COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Renewable hydrogen by aqueous-phase reforming of glucose†

Rupali R. Davda and James A. Dumesic*
University of Wisconsin, Madison, 1415 Engineering Drive, Madison, Wisconsin 53706, USA.
E-mail: dumesic@engr.wisc.edu; Fax: 1 608 262 5434; Tel: 1 608 262 1095

Received (in Cambridge, UK) 26th August 2003, Accepted 6th November 2003
First published as an Advance Article on the web 20th November 2003

Hydrogen can be produced from aqueous solutions containing 10 wt% glucose with high selectivities through the combined use of a hydrogenation reactor for conversion of glucose to sorbitol, followed by a reforming reactor for conversion of sorbitol to H_2 and CO_2 and then a gas–liquid separator for the removal of high-pressure H_2-rich reformate gas, ready for use in a fuel cell.

Biomass is a promising source for the sustainable production of hydrogen in an age of diminishing fossil fuel reserves; however, conversion of biomass to hydrogen remains a challenge, since processes such as enzymatic decomposition of sugars, steam-reforming of bio-oils and gasification suffer from low hydrogen production rates and/or complex processing requirements.[1]

We have recently reported[2] that hydrogen can be generated by catalytic reforming of oxygenated hydrocarbons in liquid water at temperatures near 500 K. Of particular interest in this class of reactants is glucose ($C_6O_6H_{12}$), because this sugar makes up the major energy reserves in plants and animals. While the selectivity for hydrogen production is insensitive to the liquid-phase concentration of sugar-alcohols such as sorbitol ($C_6O_6H_{14}$), the hydrogen selectivity from reforming of glucose decreases as the liquid concentration increases from 1 to 10 wt% because of undesired hydrogen-consuming side reactions that occur in the liquid phase.[3] This decrease in selectivity is an important limitation, because processing dilute aqueous solutions involves the processing of excessive amounts of water.

Fig. 1 depicts various reaction pathways that take place during aqueous-phase reforming of glucose and sorbitol. Production of H_2 and CO_2 from glucose (G) and sorbitol (S) takes place on metal catalysts such as Pt or NiSn alloys (pathways G1 and S1) *via* cleavage of C–C bonds followed by water-gas shift processes.[2] Undesired alkanes are formed by cleavage of C–O bonds on the metal catalyst and by dehydration processes on acidic catalyst supports (pathways G2, S2).[4] In the case of glucose, undesired reactions can also take place in the aqueous phase to form organic acids, aldehydes and carbonaceous deposits (pathway G3).[3] These undesirable homogeneous decomposition reactions are first order in glucose concentration, whereas the desirable reforming reactions on the catalyst surface are fractional order;[5] therefore, high concentrations of glucose lead to low hydrogen selectivities. Another reaction that links the aforementioned pathways is the hydrogenation of glucose to sorbitol (pathway G–S), which takes place on metal catalysts with high selectivity at low temperatures (*e.g.*, 400 K) and high H_2 pressures.[6]

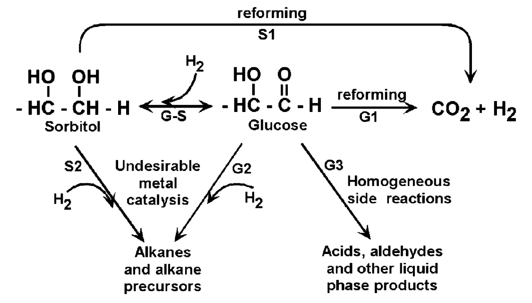

Fig. 1 Reaction pathways involved in glucose and sorbitol reforming.

The rates of pathways G1, G2, G3 increase more rapidly with temperature than does the rate of pathway G–S. Accordingly, a strategy for improving the hydrogen selectivity from aqueous-phase reforming of glucose is to employ a dual-reactor system involving a low-temperature hydrogenation step followed by a higher-temperature reforming process. To implement this two-step process, it is important to understand how the pressure of H_2 depends on the system pressure. Aqueous-phase reforming leads to the production of gas bubbles containing H_2, CO_2 and alkanes. The pressure in these bubbles is approximately equal to the total pressure of the system, and the partial pressures of the gaseous reaction products and water vapour depend on the composition of the feed stream and the saturation pressure of water at the reactor temperature.[7] For this study, the partial pressures of the gas phase products in the reactor were varied by co-feeding a gas stream (N_2 or H_2) with the liquid feed at the inlet of the reactor. The performance of the reactor in this mode can then be compared to the case where only liquid is fed to the reactor and N_2 sweep gas is combined with the effluent stream at the exit of the reactor.

Table 1A and B shows the results of aqueous-phase reforming of 10 wt% sorbitol and glucose solutions at 538 K and 52.4 bar over a Pt/Al_2O_3 catalyst. All runs were conducted at high conversions of the feed to gas-phase products, from which the reaction selectivities were calculated. We report the hydrogen selectivity, which is defined as the number of moles of H_2 in the effluent gas normalized by the number of moles of H_2 that would be present if each mole of carbon in the effluent gas had participated in the sorbitol or glucose reforming reaction to give 13/6 or 2 moles of H_2, respectively. When H_2 is co-fed with the liquid reactant stream to the reactor, the hydrogen selectivity reported is based on the calculated moles of hydrogen produced, using the composition of the carbon-containing products in the effluent gas stream. We also report the alkane selectivity, which is defined as the moles of carbon in the gaseous alkane products normalized by the total moles of carbon in the gaseous effluent stream.

The highest rates of aqueous-phase reforming were obtained for runs where N_2 was combined with the liquid feed at the reactor inlet. Also, since glucose is less reactive than sorbitol for aqueous-phase reforming over Pt/Al_2O_3,[2] lower weight hourly space velocities (WHSV; grams of reactant per gram of catalyst per hour) of glucose were employed to achieve high conversions. Table 1 shows that the hydrogen selectivities observed for aqueous-phase reforming of glucose (~10–13%) are much lower compared to reforming of sorbitol (~60%) under similar conditions. Also higher alkane selectivities of 47–50% were observed for reforming of glucose, indicating that aqueous-phase reforming of glucose, even with hydrogen co-fed with the liquid reactant stream at the inlet of the reactor, is not selective for production of H_2. The above results indicate that co-feeding hydrogen with liquid reactants into the reforming reactor at 538 K (and 52.4 bar) does not lead to rapid hydrogenation of glucose into sorbitol and its subsequent reforming to give high H_2 selectivities. Similarly, sorbitol does not undergo rapid dehydrogenation to glucose under conditions of aqueous-

---

† Electronic Supplementary Information (ESI) available: catalyst preparation and characterization; reaction kinetics studies; acknowledgements. See http://www.rsc.org/suppdata/cc/b3/b310152e/

DOI: 10.1039/b310152e

Table 1 Experimental results for the aqueous-phase reforming of 10 wt% sorbitol and glucose at 538 K under different reactor configurations[a]

Experiment	A: Sorbitol reforming			B: Glucose reforming			C: Hydrogenation + reforming	
Gas flow at reactor inlet/outlet	N_2 sweep at outlet	N_2 fed at inlet	H_2 fed at inlet	N_2 sweep at outlet	N_2 fed at inlet	H_2 fed at inlet	Sorbitol + H_2 fed at inlet	Glucose + H_2 fed at inlet
Pressure/bar	52.4	52.4	52.4	52.4	52.4	52.4	54.8	54.8
Hydrogenation/reforming WHSV/g(feed) g(cat)$^{-1}$ h^{-1}	—/0.0963			—/0.0224			0.091/0.065	
% Carbon in gas-phase effluent	86	96	91	91.2	92.4	95.8	100	93
% H_2 selectivity	50	62	63	10.5	13.4	11.6	57.3	62.4
% Alkane selectivity	22	20	19.1	49.5	47.5	46.8	22.7	21.3
α = moles H_2/mole glucose fed (α_{max} = 12)	4.4	6.7	6.6	1.3	1.5	1.5	6.5	5.8

[a] Catalyst: 3 wt% Pt on nanofibers of γ-Al_2O_3 (BET area 500 m^2 g^{-1}) having a Pt dispersion of 70% (see ESI†).

phase reforming where H_2 is not co-fed with the liquid reactant stream to the reforming reactor, a desirable result.

Experiments were conducted by co-feeding gaseous H_2 with aqueous solutions containing 10 wt% sorbitol or glucose into a dual-reactor system consisting of a hydrogenation reactor at 393 K followed by a reforming reactor. The presence of the hydrogenation reactor did not affect the aqueous-phase reforming of sorbitol. However, when 10 wt% glucose was co-fed with gaseous H_2 to the dual-reactor system, high hydrogen selectivity (62.4%) and low alkane selectivity (21.3%) were obtained (see Table 1C), these values being similar to the selectivities obtained from the reforming of sorbitol. These results indicate that glucose was first completely hydrogenated to sorbitol before being sent to the reformer in which the sorbitol was converted with high selectivity to H_2 and CO_2.

Table 1 compares the net moles of hydrogen produced per mole of glucose (α), where the maximum theoretical value of α is 12. For sorbitol feeds, α is calculated by subtracting 1 from the moles of H_2 produced per mole of feed (to account for the extra mole of H_2 in sorbitol compared to glucose). For sorbitol reforming, α is *ca.* 6.6 when N_2 or H_2 are co-fed with the liquid reactant stream to the reactor. In contrast, α is only 1.5 for the glucose feed. The addition of a hydrogenation reactor upstream of the reformer leads to α equal to nearly 6 for glucose reforming, showing an improvement of 290% in the net production of hydrogen per mole of glucose.

A novel aspect of the approach outlined here for the generation of hydrogen from aqueous solutions of glucose is that we have identified a beneficial synergy formed by operating the hydrogenation reactor, the reformer, and the gas–liquid separator (situated downstream of the reformer) at different temperatures while maintaining the total pressure of the system, P_{tot}, at a constant value. This situation is depicted schematically in Fig. 2. An aqueous solution of glucose is co-fed with gaseous H_2 to the hydrogenation reactor, which is operated at a relatively low temperature, T_1, to minimize glucose decomposition reactions in the liquid phase. The partial pressure of hydrogen, P_{H2}, in the reactor is equal to $P_{tot} - P_{H2O}(T_1)$, where $P_{H2O}(T_1)$ is the vapor pressure of water at T_1. For example, if P_{tot} is 54.8 bar and T_1 is 393 K, then P_{H2} = 52 bar. This relatively high pressure of hydrogen is favorable for the conversion of glucose to sorbitol. The aqueous solution of sorbitol and gaseous H_2 are then fed to the reforming reactor, which is operated at the higher temperature, T_2 (*e.g.*, T_2 = 538 K), necessary to convert sorbitol to H_2 and CO_2. Finally, the liquid and gaseous effluents from the reformer are cooled and sent to a separator, which is maintained at a low temperature, T_3. The sum of the partial pressures of H_2 and CO_2 in the separator is equal to $P_{tot} - P_{H2O}(T_3)$. If the separator is at room temperature, then the sum of the H_2 and CO_2 pressures is essentially equal to P_{tot}, which is 54.8 bar. This high pressure of the reformate facilitates further removal of CO_2 from H_2 by pressure-swing adsorption. A fraction of the purified H_2 at high pressure can then be recycled to the hydrogenation reactor, and the remaining hydrogen may be directed to a fuel cell for conversion to electrical power.

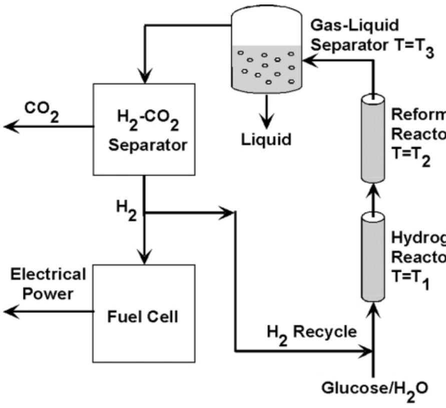

Fig. 2 Schematic representation of the recycle loop for generation of hydrogen by aqueous-phase reforming of glucose.

Notes and references

1 J. Woodward, M. Orr, K. Cordray and E. Greenbaum, *Nature*, 2000, **405**, 1014; L. Garcia, R. French, S. Czernik and E. Chornet, *Appl. Catal., A*, 2000, **201**, 225.
2 R. D. Cortright, R. R. Davda and J. A. Dumesic, *Nature*, 2002, **418**, 964; G. W. Huber, J. W. Shabaker and J. A. Dumesic, *Science*, 2003, **300**, 2075; R. R. Davda, J. W. Shabaker, G. W. Huber, R. D. Cortright and J. A. Dumesic, *Appl. Catal., B*, 2003, **43**, 13.
3 B. M. Kabyemala, T. Adschiri, R. M. Malaluan and K. Arai, *Ind. Eng. Chem. Res.*, 1999, **38**, 2888.
4 S. P. Bates and R. A. Van Santen, *Adv. Catal.*, 1998, **42**, 1.
5 J. W. Shabaker, R. R. Davda, G. W. Huber, R. D. Cortright and J. A. Dumesic, *J. Catal.*, 2003, **215**, 344.
6 P. Gallezot, P. J. Cerino, B. Blanc, G. Fleche and P. Fuertes, *J. Catal.*, 1994, **146**(1), 93.
7 R. R. Davda and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2003, **42**(34), 4068.