Selective Production of Methane from Aqueous Biocarbohydrate Streams over a Mixture of Platinum and Ruthenium Catalysts

Maria Fernanda Neira D’Angelo, Vitaly Ordomsky, John van der Schaaf, Jaap C. Schouten, and Tjeerd Alexander Nijhuis*[a]

Introduction

Replacing natural gas by a renewable equivalent is an attractive option to decrease the use of fossil fuels, minimize greenhouse gas emissions, as well as to secure the energy supply in the short–mid term. Renewable natural gas can be directly injected in the gas grid to take advantage of the existing infrastructure to provide space heating, drive combined cycle tur- bines, and to provide fuel for road vehicles.[1] The conversion of biomass to methane, which is the primary constituent of natural gas, has been the subject of significant research, mainly focused on biogas[2] (first generation) and synthetic natural gas[3] (SNG; second generation). Whereas biogas is likely to put pressure on food stocks,[4] the production of SNG requires a complex sequence of steps, including biomass pretreatment (drying is one of the most cost- and energy-intensive steps)[5], gasification at elevated temperatures (ca. 800–900 °C), gas cleaning, methanation over a nickel catalyst at high temperature, and final gas conditioning.[6]

A one-step process for the selective production of methane from wet bio-based carbohy- drates under mild conditions is proposed herein. This process is aimed at the valorization of low-value dilute streams, for example, waste streams from bio-based industries, into fuel. Herein, we have used sorbitol (SB) as a model carbohydrate to study its conversion into methane; this is interpreted as the result of two combined reactions: 1) the hydrogenolysis of SB to methane over a Ru catalyst, and 2) the in situ generation of hydrogen through the aqueous-phase reforming of part of the sorbitol over Pt. A synergistic effect of the combination of these two catalysts results in the rapid and highly selective conversion of the carbohydrate to methane. This process offers the possibility of upgrading a low-value carbohydrate stream into a valuable fuel with no addition of H₂. Exergy analysis reveals that nearly 80% of the exergy of the reactant is recovered as methane.
a limitation for the selective production of glycols, whereas it is convenient for the production of methane. Excessive C–C hydrogenolysis leads to the conversion of nearly any carbohydrate mixture into methane; this opens up the possibility to upgrade low-value carbohydrate streams into a valuable fuel.

To avoid the need for an external supply of hydrogen, we propose the in situ generation of hydrogen through the aqueous-phase reforming of part of the substrate. Aqueous-phase reforming of SB occurs under analogous reaction conditions to those required for its hydrogenolysis (ca. 200 °C), typically over a Pt-based catalyst. The production of hydrogen through aqueous-phase reforming is limited by the inhibiting effect of hydrogen on the reforming rate and on the selectivity to the desired product.[13] Hydrogenation of SB and the reaction intermediates takes place as the concentration of hydrogen increases in the reactor, which results in the formation of a complex mixture of acids, ketones, aldehydes, and so forth.[14] An alternative to maximize the yield to hydrogen in the reforming reaction is to decrease the hydrogen concentration. A larger reforming rate and a higher hydrogen selectivity can be reached. The direct consumption of hydrogen in a highly selective conversion route to methane enhances the reforming rate and suppresses the formation of a wide variety of side products.

Herein, a catalytic bed consisting of a physical mixture of Ru/C and Pt/C was used to partially convert SB into hydrogen and CO₂, and to further process the remaining SB, CO₂, and hydrogen produced into methane.

Results and Discussion

The experimental results are given in Table 1. The most relevant experimental conditions and expressions used to interpret the results are defined in the footnotes of Table 1. Further details concerning the experimental procedure are discussed in the Experimental Section.

As shown in Table 1, for runs 1, 3, 4, and 5, both Pt and Ru are active in the aqueous-phase reforming reaction to produce hydrogen, CO₂, and alkanes in the gas phase. The liquid-phase products consist of a mixture of polyhydroxy species, containing one to six carbon atoms (e.g., alcohols, polyols, organic acids, and aldehydes), produced by a sequence of dehydrogenation and decarboxylation/decarbonylation reactions, as well as by C–C/C–O hydrogenolysis of the substrate and intermediates. Some of these species may undergo further reforming reactions to produce additional hydrogen and CO₂, or further hydrogenolysis reactions to produce more alkanes in the gas phase. Therefore, the liquid-phase products can be considered intermediates towards the formation of gas-phase products. For both catalysts, an increase in the residence time (i.e., decreasing WHSV) leads to a larger conversion of SB and, in particular, a higher conversion to gas-phase products. This is why the selectivity to hydrogen increases with increasing SB conversion when using Pt as the catalyst (Table 1, runs 1 and 3). Although we observe a decrease in the rate of hydrogen production as the residence time increases, some of the liquid intermediates (e.g., glycerol) continue to be converted into hydrogen when the conversion of SB is nearly complete. This results in hydrogen production while there is no additional SB consumption, leading to an apparent increase in the hydrogen selectivity.

In agreement with the literature,[15] our results reveal that Pt is a better catalyst than Ru for the production of hydrogen in terms of activity and selectivity. This is attributed to a milder activity in C–C hydrogenolysis and methanation reactions and a higher activity for water–gas shift reactions in the case of Pt compared with that of Ru. In the range of WHSV studied, there was still a significant amount of carbon-containing species present in the liquid phase for both catalysts, although this was less for the Ru-catalyzed reactions. The high activity of Ru in C–C hydrogenolysis and hydrogenation reactions results in a significant production of light alkanes. Whereas the gaseous products in the case of the Pt-catalyzed reactions are mainly hydrogen, CO₂, and a minor amount of alkanes, in the case of the reactions with Ru, the gas contains a greater amount of methane. The selectivity to methane relative to heavier alkanes in the case of the reaction with Ru is remarkably high. Notably, the increase in the selectivity to methane over the Ru catalyst is not accompanied by a decrease in the selectivity to CO₂.

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<th>Table 1. Experimental results for the conversion of SB into methane.[a]</th>
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[a] Experiments conducted at 220 °C and 35 bar with 1 wt% SB in water. More details are given in the Experimental Section. [b] Weight hourly space velocity (WHSV) is given as the number of moles of SB per mole of metal per minute. [c] SB conversion, Xₐₚ = (flow SB fed − flow SB unreacted)/flow SB fed x 100%. [d] Hydrogen selectivity, Sₜₐₚ = flow of hydrogen produced/13×flow of SB fed×Xₐₚ×100%. [e] Carbon selectivity = moles of carbon in each product/moles of carbon in all products x 100%. [f] The amount of hydrogen measured at the outlet is smaller than the amount of hydrogen fed. [g] Pt/Ru = 1:5 on a weight basis.
Therefore, we attribute the formation of methane to hydrogenolysis reactions over the Ru catalyst instead of methanation of CO₂.

The addition of hydrogen to the reaction mixture leads to direct hydrogenolysis of the C–C and C–O bonds of the substrate over the two catalysts used. Run 1 in Table 1 reveals that hydrogenolysis of SB over Pt is a relatively slow reaction and rather selective to liquid-phase products. No significant amount of methane was formed by hydrogenolysis of SB over a Pt catalyst. In the liquid phase, a significant amount of glycols (i.e., 22% of glycerol and 14% of 1,2-propanediol) and other compounds such as acids and aldehydes (ca. 50% in total) are detected. On the other hand, run 6 in Table 1 shows that Ru presents a greater activity than Pt in the hydrogenolysis of SB to produce gas-phase products, in particular, methane; this is attributed to a very high activity in C–C cleavage reactions.

Another difference between the Pt and Ru catalysts for the hydrogenolysis reactions is the effect of hydrogen on the catalytic activity. A comparison of runs 1 and 2 (Table 1) reveals that, when Pt is used as the catalyst, the addition of hydrogen to the reactant mixture results in a decrease in SB conversion and an increase in the yield to liquid-phase products. Runs 5 and 6 (Table 1) show that the addition of hydrogen does not have the same effect in the case of the Ru catalyst. In this case, the addition of hydrogen increases both the rate of SB consumption and the selectivity to gas-phase products, in particular, methane. According to the mechanism proposed by Montassier et al.,[8] the first step in the hydrogenolysis of a polyol is dehydrogenation over the metal surface, which involves breaking of the C–H bond and later the formation of molecular hydrogen. This is also the initial step for the aqueous-phase reforming of a polyol.[15] Several studies have proposed that the rate-limiting step for polyol dehydrogenation is different over Pt than that over Ru, whereas the limiting step for dehydrogenation over Pt seems to be the dissociation of the methine bond C–H, the formation of molecular hydrogen limits the rate of dehydrogenation over Ru.[16] A plausible explanation for our observations is that higher concentrations of hydrogen inhibit cleavage of the C–H bond, but do not suppress the rate of formation of molecular hydrogen.

The hydrogenolysis of a low-value carbohydrate to methane over Ru is attractive because relatively high selectivities to the desired product can be achieved and the methane product can be easily separated from the aqueous stream. However, it is questionable whether the complete conversion to methane with an external supply of hydrogen—a highly valuable product—is energetically and economically efficient. The in situ generation of hydrogen through aqueous-phase reforming by using only Ru as a catalyst is a possibility, but a significant amount of carbon is still present as a mixture of liquid-phase products, probably due to the slow rate of hydrogen production over the Ru catalyst, which limits further conversion steps. Runs 6 and 8 (Table 1) reveal that the addition of Pt to Ru allows complete conversion of SB into gas-phase products under analogous WHSV conditions. Hydrogen is generated in situ over the Pt catalyst and further consumed in the hydrogenolysis reactions over Ru, leading to a gas mixture with methane, CO₂, and hydrogen. The molar balance of the most significant reactants and products of the reaction of SB over a mixture of Pt and Ru (Table 1, run 8) is given in Figure 2.

As shown by runs 1, 4, and 7 in Table 1, the conversion of SB over a mixture of Pt and Ru is increased with respect to that over the monometallic catalysts. We attribute this effect to a synergistic effect derived from the in situ production and consumption of hydrogen. It is believed that the direct consumption of hydrogen over the Ru surface prevents building up of the concentration of hydrogen in the reactor and acts as a promoter of the conversion of SB into hydrogen and CO₂ over Pt. Rapid production of hydrogen increases its availability to participate in the C–C hydrogenolysis reactions over Ru.

When comparing the direct hydrogenolysis of SB with the external addition of hydrogen over Ru (Table 1, run 6), with respect to the hydrogenolysis of SB with in situ hydrogen production over a mixture of Pt and Ru (Table 1, run 8), we observe that, in the latter case, a greater amount of CO₂ is produced as a result of reforming reactions. This is accompanied by a net production of hydrogen and a small decrease in the selectivity to methane. In this case, part of the SB is not converted into methane but into hydrogen and CO₂. In other words, the advantage of suppressing the demand for hydrogen as a reactant for the production of methane is counterbalanced by a slight reduction in the yield to methane when hydrogen is generated in situ.

The thermodynamic efficiency of these two routes (i.e., the production of methane from SB with and without the addition of hydrogen over Ru and Pt/Ru, respectively) was roughly estimated in this study by performing an exergy balance between reactants and products.[17] This approach to evaluate efficiency is based on the second law of thermodynamics, and therefore, takes into account the degradation of the quality of the energy during a given conversion. The amount of exergy avail-

![Figure 2. Molar balance of the reactants and products of the hydrogenolysis of SB to methane with in situ hydrogen production over a mixture of Pt and Ru catalysts (run 8 in Table 1).](image-url)
able in the products with respect to that in the reactants is considered herein to be the efficiency of the process (i.e., \( \varphi = \frac{\text{exergy}_{\text{products}}}{\text{exergy}_{\text{reactants}} \times 100\%} \)). Calculation of the exergy in the material streams was performed by following standard methodology described elsewhere.\textsuperscript{17} In the case of the external addition of hydrogen, the products (i.e., methane and CO\(_2\)) contain slightly above 50% of the exergy fed in the reactants (i.e., SB and hydrogen) stream. If hydrogen were to be generated in a separate reactor through aqueous-phase reforming of an additional amount of SB, the overall efficiency of the complete conversion route (i.e., hydrogen production and methane production) would drop below 30%. On the other hand, when hydrogen is otherwise generated in situ by using a mixture of Pt and Ru, the efficiency of the process significantly increases. The products (i.e., methane, CO\(_2\), and hydrogen) contain nearly 80% of the exergy in the feed (in this case only SB). Although thermodynamically efficient, the economic feasibility of the conversion of biocarbohydrates into methane depends on the cost of the original feed. This process is aimed at the selective conversion of low-value diluted carbohydrates streams into methane.

**Conclusions**

Methane was selectively produced by the direct conversion of SB in an aqueous medium at 220 °C over a mixture of Pt and Ru catalyst with no external addition of hydrogen. This conversion was the result of partially converting SB into hydrogen and later proceeding with the hydrogenolysis of the remaining SB towards methane. It is believed that the direct consumption of hydrogen during the hydrogenolysis reaction reduces the hydrogen concentration in the reactor, and therefore, promotes the rate of hydrogen production in the reforming pathway over Pt. At the same time, the rapid generation of hydrogen promotes the C–C scission reactions over the Ru surface, which strongly benefits the selectivity towards methane. Whereas the production of methane from polysols is understood to be an inefficient process when hydrogen needs to be added to the reactor, the in situ generation of hydrogen and high selectivities to the desired product make this process a potential application to produce a renewable equivalent of natural gas.

**Experimental Section**

Three catalysts were used: 1) 5 wt% Pt/C (Johnson Matthey, BET surface area of 10 m\(^2\) g\(^{-1}\), average Pt particle size of 14 nm), 2) 5 wt% Ru/C (Engelhard de Meern B.V., BET surface area of 802 m\(^2\) g\(^{-1}\), average Ru particle size of 4 nm), and 3) a physical mixture of catalysts 1 and 2 in a Pt/Ru ratio of 1:5 (mass basis). For the catalytic tests, the powder catalysts were pressed and sieved to give particles between 106 and 212 μm to avoid mass transfer limitations (Thiele modulus \( \varphi < 0.3 \)). Later, the powder catalyst was packed into a stainless-steel tubular reactor with an inner diameter (ID) of 2.5 mm and 10 cm long. This reactor was vertically placed inside an oven with circulating hot air and brought to the reaction temperature (i.e., 220 °C) and pressure (i.e., 35 bar). Prior to the reaction, the catalysts were reduced in situ with hydrogen for 2 h at 220 °C. The reduction procedure served to activate the metal surface as well as to test the possibility of hydrogenation reactions (e.g., methanation) of the carbon support. Since no anakes were formed during the reduction, the interaction of the carbon support in the reactions was not considered in this study. A syringe pump (Teledyne ISCO 500D) was used to feed the reactant solution with 1 wt% of SB (Sigma) in water. When applicable, a nitrogen/hydrogen gas stream was premixed with the liquid flow in a Y-mixer (VICI Valco) in a gas to liquid ratio of \( R_{\text{GS}} = \frac{2 m_{\text{gas}}}{m_{\text{liquid}}} \). Downstream, the reaction products were quenched in a cooling bath and collected in a stainless-steel vessel, in which the gas and liquid phases were separated. An argon flow was fed to this vessel as an external standard to analyze the composition of the gas stream. Analysis of the gas phase was performed online with GC (columns: Poraplot/Molsieve 5A, detectors: TCD/FID). Analysis of the liquid-phase products was performed by a combination of HPLC (column: Metacarb 67H and, detector: RI), GC (column: Cp-sil5, detector: FID), and GC-MS (column: DB-200, detector: MS) analyses. The carbon balance was closed for all cases within 5–10%. Each set of experimental conditions was tested for 24 h of time on stream to ensure stable performance. Thus, each catalyst was tested for a total operational period of at least 72 h, during which time no deactivation of the catalyst was observed.

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**Keywords:** aqueous-phase reforming · carbohydrates · heterogeneous catalysis · platinum · ruthenium


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Twice as precious: A one-step process for the selective production of methane by hydrogenolysis of low-value diluted bio-based carbohydrates with in situ hydrogen production is proposed (see picture). Sorbitol is used as a model compound that can be fully converted into methane, carbon dioxide and a minor amount of hydrogen over a Pt/Ru catalyst.