Proceeding Paper

Investigating Sustainable Hydrogen Production via Catalytic Steam Reforming of Ethanol over Stable Commercial Catalysts [†]

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Abstract: Renewable ethanol serves as a compelling source for generating clean hydrogen. In this study, we conducted an in-depth exploration of the catalytic steam reforming of ethanol to produce hydrogen employing four commercial catalysts under optimized reaction conditions, including temperature, pressure, and the steam-to-ethanol ratio. Among the catalysts investigated, two nickel-based catalysts with different nickel contents a exhibited superior performance, displaying the highest hydrogen yield, ethanol conversion, and hydrogen selectivity. Notably, these nickel-based commercial catalysts achieved a hydrogen selectivity of 75%, a hydrogen yield of 89%, and an ethanol conversion rate of 100%.

Keywords: renewable hydrogen; stable nickel catalysts; decarbonization; ethanol reforming; high pressure; molar feed ratio; performance; characterization

1. Introduction

The catalytic steam reforming of ethanol for hydrogen production has garnered significant attention in recent years, driven by the increasing demand for sustainable and clean energy sources [1]. Ethanol, sourced from renewable feedstocks, has emerged as a compelling precursor for clean hydrogen, offering environmental benefits and contributing to the transition toward a low-carbon economy [2]. Numerous studies have explored the catalytic conversion of ethanol to hydrogen, with a particular focus on optimizing the reaction conditions for enhanced efficiency [2,3]. Temperature, pressure, and the steam-to-ethanol ratio have been identified as the pivotal parameters influencing the catalytic performance of various catalysts [4,5]. These studies underscore the importance of understanding the intricate interplay between these factors to achieve optimal hydrogen yields [5]. Among the diverse catalysts explored, nickel-based catalysts have consistently exhibited a superior performance [6,7]. Nickel's catalytic activity, coupled with its cost-effectiveness, makes it an attractive choice for ethanol steam reforming. The literature highlights the versatility of nickel-based catalysts in achieving high hydrogen selectivity and ethanol conversion rates [7–9]. This study builds upon the existing knowledge by conducting an in-depth exploration of the catalytic steam reforming of ethanol using various commercial catalysts generously supplied by our industry partner, Proteum Energy. Specializing in non-methane (SnMR) steam reforming, Proteum Energy is at the forefront of advancing hydrogen production to facilitate the global transition toward clean energy. Their innovative modular hydrogen-designer fuel system is designed to generate low-carbon hydrogen, seamlessly integrating both renewable and non-renewable sources. Proteum Energy employs a diverse

range of non-methane feedstocks, including ethanol, methanol, ethane, and other non-methane hydrocarbons, to produce various grades of hydrogen. These grades encompass fuel cell hydrogen, pipeline substitute natural gas (SNG), and customized blends, complete with optional carbon dioxide (CO_2) and hydrogen (H_2) separation modules for enhanced flexibility and efficiency (refer to Figure 1 for a detailed illustration). The collaboration with Proteum Energy not only enriched our research endeavors, but also allowed us to explore the dynamic landscape of hydrogen production, particularly in the context of clean energy transitions. The incorporation of diverse feedstocks and the flexibility in hydrogen grades underscore Proteum Energy's commitment to advancing sustainable solutions for hydrogen production, aligning with the evolving demands of a clean energy sector.
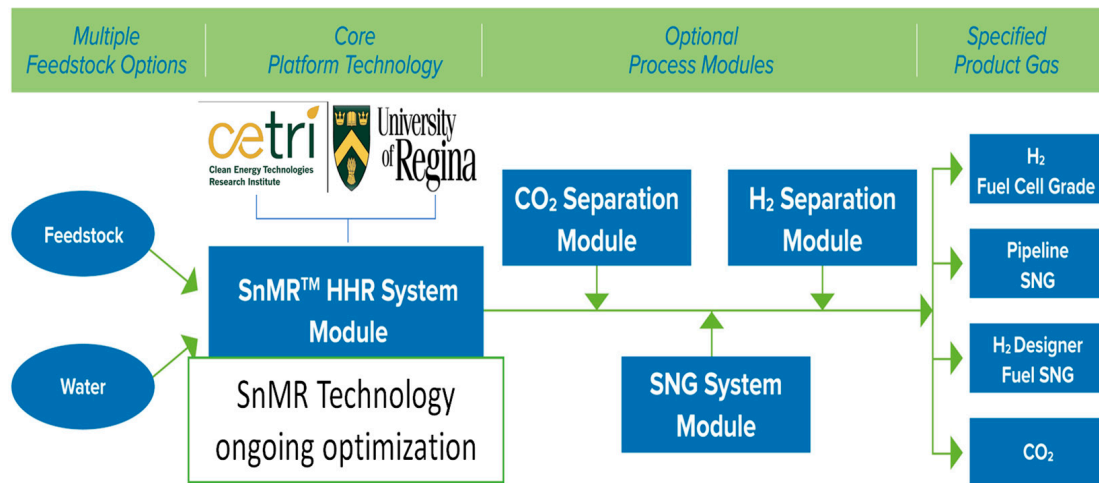
Figure 1. Proteum Energy core technology showing designer fuel system and carbon dioxide and hydrogen separation units.

Among the four commercial catalysts being studied here, two of them are nickel-based, with varying nickel contents, while the third is zinc-based, and the fourth is a lanthanum rare earth-promoted catalyst. The emphasis on optimized reaction conditions further enhances our understanding of the intricate mechanisms governing ethanol steam reforming to hydrogen. The findings of this study, particularly the exceptional performance of the nickel-based catalysts, with 75% H_2 selectivity, 89% H_2 yield, and a 100% ethanol conversion rate, align with the previous research trends [1,8,9]. Notably, the sustained activity of the catalysts over an extended period addresses a common concern in long-term catalytic processes. The investigation into the impact of nickel content variation on catalytic performance adds depth to the existing literature, opening avenues for future investigations on catalyst composition optimization. The comparative analysis of the four commercial catalysts not only reinforces the established trends, but also introduces novel insights, enriching our understanding of catalytic processes for sustainable energy solutions.

2. Experimental

2.1. Materials

The four commercial catalysts used in this study are Ar-401, NGPR-2, MS-901, and NG-608 L. All four catalysts were provided to us by our industry partner, Proteum Energy.

2.2. Catalyst Characterizations

Various characterization techniques were employed to gain crucial insights into the catalysts. Figure 2 presents SEM images of the four catalysts, with insets displaying EDX mapping that delineates distinct elements present in each catalyst. This comprehensive analysis enhances our understanding of the catalysts' structural and elemental composition.
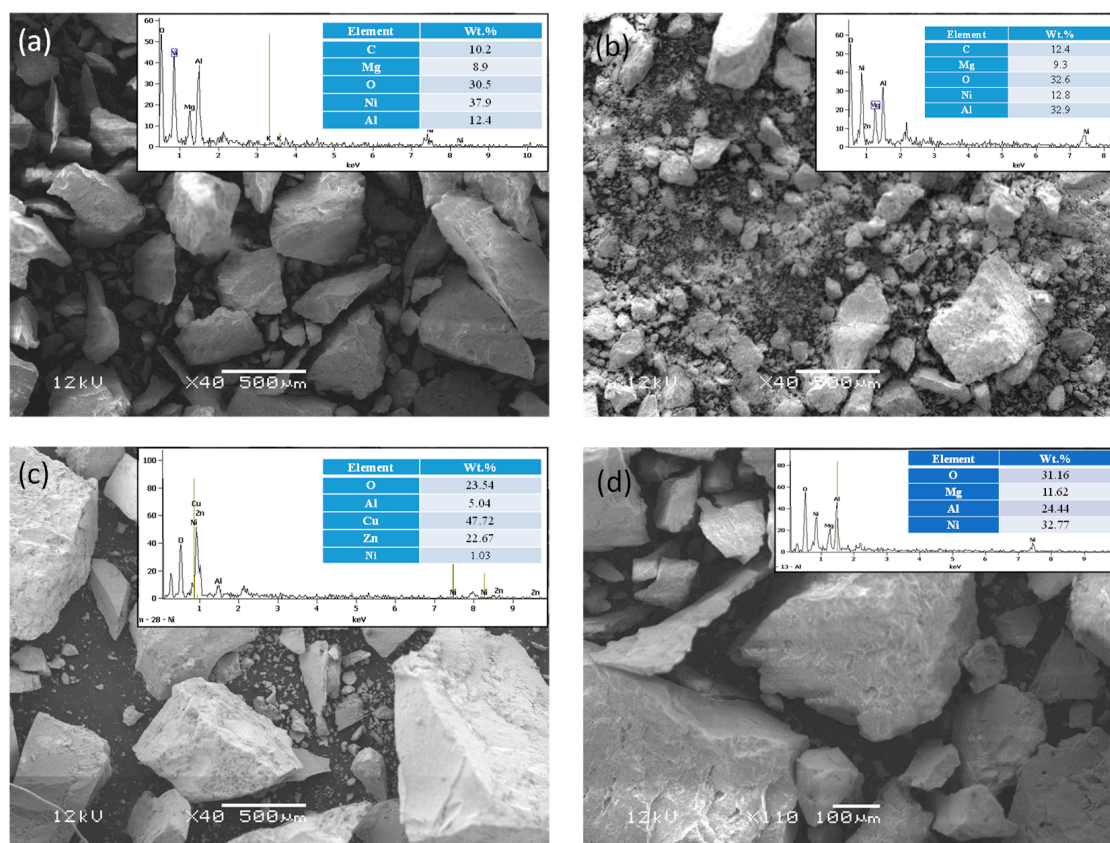
Figure 2. SEM-EDX images illustrating the morphology and compositions of the four commercial catalysts: (**a**) Ar-401, (**b**) NGPR-2, (**c**) MS-901, and (**d**) NG-608 L. The insets in the Figure illustrate the percentages of the elemental compositions.

In addition to SEM, various characterization techniques, including TEM, BET, PXRD, and TPR, were employed to extract crucial information about the catalysts. The primary emphasis was on the two most active catalysts: Ar-401 and NGPR-2. Summarized data can be found in Table 1.

Table 1. Comparative analysis of surface area, pore size, pore volume, nanoparticle size, and reduction temperature for Ar-401 and NGPR-2 catalysts.

Characterization	Ar-401	NGPR-2
BET Surface Area (m^2/g)	66.47	89.9
Pore Size (nm)	12.06	10.47
Pore Volume (cm^3/g)	0.20	0.24
Nanoparticle Size (nm)	90.3	65.4
TPR Reduction Temperature (°C)	295.3	306.2 and 828.9

2.3. Catalyst Testing Procedure

The steam reforming process was conducted in a fixed-bed reactor, as illustrated in Figure 3. Constructed from Inconel material capable of withstanding high temperatures, the reactor features external and internal diameters of 1.050″ and 0.514″, respectively. Engineered with a thickness designed to withstand pressures exceeding 500 bar, the reactor was situated within an electric furnace. To regulate the flow rates, a Cisco pump delivered the ethanol/water mixture, while the temperature of the catalyst was monitored using a thermocouple inserted into the reactor. Before assessing the catalysts' performance, a

500 mg sample placed at the center of the packed-bed reactor was reduced at 400 °C in 10% H_2 for one hour. During the reaction, the ethanol/water mixture was vaporized in a preheater before entering the reactor. Subsequently, the reaction products were condensed in a condenser and passed through a gas–liquid separator, where the liquid products were collected for analysis, while the gaseous products were sampled for analysis using online gas chromatography.
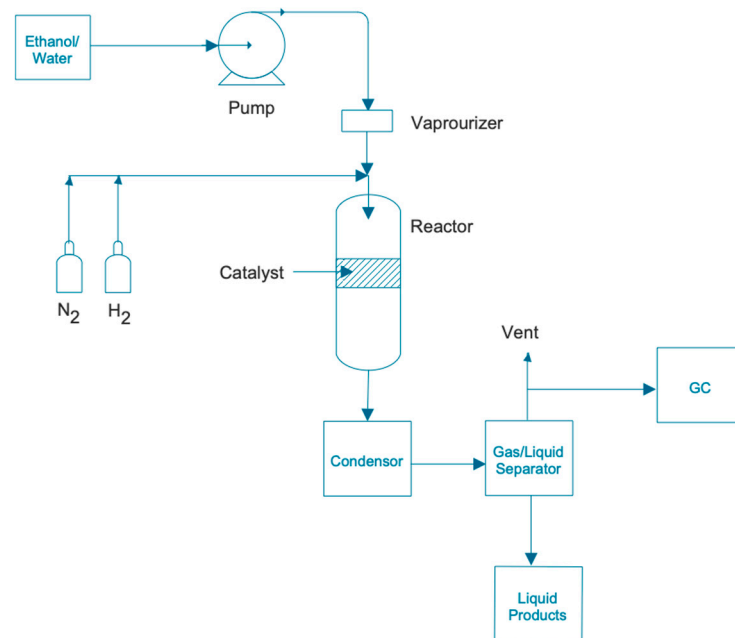
Figure 3. A schematic diagram of the reactor system, detailing the process flow and various components employed for conducting the ethanol steam reforming process.

3. Results and Discussion

This paper presents the comparative analysis of the performance of four catalysts in ethanol steam reforming. Specifically, two of these catalysts, AR-401 and NGPR-2, exhibit a nickel-based composition, while the third, MS-901 is comprised of zinc and copper, and the fourth, NG-608 L, is a lanthanum aluminate-based catalyst. AR-401 is characterized by its formulation with a low nickel content and is supported on an activated magnesium alumina spinel. In contrast, NGPR-2 functions as a pre-reformer catalyst, featuring a significantly higher nickel content compared to that of AR-401. Furthermore, the MS-901 catalyst predominantly consists of highly dispersed CuO, supplemented by a minor amount of ZnO, all supported on an alumina base. The NG-608 L catalyst is a lanthanum rare earth-promoted catalyst that contains NiO supported on magnesium aluminate. This research explores and compares the distinct properties of these catalysts, shedding light on their respective performances in the ethanol steam reforming process.

The performance parameters used to evaluate the commercial catalysts include ethanol conversion, the hydrogen yield, and hydrogen selectivity. These three performance parameters are defined according to Equations (1)–(3), where the F terms are the molar flow rates of the respective components.

$$Ethanol\ Conversion = [F(C_2H_5OH)in - F(C_2H_5OH)out]/F(C_2H_5OH)in \times 100 \quad (1)$$

$$Hydrogen\ Yield = F(H_2)out/6[F(C_2H_5OH)in - F(C_2H_5OH)out] \quad (2)$$

$$Hydrogen\ Selectivity = Moles\ of\ (H_2)out \times 100/Total\ moles\ of\ products \quad (3)$$

The performances of the four catalysts were compared under optimal reaction conditions of 700 °C, a steam-to-ethanol ratio of nine, and atmospheric pressure. The hydrogen selectivities, hydrogen yields, and ethanol conversions of the four catalysts were evaluated

and are summarized in Table 2. It was observed that the Ar-40 and NGPR-2 catalysts exhibited superior performances compared to those of the NG-608 L and MS-901 catalysts.

Table 2. Comparative performance analysis of commercial catalysts in terms of hydrogen selectivity, hydrogen yield, and ethanol conversion.

Catalysts	H_2 Selectivity (%)	H_2 Yield (%)	Ethanol Conversion (%)
Ar-401	74.8	85.1	100
NGPR-2	72.6	88.7	100
NG-608 L	63.1	79.5	94.8
MS-901	55.5	76.8	87.5

Furthermore, the product selectivities of the four catalysts were compared, as illustrated in Figure 4. In Figure 4a, Ar-401 had hydrogen, carbon dioxide, and carbon monoxide selectivities of 75% 15%, and 10%, respectively, with a negligible amount of less than 1% of CH4. The product selectivities of the NGPR-2 catalyst (Figure 4b) were similar to those of Ar-401.
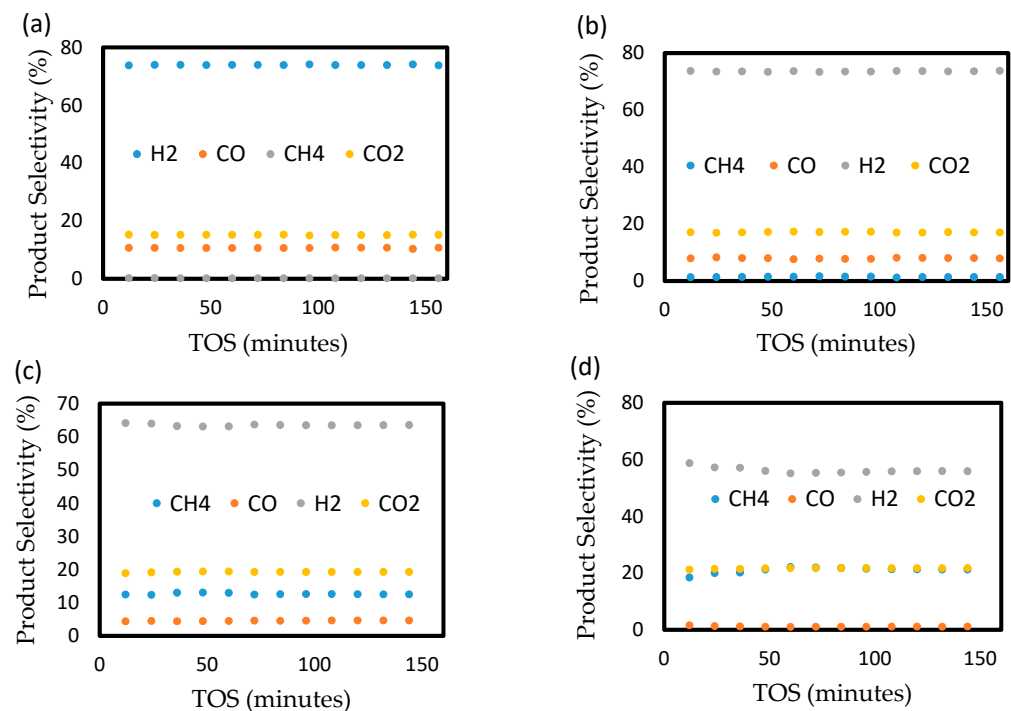
Figure 4. Product selectivities over time via stream of four commercial catalysts tested at 700 °C, with steam-to-ethanol ratio of 9, and at atmospheric pressure. (**a**) Ar-401, (**b**) NGPR-2, (**c**) NG-608 L, and (**d**) MS-901.

However, both NG-608 L (Figure 4c), and MS-901 (Figure 4d) showed hydrogen selectivities significantly lower than those of Ar-401 and NGPR-2. Consequently, the subsequent sections of this paper focus on the comparative performances of the Ar-401 and NGPR-2 catalysts. Specifically, the effects of the different parameters on the performance of the Ar-401 and NGPR-2 catalysts in terms of hydrogen selectivity, ethanol conversion, and the hydrogen yield were studied, as discussed below.

3.1. Effects of Steam-to-Ethanol Ratio

The impacts of the steam–ethanol ratio on the hydrogen selectivities and hydrogen yields of the Ar-401 and NGPR-2 catalysts were analyzed. It is important to note that the

catalysts were tested under atmospheric pressure and at 700 °C. The evaluations were conducted at steam-to-ethanol ratios of six, nine, and twelve. For Ar-401, the hydrogen selectivities were 70.3%, 74.8%, and 71.1% for the steam-to-ethanol ratios of six, nine, and twelve, respectively. In comparison, NGPR-2 exhibited hydrogen selectivities of 69.8%, 72.6%, and 70.3% for the corresponding steam-to-ethanol ratios, as illustrated in Figure 5. Furthermore, the hydrogen yields of Ar-401 were 85.2%, 85.1%, and 84.8% for the steam-to-ethanol ratios of six, nine, and twelve, respectively. Meanwhile, the hydrogen yields of the NGPR-2 catalyst were recorded as 91.2%, 92.7%, and 91.9% for the steam-to-ethanol ratios of six, nine, and twelve, respectively. This reveals a consistent trend where both the catalysts exhibit similar hydrogen selectivities, but NGPR-2 shows a higher hydrogen yield. This observation is consistent with the higher nickel content in NGPR-2, providing more active sites for breaking the ethanol C-C bonds and catalyzing the reforming reaction to produce hydrogen. Furthermore, the selectivity of each catalyst increases with an increase in steam-to-ethanol ratio from six to nine, but decreases when further increased from nine to twelve. This suggests the competitive adsorption of steam at higher concentrations, occupying more active sites and leaving fewer sites for ethanol adsorption [10]. Therefore, there is no advantage in using more water in the ethanol steam reforming reaction beyond a steam-to-ethanol ratio of nine. Notably, both the Ar-401 and NGPR-2 catalysts achieved 100% ethanol conversion at all the three steam-to-ethanol ratios.
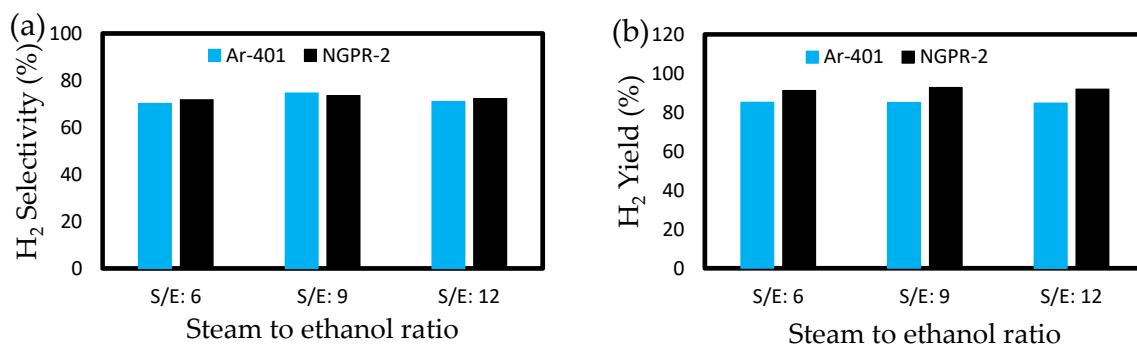
Figure 5. (**a**) The hydrogen selectivities and (**b**) the hydrogen yields as a function of the steam-to-ethanol ratio for the Ar-401 and NGPR-2 catalysts conducted at 700 °C, atmospheric pressure, and WHSV of 56.7 h-1.

### 3.2. Effects of Reaction Temperature

The impact of temperature on the performance of the Ar-401 and NGPR-2 catalysts was examined. Both the catalysts were evaluated at a steam-to-ethanol ratio of nine and atmospheric pressure. The experiments were conducted at four different temperatures, which are 400, 500, 600, and 700 °C. As depicted in Figure 6, hydrogen selectivity, the hydrogen yield, and ethanol conversion increase with rising temperature. At lower temperatures of 400 and 500 °C, the reaction by-products, such as CO_2, CO, and CH_4 resulting from ethanol decomposition predominate. Furthermore, acetaldehyde was produced at temperatures of 400 and 500 °C. Elevating the temperature to 600 and 700 °C enhances hydrogen production, accompanied by a decrease in the CH_4 and CO yields due to favorable hydrogen-producing reactions, such as water gas shift and methane reforming reactions [10]. Additionally, although CH_4 was significantly more abundant than CO in the product stream at lower temperatures, CO concentrations surpassed CH_4 at higher temperatures, accounting for approximately 10% of the gaseous reaction products' selectivity.
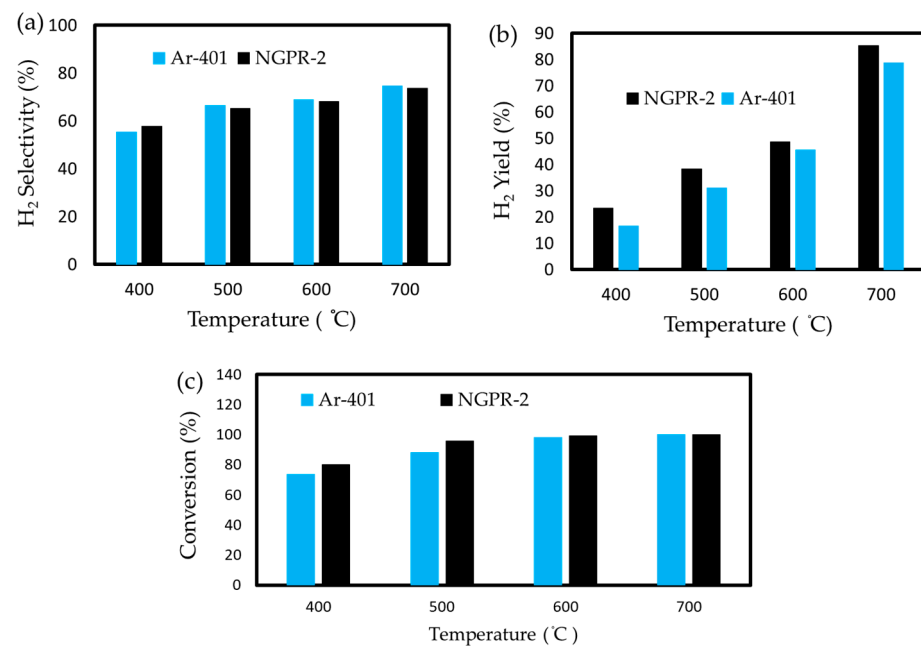
Figure 6. Variation in (**a**) hydrogen selectivity, (**b**) hydrogen yield, and (**c**) ethanol conversion with temperature for Ar-401 and NGPR-2 catalysts conducted at steam-to-ethanol ratio of 9, atmospheric pressure, and WHSV of 56.7 h-1.

3.3. Effects of Pressure

The influence of pressure on ethanol steam reforming was examined on the Ar-401 and NGPR-2 catalysts. Both the catalysts were assessed under identical conditions of 700 °C and a steam-to-ethanol ratio of nine. The pressure was systematically adjusted from atmospheric pressure to 3 bar, and finally to 6 bar. The recorded hydrogen selectivity and hydrogen yield at the different pressures are depicted in Figure 7.
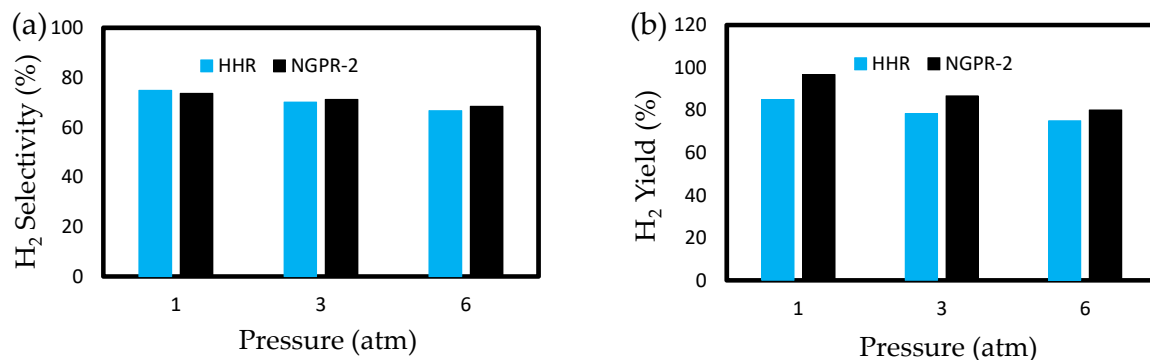
Figure 7. (**a**) Hydrogen selectivity and (**b**) hydrogen yield as function of pressure for Ar-401 and NGPR-2 catalysts conducted at 700 °C, steam-to-ethanol ratio of 9, and WHSV of 56.7 h-1.

While pressure had a negligible effect on hydrogen selectivity (see Figure 7a), its impact on the hydrogen yield was evident, as illustrated in Figure 7b.

4. Conclusions

This study conducted ethanol steam reforming experiments using commercial catalysts provided by Proteum Energy, a leading innovator in non-methane steam reforming for hydrogen production. This research compares the performances of four catalysts—AR-401, NGPR-2, MS-901, and NG-608 L—in ethanol steam reforming. The catalysts exhibit different compositions and properties. AR-401 and NGPR-2, both nickel-based, outperform NG-608 L and MS-901 in terms of hydrogen selectivity, yield, and ethanol conversion.

This research further explores the impacts of reaction parameters, such as the steam-to-ethanol ratio, the reaction temperature, and pressure, on the catalysts' performance. The results indicate that higher temperatures enhance hydrogen production, while pressure has a notable impact on the hydrogen yield. These collaborative efforts with Proteum Energy emphasize the importance of diverse feedstocks and hydrogen grades in advancing sustainable hydrogen production for a clean energy sector.

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