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Evaluating the performance of non-precious metal based catalysts for sulfur-tolerance during the dry reforming of biogas

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HIGHLIGHTS

- Evaluation of active, stable non-precious metals catalysts for sulfur tolerance for dry reforming of biogas.
- The bimetallic catalysts consisting of cobalt and nickel produced a highly stable activity.
- A bimetallic catalyst in which cobalt was impregnated before nickel gave the best overall performance.
- Statistical structure-activity relations have been designed to help explain differences in activity of various catalysts.
- Increase in pore volume/surface area ratio, metal dispersion, reducibility and support basicity increase catalyst activity.

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ABSTRACT

A portfolio of catalysts with a nominal composition 15 wt.%Ni + (0/5 wt.%)Co/M_aO_x–N_aO_x–Al_2O_3 (where M = Mg, Ca, La, Y, Gd; N = Al, Zr) were synthesized and evaluated for biogas reforming application. Structure activity relations (SARs) were designed to help explain the significant difference in activity observed among the catalysts containing monometallic (Ni) and bimetallic species (Ni–Co) and among the bimetallic catalysts impregnated by altering the sequence of impregnation. The order of activity observed among the various catalyst formulations was: bi-metallic (reverse stepwise Co → Ni) > bi-metallic (simultaneous Ni + Co) > mono-metallic > bi-metallic (stepwise Ni → Co). From SARs it is established that high pore volume to surface area ratio, high metal dispersion, high reducibility and high support basicity are the essential traits of an active and stable catalyst. Analysis of variability (ANOVA) was performed to identify the main and interaction effects of various factors on both catalyst activity and catalyst textural properties. Impregnation sequence and promoter composition are found to have significant effects on both catalysts activity and its textural properties. Also, an empirical model equation that establishes a statistical relationship between the factors and the response variable was developed. In addition, a sensitivity analysis was performed to study the effect of surfactant to metal ratio, CH_4-to-CO_2 ratio, operating temperature, H_2S concentration, cobalt amount, and support basicity on catalyst performance.

1. Introduction

Hydrogen is projected to be one of the most important clean and green energy carriers in the near future [1]. The drastic changes in the global climate occurring due to anthropogenic CO_2 emissions are the greatest environmental concerns in the present day, and switching from conventional hydrocarbon based fuels to renewable sources of energy and zero emission energy carriers like hydrogen are the best possible solutions available to humankind today [2]. Biogas, which is produced readily and easily by the anaerobic digestion of biomass, is an excellent example of a kind of renewable energy [3]. Biogas is primarily composed of methane and carbon dioxide along with trace amounts of other components like nitrogen, water vapor, hydrogen sulfide, ammonia, and siloxanes. Methane is a greenhouse gas (GHG) that is about 25 times more potent than CO_2 [4]. The main driving force for the utilization of biogas is to avoid greenhouse gas emissions and to lower gas emissions with extremely high ozone depletion potential (ODP). Its utilization will not only reduce uncontrolled emissions of greenhouse gases but will also help eliminate the wide range of pollutants found in this type of gas, which pose a threat to human health. The sustainable use of biogas for energy production does not contribute to CO_2 emission production but has a high CO_2 abatement potential [5]. Also, biogas reforming is not only necessary from an environmental point of view, but is also of commercial relevance in the hydrogen production process. Therefore, there is immense potential in developing technology to utilize as-generated biogas for energy-related applications.

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The major technological challenge for CO_2 reforming of biogas is to develop catalysts, which can tolerate contaminants such as hydrogen sulfide and siloxanes. Biogas composition varies considerably depending on the origin of the biomass and also on the method through which it is generated. Biogas can be generated at different temperatures, in an anaerobic digester i.e., thermophilic, mesophilic, and psychrophilic [6]. This implies that the biogas production rate (yield) and its methane composition (quality) can improve with increase in the temperature due to increased methane forming bacterial activity. The CH_4 potential from landfill material, animal manure, wastewater, and industrial, institutional, and commercial organic waste in the United States alone is estimated at about 7.9 million tonnes per year, which is equal to about 420 billion cubic feet [7]. Also, landfills in the United States alone produce 7.2 billion Nm^3 of methane per year of which 4.3 billion Nm^3 is currently being captured and utilized while 2.9 billion Nm^3 per year of methane is released resulting in atmospheric emissions [8] The presence of methane in $\geqslant 50$ vol.% proportion in the biogas makes it an attractive and economically viable source of renewable energy. Most of the commonly employed reforming catalysts are prone to deactivate in presence of H_2S and other sulfur compounds on account of surface oxy-sulfides and/or bulk sulfides formation [9]. Carbon formation is the other main drawback of the CO_2 reforming of biogas, but is second only to the earlier mentioned sulfur poisoning [10,11]. The CO_2 reforming of biogas uses a high C/H feedstock, which results in carbon deposition on the catalyst by CO disproportionation and/or methane decomposition reactions [11]. The catalysts possessing noble metals such as Rh, Ru and Pt, exhibit higher activity in the CO_2 reforming of biogas because noble metals are very resistant to carbon formation but are very expensive [12,13]. Earlier research has shown that Ni-based catalysts exhibit activity similar to noble metals and are also inexpensive but prone to coke formation [14–16]. To the best of our knowledge, no previous researchers have reported sulfur resistant catalysts for CO_2 reforming of biogas. Sulfur resistant catalyst in this context is intended to imply a catalyst with the potential to resist the formation of surface oxy-sulfides and bulk sulfides in the presence of sulfur compounds or maintain its catalytic function/activity in the sulfided state. Ashrefi et al., 2008 studied the steam reforming of biogas over a Sud-Chemie catalysts “G-90” and also investigated the impact of sulfur on the deactivation and regeneration of Ni-based “G-90” catalysts [17,18]. Apart from the Ashrefi et al. [17,18] 2008 report, most of the research papers dealing with biogas reforming have employed a treated biogas (H_2S free), which is also termed as model biogas [1,2,9,10,19–24].

It is to be noted that the current work will also be applicable to sub-quality natural gas commonly referred to as “dirty gas” and “landfill gas” since their compositions are somewhat similar to biogas. The aim of this paper is to evaluate the performance of non-precious metal based catalysts for their sulfur-tolerance during the dry reforming of biogas, land fill gas or dirty gas. An attempt is also made to elucidate the relationship between the catalysts’ structure and catalytic activity. The data generated in the catalyst screening, catalyst characterization and structure-performance relationships are presented and discussed in this paper.

2. Materials and methods

2.1. Support and catalyst preparation

All the supports employed for the current application are based on Al_2O_3 and their nominal composition is represented as M_aO_x–N_aO_x–Al_2O_3 (where M = Mg, Ca, La, Y, Gd; and where N = Al, Zr; and in cases where $a = 1$, then x is either 1 or 2; and when $a = 2$, then $x = 3$) were prepared by surfactant-assisted route using cetyl trimethyl ammonium bromide (CTAB) [25]. When N_aO_x is Al_2O_3 (N = Al), it results in the binary oxide supports of general formula M_aO_x–Al_2O_3. In the current study five different alumina based binary oxide supports were synthesized in 1:3 (M_aO_x/Al_2O_3) molar oxide ratio (where M = Mg, Ca, La, Y, Gd). Also, two different alumina based ternary oxide supports were synthesized in 1:1:6 ($M_aO_x/ZrO_2/Al_2O_3$) molar oxide ratio. Calculated amounts of M_aO_x nitrate (M = Mg, Ca, La, Y, and Gd), N_aO_x nitrate (N = Al, Zr) and $Al(NO_3)_3{\cdot}9H_2O$ salts were employed in the support preparation. The corresponding metal nitrates were dissolved separately in deionized water and then mixed together to form a mixed nitrate solution. Separately, an appropriate amount of cetyl trimethyl ammonium bromide (CTAB) was dissolved in warm deionised water to form the surfactant solution. The mixed nitrate and surfactant solutions were mixed together under constant stirring to form a metal nitrate-surfactant mixture solution. The ratio of surfactant/metal [CTAB/(M + N + Al)] in the mixture solution was maintained at ~0.5. The mixture solution was hydrolyzed by the addition of aqueous ammonia until the pH reached ~11.6, which resulted in the precipitation of a mixed metal hydroxide-surfactant matrix in the form of colloidal slurry. In a typical surfactant-assisted synthesis, the cationic surfactant is incorporated into the metal oxide matrix by proton exchange process, which occurs at elevated pH. Therefore, the pH of mother liquor needs to be maintained at $\geqslant 11.0$ to $\leqslant 12.0$ (optimum possible is 11.6). At pH $\geqslant 11.0$, the surface hydroxyl protons $[Al(O^-H^+)_3]$ are exchanged with the cetyl trimethyl ammonium cation $[(C_{16}H_{33})N^+(CH_3)_3]$, resulting in the incorporation of the surfactant cations into a hydrous alumina mixed hydroxide oxide gel. This incorporation decreases the interfacial energy and eventually decreases the surface tension of water that exists in the hydrous support pores. As a result, the degree of shrinkage and pore collapse that would occur in the hydrous support during drying and calcination is reduced, thereby imparting a high surface area to the sample. Thus, even though it is beneficial to operate at a higher pH, it is not probable to reach a pH of 12 whereas at much lower pH, say 7, this exchange would not occur. The slurry was rigorously stirred for 30 min and then sealed in air tight Pyrex glass bottles and aged hydrothermally at 90 °C for 5 days in a conventional air circulated oven under autogenous pressure. After a 5-day aging, the precipitate was removed from the oven, cooled to room temperature, and then filtered. The filtered precipitate was washed with warm deionised water in order to remove the unused surfactant. The precipitate was dried at 120 °C overnight and subsequently calcined at 650 °C for 3 h in an ambient air environment.

The supports were then impregnated with either nickel or both nickel + cobalt precursors so as to result in the formation of monometallic and bimetallic catalysts. In order to investigate the effect of cobalt addition and also the sequence of cobalt addition on the nickel-supported catalysts, a series of Ni–Co bimetallic catalysts were prepared by adapting simultaneous, step-wise, and reverse step-wise wet-impregnation strategies. In the simultaneous scheme, precursors of both the metallic elements, Ni and Co, were impregnated together. In the step-wise impregnation scheme, Co was impregnated after Ni (Ni → Co) and in the reverse step-wise impregnation scheme Ni was impregnated after Co (Co → Ni). These simultaneous, step-wise and reverse step-wise impregnation schemes were selected to represent the dilution of Ni active site density with Co, obstruction or coverage of Ni active site by Co, and unhindered availability of Ni active sites, respectively, for CO_2 reforming of CH_4. 0.1 M $Ni(NO_3)_2{\cdot}6H_2O$ and 0.1 M $Co(NO_3)_2{\cdot}4H_2O$ solutions were used as source of Ni and Co species, respectively. In the preparation of monometallic nickel-based catalysts, the supports were impregnated with a nominal 15 wt.% Ni using a standard wet impregnation method. The bimetallic catalysts were prepared by impregnating the supports with a