Aqueous-phase reforming of ethylene glycol over supported platinum catalysts

J.W. Shabaker, G.W. Huber, R.R. Davda, R.D. Cortright, and J.A. Dumesic *

Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706, USA

Received 4 February 2003; accepted 7 March 2003

Aqueous-phase reforming of 10 wt% ethylene glycol solutions was studied at temperatures of 483 and 498 K over Pt-black and Pt supported on TiO_2, Al_2O_3, carbon, SiO_2, SiO_2–Al_2O_3, ZrO_2, CeO_2, and ZnO. High activity for the production of H_2 by aqueous-phase reforming was observed over Pt-black and over Pt supported on TiO_2, carbon, and Al_2O_3 (i.e., turnover frequencies near 8–15 min^{-1} at 498 K); moderate catalytic activity for the production of hydrogen is demonstrated by Pt supported on SiO_2–Al_2O_3 and ZrO_2 (turnover frequencies near 5 min^{-1}); and lower catalytic activity is exhibited by Pt supported on CeO_2, ZnO, and SiO_2 (H_2 turnover frequencies lower than about 2 min^{-1}). Pt supported on Al_2O_3, and to a lesser extent ZrO_2, exhibits high selectivity for production of H_2 and CO_2 from aqueous-phase reforming of ethylene glycol. In contrast, Pt supported on carbon, TiO_2, SiO_2–Al_2O_3 and Pt-black produce measurable amounts of gaseous alkanes and liquid-phase compounds that would lead to alkanes at higher conversions (e.g., ethanol, acetic acid, acetaldehyde). The total rate of formation of these byproducts is about 1–3 min^{-1} at 498 K. An important bifunctional route for the formation of liquid-phase alkane-precursor compounds over less selective catalysts involves dehydration reactions on the catalyst support (or in the aqueous reforming solution) followed by hydrogenation reactions on Pt.

KEY WORDS ethylene glycol; reforming; hydrogen production; supported platinum catalysts; support effects.

1. Introduction

The production of hydrogen is a major issue in the implementation of hydrogen fuel cells as electrical power sources [1]. In this respect, we have recently reported that hydrogen can be produced with high selectivity in a low-temperature (e.g., 500 K), single-reactor process based on aqueous-phase reforming of light oxygenated hydrocarbons, such as methanol, ethylene glycol, and glycerol [2,3]. Ethylene glycol and glycerol are interesting feed molecules for the generation of hydrogen because they are non-volatile and convenient for transport and storage. Moreover, aqueous-phase reforming of larger, biomass-derived carbohydrates, such as glucose and sorbitol, provides a sustainable route for the production of hydrogen, in contrast to the production of hydrogen from non-renewable fossil fuels.

Ethylene glycol is a particularly relevant feed molecule for studies of aqueous-phase reforming reactions because it contains the same functionalities of larger polyols, including C–C, C–O, C–H, and O–H bonds, and also OH groups on adjacent carbon atoms. The catalytic activity and selectivity for aqueous-phase reforming of ethylene glycol are controlled by various processes, including the following stoichiometric reactions: C–C cleavage leading to CO and H_2,

$$C_2H_6O_2 \rightleftharpoons 2CO + 3H_2 \tag{1}$$

water–gas shift,

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{2}$$

dehydrogenation,

$$C_2H_6O_2 \rightleftharpoons C_2H_{6-x}O_2 + x/2H_2 \tag{3}$$

dehydration/hydrogenation,

$$C_2H_6O_2 + H_2 \rightleftharpoons C_2H_5OH + H_2O \tag{4}$$

and methanation,

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O. \tag{5}$$

In previous papers, we reported reaction kinetic studies of aqueous-phase reforming of ethylene glycol over a range of silica-supported metal catalysts [3] and detailed kinetics over Pt/Al_2O_3 catalysts [4]. In this work, we studied the effects of the support on the activity and selectivity of Pt-based catalysts for aqueous-phase reforming of ethylene glycol.

2. Experimental

2.1. Catalyst preparation

Platinum catalysts were prepared by incipient wetness impregnation of various supports with aqueous solutions

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* To whom correspondence should be addressed.
E-mail: dumesic@engr.wisc.edu

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Table 1
Catalyst characteristics and pretreatment conditions

Catalyst	Support supplier	Pt loading (wt%)	Calcination (K)	Reduction (K)	CO uptake (μmol/g)	CO/Pt ratio
Pt/SiO_2	Cabot, EH-5	0.75	533	523	16.1	0.42
Pt-black	Aldrich	99.90	none	348	27.9	0.01
Pt/ZrO_2	Alfa	0.69	533	523	30.2	0.85
Pt/C	Norit, SX 1 G	0.89	503 (He)	503	10.5	0.23
Pt/TiO_2	Degussa, P-25	0.85	533	523	16.8	0.39
$Pt/SiO_2–Al_2O_3$	Grace, MS-25	0.79	533	523	13.7	0.34
Pt/CeO_2 [a]	Aldrich	0.59	533	523	20.1	0.66
$Pt/\gamma–Al_2O_3$-sintered [b]	Grace, Catapal B	3.63	533	523	58.1	0.31
$Pt/\gamma–Al_2O_3$	Grace, Catapal B	0.59	533	523	24.5	0.81
Pt/ZnO	Alfa	0.88	533	523	4.49	0.10

[a] CeO_2 (as verified by XRD) was produced by oxidation of cerium(III) nitrate at 533 K for 2 h in flowing pure oxygen.

[b] Sintering was done by heating to 723 K over 30 min and holding for 12 h under 100 cm^3(STP)/min hydrogen saturated with water at 300 K.

of tetraamine platinum nitrate ($Pt(NH_3)_4(NO_3)_2$), followed by drying under air in an oven at 393 K for 12 h. Most catalysts were subsequently heated in a Pyrex cell in 10% O_2/He (300 cm^3(STP)/min) to 533 K (at 1.3 K/min) and held at this temperature for 2 h. Prior to collecting reaction kinetic data, each catalyst was reduced in flowing H_2 (100 cm^3(STP)/min) for 2 h at typically 523 K, after heating to this temperature at 0.5 K/min.

The number of surface Pt atoms on each catalyst was determined from the irreversible chemisorption of CO at 298 K, as described elsewhere [3]. Loadings of Pt on catalysts were determined by inductively coupled plasma atomic absorption spectrometry (ICP-AAS). The properties and treatment conditions of each catalyst are listed in table 1.

2.2. *Reaction kinetic measurements*

Reaction kinetic measurements for aqueous-phase reforming of ethylene glycol were conducted in an up-flow, packed-bed reactor as described previously [4]. Catalyst samples (0.2–2 g) were sieved to –120 mesh size (particle diameters $<63\,\mu$m) to alleviate transport limitations [4]. Aqueous feed solutions containing 10 wt% ethylene glycol were fed to the reactor at flowrates of 0.30 and 0.10 ml/min (WHSV of 3–30 and 9–90 h^{-1}, respectively) and reaction kinetic measurements were made at temperatures of 483 and 498 K and system pressures of 22.4 and 29.3 bar, respectively, (3 bar above the bubblepoint of the feed solution) over a 2-day period. Each reaction condition was maintained for at least 6 h to assure that steady state had been achieved, as determined by online gas chromatography. The liquid-phase effluent from the reactor was collected during reaction kinetic measurements at 498 K, and this liquid was analyzed via gas chromatography (FID detector), high-performance liquid chromatography (HPLC, RI and UV detectors), and total organic carbon (TOC) content. Total conversion of the ethylene glycol feed over the platinum catalysts varied from 1 to 20%, while blank runs with only quartz wool in the reactor gave no measurable products. Considerable catalyst deactivation (>20% decrease in activity over 24 h) was observed only for Pt/SiO_2 and Pt/CeO_2.

3. Results

Aqueous-phase reforming of 10 wt% ethylene glycol feed solutions produced primarily hydrogen and carbon dioxide at conversions <20%, although small amounts of liquid organic byproducts, gaseous alkanes, and carbon monoxide were also detected. Turnover frequencies for the production of hydrogen based on the irreversible CO chemisorption uptake are shown in figure 1 for various supported Pt catalysts and Pt-black. Since it has been shown elsewhere [4] that aqueous-phase reforming of methanol over Pt leads primarily to H_2 and CO_2, we have included in figure 1 the potential hydrogen that could be generated by complete reforming of the methanol byproduct. It is clear, however, that this additional amount of hydrogen that could be produced from the residual methanol is small compared with the total amount of hydrogen produced by the catalyst.

It can be seen that Pt/TiO_2 is the most active catalyst for the production of hydrogen from aqueous-phase reforming of ethylene glycol. In addition, unsupported Pt-black, as well as catalysts composed of Pt supported on Al_2O_3 and activated carbon, also show high activity. Moderate catalytic activity for production of hydrogen is demonstrated by Pt supported on $SiO_2–Al_2O_3$ and ZrO_2, whereas lower catalytic activity is exhibited by Pt supported on CeO_2, ZnO, and SiO_2. In general, the supported Pt catalysts (and Pt-black) can be ranked in the following order with respect to the rate of hydrogen production:

$$\mathrm{TiO_2} > \mathrm{Al_2O_3}, \text{carbon}, \text{Pt-black} > \mathrm{SiO_2–Al_2O_3}, \mathrm{ZrO_2} > \mathrm{CeO_2}, \mathrm{ZnO}, \mathrm{SiO_2}.$$

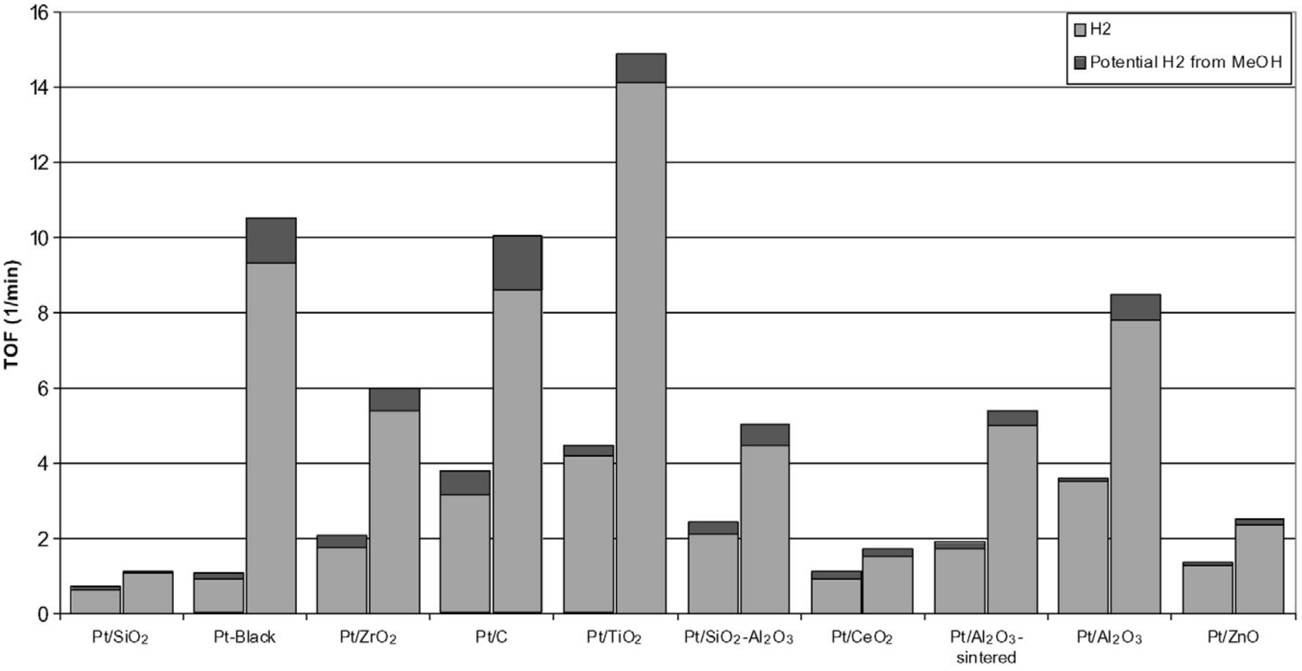

Figure 1. Hydrogen turnover frequencies for reforming of 10 wt% aqueous ethylene glycol at 483 (left columns) and 498 K (right columns) over supported Pt catalysts. The top portion of each bar is the amount of hydrogen that could be generated by total reforming of the methanol byproduct.

In addition to H_2 and CO_2, all catalysts produced smaller amounts of gaseous alkanes (methane and ethane) and liquid-phase products including alcohols (methanol and ethanol), organic acids (acetic and glycolic acids), and aldehydes (acetaldehyde and glycolaldehyde). Liquid products having a carbon atom that is not bonded to an oxygen atom, such as ethanol, acetic acid, and acetaldehyde, can be considered to be

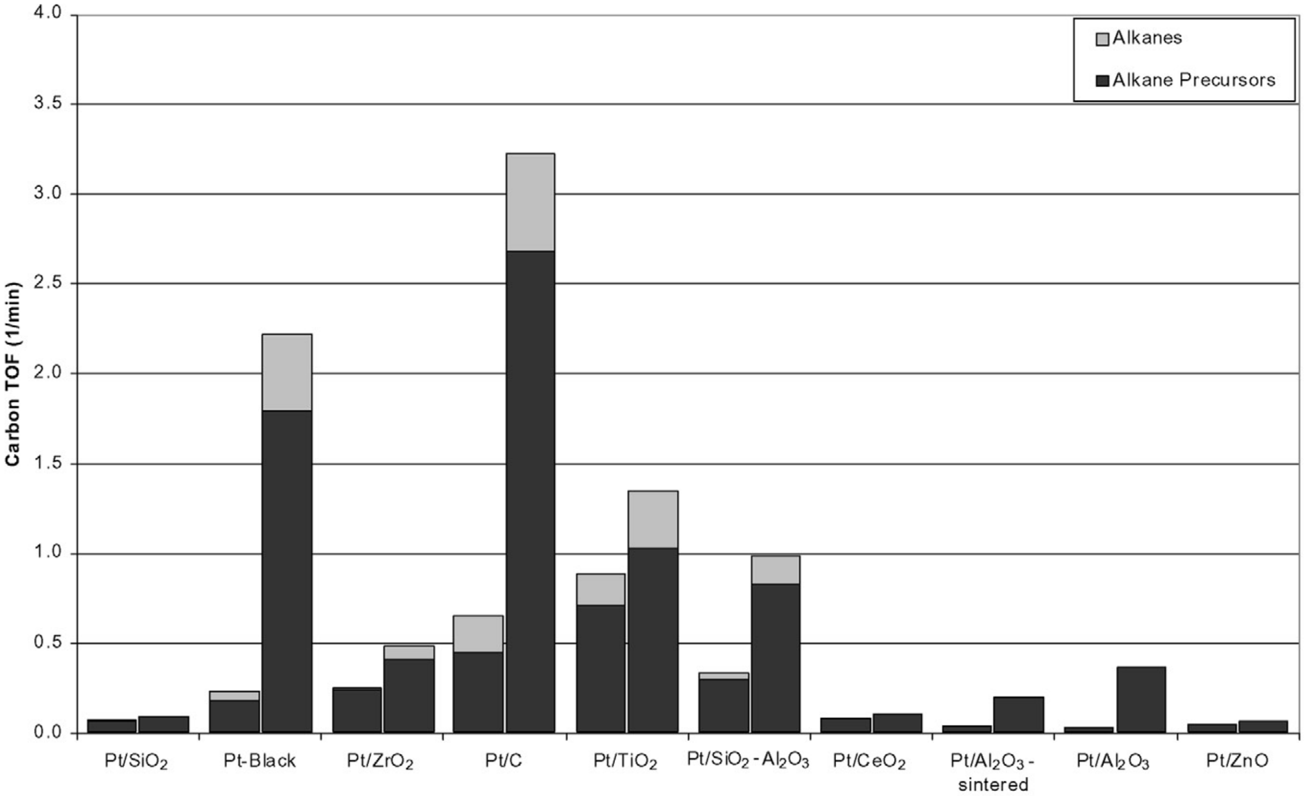

Figure 2. Production of alkanes for reforming of 10 wt% aqueous ethylene glycol at 483 (left columns) and 498 K (right columns) over supported Pt catalysts. The bottom portion of each column represents the carbon TOF for alkane precursors (acetaldehyde, ethanol, and acetic acid) and the top portion represents the carbon TOF for alkanes (methane and ethane).

precursors for the subsequent formation of gaseous alkanes, because these liquid species cannot be reformed to H_2 and CO_2 with high selectivity (>50%) [5]. In this respect, figure 2 shows the turnover frequencies for the formation of carbon in gaseous alkanes and in liquid-phase products that will subsequently lead to alkanes at higher conversions (i.e., alkane precursor compounds in the liquid phase). It can be seen that the rates of production of gaseous alkanes and liquid alkane-precursor compounds are dependent on the support. For example, platinum supported on activated carbon shows the highest rates of production of gaseous alkanes and liquid alkane-precursor compounds. These alkanes are not formed by gasification of the support because these products were not observed when the Pt/carbon catalyst was treated in flowing water at 498 K.

Comparison of figures 1 and 2 shows that Pt/Al_2O_3, and to a lesser extent Pt/ZrO_2 and Pt/TiO_2, are the most active and selective catalysts we tested for the production of H_2 from liquid-phase reforming of ethylene glycol. Interestingly, Pt/Al_2O_3, Pt/ZrO_2 and Pt/TiO_2 produce lower amounts of alkanes than unsupported Pt-black. The higher rate of alkane production over Pt-black does not appear to be caused by an effect of Pt particle size, since the rates of alkane production are similar on two Pt/Al_2O_3 catalysts with different Pt dispersions. In particular, the catalytic activity for production of hydrogen decreases by less than a factor of two and the selectivity remains nearly unchanged on alumina-supported catalysts when the CO/Pt ratio is decreased from 81 to 31%.

Figures 1 and 2 also show the effects of temperature on the rates of production of H_2, methanol, alkanes, and alkane-precursor compounds. The effective activation energy for the production of hydrogen over supported catalysts in this study varies from about 110 to 150 kJ/mol. We have reported elsewhere that the apparent activation for liquid-phase reforming of ethylene glycol over highly dispersed Pt/Al_2O_3 is about 100 kJ/mol. The variation in apparent activation energy for these different catalysts may be partially caused by differences in the Pt dispersions on these catalysts. In particular, the apparent activation observed over the highly dispersed Pt/Al_2O_3 catalyst (i.e., 125 kJ/mol) was lower than the activation energy measured over the more poorly dispersed Pt/Al_2O_3 catalyst (i.e., 145 kJ/mol). We also note that the rate of production of hydrogen depends on the selectivity of the catalyst, because the production of alkanes consumes hydrogen. Thus, changes in selectivity with temperature have some effect on the values of the apparent activation energies for the production of hydrogen.

Low concentrations of carbon monoxide (<500 ppm) were detected in the reactor effluent for each catalyst tested. Figure 3 shows the ratio of the partial pressures of CO_2, H_2, and CO expressed as a quotient Q_P $(= P_{CO_2}P_{H_2}/P_{CO})$, divided by the equilibrium constant for the water–gas shift reaction K_{WGS} $(= P_{CO_2}P_{H_2}/P_{CO}a_{H_2O})$. For the dilute solutions of the present study, the activity of liquid water is essentially equal to unity. The partial pressure of each product gas in the reactor can be found by assuming that the gas bubbles are at the system pressure and in equilibrium with water

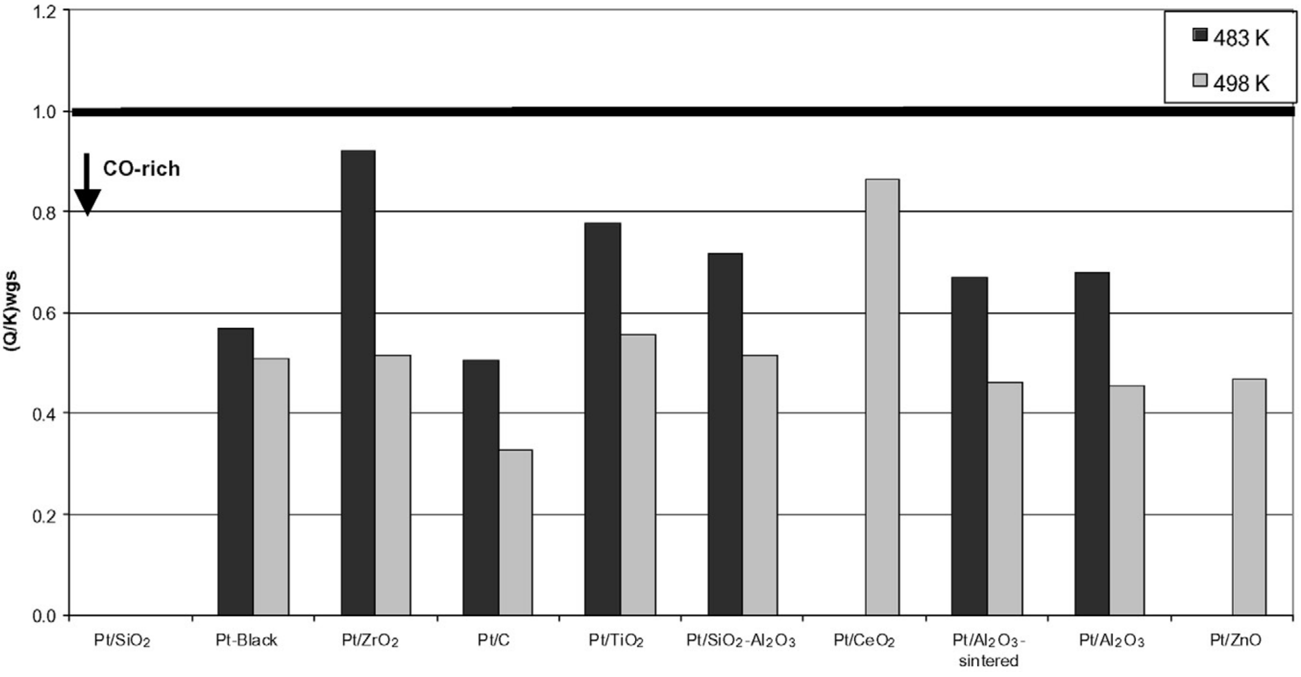

Figure 3. The ratio of the measured reaction quotient to the equilibrium constant for the forward water–gas shift reaction over Pt catalysts during aqueous reforming of 10 wt% ethylene glycol solutions at 483 and 498 K. Missing values were below the detection limits owing to low activity.

Table 2
Steady-state production rates, selectivities, carbon conversions and carbon balances for the highest conversion kinetics runs (498 K, 29.4 bar, 0.10 cm^3/min 10 wt% aqueous ethylene glycol feed solution (WHSV 3-30 h^{-1}))[a]

	H_2 TOF (min^{-1})	CH_4 TOF (min^{-1})	CO_2 TOF (min^{-1})	C_2H_6 TOF (min^{-1})	CO/CO_2 ratio	Liquid C total TOF (min^{-1})	Methanol (% liquid C)	Ethanol (% liquid C)	Acetaldehyde (% liquid C)	Acetic acid (% liquid C)	Glycolaldehyde (% liquid C)	Glycolic acid (% liquid C)	Conversion to gas (%)	Conversion to liquid (%)	C Balance, out/in (%)
Pt/SiO_2	0.70	0.00	0.33	0.00	0.0019	1.29	16.3	40.5	1.08	4.86	16.6	20.7	1.29	0.84	98
Pt-black	8.54	0.00	3.95	0.20	0.0019	8.34	9.3	46.5	2.18	6.00	4.14	31.9	8.34	1.94	101
Pt/ZrO_2	4.87	0.03	2.27	0.01	0.0018	9.34	38.8	46.2	1.48	6.55	4.88	2.14	9.34	1.98	103
Pt/C	7.52	0.51	4.30	0.07	0.0026	16.9	28.4	52.6	0.84	5.91	1.82	10.5	16.9	2.39	102
Pt/TiO_2	11.1	0.05	4.90	0.09	0.0016	16.3	13.4	62.7	0.75	20.1	3.04	0.01	16.3	4.21	103
Pt/SiO_2–Al_2O_3	4.60	0.05	2.06	0.06	0.0019	9.63	17.3	39.8	1.54	12.3	2.97	26.0	9.63	1.39	100
Pt/CeO_2	1.20	0.00	0.52	0.00	0.0019	1.88	15.0	21.1	1.75	11.5	18.8	32.0	1.88	0.44	97
Pt/Al_2O_3-sintered	3.90	0.00	1.91	0.00	0.0019	7.81	56.6	32.9	0.91	4.52	3.92	1.19	7.81	1.31	101
Pt/Al_2O_3	7.04	0.00	3.07	0.00	0.0018	12.4	57.4	29.2	0.78	8.71	3.68	0.26	12.4	1.38	102
Pt/ZnO	1.55	0.00	0.19	0.00	0.0042	0.55	1.98	0.40	0.12	3.96	5.98	87.6	0.55	2.15	97

[a] Liquid product selectivities are given as a percentage of the total liquid product carbon TOF.

vapor at the reaction temperature, as done previously [4]. The remaining partial pressure is divided among the dry gases according to the measured reaction selectivity.

As the ratio Q_p/K_{WGS} approaches unity, the water–gas shift reaction becomes quasi-equilibrated. It can be seen in figure 3 that the value of Q_p/K_{WGS} is >0.5 for most of the Pt-based catalysts in the present study, indicating that the water–gas shift reaction is nearly equilibrated for all supported catalysts. This observation suggests that the water–gas shift proceeds over the Pt metal without a major influence from the support. The presence of CeO_2, a common promoter of the water–gas shift reaction [6–8], appears to enhance that reaction, since the value of Q_p/K_{WGS} is ~0.9 over Pt/CeO_2.

More detailed analyzes of liquid-phase products were carried out for experiments conducted at lower space velocities at 498 K (i.e., liquid flow-rates of 0.1 cm^3/min), leading to ethylene glycol conversions of up to 20%. The rates of formation of liquid and gaseous products are listed in table 2. Catalysts that are active and selective for the production of hydrogen, such as Pt/Al_2O_3 and Pt/ZrO_2, make small amounts of liquid-phase products containing two carbon atoms, and they show increased selectivity toward the formation of methanol. In contrast, catalysts that are active for the production of hydrogen and gaseous alkanes, such as Pt-black, Pt/carbon, Pt/TiO_2 and Pt/SiO_2–Al_2O_3, produce larger amounts of two-carbon alkane precursors that may lead to further alkane formation at higher conversions. Catalysts that show low activity for production of hydrogen, such as Pt/ZnO, Pt/CeO_2, and Pt/SiO_2, lead to the formation of larger amounts of two-carbon aldehydes and acids, particularly glycolaldehyde and glycolic acid. The appearance of these compounds may be related to initial dehydrogenation of ethylene glycol before breaking of the C–C bond. The Pt/ZnO catalyst showed higher selectivity toward the formation of glycolic and acetic acids than all other catalysts. Carbon balances for all runs listed in table 2 were close to within 3%.

Table 3 lists equilibrium constants for several relevant hydration/dehydration and hydrogenation reactions. In addition, this table shows ratios calculated from the effluent liquid-phase concentrations and the hydrogen partial pressure, corresponding to reaction quotients

Table 3
Calculated equilibrium constants and measured reaction quotients for various liquid product reactions at 498 K

Reaction	K (498 K)	Q (498 K)	
		Range[a]	Pt/ZnO
$\text{Ethylene glycol}_{(l)} \rightleftharpoons \text{acetic acid}_{(l)} + H_{2(g)}$	3.73×10^9	0.0012–0.026	3.40×10^{-3}
$\text{Ethylene glycol}_{(l)} + H_{2(g)} \rightleftharpoons \text{ethanol}_{(l)} + H_2O_{(l)}$	6.86×10^7	$(0.30–8.63) \times 10^{-3}$	2.00×10^{-5}
$\text{Ethylene glycol}_{(l)} \rightleftharpoons \text{glycolaldehyde}_{(l)} + H_{2(g)}$		$(1.20–4.30) \times 10^{-3}$	5.10×10^{-3}
$\text{Ethylene glycol}_{(l)} \rightleftharpoons \text{acetaldehyde}_{(l)} + H_2O_{(l)}$	6.15×10^5	$(0.80–4.20) \times 10^{-4}$	3.00×10^5
$\text{Ethanol}_{(l)} + H_2O_{(l)} \rightleftharpoons \text{acetic acid}_{(l)} + 2H_{2(g)}$	54.4	0.81–5.27	155
$\text{Acetal} + H_2O_{(l)} \rightleftharpoons \text{acetic acid}_{(l)} + H_{2(g)}$	6.07×10^3	8.14–82.2	134
$\text{Ethanol}_{(l)} \rightleftharpoons \text{acetaldehyde}_{(l)} + H_{2(g)}$	8.96×10^{-3}	0.040–0.26	1.16
$CO_{2(g)} + 3H_{2(g)} \rightleftharpoons \text{methanol}_{(l)} + H_2O_{(l)}$	4.06×10^{-8}	$(0.0059–3.86) \times 10^{-6}$	4.72×10^{-9}

[a] The range of calculated reaction quotients for all catalysts *except* Pt/ZnO.

for the various hydration/dehydration and hydrogenation reactions. It can be seen that the reaction quotients are much smaller than the equilibrium constants for the production of ethanol, acetic acid, and aldehydes from ethylene glycol, indicating that these reactions are essentially irreversible. Reactions leading to conversions between ethanol, acetic acid and acetaldehyde may be reversible over the Pt-supported catalysts tested. The conversion of methanol to CO_2 and H_2 may also be reversible. Under the conditions of this study, the reaction effluents were rich in acetaldehyde with respect to the hydrogenation to ethanol or oxidation to acetic acid. Ethanol oxidation to acetic acid was only on the acid-rich side of equilibrium for Pt/ZnO.

4. Discussion

An effective catalyst for the production of hydrogen by liquid-phase reforming of ethylene glycol, such as Pt/Al_2O_3, must facilitate specific pathways toward reforming and water–gas shift. Initial dehydrogenation of ethylene glycol to form an adsorbed reaction intermediate species must be followed by rapid cleavage of the C–C bond, to avoid parallel reaction pathways leading to alkanes, such as pathways involving dehydration and hydrogenation reactions. This parallel selectivity route leads to C–O bond cleavage and the formation of alkanes through aldehyde and alcohol intermediates. After cleavage of the C–C bond, adsorbed C_1 species, such as formyl or methoxy species, may undergo further dehydrogenation to form strongly adsorbed carbon monoxide. Finally, the water–gas shift reaction may take place, leading to the formation of weakly adsorbed CO_2 species that can readily desorb from the Pt surface. In general, subsequent reaction pathways exist for the production of alkanes from methanation and Fischer–Tropsch reactions (leading to series selectivity challenges for the production of H_2 by liquid-phase reforming). Although alkanes are the thermodynamically favorable reaction products under the conditions of this study, Pt catalysts are not generally effective for methanation and Fisher–Tropsch reactions, and the series selectivity challenge for production of H_2 is not an issue in this study. A simple reaction network illustrating these selectivity trends is presented in figure 4.

In previous work [4], we showed that rate of hydrogen production is similar for liquid-phase reforming of methanol and ethylene glycol feed solutions over Pt/Al_2O_3. This observation suggests that adsorption/dehydrogenation steps may be kinetically significant and that C–C bond cleavage is relatively fast. Thus, while measurable amounts of dehydrogenated products, such as glycolaldehyde, are observed in the liquid at low conversions, the relatively fast rate of subsequent C–C bond cleavage leads to the formation of adsorbed C_1 species followed by production of hydrogen (moving to the right in figure 4), in contrast to the parallel formation of gaseous alkanes and liquid-phase alkane-precursor compounds (moving downward in figure 4). Steps following cleavage of the C–C bond appear to be reversible. In particular, the water–gas shift reaction is reversible, as indicated in figure 3 by values of ~0.5 for the reaction quotient divided by the equilibrium constant for this reaction. In addition, the conversion between methanol and CO_2 plus H_2 also appears to be reversible in view of the values in table 3 of the reaction quotient for this process.

The results of this study show that Pt/Al_2O_3 is an excellent catalyst for the production of H_2 and CO_2 from liquid-phase reforming of ethylene glycol. In this respect, Pt/Al_2O_3 shows high activity for conversion of

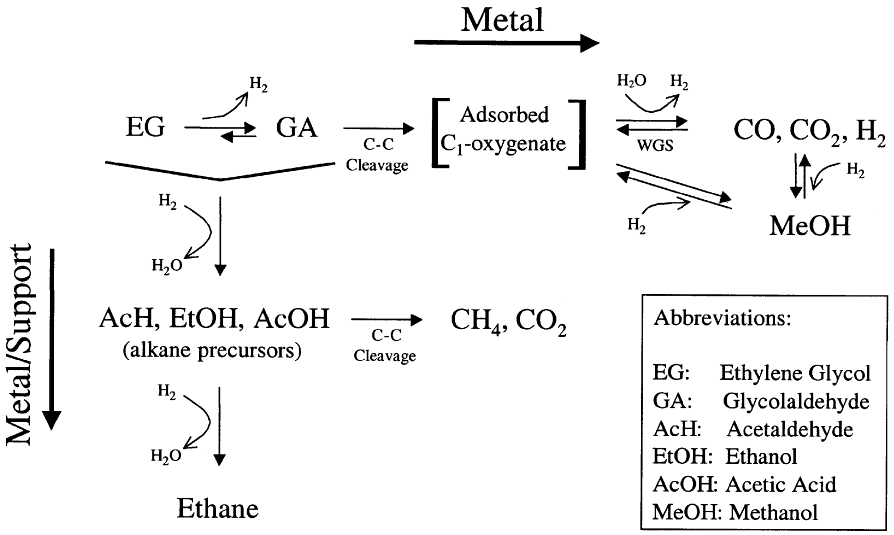

Figure 4. Schematic reaction network for aqueous-phase reforming of ethylene glycol near 500 K. Metal-catalyzed reactions move toward the right, while bifunctional metal/support reactions move downward.

ethylene glycol. The gaseous effluent from the Pt/Al_2O_3 catalyst consists primarily of H_2 and CO_2, and the predominant species formed in the liquid effluent is methanol, which can be subsequently converted with high selectivity to further amounts of H_2 and CO_2. Furthermore, this catalyst produces only small amounts of gaseous alkanes and liquid-phase alkane precursor species.

One of the most likely routes for the formation of liquid-phase alkane-precursor compounds, such as ethanol, involves dehydration of ethylene glycol followed by hydrogenation of the acetaldehyde intermediate. While both of these reactions may take place on Pt, it is also possible that the formation of ethanol may occur by a bifunctional pathway wherein dehydration is catalyzed by a Brønsted acid and hydrogenation takes place on Pt (i.e. the metal/support pathway in figure 4). The acid-catalyzed dehydration may take place on the surface of the support or in the aqueous solution. To test whether acid-catalyzed dehydration may, in fact, take place under the conditions of the present study, a blank run was carried out using a feed solution of 10 wt% ethylene glycol in 0.01 M HCl. This experiment showed that dehydration of ethylene glycol in the aqueous phase to form acetaldehyde occurs at a rate (5.4 μmol/min, or a TOF of $\sim 0.5\,\mathrm{min}^{-1}$ for typical catalytic runs) that is sufficient to contribute to a bifunctional pathway for the formation of liquid-phase alkane-precursor compounds during the aqueous-phase reforming of ethylene glycol. As supported by table 3, acetaldehyde can then be hydrogenated over the Pt metal to form ethanol. Thus, supports that can catalyze the dehydration of ethylene glycol may promote the formation of alkane precursor compounds.

After compounds such as ethanol and acetic acid have been formed from ethylene glycol, it is likely that these compounds will subsequently undergo cleavage of the C–C bond, such that one of the carbon atoms leads to methane and the other leads eventually to CO_2. For example, in the gas phase, ethanol and acetic acid are known to be reactive over Pt catalysts [5], and hydrogenolysis of ethanol and acetic acid over Pt to lead to methane and carbon monoxide (or CO_2). Conversion between ethanol and acetic acid may also take place (see table 3) in the presence of hydrogen and water on Pt surfaces.

The initial dehydrogenation of ethylene glycol to form glycolaldehyde can lead to production of a range of byproducts, in addition to the desirable C–C bond cleavage of this intermediate eventually to form H_2 and CO_2. One likely pathway, which has very favorable reaction thermodynamics, is the rearrangement of glycolaldehyde to form acetic acid. In addition, glycolaldehyde can be converted to glycolic acid, analogous to the conversion of acetataldehyde to acetic acid. Cleavage of the C–C bond in glycolic acid may lead to methanol and CO_2 over some catalysts, and this route allows for the direct formation of CO_2 without first passing through an adsorbed CO species followed by subsequent water–gas shift. This reaction pathway may possibly occur over Pt/ZnO since this catalyst appears to make significant amounts of glycolaldehyde and glycolic acid (see table 2). The production of acids over ZnO-supported catalysts has precedence in the literature. Takezawa and Iwasa detected formic acid intermediates in methanol decomposition over Group VIII metals, whereas Cu/ZnO showed no acid byproducts [9].

With the exception of Pt/SiO_2, all catalysts in the present study exhibited stable performance for the aqueous-phase reforming of ethylene glycol for the typical times on-stream employed (e.g., several days). However, it is possible that the physical stability of the catalyst support may be a concern for long periods of time in the high-temperature, perhaps slightly acidic, aqueous reaction environment. Thus, catalyst supports that dissolve or degrade in the aqueous reforming solution, such as SiO_2 [10] and CeO_2 [11], are unsuitable for long-term use [12]. In fact, traces of Si and Ce were found by ICP-AAS analysis in the reactor effluent from the Pt/SiO_2 and Pt/CeO_2 catalysts, respectively, after only 6 h on-stream at 483 K. As predicted in the literature [13], Al_2O_3 shows distinctly better hydrothermal stability against dissolution than SiO_2 because less than 1 ppm of Al was detected in the reactor effluent after 24 h on stream at 498 K. Catalyst supports, such as Al_2O_3, ZrO_2, and TiO_2, are also known to degrade over a period of weeks under high-temperature hydrothermal treatment through sintering (pore degradation) and phase transformation from high surface area metastable phases (i.e., gamma, anatase, and tetragonal, respectively) to low surface area phases (alpha, rutile, and monoclinic, respectively) [14]. Addition of dopants, such as La [15], PO_4 [16] (for Al_2O_3) and Y [15] (for TiO_2 and ZrO_2), has been shown to inhibit phase transition and sintering processes, but has unknown effects on the reforming chemistry that will need to be explored. Among the catalysts tested in this study, the order of decreasing selectivity for hydrogen production from the corresponding supported Pt catalysts would be $Pt/Al_2O_3 > Pt/ZrO_2 > Pt/TiO_2$. Despite a lower selectivity for hydrogen production, Pt/C may also show promising hydrothermal stability due to the hydrophobic nature of the support.

5. Conclusions

Platinum catalysts show high activity and selectivity for the production of hydrogen by aqueous reforming of ethylene glycol feedstocks. Turnover frequencies for the production of hydrogen are highest over Pt-black and Pt supported on TiO_2, carbon, and Al_2O_3 (i.e., 8–15 min^{-1} at 498 K for 10 wt% ethylene glycol). Moderate catalytic activity for production of hydrogen is demonstrated by Pt supported on SiO_2–Al_2O_3 and ZrO_2 (near 5 min^{-1}), and lower turnover frequencies are exhibited by Pt supported on CeO_2, ZnO, and SiO_2 (lower than about 2 min^{-1}). Catalysts consisting of Pt supported on carbon, TiO_2, SiO_2–Al_2O_3, and Pt-black also lead to the production (about 1–3 min^{-1}) of gaseous alkanes and liquid-phase compounds that would lead to alkanes at higher conversions (e.g., ethanol, acetic acid, acetaldehyde). Thus, we conclude that Pt/Al_2O_3, and to a lesser extent Pt/ZrO_2 and Pt/TiO_2, are active and selective catalysts for the production of H_2 from liquid-phase reforming of ethylene glycol.

Selectivity for the production of hydrogen versus alkanes appears to be controlled by competition between C–C and C–O bond scission reactions, i.e., with cleavage of the C–C bond leading to subsequent production of H_2 and CO_2, and cleavage of the C–O bond leading eventually to formation of alkanes. Cleavage of the C–C bond appears to be an irreversible process, whereas steps following cleavage of the C–C bond appear to be reversible, i.e., water–gas shift and the conversion between methanol and CO_2 plus H_2. An important bifunctional route for the formation of liquid-phase alkane-precursor compounds over less selective catalysts involves dehydration reactions on the catalyst support (or in the aqueous reforming solution) followed by hydrogenation reactions on Pt.

Future work on catalyst development for aqueous reforming will focus on alloy catalysts, with the addition of modifiers to inhibit C–O bond cleavage versus C–C bond cleavage, and with the addition of dopants to inhibit possible degradation of the support during long periods of time on-stream in the high-temperature, perhaps slightly acidic, aqueous reaction environment.

Acknowledgments

This work was supported by the US Department of Energy (DOE), Office of Basic Energy Sciences, Chemical Sciences Division. We also acknowledge funding from the Energy Center of Wisconsin and the University of Wisconsin Office of University–Industrial Relations.

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