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Steam reforming of glycerol to hydrogen over ceria promoted nickel–alumina catalysts

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ABSTRACT

Increased production of biodiesel in recent years has resulted in a surfeit of crude glycerol as by-product. This oversupply has triggered efforts to valorize glycerol to clean fuels such as hydrogen. In the present work, five kinds of nickel–alumina and ceria promoted nickel–alumina catalysts of different nickel and ceria loadings were prepared by wet impregnation method and tested for conversion of 30 wt.% glycerol in water. Characterization of fresh and spent catalysts were carried out with BET surface area, X-ray diffraction and scanning electron microscopy techniques. The reaction was conducted at temperatures from 550 °C to 800 °C, atmospheric pressure and weight hourly space velocity of 6.8–17 h⁻¹. Thermodynamic simulations were also made for theoretical estimates of conversion and selectivity and for deciding suitable reaction conditions for experiments. Among the tested catalysts, 10Ni/Al₂O₃/5CeO₂ was found to be the most efficient and stable for 16 h time on stream. Complete conversion of glycerol and hydrogen selectivity of 85.7% was obtained over this catalyst at 650 °C, against 95.9% thermodynamic value. Kinetic study was also done for this catalyst to get the reaction rate equation. Using power law model, the order of reaction and activation energy were determined to be 0.45 and 62.91 kJ/mol respectively.

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Introduction

Energy supply security, pollution reduction, and global warming mitigation are strong arguments for reduced reliance on fossil fuels use. With CO₂ levels in air in excess 400 ppm [1], substitute fuels are also needed for sustainability and climatic balance. In this context, biodiesel is an environmentally friendly, biodegradable fuel [2]. However, for 100 tons of biodiesel produced, 10 tons of glycerol is produced as byproduct. The current glycerol production has already exceeded market demand and given rise to disposal issues [3]. Hence glycerol valorization, to fuels like hydrogen, can lead to reduction in production costs of biodiesel and make it

sustainable [4,5]. Hydrogen is a clean and efficient fuel. Industrially, it is produced nearly 90% from methane and 5% from other hydrocarbons [6]. Therefore, its production from renewable sources such as glycerol is a prudent option.

Glycerol can be converted to hydrogen through a variety of reforming processes such as steam reforming, aqueous phase reforming, partial oxidation, autothermal reforming and dry reforming. It can also be converted to hydrogen by supercritical water gasification and pyrolysis. Hydrogen production from glycerol has been reviewed by Adhikari et al. [7], Lin [5], Dou et al. [8], Silva et al. [9] and Schwengber et al. [10]. Among the reforming techniques, glycerol steam reforming has the merit that it is a mature technique, it can be conveniently conducted at atmospheric pressure and its operation does not

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involve sophisticated control. However, the need for an efficient commercial catalyst for this process is still there [11].

In this regard, several catalysts with different support and modifiers have been studied under different reaction conditions. Both noble and transition metal catalysts have been used in glycerol steam reforming studies. Hirai et al. [12], Adhikari et al. [6], Zhang et al. [13], Doukkali et al. [14] and Wei et al. [15] have studied noble metal catalysts like ruthenium, rhodium, palladium, platinum and iridium in their works, amongst others. On the other hand, Adhikari et al. [16], Iriondo et al. [17], Cheng et al. [18], Dave and Pant [19], Sanchez and Comelli [20,21] and Lin et al. [22] have used transition metal catalysts such as nickel, copper and doped nickel with copper in their studies. In recent studies, use of Ni–alumina in combination with other metals or oxides such as Cu, Al, Co, Sn, Pd, K, Ca, Sr, Mg(II), MgO, B₂O₃, La₂O₃, as well as use of CeO₂, La₂O₃, ZrO₂, SiO₂ or their mix as support modifiers have been investigated by Ebsish et al. [23], Dieuzeide et al. [24], Seung-hoon et al. [25], Dou et al. [26], Yurdakul et al. [27], Bobadilla et al. [28], Papageridis et al. [29] and Zamzuri et al. [30].

In most of the studies, the preferred choice of catalyst support is γ -alumina due to its large surface area and thermal stability. In some cases, ceria is also used in addition to alumina. The noble metal catalysts demonstrate excellent catalytic performance, including suppression of carbon formation on the catalyst surface that results in higher catalyst life and activity. However, the main difficulty with these catalysts is the cost. As such, cheaper metallic catalysts such as nickel (in some cases copper) that show good catalytic activity are the subject of much research for glycerol steam reforming. Among the transition metal catalysts, nickel is the most studied active metal. Nickel has good activity for C–C, O–H, and C–H bond cleavage. It also catalyzes the water–gas-shift reaction involved in the steam reforming. Also, it is less expensive and more abundant than noble metals. However, Ni catalysts get deactivated during the steam reforming of oxygenated hydrocarbons due to coke deposition. How to subdue coke deposition to augment the catalytic stability is still a major concern. One of the ways to improve Ni–alumina catalyst properties and resistance to carbon/coke deposition is by modifying the support by rare earth oxides e.g. CeO₂. Ceria improves the catalytic activity of Ni/Al₂O₃ catalyst. Moreover, its basic character gives better redox delivery and storage of lattice oxygen, by which water dissociation, methane reforming, coke reduction, and water gas shift reaction can be promoted.

Various authors have investigated different aspects of ceria promoted nickel–alumina catalysts. Iriondo et al. [17] prepared and utilized Ni/Al₂O₃/CeO₂ catalyst with different ceria loadings at temperatures of 500–600 °C and a WHSV of 7.7 h⁻¹. They reported complete glycerol conversion and the maximum hydrogen yield of 80.3%. However, stability was observed up to 8 h on stream. Lin et al. [22] developed and tested 15Ni/10CeO₂/Al₂O₃ catalyst in a packed bed and PdAg/PSS membrane reactor for a range of steam to glycerol molar ratios (3:1–9:1), WHSV (1.5–5 h⁻¹) and temperatures (450–800 °C). Glycerol conversion of 96.7% and highest hydrogen yield of 5.82H₂ moles per mole of glycerol were reported. Sanchez and Comelli [24] studied the promoter effect

of Co on Ni/Al₂O₃ in the temperature range 300–500 °C, steam to glycerol molar ratio of 6:1 and WHSV 10 h⁻¹. They reported hydrogen yield of 83.6% and stability of the catalyst for 8 h on stream. Profeti et al. [31] also developed and evaluated Ni/CeO₂–Al₂O₃ catalysts doped with the noble metals (platinum, palladium, ruthenium, iridium) at glycerol to water molar ratio of 1:6, a flow rate of 2.5 cm³/h and temperature of 700 °C. The gaseous product distribution was reported to be similar for all catalysts, 55–60% H₂, 20% CO₂, 15–25% CO and 25% CH₄.

Thus it is seen that several studies have been made on the Ni–alumina/ceria catalysts and their performance. However, in view of its potential as an effective and less costly catalyst, there is need for further investigation on its activity and stability over different Ni, ceria content and extended range of reaction conditions. In the present work therefore experimental measurement of catalyst activity has been made for different Ni, ceria loadings. A thermodynamic simulation analysis has been made to indicate suitable conditions for study. Stability is also examined over a longer time period. Moreover, from engineering point of view kinetic model and rate equation are needed for process calculations. A higher weight hourly space velocity (WHSV) range has been studied to keep mass transfer effects insignificant and get the kinetic rate equation, not often reported in literature.

Materials and methods

Experimental

Catalyst preparation

The nickel–alumina catalysts used in this study are of 5, 10 and 15 percent nickel loading by weight over γ -alumina and are represented as 5Ni/Al₂O₃, 10Ni/Al₂O₃, and 15Ni/Al₂O₃. These were prepared by wet impregnation techniques [32]. An aqueous solution of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98% from Sigma–Aldrich) was used as precursor of nickel for impregnation onto commercial γ -Al₂O₃ support (Sigma–Aldrich). Likewise, CeO₂ promoted nickel–alumina catalysts with 5 and 10 percent loading of ceria by weight (10Ni/Al₂O₃/5CeO₂ and 10Ni/Al₂O₃/10CeO₂) were prepared by a two-step procedure. First same as above for Ni/Al₂O₃, then impregnation of aqueous solution of Ce(N-O₃)₃·6H₂O (Jonhson Mathew Chemicals, India). After impregnation, the catalysts were dried for 8 h at 125 °C followed by calcination at 550 °C for 5 h. Then the catalysts were crushed and sieved to 95–130 μ m size, for use in the reaction evaluation study.

Catalyst characterization

The surface areas and pore volumes of the prepared catalysts were determined by ASAP 2010 Micromeritics surface area analyzer using adsorption with nitrogen at –196.15 °C. X-Ray diffraction (XRD) analysis of the calcined and powdered samples were carried out to examine crystal structure of materials with Rigaku Miniflex 600 diffractometer. Measurements were made using Cu-K α radiation operating at 30 kV voltage, 40 mA current, 2°/min scanning rate and 1.54 Å. The 2 θ diffraction angle ranged from 20° to 80°. For surface morphological study of catalysts, Scanning Electron

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