Catalytic hydrogen production from 2-propanol in supercritical water: Comparison of some metal catalysts

Mesut Akgün*, Ekin Kıpçak

Chemical Engineering Department, Yıldız Technical University, Davutpasa Campus, No. 127, 34210 Esenler, Istanbul, Turkey

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ABSTRACT

The gasification of organics in supercritical water is a promising method for the direct production of hydrogen at high pressures, and in order to improve the hydrogen yield or selectivity, activities of various catalysts are evaluated. In this study, hydrogen production from 2-propanol over Ni/Al_2O_3 and Fe–Cr catalysts was investigated in supercritical water. The experiments were carried out in the temperature range of 400–600 °C and in the reaction time range of 10–30 s, under a pressure of 25 MPa. The hydrogen yields and selectivities of Ni/Al_2O_3 and Fe–Cr used in this study, and those of Pt/Al_2O_3 and Ru/Al_2O_3 used in our previous work were compared. The hydrogen contents of the gaseous products obtained by using Ni/Al_2O_3 and Fe–Cr were measured as 62 mol% and 70 mol%, respectively, at low temperatures and reaction times. However, the hydrogen yields remained in low levels when compared with that of Pt/Al_2O_3 used in previous study. Pt/Al_2O_3 was established to be the most effective and selective catalyst for hydrogen production. During the catalytic gasification of a 0.5 M solution of 2-propanol, hydrogen content up to 96 mol% and hydrogen yield of 1.05 mol/mol 2-propanol were obtained.

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1. Introduction

Hydrogen is an important chemical in many industries such as the chemical industry (production of ammonia, hydrogenation, etc.), petrochemical industry, food processing, semiconductor industry, and in the metallurgical industry. The growth in hydrogen demand is already increasing significantly, and since hydrogen fuel cells is now near commercialization, hydrogen is expected to become one of the major fuels for energy generation in the future. Unfortunately, hydrogen does not exist in nature in its elemental form and, therefore, has to be produced from coal, petroleum, water or any other hydrogen-containing compounds, such as alcohols and hydrocarbons. Although electrical, thermal, biochemical and photonic energy or combinations of these are identified as the key commodities to drive hydrogen production process, there are currently four routes for hydrogen production: steam reforming, cracking, water electrolysis and gasification [1].

Supercritical water gasification (SCWG) has recently received much attention as a potential alternative to energy conversion methods applied to aqueous/non-aqueous biomass sources [2–4] or fossil fuels such as coal [5], due to the unique physical properties of water above its critical point (i.e. 374 °C and 22.1 MPa). In addition, water behaves as an acidic and alkaline precursor for acidic or basic reactions, since the formation of both H_3O^+ and OH^- ions takes place due to its self-dissociation at temperatures of near-critical and above critical point. Therefore, supercritical water is considered either as a solvent or as a reactant in the gasification processes of aqueous organic solutions [6].

In order to either manipulate the selectivity to produce the desired products in the gas effluent or to reduce the activation energy of the reactions, the use of catalysts is common in the gasification reactions at supercritical conditions of water. Moreover, reducing the activation energy of the reactions provides to obtain a hydrogen-rich gas at even low temperatures [7]. Increasing the gas product yields by the degradation of the organics and the intermediates, in this sense, along with the reduction to the lowest levels of tar and smut formations are also other advantages that the catalytic gasification processes have.

Many researchers have tested the effects of different catalysts like Pt, Ni, Ru, Rh and Pd supported with some metal oxides, for hydrogen production from different feedstock such as glucose, cellulose, lignin and some real biomass compounds [7]. However, these catalysts exhibit different catalytic activities or gas compositions, depending on the feedstock used. Kruse et al. [8] have investigated the effects of Raney nickel as a catalyst during the gasification of pyrocatechol solutions in supercritical water.

They have reported that Raney nickel increased the formations of hydrogen and carbon dioxide, decreased the formation of carbon monoxide and did not affect the formation of methane. In another study regarding the gasification of glucose by using Raney nickel, hydrogen formations in greater amounts were observed [9]. Osada et al. [10] have used Ni/Al_2O_3 as a catalyst during the gasification of lignin, glucose and formaldehyde. According to their results, Ni/Al_2O_3 increased hydrogen formation for each biomass; however, it was observed that methane formation did not change significantly. In another study of the same authors, the use of Ni/Al_2O_3 increased hydrogen formation during the gasification of lignin [11]. At the same time, the formation of carbon dioxide and C_2-C_4 hydrocarbons increased, whereas methane and carbon monoxide decreased. As a result of the experiments made for the gasification of glucose at the conditions of 400 °C and 24.5 MPa by Lu et al. [12], it was mentioned that hydrogen, methane and carbon dioxide formations increased. Similar conclusions were also obtained by Therdthianwong et al. [13].

Ruthenium catalysts are especially preferred for the catalytic gasification processes carried out at low temperatures. A remarkable increase in methane formation has been observed during the gasification lignin, cellulose and formaldehyde by using Ru/TiO_2 at 400 °C [10]. However, it was mentioned that the selectivity of this catalyst toward hydrogen production was not adequate. During the gasification of glucose using Ru/TiO_2, the carbon conversion increased significantly [14]. The formations of hydrogen, methane and carbon dioxide increased; contrarily, the formation of carbon monoxide decreased. At the same time, Osada et al. [15] have reported that the formations of methane and carbon dioxide increased, and the formations of hydrogen and C_2-C_4 hydrocarbons decreased during the gasification of lignin by using Ru/TiO_2 at 400 °C. In another study, which involved the gasification of cellulose and sawdust by using Ru/C, it has been observed that both the gasification, hydrogen and methane yields increased [16]. Byrd et al. [17] have mentioned that Ru/Al_2O_3 increased the formation of hydrogen during the gasification of glucose at 700 °C and 24.8 MPa, and decreased the formations of methane, carbon dioxide and monoxide. In another study carried with ethanol, the same catalyst caused a change in the gas product composition [18]. According to authors' comments, the reason of the decrease in methane content was its transformation into hydrogen via the reforming reaction. Onwudili and Williams [19] have reported that Ru/Al_2O_3 increased the formation of both hydrogen and methane. However, they have observed that the formations of carbon dioxide and C_2-C_4 hydrocarbons decreased.

Osada et al. [20] have investigated the effects of Rh/C, Pt/C, Pt/Al_2O_3, Pd/C and Pd/Al_2O_3 as catalysts on the gasification reactions taking place at 400 °C and 37.1 MPa. The authors stated that the greatest methane selectivity was obtained when Rh/C was used as a catalyst, and the lowest selectivity for methane was obtained for the cases of Pd/C and Pd/Al_2O_3. On the contrary, the hydrogen selectivity of Pd catalyst was mentioned to be much more when compared with other catalysts. During the gasification of lignin with Rh/C, Pt/C and Pd/C catalysts, similar hydrogen and methane selectivities were obtained [21]. Karakuş et al. [22] have reported that although Ru/Al_2O_3 exhibited much more catalytic activity for the gasification of 2-propanol in supercritical water, its selectivity toward hydrogen production was not high enough when compared to Pt/Al_2O_3 in the experimental conditions. On the other hand, Pt/Al_2O_3 exhibited a very high selectivity toward hydrogen production at low temperatures and fast reaction times.

In this work, hydrogen production from 2-propanol over Ni/Al_2O_3 and Fe–Cr catalysts was studied in supercritical conditions of water. Ni/Al_2O_3 was chosen because it is a frequently encountered catalyst in SCWG studies published in literature; and Fe–Cr was chosen due to its rare use in this field of research and Fe

Table 1
Elemental compositions of the catalysts.

Ni/Al_2O_3 (wt.%)	Fe–Cr (wt.%)
82.16 Ni	87.5 Fe
9.30 Al	7.84 Cr
8.54 Ca	0.68 Al
	0.24 Si
	3.78 Cu

being a common catalyst in processes like syngas production by Fischer–Tropsch synthesis. The gasification yields, hydrogen yields and selectivities were investigated in the temperature range of 400–600 °C and in the reaction time range of 10–30 s. Since the experimental results obtained in our previous study [22] revealed that both the gasification and hydrogen yields decreased with decreasing pressure, all of the experiments were performed at a constant pressure of 25 MPa. The hydrogen yields and selectivities of Ni/Al_2O_3 and Fe–Cr used in this study, and those of Pt/Al_2O_3 and Ru/Al_2O_3 used in our previous work [22] were compared.

2. Materials and methods

2.1. Materials

Ni/Al_2O_3 and Fe–Cr were supplied commercially (Alfa Aesar) and used without further processing. SEM photos and the content analyses of the catalysts are showed in Fig. 1. SEM images were obtained from scanning electron microscope (JEOL-5410LV) by using a Bath Scatter Electron Detector and a Secondary Electron Detector. XRF spectrums were obtained by using Energy Dispersive Spectroscopy (EDS) and the elemental compositions of the catalysts are given in Table 1. 2-Propanol (Merck) was used in the experiments after it was diluted with deionized water to the desired concentrations.

2.2. Experimental procedure

Catalytic gasification of 2-propanol in supercritical water was performed in a packed bed reactor system as described in previous work [22]. The experimental apparatus consisted of a packed bed reactor (10 cm length × 2 cm i.d.) and a pre-heating line (50 cm × 4.35 mm i.d.), which were placed into a PID controlled split furnace (Protherm). The weights of Ni/Al_2O_3 (d_{cat} = 2.17 g/cm^3) and Fe–Cr (d_{cat} = 2.0 g/cm^3) used in the reactor were 13.83 g and 27.53 g, and their shapes were in ring ribbed with hole form and in cylindrical form, respectively. From the feed pump to the gas–liquid separator, all of the wetted parts of the system were made of 316 SS. 2-Propanol solution in desired concentration was pumped into the pre-heating zone and the reactor placed in the furnace by using a high pressure pump (Autoclave Engineers). The feed flow rates were determined according to the reaction conditions for chosen reaction times (Eq. (1)). The temperature of the 2-propanol solution was provided to reach the desired value by passing through the preheating zone, before coming upon the catalyst in the reactor. At the exit of the furnace, the effluent was cooled rapidly by a heat exchanger and the possible reactions immediately stopped. The system pressure was maintained at the desired value in a precision of ±0.1 MPa by a back pressure regulator (GO Regulator Inc.). The products leaving the back pressure regulator were separated by a gas–liquid separator. The gaseous effluent taken from the top of the separator was transported for quantitative analysis to a gas chromatograph capable of online sampling. After gas sampling, the flow rate of the gaseous effluent produced was measured at each experiment by a digital volumetric gas flow meter (Agilent, ADM2000), the ratio of which to the feed flow rate was used to