



Review:

Progress in the aqueous-phase reforming of different biomass-derived alcohols for hydrogen production*

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Abstract: Hydrogen as a clean, efficient, and sustainable energy has attracted considerable attention in recent years. Hydrogen production from aqueous-phase reforming (APR) of biomass-derived alcohols is preferable to other methods because of its wide renewable resource, mild reaction conditions, and low processing cost. In this paper, the progress in the APR process of different biomass-derived alcohols for H₂ production is reviewed, and the reaction mechanisms are briefly discussed for different catalysts. Pt-based catalysts exhibit high H₂ selectivity but low conversion of the alcohols. Ni-based catalysts exhibit high activity and conversion but low H₂ selectivity and yield.

Key words: Biomass, Alcohols, Hydrogen production, Aqueous-phase reforming (APR), Reaction mechanism, Catalysts
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1 Introduction

Because of increasing fossil fuel consumption and its associated serious environmental pollution, hydrogen, a clean, quiet, and highly efficient energy with a flexible number of applications, including power generation, calorification, and power automobiles, has received wide attention. Hydrogen can be obtained through fossil fuels by various techniques. Currently, almost 97% of hydrogen is made by reforming fossil fuels, including natural gas, oil, coal, and naphtha, which will lead to a high carbon footprint. Further, hydrogen production by means of a

water electrolysis method usually results in immense power consumption.

Hydrogen can also be produced from renewable sources such as solar energy, wind energy, hydro-power, nuclear energy, and biomass. In contrast, some unique characteristics of biomass, including large storage capacity, low price, great potential for commercialization, carbon neutral, and mild reaction condition, make it feasible for hydrogen production. However, current methods for hydrogen production require immense power consumption, high temperature and pressure. Aqueous-phase reforming (APR), proposed by Dumesic (Cortright *et al.*, 2002), generated hydrogen and alkanes from biomass-derived resources in liquid water. The major advantages of the APR process include three aspects. First, this process is applicable for either wet or water soluble feedstock. Second, owing to the superiority of the water-gas shift (WGS) reaction, the production of CO, which is a major byproduct, can be reduced effectively (Davda *et al.*, 2005). Third, compared with conventional alkane stream reforming processes, this

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reforming process is performed at a relatively low temperature (i.e., 500 K) and elevated pressure (i.e., 2.5 MPa). Notably, these conditions preclude the evaporation of water. To date, the model compounds that have been studied include methanol, ethanol, ethylene glycol, glycerol, butanol, sorbitol, mannitol, and xylitol. Research on the catalysts used in the APR process is also an active area.

In this paper, the research progress of the APR of alcohols for hydrogen production is reviewed. We also discuss the use of different alcohols as substrates for these reactions. Additionally, perspectives to the future for hydrogen production are briefly examined.

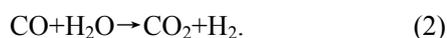
2 Mechanism of the aqueous-phase reforming of alcohols

In 2002, Dumesic (Cortright *et al.*, 2002) proposed catalytic bio-conversion and bio-refinery methods to obtain hydrogen, thus making a breakthrough in hydrogen generation. Hydrogen was produced through a direct biomass reforming reaction at 550 K by using aqueous-phase sugar and alcohols as the raw materials. The entire reaction is performed in the aqueous phase whereby cellulose and hemicellulose are reduced to sugar via hydrolyzation with the assistance of heat and acid. Then, the sugar is used as a workable feedstock in biological fermentation processes. Thus, an aqueous-phase biomass reforming process such as this could result in a higher biomass utilization rate compared to physical, chemical or biological methods (Cortright *et al.*, 2002; Huber *et al.*, 2003; 2006; Davda *et al.*, 2005).

For example, the alcohols can be reformed to produce H₂ and CO₂ through the following reaction (Huber *et al.*, 2004):



CO and H₂ can be formed by breaking C-C bonds. Then, CO will react with H₂O to produce CO₂ and H₂ by WGS reaction:



Some secondary reactions will also occur when the formation of H₂ and CO₂ by the APR method is

performed at relatively low temperatures. For example, CO₂ and H₂ will be converted to methane at 500 K through the methanation and Fischer-Tropsch reactions (Vannice, 1977; Kellner and Bell, 1981; Dixit and Tavlarides, 1983; Iglesia *et al.*, 1992):

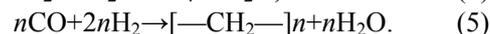
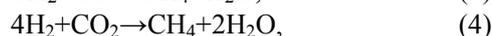


Fig. 1 shows an outline of the APR process, the H₂ formation paths and the production of alkanes from alcohols. First, the alcohols transform into the adsorbed intermediates on the catalyst surface after dehydrogenation steps, followed by cleavage of the C-C or C-O bonds. Second, the optimal situation is that cleavage of the C-C bonds is followed by the WGS reaction, which will produce H₂. However, the scission of C-O bonds will possibly make organic acids, which are stable and cannot be reformed easily. Moreover, the produced organic acids can corrode the equipment and inactivate the catalysts (Davda *et al.*, 2003). Therefore, effective catalysts for the APR process should demonstrate high activity in cleaving C-C bonds, high capacity to promote the subsequent WGS reaction, and low activity in the methanation reactions. The present studies on the APR of biomass-derived alcohols for hydrogen production focus on promoting the catalytic activity.

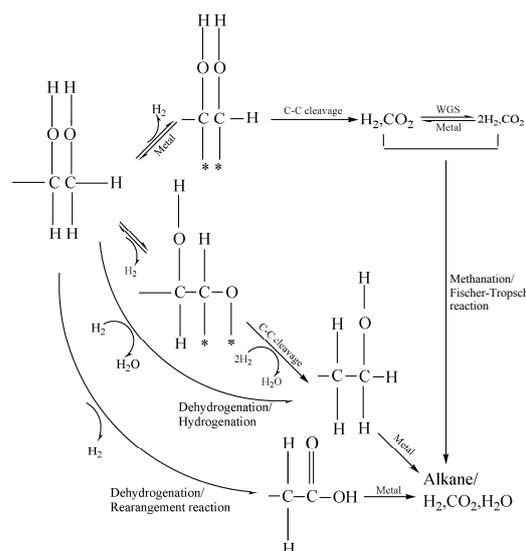


Fig. 1 Reaction pathways for production of H₂ by an aqueous-phase reforming process

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3 Hydrogen production from the aqueous-phase reforming of biomass-derived alcohols

Many biomass-derived alcohols, such as methanol, sorbitol, glycerol, butanol, and ethylene glycol, have been used in APR process for H₂ production (Cortright *et al.*, 2002; Davda *et al.*, 2005). Different catalysts were used in these systems. The performances of noble metal catalysts, non-noble metal catalysts, and different supports strongly affected the efficacy of these catalysts. More specifically, the chemical state and load of the catalyst are the primary factors that influence the activity of these catalysts.

3.1 Aqueous-phase reforming of ethylene glycol

In early studies, ethylene glycol was mainly a feed molecule for the APR process. It possesses the typical structure of alcohols including C-C, C-O, C-H, O-H bonds, and OH groups. The production of CO is favorable, and can undergo a methanation or Fischer-Tropsch synthesis to produce alkanes. Alternatively, ethylene glycol can be converted to H₂ and CO₂ by the WGS reaction, or even react with H₂ to form methanol. Ethylene glycol can also generate acetic acid by dehydrogenation or isomerization, or via an acetaldehyde intermediate (Fig. 2).

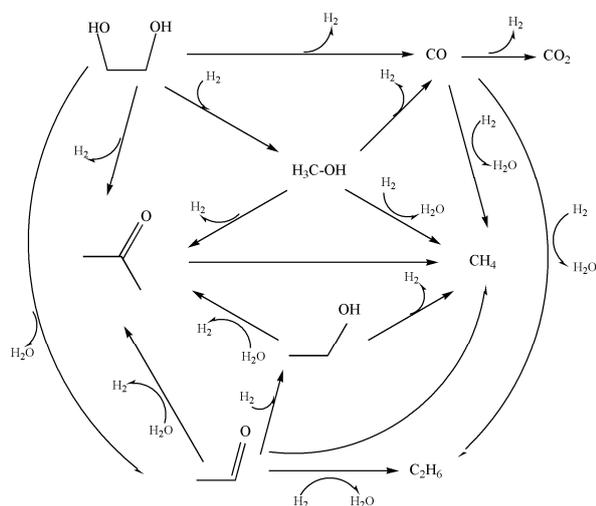


Fig. 2 Reaction pathways for ethylene glycol reforming (Reprinted from (Shabaker and Dumesic, 2004), Copyright 2004, with permission from American Chemical Society)

Different types of catalysts were applied in the APR of ethylene glycol, including noble metal-based catalysts, such as Pt, Pd, Rh, Ru, and Ir (Liu *et al.*,

2008; Skoplyak *et al.*, 2009; Kim *et al.*, 2011; 2012a), Sn modified Raney Ni (Huber *et al.*, 2003; Shabaker and Dumesic, 2004; Shabaker *et al.*, 2004; 2005), NiMgAl layered double hydroxide catalysts, Ni/Sn/Al hydrotalcite derived catalysts (Pan *et al.*, 2012), rapidly quenched skeletal Ni (Xie *et al.*, 2006), non-pyrophoric Ni catalysts (Zhu *et al.*, 2008), and Co/ZnO catalysts (Chu *et al.*, 2011).

3.1.1 Noble metal catalysts

Davda *et al.* (2003) tested the catalytic activity of the catalysts Ni, Pd, Pt, Ru, Rh, and Ir supported on silica for the APR of ethylene glycol, and found that the activity decreased in the following order: Pt~Ni>Ru>Rh>Pd>Ir. All of the H₂ selectivity on Rh, Ru, and Ni/SiO₂ was low, whereas the alkane selectivity was high. In contrast, it was found that Pt and Pd catalysts supported on silica presented higher H₂ selectivity and lower alkane selectivity.

Among all of the noble metal utilized in the APR, Pt consistently demonstrates higher hydrogen selectivity. Kim *et al.* (2011) examined a series of Pt-based catalysts supported on ordered mesoporous carbon (CMK-3) with different Pt loadings. The catalytic performance of these materials with different supported catalysts for the APR reaction is shown in Table 1. The optimal Pt loading with the highest hydrogen production rates was 7% (in weight, unless otherwise stated) for CMK-3, which results from the high dispersion of Pt nanoparticles, good hydrothermal stability, and a 3D highly opened mesoporous structure. The catalytic performance would be enhanced by a Pt catalyst supported on a hollow-type ordered mesoporous carbon (OMC) with a 3D pore structure because of the synergistic effect between the low amount of metal sintering during the reaction process and the favorable transport and diffusion of the reactants and products (Kim *et al.*, 2012b; Jeong *et al.*, 2014).

A support improves the metal dispersion of a supported catalyst. The promoter is also very important. In the APR reaction, not only the nature of the support has an influence on the activity but also the distribution of the products on the surface affects the activity. Kim *et al.* (2011; 2012a) examined the APR catalytic activity over monometallic Pt catalysts and bimetallic Pt-Mn catalysts on different supports. The hydrogen production rates among

these catalysts followed the order: Pt/CMK-3>Pt/activated carbon (AC)>Pt/ γ -Al₂O₃>Pt/Catapal B. Relative to oxide-based catalysts, the stability of carbon-based catalysts under severe hydrothermal reactions leads to superior hydrogen production than alumina-based supports. These data suggest that the catalytic activity of APR is affected greatly by the structural properties of the supports. Kim *et al.* (2012c) made similar conclusions. The activity of supported catalysts followed the order: CMK-3>AC>SiO₂>Al₂O₃. The reaction data of the Pt-based catalysts on different supports are listed in Table 2. Both carbon-based catalysts (i.e., CMK-3 and AC) showed higher H₂ yield than the Al₂O₃ and SiO₂

catalysts, which is because of the high surface area and thermal stability of the carbon-based catalysts relative to the oxide-based catalysts. In addition, a higher H₂ yield and ethylene glycol conversion on the carbon-based catalysts indicated that the metal oxide supports sintered during the APR reaction because of their weak hydrothermal stability at high temperatures. Finally, for the Al₂O₃ support, *in situ* generation of the acid sites formed the H₂ spillover, and the high acidity of Al₂O₃ led to low H₂ formation and high alkane selectivity. Additionally, Liu *et al.* (2008) synthesized a Pt-based Fe-Cr catalyst. The X-ray diffraction (XRD) results demonstrated that the addition of Cr could promote the phase

Table 1 Catalytic performance of APR over different Pt-based catalysts

Catalyst	Loading (%)	Conversion (%)	H ₂ yield (%)	Alkane selectivity (%)	Gas products (%)				Reference
					H ₂	CO ₂	CO	Alkanes	
Pt/CMK-3	1	32.5	24.9	5.0	65.8	32.7	ND ^a	1.5	Kim <i>et al.</i> , 2011 ^b
Pt/CMK-3	2	41.8	32.2	3.3	65.9	33.1	ND ^a	1.0	
Pt/CMK-3	5	59.1	43.9	4.3	66.1	32.5	ND ^a	1.4	
Pt/CMK-3	7	75.8	56.7	6.8	65.4	32.6	ND ^a	2.0	
Pt/CMK-3	10	79.4	57.5	6.5	64.7	33.3	ND ^a	2.0	
Pt/CMK-3	7	69.8	72.1	7.1	71.0	27.6	ND ^a	1.5	Kim <i>et al.</i> , 2012b ^b
Pt/CMK-5	7	79.5	77.0	5.7	71.2	27.3	ND ^a	1.4	
Pt/CMK-8	7	85.8	84.7	4.7	71.4	27.4	ND ^a	1.2	
Pt/CMK-9	7	89.2	94.2	4.4	72.1	27.0	ND ^a	0.9	
Pt/CMK-3-MCM	7	78.6	60.4	16.1	66.2	28.9	ND ^a	4.9	Jeong <i>et al.</i> , 2014 ^b
Pt/CMK-3-MCN-R	7	84.7	71.7	6.1	68.1	30.2	ND ^a	1.7	
Pt/CMK-5-MCM	7	83.0	76.8	5.3	70.0	28.7	ND ^a	1.4	
Pt/CMK-5-MCN-R	7	88.0	86.3	5.9	71.2	27.3	ND ^a	1.3	

^a ND: not detected (below the gas chromatography (GC) detection limit); ^b Reaction conditions: 10% ethylene glycol, 523 K, 4.56 MPa, weight hourly space velocity (WHSV) of 2.0 h⁻¹, 24 h

Table 2 Catalytic performance of different supported Pt-based catalysts in the APR of 10% ethylene glycol

Catalyst	Loading (%)	Conversion (%)	H ₂ production rate (cm ³ /(g _{cat} ·min))	H ₂ yield (%)	Alkanes selectivity (%)	Reference
Pt/CMK-3	7	75.8	37.8	56.7	6.8	Kim <i>et al.</i> , 2011 ^a
Pt/AC	7	38.1	18.0	27.0	5.8	
Pt/ γ -Al ₂ O ₃	7	38.6	14.3	21.5	10.8	
Pt/Catapal B	7	25.4	10.1	15.1	7.4	
Pt-Mn/CMK-3	1	39.7	26.8	40.2	2.9	Kim <i>et al.</i> , 2012a ^a
Pt-Mn/AC	1	34.2	22.7	34.1	5.5	
Pt-Mn/ γ -Al ₂ O ₃	1	27.7	19.6	29.4	3.8	
Pt-Re/CMK-3	3	89.3	36.6	55.0	26.4	Kim <i>et al.</i> , 2012c ^a
Pt-Re/AC	3	80.0	30.4	45.7	29.2	
Pt-Re/Al ₂ O ₃	3	43.8	22.4	33.7	12.9	
Pt-Re/SiO ₂	3	63.1	25.9	38.9	25.2	

^a Reaction conditions: 523 K, 4.56 MPa, WHSV of 2.0 h⁻¹

composition of iron oxide, and the formation of amorphous Cr oxides improved the BET surface area of Fe-Cr mixed oxides.

The addition of other metals to Pt-based catalysts is growing interest. The cost of the catalyst might be reduced while maintaining the catalytic activity. As in the case of Kim *et al.* (2012a), a series of metal were doped on Pt-based catalysts. The activities of these catalysts are shown in Table 3. The rate of hydrogen production and hydrogen yield decreased in the following order: Pt-Mn>Pt-Fe>Pt-Re>Pt>Pt-Cs>Pt-Ba>Pt-Ga>Pt-Mo>Pt-Ag. The addition of Mn to a Pt-based catalyst had a higher catalytic activity than the Pt/CMK-3 catalyst. This indicated that Mn could increase the reduction behavior and consequent alloy formation that was responsible for the enhancement of the catalytic activity in the APR, especially for the hydrogen production rate. Bai *et al.* (2006) utilized the Pt-Ce/ γ -Al₂O₃

and Pt-Mg/ γ -Al₂O₃ catalysts in the APR of ethylene glycol. It was suggested that both bimetallic catalysts showed higher catalytic activities than Pt/ γ -Al₂O₃, and the conversion of ethylene glycol was increased from 72.3% to 100% with an almost 100% H₂ selectivity. The presence of Ce increased the dispersion of Pt on the surface of γ -Al₂O₃ and improved the adsorption cracking of ethylene glycol on Pt and the WGS reaction. At the same time, the presence of Mg could neutralize the acidity of γ -Al₂O₃, promote the dispersion of PtAl₆²⁻, and inhibit the dehydration of ethylene glycol. de Vlieger *et al.* (2012) found that the formation of acetic acid could be suppressed by Pt-Ni catalyst during the APR of ethylene glycol, and the H₂ selectivity and catalyst lifetime would be increased. Huber *et al.* (2006) suggested that alloying Pt with either Ni, Co or Fe could promote the activity for hydrogen production by decreasing the heats of adsorption of CO and hydrogen, which

Table 3 Effect of doped metals on the catalytic activity of ethylene glycol APR

Catalyst	Proportion of Pt-M	Conversion (%)	H ₂ production rate (cm ³ /(g _{cat} ·min))	Alkanes selectivity (%)	Reference
Pt-Re/CMK-3	1:1	44.2	19.9	19.8	Kim <i>et al.</i> , 2012a ^a
Pt-Mn/CMK-3	1:1	39.7	26.8	2.9	
Pt-Fe/CMK-3	1:1	30.4	22.1	2.0	
Pt-Cs/CMK-3	1:1	20.1	12.5	1.5	
Pt-Ba/CMK-3	1:1	15.3	10.6	2.7	
Pt-Ga/CMK-3	1:1	5.7	5.5	3.85	
Pt-Ag/CMK-3	1:1	0.2	0.3	0	
Pt-Mo/CMK-3	1:1	5.8	3.1	18.9	
Pt	1:0	25.4	17.7	4.5	Bai <i>et al.</i> , 2006 ^b
Pt-Mg/ γ -Al ₂ O ₃	1.79	100	1.2	–	
Pt-Ce/ γ -Al ₂ O ₃	1.82	100	1.3	–	
Pt-Ni/ γ -Al ₂ O ₃	3.29	80	–	–	Vlieger <i>et al.</i> , 2012 ^c
Pt-Ni/ γ -Al ₂ O ₃	1	3.9	0.60	0.0	Huber <i>et al.</i> , 2006 ^d
Pt-Ni/ γ -Al ₂ O ₃	0.2	2.3	0.07	0.0	
Pt-Ni/ γ -Al ₂ O ₃	0.125	3.0	0.84	1.2	
Pt-Co/ γ -Al ₂ O ₃	0.2	3.8	0.50	0.0	
Pt-Co/ γ -Al ₂ O ₃	0.11	3.6	0.06	0.0	
Pt-Ni/ γ -Al ₂ O ₃	1	5.9	0.96	0.0	
Pt-Ni/ γ -Al ₂ O ₃	0.2	3.6	1.12	0.9	
Pt-Ni/ γ -Al ₂ O ₃	0.125	3.5	1.01	2.0	
Pt-Co/ γ -Al ₂ O ₃	0.2	8.4	0.93	0.5	
Pt-Fe/ γ -Al ₂ O ₃	0.11	26.9	0.03	0.0	
Pt-Fe/ γ -Al ₂ O ₃	0.11	48.1	0.06	1.1	
Pt-Re/CMK-3	1	89.3	36.6	–	Kim <i>et al.</i> , 2012c ^e

Reaction conditions: ^a 10% ethylene glycol, 523 K, 4.56 MPa; ^b 10% ethylene glycol, 498 K, 2.58 MPa; ^c 1% ethylene glycol, 458 K, 2.0 MPa; ^d 10% ethylene glycol, 483 K, 2.54 MPa; ^e 10% ethylene glycol, 523 K, 4.58 MPa

would increase the fraction of the surface available for its reaction with ethylene glycol. Dispersion of Pt on the supports could be improved by the addition of Re or Co (Wang *et al.*, 2009; Kim *et al.*, 2012c). The Pt-Re/CMK-3 catalyst has much higher activity on the APR of ethylene glycol. The Pt-Co/single-walled carbon nanotube bimetallic catalyst obtained by sequential impregnation exhibited a core-shell structure with Co as the core and a Pt-Co alloy phase as the shell, where Pt was atomically dispersed and Co acted as a co-catalyst or promoter.

3.1.2 Non-noble metal catalysts

Although noble metal-based catalysts such as Pt/ γ -Al₂O₃ demonstrated high catalytic activity and H₂ selectivity, their expense limits their technological viability. Therefore, numerous studies have been performed to search for inexpensive materials with good catalytic characteristics for the APR process.

Chu *et al.* (2011) prepared Co/ZnO catalysts with four different Co/Zn molar ratios by the co-precipitation method. The APR experiments showed that the catalyst activity and the H₂ selectivity increased with the amount of ZnO, and there was much less CO in the gas products. Moreover, the bimetallic catalysts showed high catalytic activity in the APR process.

Chu *et al.* (2009) reported that the addition of Sn had a remarkable effect not only on the chemical composition, texture, and structure of the catalyst but also on its active site. The Sn modified catalyst had a higher hydrogen production rate and selectivity, and the formation of alkanes was substantially suppressed. Pan *et al.* (2012) proposed that Sn existed in a SnO phase on the Ni/Sn/Al hydrotalcite catalyst synthesized by a co-precipitation method. Ni₂₀SnAl₇-hydrotalcites showed a good H₂ selectivity of nearly 100% and a good catalytic stability over 120 h.

The main research was focused on the noble catalyst with high H₂ selectivity and high ethylene glycol conversion. Because ethylene glycol is more difficult to convert and the APR process requires a water-resistance catalyst, most oxide-based materials cannot function properly when H₂O is at high temperatures. Ethanol is easier to convert under the same conditions. Thus, the application of bio-ethanol has become more important in biomass applications. Consequently, research into ethanol APR has increased in importance.

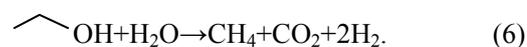
3.2 Aqueous-phase reforming of ethanol for hydrogen production

Bio-ethanol is widely used as the substrate in the production of hydrogen because it is a direct product from the fermentation process of the biomass. In addition, bio-ethanol has high hydrogen content and is nontoxic. The CO₂ generated during the hydrogen production process can be consumed by the photosynthesis of the biomass growth, which is formed in a CO₂ cycle.

There are many methods available for hydrogen production by using ethanol as the substrate, including steam reforming, oxidative reforming, and auto-thermal catalytic reforming. However, these methods possess many drawbacks, such as high reaction temperatures (573–873 K), incomplete WGS reactions, high CO concentrations in the gas products (5%–20%), complicated equipment for H₂ purification, low ethanol conversion, H₂ selectivity, and alkylation side reactions. For these reasons, APR of ethanol for hydrogen production has been investigated because of its modest and straightforward reaction conditions.

3.2.1 Noble metal catalysts

In the APR of ethanol, a noble metal, such as Pt, is always used as the catalyst. Tokarev *et al.* (2010) utilized a Pt/Al₂O₃ catalyst in the APR process of bio-ethanol to produce hydrogen, and they compared its efficiency by using glycerol and sorbitol as the substrates. The results showed that ethanol conversion could reach 98.3% and that methane will be formed from the ethanol transformation.



Only ethanol and acetic acid were detected in the liquid products. When there was glycerol or sorbitol in the substrate, similar amounts of acetic acid and acetaldehyde were present, though they were lower than the quantities present in the reaction that used only ethanol as the substrate. The conversion of ethanol with APR was high, but the hydrogen yield decreased when there was either a fraction or full measures of glycerol and sorbitol in the substrate. The amounts of acetic acid and acetaldehyde were similar, which are much lower than the ethanol concentration present in glycerol or sorbitol. This is

because of the inhibition of ethanol for converting aldehydes to hemiacetals and acetals. Consequently, aldehydes could not be concentrated to form larger by-products.

3.2.2 Non-noble metal catalysts

The industrial application of noble metal catalysts was limited by its high cost. For this reason, the development of nickel catalysts has attracted more attention in recent years. Roy *et al.* (2010) prepared a Ni/Al₂O₃ catalyst by a solution combustion synthesis method, and modified its surface using a non-thermal radio frequency (RF) plasma. Liu *et al.* (2002) found that the surface modification could reduce the energy requirements and shorten the preparation time without altering the bulk properties of the catalyst. In addition, it has been reported that such modifications could: i) avoid the particles sintering, ii) increase the activity of the catalyst, iii) promote the metal dispersion, and iv) improve the stability of the catalyst by restraining carbon deposition on its surface, which would prolong its lifetime (Dadashova *et al.*, 1991; 1993; Yagodovskaya and Lunin, 1997; Zhang *et al.*, 2000; Li *et al.*, 2004). After comparing the catalytic activity of the modified and unmodified Ni/Al₂O₃ catalysts, the results showed that the ethanol conversion and H₂ production of the modified catalyst were higher than the unmodified catalyst. The modified catalyst did not show any deactivation after 144 h of continuous use.

The effect of the preparation method and microstructural and compositional phase differences on the activity of Ni/Al₂O₃ catalysts for the APR of methanol has been investigated (Roy *et al.*, 2012a; 2012b). An SCS-Al₂O₃ (Al₂O₃ support was made by a solution combustion synthesis route) sample with smaller Ni particles was found to be superior for methanol conversion, H₂ selectivity, and CO₂ production. The same phenomenon was observed on the Ru/TiO₂ catalyst in the APR of methanol (Nozawa *et al.*, 2014).

3.2.3 Different supports of catalysts for non-noble catalysts

It has been observed that some types of basic supports, such as MgO, ZnO, can promote the hydrogen yield and the stability of catalysts in the APR process. Cruz *et al.* (2008) prepared a catalyst with

Ni loaded onto the derived hydrotalcite (NiHTC), and found that this catalyst showed higher activity in the APR process than a NiAl catalyst because of its larger surface area and pore volume. The XRD results showed that the lamellar structure of hydrotalcite-like compounds (HTLCs) disappeared and formed a poorly crystallized MgO-periclase phase after calcination. The dispersions of Ni and Al in the MgO matrix were good for the NiAl catalyst on a MgO support. Davidson *et al.* (2014) also reported that the Co/C catalyst led to an effective cleavage of the C-C bond, and the addition of ZnO provided more surface sites and enhanced the activation of H₂O.

3.3 Aqueous-phase reforming of glycerol

To solve the energy crisis in the world, biodiesel, which can be generated from vegetable oils, has become a substitute for petroleum. As the main by-product, the production of glycerol has increased rapidly and its subsequent utilization becomes more important (Pagliaro *et al.*, 2007; Balat and Balat 2010; Huang *et al.*, 2010; Wen *et al.*, 2010). The APR of glycerol for hydrogen production is one attractive approach (Iriundo *et al.*, 2008; Lehnert and Claus, 2008; Wen *et al.*, 2008).

The mechanism of glycerol APR over Pt-based catalysts has been discussed (King *et al.*, 2010; Wawrzetz *et al.*, 2010; Zhang *et al.*, 2012), and the possible reaction pathways are shown in Fig. 3. The differences of the pathways are dependent on the properties of the catalysts. The Pt/Al₂O₃ catalyst possessed both metal and acid functions and enhanced glycerol dehydration to 3-hydroxypropanal. Moreover, Wawrzetz *et al.* (2010) proposed that the transformation of Al₂O₃ into boehmite supplied an acid-base site that promoted disproportionation in the reaction. The active phase of the Pt-Re/AC catalyst was Pt-Re alloy and ReO_x. King *et al.* (2010) indicated that the Pt-Re alloy acted as a metal-functionalized site resulting in C-C bond cleavage, and ReO_x was intended to promote glyceroldehyde dehydration to produce pyruvaldehyde.

3.3.1 Pt-based catalysts

The catalyst Pt/Al₂O₃ remains the most commonly applied catalyst in the APR of glycerol (Luo *et al.*, 2008). Meryemoglu *et al.* (2012) used APR of

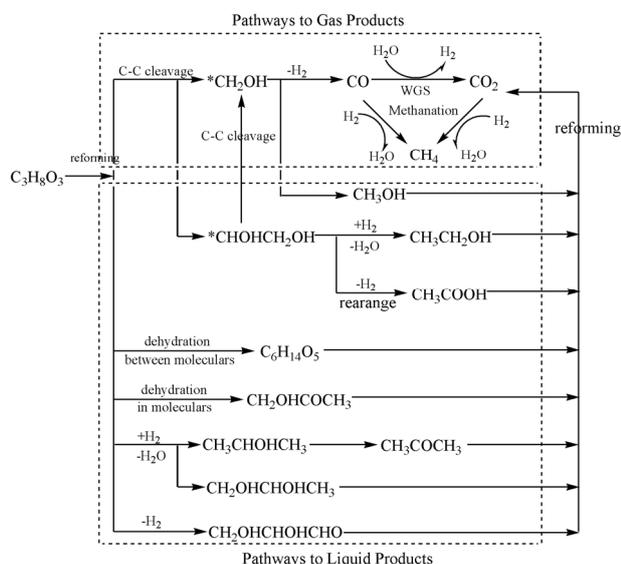


Fig. 3 Possible reaction network for the aqueous-phase reforming of glycerol (Reprinted from (Luo *et al.*, 2008), Copyright 2008, with permission from Elsevier)

glycerol over Pt/ Al_2O_3 and Pt/carbon catalysts at 523 K and obtained larger gas volume. However, Pt/ Al_2O_3 produced less gas than a Pt/carbon catalyst at 573 K. The effects of metal loadings and operation conditions to the APR process of glycerol for H_2 production on Pt/ Al_2O_3 were investigated, and the results showed that a 0.9% Pt loading possessed the highest activity for hydrogen generation. The optimal temperature was determined at 493 K, which was similar to the 503 K temperature reported earlier (Özgür and Uysal, 2011). The amount of CO was expected to be as low as possible, but this would not always be achieved because of limitations of the reaction equipment. Thus, although CO_2 concentration increased with increasing temperature, the WGS reaction could not go to completion.

The APR reaction is usually sensitive to particle size and the metal surface. Catalysts showed similar activity under the same reaction conditions, and no significant deactivation of the catalysts or formation of higher alkanes could be observed on Pt-based Al_2O_3 catalysts (Lehnert and Claus, 2008). In contrast, an increase in Pt particle size led to a decrease of the formation of H_2 and CO_2 . This was identified with a decreasing concentration of metal sites, which favor the dehydration reactions (Wawrzetz *et al.*, 2010). Barbelli *et al.* (2013) also observed the same experimental phenomenon on Pt-based catalysts. In

addition, they suggested that small particle size would favor C-C bond cleavage over C-O bond cleavage and the hydrogenation reactions.

Doping of certain metals can improve the activity of catalysts. King *et al.* (2010) performed experiments for the APR of glycerol over Pt/C and Pt-Re/C catalysts, and found that adding Re to Pt promoted the conversion of glycerol and H_2 selectivity. It was suggested that Re might have a dual effect on Pt: first, the formation of the Pt-Re alloy led to an increased rate of dehydrogenation and decarbonylation; second, ReO_x led to liquid products and alkanes. Another explanation was that carbon-supported alloys of Pt with a Re catalyst were substantially more active in C-C bond cleavage than monometallic Pt/carbon catalysts. Further, such bimetallic catalysts increased WGS activity by rapidly removing CO from the surface (Ciftci *et al.*, 2014). Dietrich *et al.* (2012) prepared a PtMo bimetallic nanoparticle catalyst for APR of glycerol. The result showed that the formation of this catalyst was Pt-rich in the core and Mo-rich at the surface. The PtMo nanoparticles increased slightly in size from 2 to 5 nm after 30 d of glycerol APR, and the structure can retain the Pt core-Mo shell morphology. The intermediates and products were related to both C-C and C-OH bond cleavage to give H_2 , CO_2 , and CH_4 . At low glycerol conversion and high H_2 selectivity, cleavage of the C-OH bonds led to liquid products with saturated carbon atoms, whereas additional CH_4 would be obtained and reduce the H_2 yield and selectivity at high conversions. This was in contrast to PtMo/multi-walled carbon nanotube catalysts (Dietrich *et al.*, 2014). In this case, Mo promoted the C-O cleavage and reduced the H_2 yield at over 60% conversions. The difference could be on account of their different structures. Indeed, PtCo loaded onto the same support had a 4.6 times higher glycerol conversion than the Pt monometallic catalyst.

Nickel was sometimes utilized as a co-active component in Pt-based catalysts. The Pt-Ni/ $\gamma-Al_2O_3$ catalyst prepared by modified sol-gel preparation methods decreased the sintering effect on the Pt and Ni particles and avoided the formation of coke highly structured on the catalyst's surface (El Doukkali *et al.*, 2012; 2014). He *et al.* (2015) indicated that Pt-Ni/multi-walled carbon nanotube bimetallic catalysts improved the dehydrogenation-decarboxylation

and dehydration-hydrogenation reactions, leading to the highest glycerol conversion rates observed to date (81.21%).

3.3.2 Ni-based catalysts

Although the deactivations of Ni catalysts were observed in the APR process, Ni is still widely used as the main reactive species because of its low cost. However, several modifications to Ni catalysts have been reported in recent years to reduce such deactivations (Wen *et al.*, 2008; King *et al.*, 2010; Luo *et al.*, 2010; Guo *et al.*, 2012b).

Manfro *et al.* (2011) investigated the influence of the preparation method of Ni-based catalysts supported on CeO₂ in the APR of glycerol (Table 4). The characterization showed that a lower specific surface area and better metal dispersion would be obtained for the catalyst prepared by combustion. Further, higher glycerol conversion and hydrogen production were also obtained when this method was used.

Guo *et al.* (2012b) used boron (B) to form a Ni-B alloy catalyst. The hydrogen production rate and hydrogen selectivity were higher than those on the Raney Ni catalyst because the doping of B would result in the formation of hexagonal closed-packed Ni crystallites and B₂O₃, which inhibit the sintering of Ni particles and impart better stability to the catalyst.

A Ni-Co bimetallic catalyst was prepared by urea matrix combustion. It was found that the C-C bond cleavage ability was good because of Ni and an improvement of hydrogen selectivity was observed because of Co. Moreover, the addition of Co could suppress the sintering phenomenon, restrain methane selectivity, and improve the activity of the catalyst (Luo *et al.*, 2010). Tuza *et al.* (2013) found that the addition of Cu decreased the formation of methane

in the APR of glycerol, and also decreased the conversion of glycerol.

3.3.3 Different supports for catalysts

The supports also play an important role in the APR of glycerol. Pt- and Ni-based catalyst supports, such as Al₂O₃, CeO₂, MgO, and SiO₂, were prepared to investigate the effect of supports on the activity of the catalysts for hydrogen production by APR of glycerol. The results are shown in Table 5.

Menezes *et al.* (2011) prepared supported Pt catalysts using Al₂O₃, CeO₂, ZrO₂, and MgO as the carriers and tested their catalytic activity. In these Pt catalysts, Al₂O₃ and ZrO₂ were amorphous, whereas CeO₂ adopted a fluorite phase and MgO formed a periclase phase. The experimental results showed that all of the supports could result in an increase in the hydrogen production and a decrease in the concentration of undesired hydrocarbons, irrespective of the phase of the four supports.

Guo *et al.* (2012a) investigated the effect of the identity of the supports (i.e., MgO, Al₂O₃, CeO₂, TiO₂, and SiO₂) on the catalytic activity of the Pt-based catalyst in the APR process of glycerol. The catalytic activities of Pt-based catalysts decreased as Pt/MgO>Pt/Al₂O₃>Pt/CeO₂>Pt/TiO₂>Pt/SiO₂. The WGS reactions played a key role in the APR process, which were enhanced by the acid-basic sites on the surface of the catalyst. Thus, the Pt/MgO catalyst exhibited the best reaction activity. However, the trend reported by Wen *et al.* (2008) was different as follows: Pt/Al₂O₃>Pt/MgO>Pt/SiO₂>Pt/HUSY>Pt/AC>Pt/SAPO-11. A basic support resulted in high activity and hydrogen yield, whereas the acidic Al₂O₃ support and neutral support increased the formation of alkanes.

Table 4 Catalytic performance of different metal-doped Ni-based catalysts (Reprinted from (Manfro, 2011), Copyright 2011, with permission from Elsevier)

Catalyst	NiO (%)	S _{BET} (m ² /g)	V _{por} (m ³ /g)	Reaction temperature (K)	Reaction pressure (MPa)	Conversion (%)	H ₂ selectivity (%)
NiCe-Imp ^a	21.7	62	0.15	523	3.75	21.0	88.0
NiCe-Cp ^b	20.6	51	0.20	523	3.75	16.0	122.2
NiCe-Com ^c	19.6	<10	0.01	523	3.75	12.0	186.8
NiCe-Imp	21.7	62	0.15	543	5.27	18.8	71.4
NiCe-Cp	20.6	51	0.20	543	5.27	17.5	82.4
NiCe-Com	19.6	<10	0.01	543	5.27	27.5	60.6

^a Imp: wet impregnation; ^b Cp: Co-precipitation; ^c Com: combustion

Iriondo *et al.* (2008) indicated that the structure and morphology of Ni catalysts could be modified by doping with Zr, Ce, La, or Mg. Mg modified the synergistic effect between Ni and Al₂O₃, and it enhanced the cooperation of Ni with the Al₂O₃ phase. The presence of Zr weakened the dispersion of Ni and displayed a strong Ni-ZrO₂ interaction. Ce and La partially covered the Ni phases. However, although the catalysts showed high activities at early reaction times, they deactivated quickly, which was ascribed to the change of Ni to an oxidized state with the formation of surface NiAl₂O₄.

3.4 Aqueous-phase reforming of other alcohols

Thus far, most feedstocks of APR processes for hydrogen production were alcohols derived from biomass, such as ethylene glycol and glycerol. However, studies of other alcohols in the APR process, such as methanol, butanol, sorbitol, mannitol, and xylitol, remain important branches of investigation.

Recently, *n*-butanol (*n*-BuOH) has been considered to be a potentially significant source of H₂ because of its higher weight percent of H (13.5%)

compared with ethanol (13.0%) and methanol (12.5%), low vapor pressure, flammability, and ease of handling. Additionally, *n*-BuOH (or biobutanol) can be produced by fermenting sugar beets, sugar cane, corn, wheat, lignocellulosic biomass, and aqueous fractions of biomass pyrolysis liquids (i.e., bio-oil). Roy *et al.* (2011) studied the APR of *n*-BuOH over Ni (20%) loaded onto Al₂O₃ and CeO₂ catalysts. The Ni/CeO₂ catalyst demonstrated higher selectivity for H₂ and CO₂, lower selectivity to alkanes, and a lower amount of C in the liquid phase compared with the Ni/Al₂O₃ sample because of higher oxygen mobility in the Ni doped non-stoichiometric CeO₂ lattice. For the Ni/CeO₂ and Ni/Al₂O₃ catalysts, the highest *n*-BuOH conversion was 5.77% and 2.76% on the Ni/CeO₂ and Ni/Al₂O₃ catalysts at 488 K, respectively. The low conversion led to a few subsequent investigations.

Sorbitol as a starting material for the APR process has attracted considerable interest because of its relatively large number of successive C-C and C-O bonds (Cortright *et al.*, 2002; Huber *et al.*, 2003; Tanksale *et al.*, 2008). Li and Huber (2010)

Table 5 Effect of the support for different catalysts on the APR process

Catalyst	Pt loading (%)	S_{BET} (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)	Conversion (%)	H ₂ selectivity (%)	Yield rate of H ₂ production (μmol/(g _{cat} ·min))	Reference
Pt/Al ₂ O ₃	1.22	–	–	–	23	49.3	–	Menezes <i>et al.</i> , 2011 ^a
Pt/CeO ₂	1.49	–	–	–	13	52.5	–	
Pt/ZrO ₂	1.13	–	–	–	26	46.1	–	
Pt/MgO	1.44	–	–	–	20	73.3	–	
Pt/MgO	0.79	42	0.20	3.82	48	60	–	Guo <i>et al.</i> , 2012a ^b
Pt/Al ₂ O ₃	0.74	228	0.34	3.43	38	66	–	
Pt/CeO ₂	0.75	58	0.01	3.82	35	61	–	
Pt/TiO ₂	0.72	35	0.18	5.46	27	56	–	
Pt/SiO ₂	0.76	259	0.70	5.51	20	70	–	
Pt/Al ₂ O ₃	4.38	229.0	0.663	9.6	18.9	65.7	572.2	Wen <i>et al.</i> , 2008 ^c
Pt/SiO ₂	4.34	105.2	0.400	6.6	10.8	72.8	369.4	
Pt/AC	4.23	721.3	0.098	3.8	17.2	65.7	307.7	
Pt/MgO	9.84	302.9	0.732	5.6	13.8	113.0	431.9	
Pt/HUSY	5.10	436.8	0.133	3.8	22.0	72.6	337.0	
Pt/MSAPO-11	5.31	137.1	0.124	2.8	13.3	76.8	222.1	
Ni/Al ₂ O ₃	14.5	207	0.77	14.8	25	–	–	Iriondo <i>et al.</i> , 2008 ^d
Ni/Al ₂ O ₃ -ZrO ₂	15.4	229	0.81	14.0	30	13.4	–	
Ni/Al ₂ O ₃ -CeO ₂	14.5	215	0.81	14.3	36	13.4	–	
Ni/Al ₂ O ₃ -MgO	14.5	218	0.82	14.1	15	26.4	–	
Ni/Al ₂ O ₃ -La ₂ O ₃	15.4	225	0.81	14.3	37	13.4	–	

Reaction conditions: ^a 10% glycerol, 503 K, 3.2 MPa; ^b 1% glycerol, 498 K, autogenous pressure; ^c 5% glycerol, 498 K, 2.76 MPa; ^d 1% glycerol, 498 K, 3.0 MPa

proposed that a closed-loop dehydration of sorbitol into C_6 was the first reaction to occur on acidic centers, and cleavage of the C-C bond of sorbitol into C_3 fragments was easier on the Pt-based catalysts. Tanksale *et al.* (2008) combined small quantities of Pt or Pd with a Ni catalyst to prepare the alloy catalysts for the APR process of sorbitol. The results showed that the hydrogen formation rate for the alloy catalysts were 3–5 times higher than that measured for the monometallic Ni catalysts. The results were rationalized as follows: first, the increase of reduction of Ni led to a higher number of active sites; second, the alloying of Pt/Ni decreased the C-O binding energy on the active metal. In other words, poisoning the catalyst was inhibited and the available number of active sites was increased. Aiouache *et al.* (2013) added Pd to the Ni/ γ - Al_2O_3 catalyst and found that the nickel dispersion and reducibility were increased, made the H_2 production higher, and led to a lower CO_2 production. The introduction of a small amount of Pd appeared to inhibit the remaining reactions via surface carbon intermediates that were tightly bound to the surface of the catalyst. In (Tanksale *et al.*, 2009)'s investigation, different supports (i.e., alumina nano-fibre (Alnf), ZrO_2 , and mixed oxides of ceria-zirconia-silica (CZ_xS)) were chosen to prepare bimetallic Pt-Ni catalysts for the APR of sorbitol. It was observed that the rate of H_2 production for the co-impregnated Ni/Pt catalysts was higher than the sequentially impregnated Pt/Ni catalysts and monometallic Ni catalysts. Silica did not form any compound with ceria-zirconia but instead existed as an amorphous layer on the $Ce_xZr_{1-x}O_2$ crystals. The hydrogen activity decreased in the following order of the supports: Alnf > ZrO_2 > CZ3S > CZ7S.

Although xylitol is the second most abundant sugar alcohol, which is produced by the catalytic hydrogenation of xylose monomers generated from hemicelluloses, it has attracted very little attention (Sjöström, 1993). A Pt/ Al_2O_3 catalyst presented good stability (only 10% decreased after 120 h time-on-stream) in the APR of xylitol, and could be improved by regeneration. No deactivation was observed on Pt/ TiO_2 (Kirilin *et al.*, 2012). In the following study, Kirilin *et al.* (2014) found that the addition of Re to the Pt/ TiO_2 catalyst decreased the number of surface acid sites, and this could result in

the formation of hydrocarbons. Kim *et al.* (2014) proposed that the pore structure of the support played a more critical role in the APR of xylitol. Three-dimensionally mesoporous carbon with larger secondary mesopore Pt supported catalysts was more favorable for the production of H_2 because of its unique mesoporous structure. H_2 selectivity was higher and alkane selectivity was lower for glycerol than for xylitol. Because xylitol has a longer carbon chain than glycerol, it is likely that the frequency of some side reactions, such as methanation/Fischer-Tropsch synthesis, would increase and consume the hydrogen previously generated. This conclusion is relevant for the other alcohols as well. Indeed, higher H_2 yields and H_2 selectivities were observed in the APR of xylitol compared with sorbitol, which has a longer carbon chain (Kirilin *et al.*, 2012).

3.5 A comparison of reaction mechanisms for different types of alcohols

As the simplest model of alcohols, early studies of hydrogen generation through the APR reaction mainly focused on ethylene glycol. The catalytic performance of ethanol appeared to be an excellent strategy to obtain hydrogen by the steam reforming reaction, and some scholars attempted to utilize ethanol in the APR reaction as a raw material and obtained high production efficiency. In recent years, because of the rapid development of biodiesel technology, the transformation of its main by-product (i.e., glycerol) has prompted a considerable number of investigations. For other alcohols that have more complicated structures, such as sorbitol and xylitol, studies on the APR reaction have only just begun. Although it is not a direct derivative of biomass, methanol was often chosen as a reference material to investigate the C-C bond cleavage efficiency for different catalysts because no C-C bond cleavage would occur during the APR process. To investigate the differences between the alcohols discussed above in the APR reactions for hydrogen production, some investigators performed parallel investigations.

Shabaker *et al.* (2003) measured the reaction rates of the APR process of methanol and ethylene glycol for H_2 and CO_2 production under kinetic control on Pt/ Al_2O_3 catalysts. The similar results for methanol and ethylene glycol suggested that the C-C bond cleavage was not the decisive step in the APR

process. The H₂ production rate for methanol was higher than ethylene glycol because the reaction involving the former would be weakly inhibited by the surface active sites occupied by hydrogen atoms and other intermediate species derived from ethylene glycol.

Liu (2011) prepared five different types of catalysts (i.e., Pt/ γ -Al₂O₃, Pt/ δ -Al₂O₃, Pt/ α -Al₂O₃, Pt/ α -Fe₂O₃, and Pt/CeO₂) for the APR process involving methanol and ethylene glycol. The results from these reactions are shown in Table 6. The conversion of ethylene glycol was higher than that of methanol, suggesting that the effect of the C-C bond cleavage on the catalysts was not clear. In addition, both the conversion and H₂ selectivity for ethylene glycol were higher than they were for methanol, which demonstrated that the reforming of ethylene glycol on the supported catalysts was not only a simple C-C bond cleavage combined with the methanol APR reaction but also the reaction mechanism of the

reforming of methanol and ethylene glycol were completely different. The conclusion that C-C bond cleavage was not the decisive step in the APR process was demonstrated once again.

Cortright *et al.* (2002) found that the hydrogen concentration and selectivity from methanol achieved the highest level among some alcohols (Table 7). The hydrogen selectivity of these alcohols increased in the order: sorbitol<glycerol<ethylene glycol<methanol. However, CO₂ formation and hydrocarbon conversion followed the opposite order: methanol<ethylene glycol<glycerol<sorbitol. This observation can be related to the number of carbon atoms of the alcohols. With an increase in the number of carbons, the by-reactions decreased and condensation of the alcohols became easier, which results in the reduction of hydrogen production and the promotion of the formation of CO₂ and hydrocarbon compounds. This theory is consistent with the results reported by Tang *et al.* (2009) and Wen *et al.* (2009).

Table 6 Catalytic activity for the APR of methanol/ethylene glycol on supported catalysts (Liu, 2011)

Catalyst	Feedstock	Conversion (%)	Rate of production ($\mu\text{mol}/(\text{g}_{\text{cat}} \cdot \text{min})$)			
			H ₂	CO	CH ₄	CO ₂
Pt/ γ -Al ₂ O ₃	Methanol	13.1	197	0.017	0.97	62.3
Pt/ γ -Al ₂ O ₃	Ethylene glycol	15.2	218	0.30	1.42	90.3
Pt/ δ -Al ₂ O ₃	Methanol	13.8	164	0.01	1.01	28.6
Pt/ δ -Al ₂ O ₃	Ethylene glycol	20.9	321	0.42	1.87	106.7
Pt/ α -Al ₂ O ₃	Methanol	10.5	145	0.01	1.10	40.8
Pt/ α -Al ₂ O ₃	Ethylene glycol	18.1	452	0.50	1.95	77.9
Pt/ α -Fe ₂ O ₃	Methanol	4.5	24	0.007	0.02	17.9
Pt/ α -Fe ₂ O ₃	Ethylene glycol	13.8	116	0.11	0.21	48.1
Pt/CeO ₂	Methanol	3.8	41	0.03	0.20	20.1
Pt/CeO ₂	Ethylene glycol	6.1	85	0.58	0.62	38.8

Table 7 APR reaction data for different alcohols (Reprinted from (Cortright *et al.*, 2002), Copyright 2002, with permission from Nature)

Feedstock	Concentration (%)	Temperature (K)	Pressure (MPa)	Carbon in liquid-phase effluent (%)	Carbon in gas-phase effluent (%)	Gas-phase composition (%)			H ₂ selectivity (%)	Alkane selectivity (%)
						H ₂	CO ₂	CH ₄		
Methanol	12.5	498	2.9	6.5	94	74.6	25	0.0	99	1.7
		538	5.6	6.4	94	74.8	24.6	0.0	99	2.7
Ethylene glycol	9.7	498	2.9	11	90	70	29.1	0.1	96	4
		538	5.6	2.9	99	68.7	29	0.3	88	8
Glycerol	8.6	498	2.9	17	83	64.8	29.7	0.9	75	19
		538	5.6	2.8	99	57	32	2.0	51	31
Sorbitol	7.6	498	2.9	29	61	61	35	2.3	66	15
		538	5.6	12	90	54	36	0.7	46	32

4 Conclusions

The APR of biomass-derived alcohols for hydrogen production has been considered a promising approach because of its wide renewable resource, mild reaction conditions, and low processing cost. In this process, increasing attention is focused toward ethylene glycol, and glycerol rather than other alcohols, such as methanol, ethanol, sorbitol, and xylitol.

The APR of ethylene glycol and ethanol on Pt-based catalysts presented high conversion but low H₂ yield, and little research on non-noble metal catalysts was performed. For the complex structure of glycerol, the major studies focused on bimetallic catalysts to improve H₂ selectivity and conversion. However, the H₂ yield on the noble metal catalysts remained low. The conversions of *n*-butanol on the Ni/CeO₂ and Ni/Al₂O₃ catalysts were rather low, at approximately 5.77% and 2.76%, respectively, whereas the H₂ selectivity was high. For APR of other alcohols, 99% H₂ selectivity was obtained by small molecule polyols. Degradation and condensation took place with an increase in molecular weight of the alcohols, resulting in a decline in H₂ selectivity from 99% to 46% and a rise in alkane formation from 1.7% to 32%.

In the APR reaction of alcohols, the main catalysts are noble-metal catalysts and nickel catalysts. Noble-metal catalysts, including Pt, Pd, Ru, and Ir, show high selectivity in H₂ production but the conversion of alcohols is low. Ni-based catalysts show high conversion of alcohols but low H₂ selectivity and yields. The addition of Re, Ce, Mg, Mo, and Co to Pt-based catalysts can improve the conversion of alcohols to varying degrees, but the H₂ selectivity and yield decreased for the PtMo catalyst. The H₂ selectivity would be enhanced with Pt, Sn, Ce, B, and Co on Ni-based catalysts, whereas the conversion of alcohols would reduce on NiCu catalyst. If an appropriate support could improve the dispersion of metal and increase the utilization rate of the active sites, then the activity and stability would also be influenced.

At present, the APR process to convert biomass into hydrogen is only at the research and development stage. Future work should focus on developing catalysts of high efficiency, stability, and low cost. Moreover, movement away from micro reactors to

new reactor designs that can rapidly separate products but can accommodate larger volumes and concentrations of reactants should be pursued.

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中文概要

题目: 生物质衍生醇类水相重整制氢研究进展

概要: 氢气作为一种清洁、高效的可持续能源,近年来得到了广泛关注。水相重整技术以生物质衍生醇类制备氢气,具有来源广泛、反应条件温和、运行成本较低等优点,相较于其他制氢方法更有优势。本文详细阐述生物质衍生醇类水相重整制氢的研究进展,同时讨论不同催化剂的反应机理。Pt系催化剂表现出较高的氢气选择性,但是醇类转化率较低。Ni系催化剂反应活性和转化率均较高,但仍存在氢气选择性和氢气产率较低等问题。

关键词: 生物质; 醇类; 制氢; 水相重整制氢; 反应机理; 催化剂