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Autothermal reforming of isobutanol over promoted nickel xerogel catalysts for hydrogen production

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ABSTRACT

Autothermal reforming (ATR) of isobutanol, a bio-based fuel, was investigated for hydrogen production on Ru- promoted Ni xerogel catalysts and under optimized operating conditions to attain lower carbon formation on the catalysts. All the catalysts were prepared by the sol–gel technique. Catalysts were characterized by X-ray diffraction (XRD), pore size, BET surface area, temperature-programmed reduction (TPR), and temperature-programmed desorption of H₂ (TPD of H₂), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and temperature-programmed oxidation (TPO) studies to investigate the physicochemical changes occurring due to the reaction. Catalytic autothermal reforming reactions were carried out in a fixed-bed reactor operating at atmospheric pressure. The reforming conditions were varied in the temperature range from 600 to 750 °C, space velocity range of 130,000–650,000 h⁻¹, H₂O/C molar ratio in the feed between 0 and 4.0, and O/C ratio of 0–1. The 0.3 wt% Ru/10 wt% Ni/Ce(3 wt%) O₂/ZrO₂/Al₂O₃ catalyst showed high catalytic activity, low carbon deposition, good resistance to sintering and prolonged stability. Ru promotion not only improved hydrogen production appreciably, but also reduced the coke formation under the conditions studied.

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Introduction

The development of alternative fuels is necessary due to the limited fossil fuel reserves and growing demand for energy. Hydrogen energy is one of the clean alternative energy options. Due to the fact that the storage and direct distribution of hydrogen is risky, onboard hydrogen production is a viable option. Research is being undertaken on the production of hydrogen from catalytic reforming of hydrocarbons and alcohols. Alcohols, like methanol, ethanol, and butanol were

studied for cleaner hydrogen production for fuel cell applications [1–3]. Among these alcohols, butanol/isobutanol is receiving more attention recently due to its attributes such as high energy density compared to other alcohols, lower volatility, diminished flammability, hygroscopicity, and compatibility with gasoline [4]. Isobutanol can be produced in two ways, namely, synthetic chemical process (carbonylation and hydrogenation), and fermentation of biomass by microorganisms like *Clostridium Acetobutylicum* *Escherichia Coli* and *Algae* etc ... [4–6]. Bio based fuels are renewable resources and among them isobutanol/bio-butanol is an emerging future

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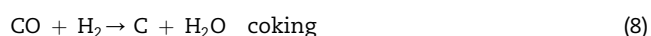
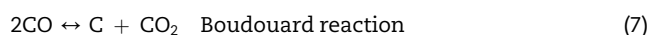
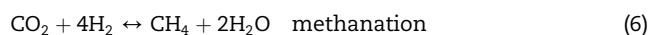
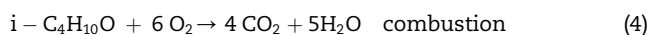
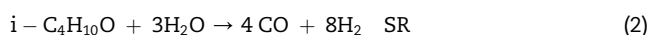
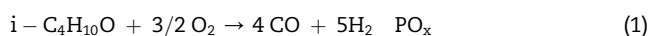
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fuel according to US-DOE, which can be produced from the abundantly available biomass (corn, sugarcane etc ...) feed-stock [7]. Bio-butanol has more advantages compared to the bio-ethanol which is the present leader in the bio fuels. Bio-butanol has more energy density per liter i.e., 29.2 MJ/L to the ethanol (24 MJ/L). In comparison to ethanol and other alcohols, it is less toxic, less volatile, less corrosive and can be directly blended into gasoline at higher concentrations [8]. Butanol has a high flash point of 35 °C, which is a benefit for fire safety. Till now bio-butanol studies were not carried out thoroughly and development of bio-butanol based technologies is one of the major concerns.

Among the methods available for hydrogen production from alcohols, catalytic reforming is gaining more attention. Even though steam reforming method produces more hydrogen compared to partial oxidation and autothermal reforming, it produces appreciable coke, other undesired by-products, and it is an endothermic reaction. Partial oxidation is an exothermic reaction but hydrogen production is low; coke formation reduces the catalyst activity in the long run and it deactivates the catalyst. Hence development of new catalysts for higher hydrogen production and lower or no coke formation is of great interest. Autothermal reforming (ATR) of alcohols is one of the best options to overcome the problems cited above. ATR is a combination of steam reforming and partial oxidation, with the addition of oxygen into the reaction preventing coke formation and with comparatively high hydrogen yield; it also requires less energy compared to the conventional processes; but thermal sintering of active and support materials makes this process more challenging.

In the ATR of alcohols, many complex reactions occur, but mainly catalytic partial oxidation, steam reforming and water gas shift processes, transforming isobutanol into final products i.e, hydrogen and CO. Some other/side/chain reactions like combustion, coking and methanation reactions also occur during ATR due to its complex nature and the plausible equations occur in ATR reactor are given below:



In the reforming reaction of alcohols, to avoid coke formation, and thus, deactivation, and achieve a high yield of hydrogen, various approaches are studied. Noble metals like Rh, Pt and Ru [1–3] as supported catalysts have been found to

be active and stable for reforming of alcohols, but their cost plays a negative role in the commercialization of the process. Hence, Ni-based catalysts are used as the best alternative.

Steam and oxidative steam reforming of raw butanol and isobutanol were investigated using noble metals like Pt, Rh etc ... [9–11] and various metal oxides like Co, Ni [3,12–15] in combination and with promoters. Among them, Ni-based catalysts were found to be more active for butanol reforming [13,16]. Ni catalysts are developed with various preparation methods like precipitation, incipient wetness, sol–gel and surfactant-assisted methods with supports like oxides of Al, Mg, Ce, Zr, Ir and in their combinations [13–16]. Among these supports for alcohol reforming, Ce–Zr–O support exhibited higher resistance to coke formation due to its oxygen storage capacity, redox property, thermal stability, and catalytic activity [13,17]. Catalysts which have high surface area and high dispersion will also lead to highly active catalysts [18]. In our previous work, we prepared catalysts by sol–gel method; those catalysts displayed high surface area and good activity towards autothermal reforming of n-dodecane, and also suppressed coke formation significantly [19]. The above mentioned studies of butanol are using high loadings of Ni, Zr, Ce, Ir and precious noble metals like Rh and Pt which increase the cost of the catalyst. According to our knowledge very few studies were carried out on butanol/isobutanol reforming and there is a need to study the parameters in depth for better understanding. The performance of sol–gel catalysts for the catalytic autothermal reforming of isobutanol also has not yet been understood properly. Therefore, in the present study, our goal was a systematic study for development of a high stability catalyst having the ability for higher hydrogen production with less coking at the same time reduce the cost without compromising on performance. Hence, in the present investigation, a sol–gel method derived for Ni-based catalysts with low loadings of Ni, Ce and Zr and low cost precious metal like Ru were studied with various parameters in a systematic way for autothermal reforming of isobutanol. Ni-based catalysts were prepared by a sol–gel method with supports like Al₂O₃, Ce–Zr–O and promoter Ru. Catalysts were screened and the operating conditions were optimized for the ATR of isobutanol for high hydrogen production and lower or no coking. The synergy exhibited by the support composition for the ATR reaction are explained by catalyst characterization obtained from BET surface area and pore size measurements, and TPR, TPD, XRD, SEM, TEM, and TPO techniques. The main objective of the study is to find an active, stable catalyst exhibiting good resistance to carbon formation.

Experimental

Preparation of catalysts

Aluminum trisec-butoxide (ATSB), nickel acetate, cerium ammonium nitrate, zirconium (IV) butoxide and ruthenium chloride were used as precursors for the aluminum (Al), nickel (Ni), cerium (Ce), zirconium (Zr) and ruthenium (Ru), respectively. All the chemicals used in the preparation of catalysts were obtained from Sigma–Aldrich, USA. Catalysts were prepared by a sol–gel method and the typical procedure is

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