for steam reforming the hydrocarbons present in tar-laden biomass gasifier-derived syngas. For more information on tar removal catalysts, readers are directed to excellent reviews by Yung et al. [2], Torres et al. [5], and Dayton [6].

Previously, we showed that the nature of the support (i.e., $MgAl_2O_4$ vs. Al_2O_3) affects significantly the Ir and Rh catalysts stability and coking for methane steam reforming [12]. We found that Ir and Rh metals supported on $MgAl_2O_4$ are more active and coke resistant than their counterparts supported on Al_2O_3. Our computational study has demonstrated that a stronger metal-support interaction exists with the $MgAl_2O_4$ support leading to smaller Ir and Rh metal particles ($\leq\sim$2 nm). These small metal particles activate both water and methane more effectively than the larger metal particles interacting with the Al_2O_3 support which leads to better resistance to coking. For this present work, we have thus focused our research work on $MgAl_2O_4$ supported catalysts. In our preceding studies where extensive computational work coupled with some experimental data were presented, highly dispersed ~1-nm Ir and ~2-nm Rh nanoparticles supported on $MgAl_2O_4$ were shown to be active and stable for methane [12] and benzene [13] steam reforming. This encouraged us to investigate these catalysts under more realistic conditions. This study presents the results of our experimental investigation for the steam reforming of a model biomass-derived syngas (steam reforming of tars) over $MgAl_2O_4$ supported catalysts. The performance of the $MgAl_2O_4$ supported Rh and Ir catalysts is first briefly compared to the one for a commercial Ni-based reforming catalyst and other conventional noble metal (i.e., Ru, Pt, and Pd) catalysts supported on $MgAl_2O_4$. Although the supported Ir and Rh catalysts are significantly more efficient, we show how their stability can be altered under realistic reaction conditions. Beneficial effects have been reported when adding noble metals such as Au to Ni catalysts for other reforming reactions [14]. We have thus designed bimetallic IrNi catalysts supported on $MgAl_2O_4$ and present for the first time their performance for the steam reforming of tars. Our comprehensive investigation demonstrates the potential of IrNi catalysts for steam reforming reactions as improved stability is observed as compared to $MgAl_2O_4$ supported monometallic Ni and Ir catalysts. To complete our experimental investigation, a concise theoretical study is finally shown to provide some insight into the catalyst performance of the bimetallic IrNi catalysts.

2. Experimental and theoretical methods

2.1 Experimental details

2.1.1. Catalysts preparation

A series of supported noble metals catalysts were prepared by incipient wetness impregnation of $MgAl_2O_4$ (Sasol Puralox 30/140), pre-calcined at 500 °C, with solutions of rhodium nitrate (10 wt%), platinum nitrate (13 wt%), ruthenium nitrosyl nitrate (10.19 wt%), palladium nitrate (20 wt%), and iridium acetate (14 wt%) dissolved in deionized water. After impregnation, the catalysts were dried at 110 °C for 8 h and calcined under air at 500 °C for 3 h. The metal loading was 5 wt% for all of the catalysts that are designated as 5%Rh/$MgAl_2O_4$, 5%Pt/$MgAl_2O_4$, 5%Ru/$MgAl_2O_4$, 5%Pd/$MgAl_2O_4$, and 5%Ir/$MgAl_2O_4$.

A series of bimetallic IrNi catalysts were prepared by incipient wetness impregnation of the $MgAl_2O_4$ (Sasol Puralox 30/140) pre-calcined at 500 °C with solutions of nickel nitrate hexahydrate and iridium acetate dissolved in deionized water. After impregnation, the catalysts were dried at 110 °C for 8 h and calcined under air at 500 °C for 3 h. The nickel loading was 15 wt% for all the catalysts, and the Ir loading was between 0 and 5 wt%. The catalysts are designated as x%Ir15%Ni/$MgAl_2O_4$ where "x" represents the Ir loading except for the catalyst with 0%Ir designated as 15%Ni/$MgAl_2O_4$. A commercial methane steam reforming catalyst obtained from United Catalysts Inc., (C11-9-02, nominal composition: 12%Ni, 88% Al_2O_3 support) also was tested for comparison purposes.

2.1.2. BET surface area

Nitrogen adsorption was measured at 77 K with an automatic adsorptiometer (Micromeritics ASAP 2000). Samples were pretreated at 150 °C for 12 h under vacuum. The surface areas were determined from adsorption values for five relative pressures (P/P_0) ranging from 0.05 to 0.2 using the Brunauer–Emmett–Teller (BET) surface method. The pore volumes were determined from the total amount of N_2 adsorbed between $P/P_0 = 0.05$ and $P/P_0 = 0.98$.

2.1.3. Temperature programmed reduction

Temperature programmed reduction (H_2-TPR) experiments were performed on an automated catalyst characterization unit (Micromeritics Autochem 2910) equipped with a thermal conductivity detector. The catalyst (0.1 g) was loaded in a U-type quartz tube. Then, a 5% H_2/Ar mixture was flowed through the sample starting at 50 °C and ramping up the temperature to 900 °C at a rate of 10 °C/min.

2.1.4. Scanning transmission electron microscopy

Scanning transmission electron microscopy (STEM) measurements were conducted with an FEI Titan 80-300 operated at 300 kV. The FEI Titan is equipped with CEOS GmbH double-hexapole aberration corrector for the probe-forming lens, which allows imaging with ~0.1 nm resolution in STEM mode. The STEM images were acquired on high angle annular dark field (HAADF) with an inner collection angle of 52 mrad. In general, the STEM sample preparation involved mounting powder samples on copper grids covered with lacey carbon support films and then immediately loading them into the STEM airlock to minimize an exposure to atmospheric O_2. STEM images were used to determine average metal particle sizes after reduction at 850 °C or after stability measurements under methane steam reforming reaction conditions. For the samples analyzed after reaction, the term "spent" sample/catalyst is used throughout this manuscript. Approximately 200 particles were counted in determining the average size.