

Hydrogen Generation by Catalytic Reforming of Oxygenated Hydrocarbons in Liquid Water; J. A. Dumesic, R. R. Davda, R. Alcalá, J. Shabaker, G. Huber, R. D. Cortright, and M. Mavrikakis; Department of Chemical Engineering, University of Wisconsin, 1415 Engineering Drive, Madison, WI 53706, USA

Introduction

Fuel cells have emerged as one of the most promising technologies for meeting future global energy needs. The full environmental benefit of generating power from hydrogen fuel cells is achieved when the hydrogen fuel is produced from renewable sources such as solar power and biomass. Indeed, the production of hydrogen from renewable biomass-derived resources is a major challenge as global energy generation moves towards a “hydrogen society”. In this presentation, we show that it is possible to generate hydrogen by catalytic reforming of oxygenated hydrocarbons in liquid water at temperatures near 500 K. These reforming reactions lead to high selectivities for the production of hydrogen over Pt-based catalysts from oxygenated hydrocarbon reactants having a C:O stoichiometry equal to 1:1. For example, glucose can be converted to hydrogen and gaseous alkanes over platinum-based catalysts, with hydrogen selectivities of 50 %. Higher selectivities of hydrogen can be achieved from sorbitol and glycerol, and nearly 100 % selectivity for hydrogen production can be achieved for aqueous-phase reforming of ethylene glycol and methanol. This aqueous-phase reforming process (i) generates hydrogen without the need to volatilize water, which represents a major energy saving compared to conventional, vapor-phase, steam-reforming processes, (ii) occurs at temperatures where the water-gas shift reaction is favorable, making it possible to generate hydrogen with low amounts of CO in a single chemical reactor, (iii) utilizes safe transportable non-flammable feedstocks, (iv) can utilize renewable biomass derived feedstocks, and (v) takes place at low temperatures which minimize undesirable decomposition reactions typically encountered when carbohydrates are heated to elevated temperatures.

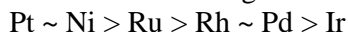
Methods

Details of our experimental studies of silica and alumina-supported catalysts for aqueous-phase reforming of ethylene glycol have been reported elsewhere [1-3]. Catalysts were loaded in a tubular stainless-steel reactor connected to a high pressure flow system and reduced in flowing hydrogen at 723 K. The system was then purged and pressurized to 22 or 29 bar with nitrogen for reaction studies at 483 or 498 K, respectively. An HPLC pump was used to feed the reactor with 10 wt% ethylene glycol in water at a rate of 0.06 cm³/min. The effluent liquid was drained periodically for analysis, and the off-gas stream was analyzed with several different gas chromatographs to determine the concentrations of hydrogen, carbon monoxide, carbon dioxide, methane, ethane and higher alkanes.

Self-consistent periodic slab calculations based on gradient-corrected density functional theory were conducted for two-layer Pt(111) slabs. The details of these calculations are presented elsewhere [4]. In brief, the total energy calculations were performed using DACAPO [5]. The 2x2 two-layer unit cell, containing a total of 8 metal atoms, was repeated periodically, with four equivalent layers of vacuum between any two successive metal slabs. The metal atoms were fixed in their bulk-terminated positions and all adsorbate atoms were allowed to relax. Transition states were identified using constrained optimizations, where the bond length representing the reaction coordinate was constrained and all other degrees of freedom were optimized.

Results and Discussion

The overall catalytic activity of aqueous-phase reforming of ethylene glycol decreases in the following order for silica-supported metals:



Silica supported Rh, Ru and Ni showed low selectivity for production of H₂ and high selectivity for alkane production, whereas silica-supported Pt and Pd based catalysts exhibited higher selectivity for production of H₂, with lower rates of alkane production. Thus, Pt appears to be an appropriate metal for hydrogen generation by liquid-phase reforming, since it displays high activity combined with good selectivity. It is noteworthy that relatively low levels of CO were produced compared to the amount of CO₂ formed from the aqueous-phase reforming of ethylene glycol over the Pt/SiO₂ catalyst (CO/CO₂<0.004). It can be concluded that an effective catalyst for the production of H₂ from aqueous-phase reforming of ethylene glycol should be active for C-C bond cleavage in ethylene glycol and be active for water-gas shift of CO to CO₂. Importantly, the catalyst must not perform the subsequent methanation and/or Fisher-Tropsch synthesis reactions to produce alkanes, which consume hydrogen, and decrease the hydrogen selectivity.

Reaction kinetics measurements on Pt/Al₂O₃ catalysts with different metal loadings were carried out (employing the Madon-Boudart test) to determine kinetically-controlled rates for aqueous-phase reforming of ethylene glycol at 483 and 498 K. The turnover frequency is approximately equal to 10 min⁻¹ at 498 K for an aqueous feed containing 10% ethylene glycol. The rate of hydrogen production is fractional order in ethylene glycol (0.3-0.5) and it is weakly inhibited by hydrogen (-0.6 order). The apparent activation energy is approximately 100 kJ/mol.

Ethanol was used as a probe molecule to investigate trends in C-C and C-O bond scission reactivities on Pt(111) using density functional theory (DFT), since ethanol is the simplest saturated alcohol having a C-C bond. The primary route for cleavage of the C-C bond is through adsorbed ketylenyl species (HCCO). The primary route for cleavage of the C-O bond is through adsorbed 1-hydroxyethylidene species (CH₃COH). Importantly, we calculate that cleavage of the C-C bond in species derived from ethanol should be faster than cleavage of the C-O bond on Pt(111), since the energies with respect to ethanol of the lowest transition states for these reactions are equal to 4 and 42 kJ/mol, respectively. In addition, it appears that cleavage of the C-C bond in species derived from ethanol should be faster than cleavage of the C-C bond in ethane on Pt(111). Thus, while Pt is not a particularly active metal for ethane hydrogenolysis, this metal exhibits high activity for cleavage of C-C bonds in oxygenated hydrocarbons.

References

- [1] R. D. Cortright, R. R. Davda, J. A. Dumesic, *Nature* **418** (2002) 964-967.
- [2] R.R. Davda, J.W. Shabaker, G.W. Huber, R.D. Cortright, J.A. Dumesic, accepted in *Appl. Catal. B: Env.* (2002).
- [3] J.W. Shabaker, R.R. Davda, G.W. Huber, R.D. Cortright, J.A. Dumesic, submitted to *J. Catal.*
- [4] R. Alcalá, M. Mavrikakis, J.A. Dumesic, submitted to *J. Catal.*
- [5] B. Hammer, L.B. Hansen, J.K. Nørskov, *Phys. Rev. B* **59** (1999) 7413-7421.