

Catalyst development for water-gas shift

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Chapter 16

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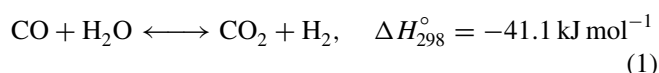
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1 HISTORIC PERSPECTIVE

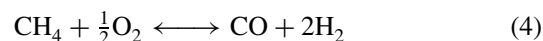
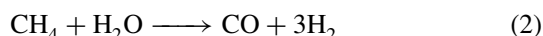
1.1 Introduction

For many years the development of fuel efficient low or zero emission engines has been a major objective of automobile, refinery and catalyst industries. Although important improvements in fuel economy and emission control of internal combustion engines has been achieved, further steps are necessary in order to meet the coming stringent legislation. Of all the fuel cell concepts discussed, the development of the polymer electrolyte membrane (PEM) fuel cell technology for transport applications appears to be most promising however they are deactivated by low levels of carbon monoxide.^[1, 2] Obviously the technical challenges with hydrogen production capacity, storage, and distribution must be addressed. To achieve an acceptable and economic lifetime of the fuel cell it is essential to reduce the amount of carbon monoxide entering the cell. Latest technology anodes are typically tolerant up to 100 ppm CO in the feed gas but the typical reformat coming from a fuel processor contains hydrogen, carbon dioxide and 1–3 vol% of carbon monoxide.^[3–5] In order to minimize the reformat CO concentration for PEM fuel cell applications, methanation of the excess CO, the selective oxidation in the presence of oxygen or water has been considered. The topic of the following summary is the oxidation reaction of carbon monoxide with steam herein referred to as the water gas shift (WGS) reaction.

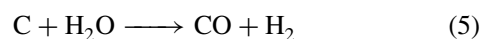
Since the early 1940s the WGS reaction has represented an important step in the industrial production of hydrogen:



The essential role of the industrial WGS reaction is to increase the production of hydrogen for refinery hydro-processes, bulk storage and redistribution. This includes the need for gases of appropriate H₂/CO ratios in the production of organic bulk chemicals such as ammonia, methanol, and alternative hydrocarbon fuels through Fischer–Tropsch synthesis. These gas mixtures applied in industry are usually referred to as synthesis gas, or syngas, and are produced in large scale facilities by high temperature reaction of carbonaceous materials in presence of water or oxygen where supported nickel catalysts are in use (see equations (2)–(4)):



or by gasification of coal (equation (5)):^[6]



In the subsequent WGS reaction the composition of the so-called water gas can be adjusted to the desired ratio of hydrogen and carbon monoxide. More detailed reviews on synthesis gas generation and application can be found elsewhere.^[7–10] Although the WGS reaction is

not the primary reaction, it must be considered in methanol synthesis, hydrocarbon conversion by reforming, Fischer–Tropsch synthesis, automotive exhaust catalysis, and selective CO oxidation for fuel cells.

1.2 Industrial applications

Two stage CO conversion systems employing WGS using Fe/Cr oxide catalysts and methanation using nickel based catalysts with CO₂ removal between the stages was the common and economical design for ammonia synthesis gas up to the late 1950s. Most of these plants employed the Fe/Cr oxide high temperature shift (HTS) catalyst as well in the second stage converter at temperatures as low as 320 °C but more typically at 330°. The conventional HTS catalysts worked extremely well in these applications. The success of these catalysts at low temperature led to its use as a second, lower temperature bed. This became the basis for the next evolution in ammonia plant design. The two stage converter systems easily and consistently reduced the CO level to 3000–4000 ppm compared to the single stage converters that could not reduce the CO to much less than 1%.

The relatively poor performance of the Fe/Cr HTS catalyst applied in the lower temperature second bed of these

systems motivated further investigations. In the work of Bohlbro, the CO₂ partial pressure in the reacting gas was found to exert a retarding effect on the forward reaction rate constant of the WGS reaction.^[11] Experiments demonstrated that the effect of CO₂ was negligible on the forward reaction rate constant over copper based catalysts developed by Larson and patented as early as 1931.^[12] The unsupported metallic copper catalysts or copper supported on Al₂O₃, SiO₂, MgO, pumice or Cr₂O₃ of the early days were characterized by relatively short life (6–9 months) and low space velocity operation (400–1000 h⁻¹). Important progress was made by the addition of ZnO or ZnO/Al₂O₃; not only did the lifetime of these catalysts increase considerably, but also due to a strong support effect an increase of the turnover numbers in the order of magnitudes were observed.^[13] For example, the turnover number of copper on alumina is approximately three orders of magnitude higher than in the case of iron on alumina.

Today the industrial realization of WGS takes place in a series of adiabatic converters where the effluent from the reformer system is converted in two steps with the second at a significantly lower temperature in order to shift the equilibrium towards the favored hydrogen product (Figure 1).

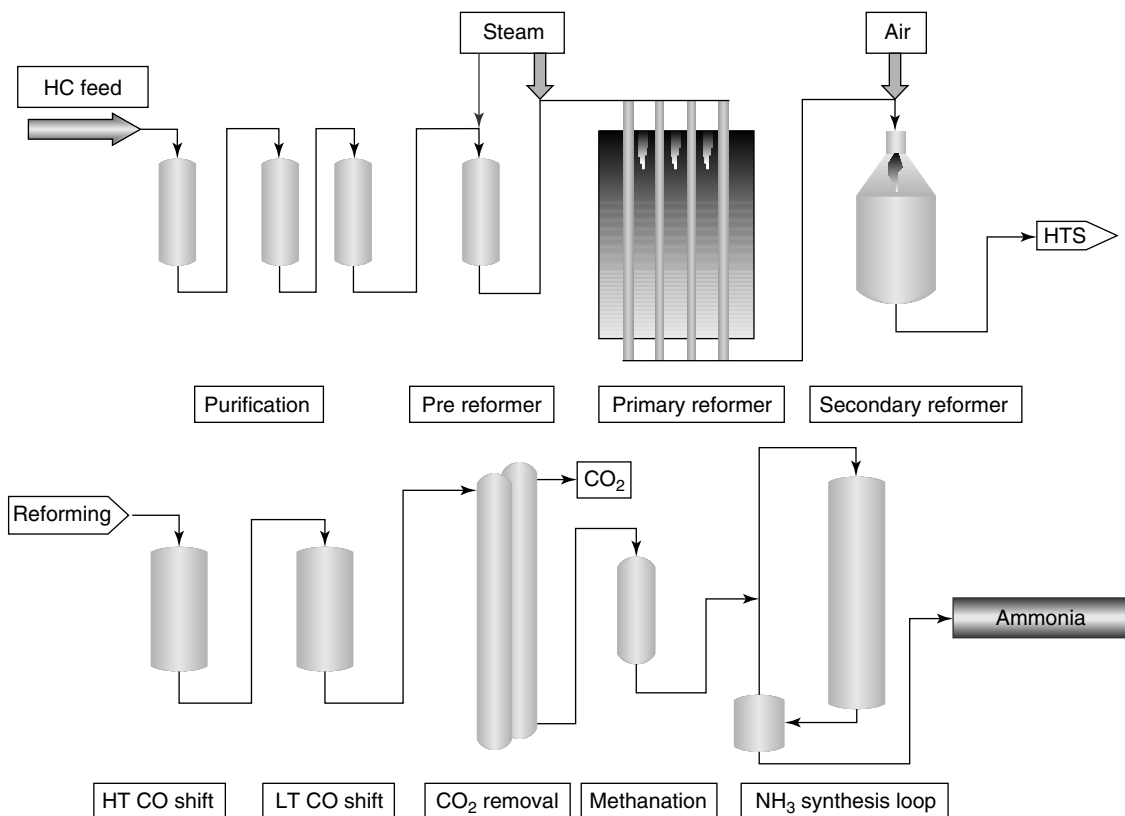


Figure 1. Syngas generation for ammonia synthesis: reforming, HTS, LTS.

In the first step, promoted Fe/Cr oxide catalysts are applied at a reactor inlet temperature of 300–360 °C and a total pressure between 10 and 60 bar. Due to the exothermic nature of the reaction and depending on the origin of the synthesis gas, which determines the inlet concentration of CO, great care has to be taken to avoid overheating the catalyst, e.g., by intercooling the catalyst beds or by the addition of quench water. Under normal operating conditions the temperature rises progressively through the converter bed and can increase to 500 °C especially if the CO inlet concentration is about 45 vol%. At exit gas temperatures of 400–500 °C the CO content can be reduced in an industrial HTS converter to 4 vol% or lower. Similar to HTS the low temperature shift (LTS) is performed in industrial scale using adiabatic converters. Here the inlet temperatures range between 190 and 230 °C at a total pressure up to 60 bar in some special applications, but usually not exceeding 40 bar. Inlet CO concentrations vary between 1 and 5% depending on the performance of the HTS installed upstream. Exit temperatures can reach 280 °C and the CO content is typically reduced to <0.5%. Due to its industrial importance, the WGS catalysts were the topic of numerous studies. Newsome in 1980 and later other authors published important and comprehensive reviews on the industrial application of the WGS reaction.^[6, 7, 14, 15]

Industrial HTS converters exclusively apply Fe-based catalysts because of their excellent thermal stability, poison

resistance and good selectivity especially in the case when low steam to CO ratios are applied where the formation of hydrocarbons is favored.^[7] The commercially available catalysts are applied in the form of pellets, containing 8–12% Cr₂O₃ and a small amount of copper as an activity and selectivity enhancer. Cu/Zn/Al commercial catalysts are applied in the form of tablets, extrusions, or spheres and are usually produced by co-precipitation of metal nitrates. Summers *et al.* describes as well the replacement of Al₂O₃ by rare earth metal oxides like La₂O₃ and Ce₂O₃; sufficient crush strength was obtained by the addition of cement.^[16]

It is important to note that the commercial Fe/Cr/Cu and Cu/Zn/Al catalysts must be activated before operation using a specific process to control reduction of the oxides to the catalytically active state. Improper activation detrimentally affects the activity and life of the catalysts. Care must be taken to avoid steam condensation and to minimize the re-oxidization of the catalysts upon shutdown. One of the greatest impacts on increasing the lives of industrial WGS catalysts was the training of plant operators on the careful startup, inert purging to prevent condensation and sequestration during shutdown of industrial reactors. These process improvements increased the lives of WGS catalysts dramatically from months to years.

As seen in Table 1, the typical plant size for Syngas generation cover a wide range of scale depending on the application.^[10] Present commercialized stationary fuel cell

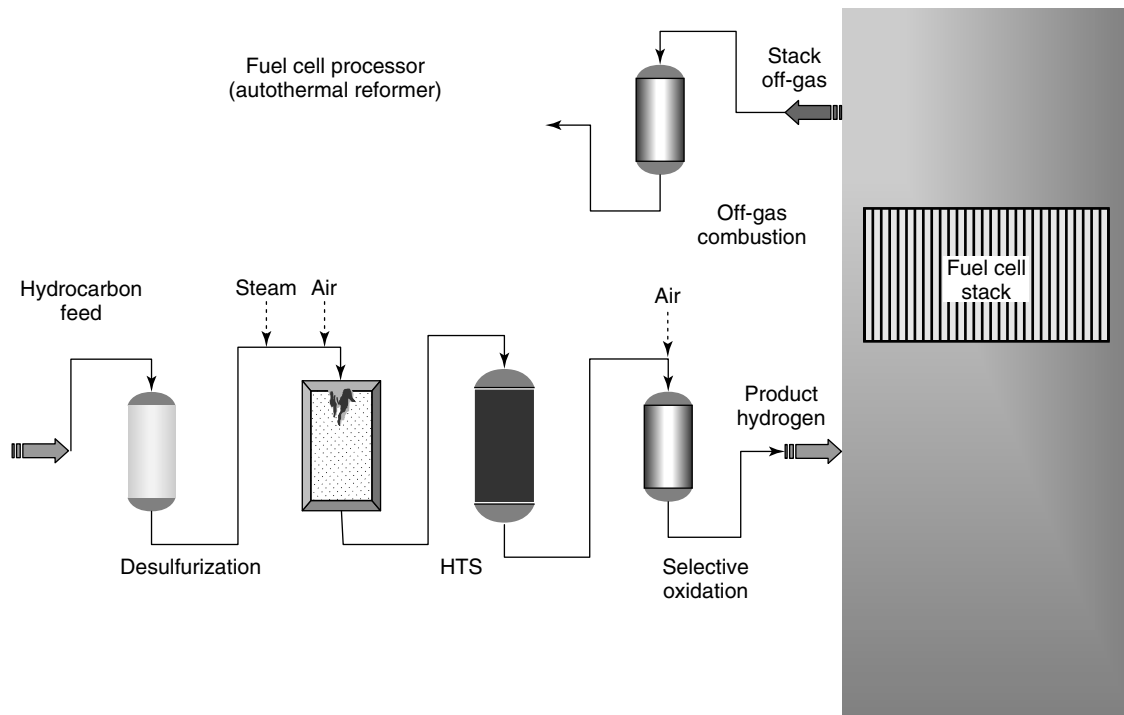


Figure 2. Fuel processor: reforming, WGS.

Table 1. Syngas application typical plant sizes.^[10]

	Plant capacity	Reformer catalyst volume (m ³)
Gas-to-liquids/FT	20 000 Bbl day ⁻¹	240
Methanol	2700 t day ⁻¹	85
Refinery hydrogen	50 t day ⁻¹ 21 mmscfd	12
Ammonia	1000 t day ⁻¹	30
Reducing gas (DRI)	1000 t day ⁻¹	109
Carbon monoxide	40 t day ⁻¹	2
Stationary fuel cells	250 kW	0.1
Mobile fuel cells	25 kW	0.01

power units on the order of 100–500 kW use hydrogen generated from natural gas or liquid fuel. International Fuel Cell (IFC) for instance, is manufacturing phosphoric acid fuel cell based systems where the hydrogen is generated by internal catalytic steam reforming and WGS reactions. Although the design of fuel processors for stationary fuel cells are less constrained by the need for compactness and fast response as it is for automotive applications, compared to industrial systems a reduction in reformer size and other catalytic reactors of over three orders of magnitude is necessary. The transition to the new age of hydrogen production will only be successful with the development of novel reactor technology and new catalyst inventions.

In 1994 Jamal and Wyszynsky reviewed the onboard generation of hydrogen as an alternative fuel for combustion engines.^[17] Applying hydrogen as a combustion fuel is still an attractive alternative; only slight modifications of spark ignition engines are necessary and car manufacturers have already demonstrated performing engines. The application of hydrogen for onboard fuel cells requires much purer hydrogen that can only be directly delivered in the desired purity by voltaic decomposition of water. The processing of methane and other hydrocarbon fuels requires highly selective processes and catalysts as well as additional purification steps in order to supply the needed purity. Figure 2 gives a scheme of a fuel processor where the WGS part is located between reforming and selective oxidation.

2 THEORY

The WGS reaction is a critical step in reducing the CO concentration for low temperature fuel cells that are not tolerant to CO. In most fuel processor designs the WGS reaction must deliver a CO concentration of <1% to the selective CO oxidation reactor. Any further reduction in CO concentration eases the load on the CO oxidizer. High temperature fuel cells are not as dependent on the WGS shift reaction to reduce CO since they are able to withstand

the high CO concentrations expected from the reforming reaction. The WGS reaction is very desirable for fuel processing as it provides two benefits. In addition to effectively reducing the CO concentration, a mole of H₂ is produced for every mole of CO that is converted in the WGS reaction (equation 1). The WGS reaction increases the fuel cell efficiency by generating H₂ from water. A detailed understanding of the thermodynamics and kinetic limitations of the catalyst must be mastered to fully utilize the benefits of the WGS reaction. Temperature, water concentration and methods of reforming must be considered when designing a WGS reactor system and catalysts.

2.1 Thermodynamic aspects

Due to the exothermic nature of the WGS reaction, higher CO conversions are favored at lower temperatures. The WGS equilibrium constant is nearly 80 times greater when the temperature is decreased from 600 to 200 °C. The WGS equilibrium constants at various temperatures are summarized in Table 2.^[18] The water content has a strong influence in converting CO. The water entering the WGS reactor can be varied by controlling the amount added at the reformer or by injecting water before or between stages of the WGS reaction. In contrast, the CO, CO₂ and H₂ concentrations are more dependent on the reformer operation, which in turn determines the thermodynamic limitations. The effect of temperature and water concentration on the equilibrium CO concentration is shown in Figures 3 and 4 for a typical HTS and LTS gases. The gas composition used for these calculations are shown in Table 3 and represent a syngas generated from autothermal reforming and excludes any residual hydrocarbon. By increasing the molar steam to dry gas ratio (S/G) from 0.25 (20% H₂O) to 0.75 (42.9% H₂O) the equilibrium temperature increases by 100 °C while maintaining 1% CO. By operating at 100 °C higher temperature a significant reduction of the reactor size can be achieved by utilizing more favorable kinetics.

Single stage WGS is desired but difficult to accomplish due to the adiabatic temperature rise. To account for the

Table 2. WGS equilibrium constants.^[18]

Temperature (°C)	K _p	Temperature (°C)	K _p
93.3	4523	426.7	9.030
148.9	783.6	482.2	5.610
204.4	206.8	537.8	3.749
260.0	72.75	593.3	2.653
315.6	31.44	648.9	1.966
371.1	15.89	704.4	1.512

Table 3. Representative inlet gas compositions for HTS and LTS reactions, from autothermal reforming, methane free.

	HTS gas (%)	LTS gas (%)
CO	9	3
CO ₂	7	13
H ₂	24	30
N ₂	28	28
H ₂ O	32	26

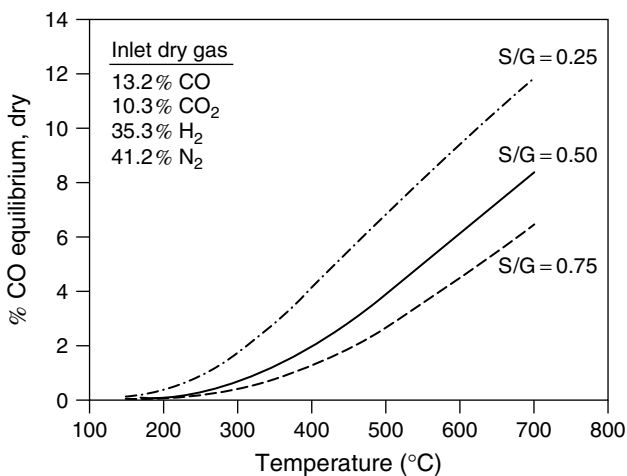


Figure 3. CO equilibrium of HTS gas from auto thermal reformer (ATR) at various S/G ratios.

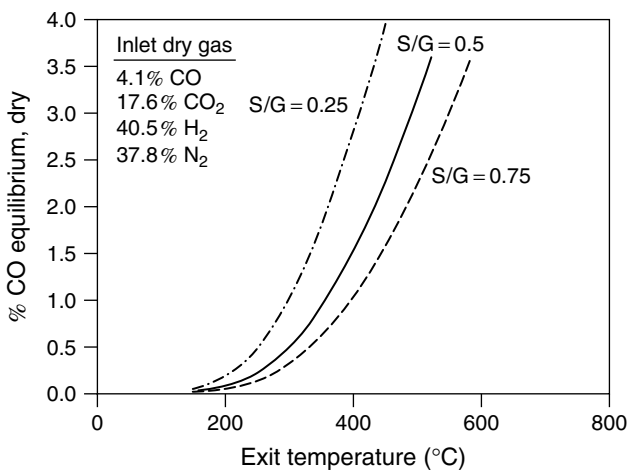


Figure 4. CO equilibrium of LTS gas from ATR at various S/G ratios.

increasing temperature, the inlet temperature to the catalyst must be relatively low where existing catalysts may reach kinetic limitations. Assuming a H₂ flow rate out of the WGS catalyst of 500 standard liter per minute, which is

approximately equal to that needed to operate a 50kW fuel cell, the adiabatic temperature rise can be calculated. At a moderate S/G ratio of 0.50, an inlet temperature of 243 °C is needed to achieve the equilibrium CO concentration of 1% at an exit temperature of 334 °C. However when the S/G ratio is reduced to 0.25, an inlet temperature of 143 °C needed to achieve 1% CO at an exit temperature of 260 °C. In this case the WGS catalyst will be kinetically limited. Commercial LTS catalysts are kinetically limited at <190 °C even at moderate space velocities. An actively cooled reactor can operate in a quasi-isothermal mode to increase the inlet temperature. In this case the reactor volume and complexity increase to account for heat exchange surface area and reactor control, respectively.

Two stages of WGS are traditionally used to take advantage of kinetics and thermodynamics. By operating an HTS catalyst at higher temperatures the favorable kinetics can be exploited and the volume of the catalyst can be minimized. By cooling the syngas between the HTS and LTS stages an active catalyst can take advantage of the thermodynamic equilibrium at low temperature. A two-stage WGS configuration can produce an exit CO concentration of much less than 1%. At this time both single and two bed concepts are being considered in fuel processor designs.

The method of producing the syngas will effect the WGS equilibrium. Autothermal reforming produces a syngas with lower H₂ concentration due to the dilution of nitrogen as compared to steam reforming. The lower H₂ concentration improves the equilibrium CO conversion whereas the high H₂ concentration expected with steam reforming lowers the WGS reaction equilibrium conversion. Figures 5 and 6 show the equilibrium CO as a function of H₂ content at constant CO and CO₂ concentrations for HTS and LTS gases.

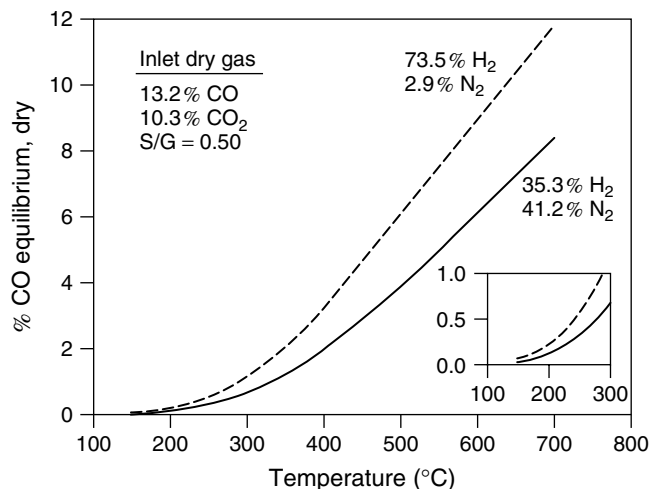


Figure 5. CO equilibrium of HTS gas from autothermal vs steam methane reformer (SMR): effect of H₂ concentration.

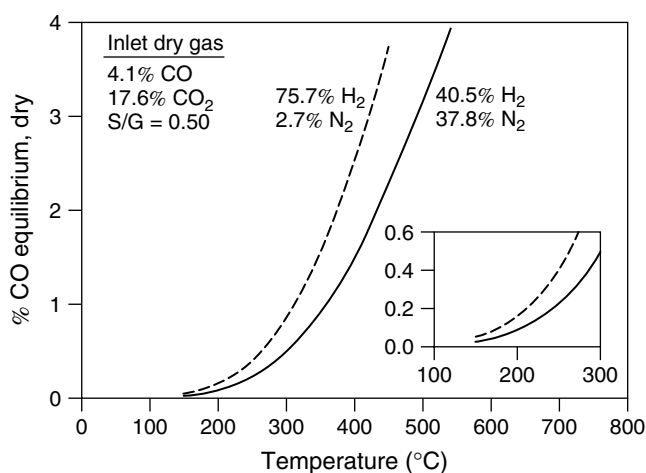


Figure 6. CO equilibrium of LTS gas from ATR vs SMR: effect of H₂ concentration.

Table 4. Effect of pressure on equilibrium CO concentrations (inlet dry gas: 13.2% CO, 10.3% CO₂, 35.3% H₂, 41.2% N₂, S/G = 0.5).

Temperature (°C)	<i>P</i> = 3 atm (% CO)	<i>P</i> = 30 atm (% CO)	<i>P</i> = 300 atm (% CO)
200	0.12	0.12	0.07
300	0.68	0.65	0.48
400	1.98	1.94	1.61
500	3.93	3.88	3.46
600	6.15	6.10	5.68
700	8.38	8.34	7.95

To achieve 1% CO the temperature must be decreased by nearly 40 °C when the H₂ is increased from 35% to 74%. Or in other words the CO concentration would be 1.66% for steam reforming at the same temperature required to achieve 1% CO for autothermal reforming. The effect of H₂ concentration is not as significant as the S/G ratio, but it is not trivial and must be considered when trying to maximize efficiency and minimize volume of the WGS reactor volume.

Since the WGS reaction is equimolar (equation 1) the effect of pressure is minimal considering the range of pressure used for fuel processing. By increasing the pressure from 3 to 30 atm there is negligible effect on the thermodynamic CO conversion (Table 4). But if the pressure is increased to 300 atm the equilibrium CO concentration is lower. However it is not practical to increase the pressure to take advantage of the slightly higher equilibrium CO conversion.

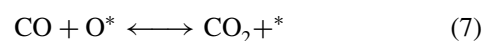
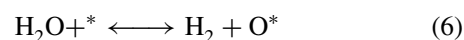
From a thermodynamic perspective, the efficiency of the WGS reaction is maximized at low temperature, high water and a low hydrogen concentration. However under some

conditions the catalysts available today are kinetically limited at the low temperatures needed for high CO conversion while striving to minimize reactor volumes.

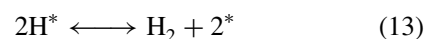
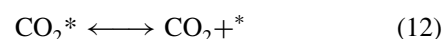
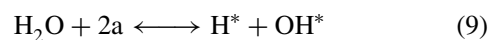
2.2 Mechanisms and kinetics

The kinetics and mechanisms of the WGS reaction with various catalyst systems were studied in the past by many authors and excellent summaries can be found in “Handbook of Heterogeneous Catalysis” by Ertl, Knözinger and Weitkamp and also by Barbier and Duprez.^[7, 19]

Based on kinetic results two types of mechanisms were proposed.^[6] The oxidation-reduction, or regenerative mechanism of Rideal-Elay type, in which water oxidizes the surface and CO re-reduces the oxidized surface.^[15, 19] Others describe a bi-functional process where the adsorbed CO on the precious metal or mixed metal oxide is oxidized by the support and then water fills the support oxygen vacancy.^[19–21]



where * is an active metal site. The multi-step Langmuir–Hinshelwood type or “associative” mechanism where adsorbed or dissociated water form reactive hydroxyl groups that combine with CO to produce a formate that decomposes to CO₂ and H₂. Others describe the bi-functional nature where CO adsorbed on the reduced metal migrates to react with hydroxyl groups to produce the formate intermediate.^[13, 19] FTIR analysis has been commonly used to confirm the presence of the formate intermediate:



The rate-determining step was found to be the decomposition of the formate. An increase in the water partial pressure increased the rate of formate decomposition and the activation energy decreased.^[22]

Based on adsorption/desorption measurements and inter-conversion of CO and CO₂ by isotope exchange on a Fe/Cr catalyst, Tinkle and Dumesic concluded that the WGS on Fe/Cr catalyst proceeds via the regenerative mechanism.^[23]

The question of the reaction mechanism over Cu based catalysts is still debated today. The catalyst composition, catalyst precursors, its resulting surface properties as well as the reaction conditions obviously play a decisive role. Most authors propose the regenerative mechanism, which is in good agreement with results obtained from WGS reaction performed on single crystal Cu surfaces and water adsorption experiments on poly-crystalline copper.^[24–27]

Several different kinetic expressions used for the WGS reaction over copper catalysts have been summarized previously.^[26] Ovensen *et al.* showed the influence of pressure on the activation energy and reaction orders based on macro and microkinetic models for Cu/Zn/Al catalysts.^[28] Grenoble *et al.* studied the WGS reaction over a number of supported metals in detail at atmospheric pressure and in a temperature range from 270 to 380 °C.^[13] Alumina supported Group VIIB, VIII, and IB metals were examined and for these metals the range of activity differed by more than three orders of magnitude and the reaction orders of water varied from 0 to +0.8 and from –0.4 to +0.6 for carbon monoxide. Alumina supported metals exhibit much higher activity than catalysts prepared on silica or active carbon. The turnover number of Pt supported on Al₂O₃ is an order of magnitude higher than the turnover number of Pt on SiO₂ and almost two magnitudes higher than Pt on active carbon. Other researchers have shown carbon monoxide reaction order of 0 and water order from 0 to 0.5 and –0.5 for carbon dioxide and –1 for hydrogen over Pd/CeO₂ catalysts.^[22, 29]

Equation (14) represents the rate expression from Moe *et al.*^[30] and is considered for discussion.^[34] Equation (15) is used to represent Pd/CeO₂ and is based on the reaction orders reported by Hilaire *et al.*^[29]

$$r_{\text{Cu}} = k_{\text{Cu}} P_{\text{CO}} P_{\text{H}_2\text{O}} (1 - \beta) \quad (14)$$

$$r_{\text{Pd}} = \frac{k_{\text{Pd}} (P_{\text{H}_2\text{O}}^{0.5})}{(P_{\text{CO}_2}^{0.5} P_{\text{H}_2})} (1 - \beta) \quad (15)$$

where

$$\beta = \frac{(P_{\text{CO}_2} P_{\text{H}_2})}{(P_{\text{CO}} P_{\text{H}_2\text{O}}) K_{\text{eq}}} \quad (16)$$

$$\frac{r_{\text{Cu}}}{r_{\text{Pd}}} = \frac{k_{\text{Cu}}}{k_{\text{Pd}}} P_{\text{CO}} P_{\text{H}_2\text{O}}^{0.5} P_{\text{CO}_2}^{0.5} P_{\text{H}_2} \quad (16)$$

To compare the relative rate of copper and palladium catalysts, equations (14) and (15) are divided resulting in equation (16). The relative WGS rate of supported Pd catalyst compared to copper is negatively effected by pressure, a higher activation energy and to a lesser extent the gas composition. The activity can be calculated by evaluating the relative reaction improvement needed to make

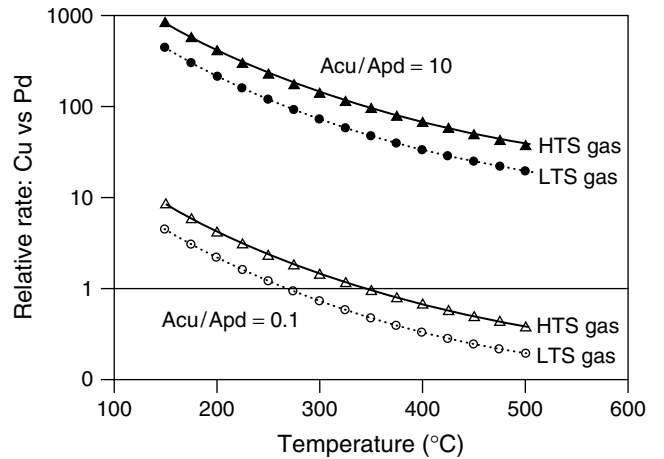


Figure 7. Relative reaction rates of Cu and Pd catalysts with variation of pre-exponential factors and gas composition. $P = 3$ atm, (\blacktriangle , \bullet) $A_{\text{Cu}}/A_{\text{Pd}} = 10$; (\triangle , \circ) $A_{\text{Cu}}/A_{\text{Pd}} = 0.1$. A_{Cu} and A_{Pd} are the pre-exponential factors for copper and palladium, respectively.

the Pd catalyst viable. The activation energies reported by Grenoble for Cu/Al and Pd/Al will be used and are 55.6, 79.9 kJ mol⁻¹ respectively and are relatively consistent with other references.^[13, 28, 31] The ratio of pre-exponential factors were varied from $A_{\text{Cu}}/A_{\text{Pd}} = 10$ to $A_{\text{Cu}}/A_{\text{Pd}} = 0.1$. Figure 7 shows the relative reaction rates with different gas compositions and over a broad temperature range. Nominal HTS and LTS gas compositions are used for this comparison (Table 2). By comparing the effect of temperature and gas composition the relative rate of copper versus palladium is greatest at lower temperatures and higher CO content. The kinetic limitations of the current WGS catalyst technology at low temperature where thermodynamics are most favorable was also described by Sun.^[32] It is safe to say that precious metal catalyst activity must be improved by at least two orders of magnitude to become useful in fuel processing.

3 ROLE OF WGS FOR AUTOMOTIVE EXHAUST GAS CLEANING SYSTEMS

In contrast to conventional base metal catalysts, supported precious metal catalysts have been known to be active for the WGS reaction for many years with early research performed in 1925 by Prichard and Hinshelwood^[33] who studied the reverse WGS reaction over supported Pt.^[31] Much attention was focused on the WGS reaction as it applied to automotive exhaust catalysts with respect to CO emissions in the 1970s and 1980s.^[19, 34–40] Detailed and excellent reviews of the early work are given by Kummer and Taylor.^[34, 35, 41]

Many have reported that CeO₂ promoted the WGS reaction.^[34, 36, 41, 42] It was shown that Pt was most active for WGS reaction followed by Pd and Rh on alumina and activity was improved with the incorporation of 12% CeO₂ with alumina.^[36, 42] Currently CeO₂ is generally added to three-way catalysts in order to promote the WGS reaction and to store oxygen under lean conditions for use under rich conditions.^[16, 43, 44] The literature provides useful information for the development of precious metal WGS catalysts for fuel processing but there are important differences that must be noted. Most WGS activity evaluations made with respect to exhaust catalyst typically were studied in an oxidative atmosphere and at temperatures >400 °C. The effect of CO₂ and H₂ were not often considered. The WGS fuel processing environment is more reducing where the partial pressures of CO₂ and H₂ are much greater and operating temperatures are generally lower, 180–450 °C.

4 WGS CATALYSTS FOR FUEL PROCESSING

Compared to the industrial use of WGS catalyst the requirements for fuel processing are quite different. Industrially the Fe/Cr and Cu/Zn/Al catalysts are activated before operation by a slow and controlled reduction process. Also upon shutdown the catalysts must be purged with inert gas to prevent condensation and re-oxidation. If any of these conditions are not met, the performance of the catalyst is significantly limited. Ease of operation is the key for WGS catalyst for fuel processing applications.

4.1 Catalyst requirements

To apply WGS catalysts successfully to fuel processing many obstacles must be overcome. The desired requirements of WGS catalysts used to produce hydrogen for fuel

cells are far different from the traditional industrial applications (Table 5). The requirements for mobile applications must compete with the standards set by internal combustion engines, therefore the operability, size, weight and cost targets are rigorous. For stationary applications the catalyst attributes are less constrained and larger volumes and higher costs are acceptable to compete with the cost of electricity from the grid, especially in premium power applications. But it is clear that catalyst and reactor technology developed for mobile fuel cells will be integrated into stationary applications making them more economically viable.

Industrial WGS catalysts are designed to operate at steady state conditions for months to years on end without interruption. It is expected that fuel processor WGS catalysts will be exposed to many startup/shutdown cycles where the catalyst will be exposed to redox cycles and condensing steam. As mentioned previously, care must be taken to prevent such exposure to industrial WGS catalysts. A commercial Cu/Zn/Al catalyst was exposed to condensing synthesis gas. The results show dramatic deactivation when tested as a powder in a micro-activity test after a few condensation cycles. Figure 8 shows the CO conversion dropping 40–50% of the fresh catalyst activity after 3 cycles.

It has been shown that the Cu/Zn/Al catalysts also deactivate rapidly when exposed to an oxidizing environment.^[45] In addition, the catalyst activity per volume and mass must be increased orders of magnitude over conventional technology to meet automotive targets. The WGS reactor targets based on Department of Energy projections for 2004 transportation fuel cells are <0.11 kWe⁻¹, <0.1 kg kWe⁻¹ at a cost of <\$1 kWe⁻¹. These targets are at least 10 times lower than expected using conventional WGS catalysts.^[46] Based on the desired attributes for WGS catalysts used for fuel processing, new catalysts must be developed.

Conventional Cu/Zn/Al and Fe/Cr/Cu WGS catalysts may continue to have a place in fuel processing due to

Table 5. WGS catalyst requirements for mobile and stationary applications.

WGS catalyst attribute	Mobile application	Stationary application
Volume reduction	Critical, <0.11 kW ⁻¹	Not as constrained
Weight reduction	Critical, <0.1 kg kW ⁻¹	Not as constrained
Cost	Critical, <\$1 kW ⁻¹	Not as critical
Rapid response	Critical, <15 s	Load following
Nonpyrophoric	Important	Eliminate purging
Attrition resistance	Critical	No constraint
Selectivity	Critical	Important
No reduction required	Critical	Important
Oxidation tolerant	Critical	Important
Condensation tolerant	Important	Important
Poison tolerant	Desired	Desired
Pressure drop	Important	Important

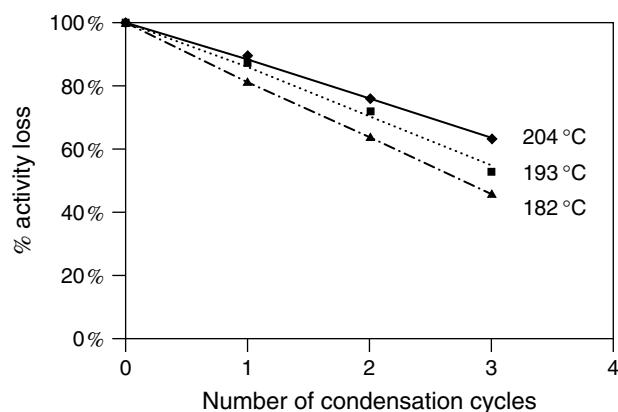


Figure 8. Effect of condensing synthesis gas on commercial Cu/Zn/Al catalyst.

their proven success with long term performance. Fe/Cr/Cu catalysts are known to be poison tolerant, selective and stable at high temperature. The low temperature activity of commercial Cu/Zn/Al catalysts continue to be the benchmark for new developments. The Cu/Zn/Al catalyst has been used successfully in the ONSI Corporation/International Fuel Cell commercial PC25 200 kW power plants with several million hours operating experience. As well, new interest in Cu/Zn/Al catalysts for fuel processing has been generated with the application of low temperature oxygen assisted WGS that combines the WGS and CO oxidation reactions.^[47] Even though the conventional catalysts must be treated with special care, engineered solutions are possible that take advantage of the low temperature activity, low cost, and proven performance.

4.2 Catalyst developments

Recently new formulations have been studied specifically to meet fuel processing requirements. A majority of the published work has focussed on precious metal catalysts. Ru/Fe₂O₃, Au/Fe₂O₃ and Au/TiO₂ all were reported to have high CO conversion activity at 200 °C.^[48–50] As found by Gorte *et al.* and other groups, precious metals supported on ceria exhibit surprisingly high WGS activities.^[20, 22, 29, 51, 52] Other groups investigated precious metals supported on zirconia.^[45, 52–54] As opposed to the very selective conventional catalysts, the formation of methane can be significant for precious metal catalysts causing a decrease in hydrogen production and extreme heat release.^[52, 54] The selectivity of commercial Fe/Cr/Cu and a model 2% Pt/CeO₂ catalyst is compared in Figure 9. At moderately high space velocity the ceria catalyst operated at equilibrium but produced nearly 2% CH₄ at 400 °C in the dry gas. In comparison the Fe/Cr/Cu catalyst did not reach equilibrium conversion until 450 °C but no CH₄

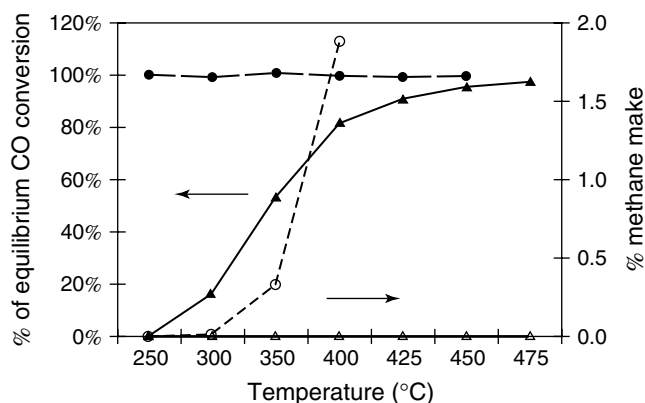


Figure 9. Selectivity of WGS catalysts. (▲, △) Commercial Fe/Cr/Cu, (●, ○) 2% Pt/CeO₂. HTS syngas, total gas SV = 45 000 h⁻¹, S/G = 0.5.

was detected. The selectivity at high temperatures is even more critical when considering fuel processors will have to operate at 5–100% power ratings. The methane leakage will increase when operating at lower turndown ratios due to the longer contact time. It is apparent that precious metal catalysts have potential to replace conventional catalysts, however the activity must be increased greatly to overcome the implied high cost while maintaining high selectivity.

Not all WGS catalyst development has focussed on precious metals. Several groups have investigated lower cost base metal formulations while striving to overcome the pyrophoricity of commercial catalysts. Alternative concepts include transition metal carbides, copper or nickel supported on ceria, cobalt on perovskite and other proprietary base metal formulations.^[21, 46, 55] In general the activities at higher temperature, typically >300 °C show dramatic improvement compared to Fe/Cr catalysts. In some cases the low temperature activities are comparable to commercial Cu/Zn/Al catalysts, but they offer no relief in reducing the low temperature WGS catalyst volume. The interest in these formulations is to develop a catalyst that requires no activation and does not generate significant heat when exposed to air at elevated temperatures. This simplifies the control of the fuel processor and allows air to be used as a purge gas during shut-down cycles. Precious metal catalysts are typically successful meeting these criteria, but it is the low cost of the base metal formulations that make them attractive. It is clear that no WGS catalyst system has met all criteria demanded for fuel processing especially at low temperatures where low CO concentrations are favored by thermodynamics.

4.3 Catalyst poisons and contaminants

The lifetime of industrial Cu/Zn/Al WGS catalysts is typically determined by deactivation due to sulfur poisoning.^[15] Commercially natural gas feedstocks are desulfurized using a Co/Mo or Ni/Mo hydrotreating catalyst with ~5% H₂ in the feed. The resulting H₂S is readily removed over ZnO operating at ~370 °C. Zinc oxide is very effective for H₂S sorption but removal is not complete. Approximately 50 ppb H₂S slips through hot zinc oxide and enters the reformer. Due to the high temperatures in the reformer and the low capacity of Fe/Cr/Cu catalysts for sulfur adsorption, nearly all sulfur is removed by the Cu/Zn/Al low temperature WGS catalyst. After the volume expansion due to the reforming reaction the resulting H₂S concentration is about 10 ppb entering the WGS catalyst reactor. Normally the Cu/Zn/Al LTS catalyst reactors are designed at a space velocity of 1000–2500 h⁻¹ to account for sulfur poisoning. This represents approximately three times the kinetic volume. The Cu/Zn/Al WGS catalyst acts as a total sulfur purifier protecting downstream processes in industrial applications.^[56] Cu/Zn/Al WGS catalysts are highly susceptible to sulfur poisoning but they do provide a purification step that still may be of interest for fuel processing depending on the sulfur removal philosophy. Even if Cu/Zn/Al catalysts are not applied as WGS catalysts they may find application as a total sulfur removal sorbent where sulfur adsorption continues even at zero WGS activity.

The desired desulfurization operating conditions for fuel processing are ambient temperature without hydrogen recycle. There is also interest to reform sulfur bearing fuels followed by sulfur removal in the resulting wet syngas. In either case it is safe to assume that the WGS catalyst will be exposed to H₂S during its lifetime. Only a few publications have investigated the effect of H₂S poisoning on WGS catalyst under fuel processing conditions.^[45, 53, 54] The literature indicates that the Pt/ZrO₂ catalysts are deactivated by the presence of H₂S, but once the sulfur is removed from the reaction gas the fresh catalyst activity is regained. A similar observation was made for Fe/Cr catalyst however they were relatively less susceptible to sulfur poisoning. In comparison the Cu/Zn catalyst was rapidly deactivated to zero WGS activity with the deactivation being irreversible once the sulfur was removed from the gas stream. It is surprising to note that the Pt/ZrO₂ catalyst exhibited a higher activity at 50 ppm H₂S than the fresh Fe/Cr catalyst even when operated at 50 °C higher temperature. It is encouraging that the activity can be maintained at reasonable levels even under extremely high H₂S concentrations and that the effect is reversible.

Other poisons or contaminants may be present in the fuel processor. It is likely that ammonia will be produced

when using autothermal reforming or partial oxidation due to the addition of nitrogen and high temperature operation. Also it is likely that unconverted hydrocarbons may slip from the reforming section especially when using heavy hydrocarbon feedstocks. The exposure of a Pt/ZrO₂ catalyst to low levels of ethylene or benzene did not show any significant deactivation.^[54] Possible contaminants such as chloride, sulfate, calcium, magnesia, etc., may be introduced from the air and water fed to the reforming section or if quench water is added before the WGS reactor. Care must be taken to purify these feeds to eliminate potential poisons of the WGS or eventually the fuel cell stack itself. Recently Hilaire described the formation of a carbonate or bicarbonate species on Pd/CeO₂ after exposure to a WGS reaction gas.^[29] The implication is that the carbonate species may impair the reducibility of the support and therefore decrease the activity. More research is needed to develop a better understanding of the effects of poisons and contaminants on the WGS catalysts before reactor volumes and catalyst lives can be predicted with any certainty.

5 SUMMARY AND OUTLOOK

To achieve the maximum performance, opportunities exist to apply novel reactor concepts to fuel processing. If the exothermic heat of reaction can be removed from the reactor, the thermodynamics can be exploited by driving down the exit temperatures. Micro-channel reactors appear to be able to accomplish the formidable heat transfer task while achieving small reactor volumes.^[52] However, it will require high performance catalysts to take advantage of the favorable low temperature equilibria.

The catalyst cost is worth some discussion especially when considering precious metal formulations. Making the following assumptions an estimate about the relative costs of precious metal vs conventional catalysts can be made:

- cost of Fe/Cr/Cu and Cu/Zn catalysts are \$10.61⁻¹ and \$17.31⁻¹, respectively
- precious metal loading at 2 wt% and washcoat loading of 150 g l⁻¹
- precious metal cost is 40% of the total catalyst cost
- precious metal cost \$600 troy ounce⁻¹.

On an equal volume basis the precious metal is about 14 times that of Fe/Cr/Cu catalyst and is sensitive to precious metal price. Therefore the precious metal catalyst activity must be increased at least 10 times to be competitive on a cost basis, but previous discussion has shown that the activity must be improved over 100 times to meet activity requirements for fuel processing. Precious metal catalysts may offer benefits over the Cu/Zn and Fe/Cr/Cu catalysts

that a higher cost may be acceptable if the durability and redox resistance can be proven. Substantial progress has been made in developing novel base metal formulations that can meet some of the criteria necessary for fuel processing but significant activity improvements are needed.

The challenges to meet all the demands of the WGS catalyst for fuel processing applications are great. The largest obstacles are increasing the activity by orders of magnitude to reduce the volume and weight and to retain activity after exposure to condensing and oxidizing conditions during the many expected startup and shutdown cycles. The catalyst must not require a special activation procedure or generate substantial heat when switching from reducing to oxidizing conditions at elevated temperatures. For these reasons conventional catalysts are not applicable for most fuel processing applications without significant engineering and control strategies.

The issues of thermal deactivation and poisoning are rarely addressed in the open literature. Without a detailed understanding of these issues, prediction of reactor volume and life are difficult. Even though WGS catalysts cannot achieve the low carbon monoxide concentrations needed to prevent the deactivation of the current PEM fuel cell stacks, they are able to decrease the carbon monoxide concentrations while increasing hydrogen to a level where selective CO oxidation is effective. At this time, catalyst performance is the driving force to prove the concept of fuel processing for fuel cells as integrated fuel processors are now being tested in the field.

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