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Abstract

This project involved fundamental research and development of novel cerium oxide-based catalysts for the water-gas-shift reaction and the integration of these catalysts with Pd-alloy H₂ -separation membranes supplying high purity hydrogen for fuel cell use. Conditions matching the requirements of coal gasifier-exit gas streams were examined in the project.

Cu-cerium oxide was identified as the most promising high-temperature water-gas shift catalyst for integration with H₂-selective membranes. Formulations containing iron oxide were found to deactivate in the presence of CO₂. Cu-containing ceria catalysts, on the other hand, showed high stability in CO₂-rich gases. This type gas will be present over much of the catalyst, as the membrane removes the hydrogen produced from the shift reaction.

The high-temperature shift catalyst composition was optimized by proper selection of dopant type and amount in ceria. The formulation 10at%Cu-Ce(30at%La)O_x showed the best performance, and was selected for further kinetic studies. WGS reaction rates were measured in a simulated coal-gas mixture. The apparent activation energy, measured over aged catalysts, was equal to 70.2 kJ/mol. Reaction orders in CO, H₂O, CO₂ and H₂ were found to be 0.8, 0.2, -0.3, and -0.3, respectively. This shows that H₂O has very little effect on the reaction rate, and that both CO₂ and H₂ weakly inhibit the reaction. Good stability of catalyst performance was found in 40-hr long tests.

A flat (38 cm²) Pd-Cu alloy membrane reactor was used with the catalyst washcoated on oxidized aluminum screens close coupled with the membrane. To achieve higher loadings, catalyst granules were layered on the membrane itself to test the combined HTS activity/ H₂ -separation efficiency of the composite. Simulated coal gas mixtures were used and the effect of membrane on the conversion of CO over the catalyst was evidenced at high space velocities. Equilibrium CO conversion at 400 °C was measured at a space velocity of 30,000 h⁻¹ with the 10µm- thick Pd₆₀Cu₄₀ membrane operating under a pressure differential of 100 psi. No carbon deposition took place during operation. The performance of the coupled Cu-ceria catalyst/membrane system at 400°C was stable in ~ 30 h of continuous operation.

The overall conclusion from this project is that Cu-doped ceria catalysts are suitable for use in high-temperature water-gas shift membrane reactors. CO₂-rich operation does not affect the catalyst activity or stability; neither does it affect hydrogen permeation through the Pd-Cu membrane. Operation in the temperature range of 400-430 °C is recommended.

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Executive Summary

Optimization of the water-gas shift (WGS) reaction system for hydrogen production for fuel cells is of particular interest to the energy industry. To this end, it is desirable to couple the WGS reaction to hydrogen separation using a semi-permeable membrane, with both processes carried out at high temperatures to improve reaction kinetics and permeation. Reduced equilibrium conversion of the WGS reaction at high temperatures is overcome by product H₂ removal via the membrane.

This project involved fundamental research and development of novel cerium oxide-based catalysts for the water-gas-shift reaction and the integration of these catalysts with Pd-alloy H₂ -separation membranes supplying high purity hydrogen for fuel cell use. Conditions matching the requirements of coal gasifier-exit gas streams were examined in the project.

The first-year scoping studies of WGS catalysts identified Cu-cerium oxide as the most promising high-temperature shift catalyst for integration with H₂-selective membranes. Formulations containing iron oxide were found to deactivate in the presence of CO₂, and were thus eliminated from further consideration. Cu-containing ceria catalysts, on the other hand, showed high stability in CO₂-rich gases. This type gas will be present over much of the catalyst, as the membrane removes the hydrogen produced from the shift reaction. Several catalyst formulations were prepared, characterized and tested in the first year of the project.

Hydrogen permeation through Pd and Pd-alloy foils was investigated in a small flat- membrane reactor. The effect of temperature on the hydrogen flux through pure Pd, Pd₆₀Cu₄₀ and Pd₇₅Ag₂₅ alloy membranes, each 25 μm thick, was evaluated in the temperature range from 250°C to 500°C at upstream pressure of 4.4 atm and permeate hydrogen pressure of 1 atm. Flux decay was observed for the Pd-Cu membrane above 500 °C. From 350-450 °C, an average hydrogen flux value of 0.2 mol H₂/m²/s was measured over the Pd-Cu membrane. These results are in good agreement with literature data.

During the second and third years of the project, we conducted reaction rate measurements, optimized the catalyst kinetics by proper choice of the dopant oxide (lanthanum oxide) in ceria, conducted long-term stability studies, and collected H₂ permeation data using unsupported flat, 10 μm-thick Pd-Cu membranes over a wide temperature window and in various gas mixtures. A special wet etching technique was used to produce defect-free thin membranes from 25 μm-thick Pd-Cu foils.

The high-temperature shift catalyst composition was optimized by proper selection of dopant type and amount in ceria. The formulation 10at%Cu-Ce(30at%La)O_x showed the best performance, and was selected for further kinetic studies. WGS reaction rates were measured in a simulated coal-gas mixture. The apparent activation energy, measured over aged catalysts, was equal to 70.2 kJ/mol. Reaction orders in CO, H₂O, CO₂ and H₂ were found to be 0.8, 0.2, -0.3, and -0.3, respectively. This shows that H₂O has very little effect on the reaction rate, and that both CO₂ and H₂ weakly inhibit the reaction. Good stability of catalyst performance was found in 40-hr long tests.

A series of hydrogen permeation tests were conducted in the small flat-membrane reactor using 10 μm-thick Pd-Cu membranes. Minor inhibitory effects of CO and CO₂ were found at temperatures above 350 °C, while H₂O vapor had no effect on hydrogen permeation. No carbon deposition took place during

many hours of membrane operation. The reaction extent on the blank (catalyst-free) membrane was also negligible. A larger (38 cm²) flat- membrane reactor was used with the catalyst supported on screens close coupled with the Pd-Cu membrane. To achieve higher loadings, catalyst granules were layered on the membrane itself to test the combined HTS activity/ H₂ -separation efficiency of the composite. Simulated coal gas mixtures were used and the effect of membrane on the conversion of CO over the catalyst was evidenced at high space velocities. Equilibrium CO conversion at 400 °C was measured at a space velocity of 30,000 h⁻¹ with the 10µm- thick Pd₆₀Cu₄₀ membrane operating under a pressure differential of 100 psi. Operation of the coupled Cu-ceria catalyst/membrane system at 400°C was stable in ~ 30 h of continuous operation.

The overall conclusion from this project is that Cu-doped ceria catalysts are suitable for use in high-temperature water-gas shift membrane reactors. CO₂-rich operation does not affect the catalyst activity or stability; neither does it affect hydrogen permeation through the Pd-Cu membrane. Operation in the temperature range of 400-430 °C is recommended.

Introduction

The water-gas shift (WGS) reaction, $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$, is used industrially for the production of hydrogen for ammonia synthesis and for adjusting the CO/H_2 ratio for the subsequent synthesis of methanol. Recently, there has been a renewed interest in WGS reaction because of its potential use in supplying hydrogen for fuel cell power generation. Fuel cells are currently undergoing rapid development for both stationary and transportation applications.

Industrially, WGS is carried out at two temperature regimes; the high-temperature shift reactors use a $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalyst, which can effectively reduce CO from several percentage points to the equilibrium CO value dictated by the operating temperature; further reduction of CO takes place at low temperatures over a more active catalyst based on Cu-ZnO. This catalyst is very sensitive to temperature excursions, operating in the narrow temperature window of 200-250°C, requires careful activation (in H_2 gas), and is readily deactivated by exposure to air or by water condensation. Thus, this type catalyst is unsuitable for use with low-temperature PEM fuel cells, under development for residential and automotive applications.

Optimization of the WGS reaction system for hydrogen production for fuel cells is of particular interest to the energy industry. High-temperature shift may be used to increase the hydrogen content of coal-derived gas produced by gasification or of reformat gas produced by autothermal reforming of fuel oils. Conversion of CO over the high-temperature shift (HTS) catalyst is limited by the equilibrium of the shift reaction. To overcome the equilibrium limitation, a highly selective membrane may be used to remove hydrogen from the product gas. Thus, a HTS membrane reactor is envisioned for pure hydrogen generation to feed a number of fuel cells, including the solid oxide fuel cell (SOFC) and the PEM fuel cell types. There are several challenges in developing a HTS membrane reactor that is small and cost-effective. The membrane should comprise a minimal amount of Pd, and the catalyst should be both robust and active in the presence of large amounts of CO_2 , since H_2 will be continuously removed by the membrane. Finally, the membrane permeance must match the hydrogen flux dictated by the catalyst activity.

In an economical analysis of palladium membrane reactors for the WGS reaction¹, costs of different membrane systems were compared with costs of conventional systems (high temperature shift followed by low temperature WGS and separation) for a fixed pure hydrogen recovery. The results showed that to make membrane reactors possible as alternatives to traditional reactor systems, the Pd thickness should be less than or equal to 20 μm , or some new material or alloy more permeable to hydrogen and less expensive than palladium should be found.

This project involved fundamental research and development of novel shift catalysts and the integration of these catalysts with H_2 -separation membranes supplying high purity hydrogen for fuel cell power generation. The approach taken here was to treat the WGS catalyst and membrane as a single, tightly coupled system designed to operate efficiently over a wide temperature window.

The first-year screening studies of WGS catalysts identified Cu-cerium oxide (ceria) as the most promising high-temperature shift catalyst for integration with H_2 -selective membranes². Formulations containing iron oxide were found to deactivate in the presence of CO_2 , and were thus eliminated from further consideration. This is in agreement with a recent report from SUNY-Buffalo³. Cu-containing ceria catalysts, on the other hand, showed high stability in CO_2 -rich gases. This type gas will be present over much of the catalyst, as the membrane removes the hydrogen produced in the shift reaction. Several catalyst formulations were prepared, characterized and tested during the course of the project.

Reaction rate measurements over a selected catalyst composition were carried out in a lab –scale packed bed reactor. H₂ permeation data were collected with unsupported, 10 μm -thick flat Pd-Cu membranes over a wide temperature range and in various gas mixtures.

Experimental

1. Catalyst preparation

The Cu- and Fe-containing ceria catalysts were prepared by an adaptation of the urea gelation co-precipitation (UGC) method for ceria-based mixed oxides. This method produces more homogeneous mixed oxides with finer particle size than conventional co-precipitation^{4,5}. The following steps are involved in the UGC method: dissolving urea and (NH₄)₂Ce(NO₃)₆, La(NO₃)₃ or ZrO(NO₃)₂, and Cu(NO₃)₂·3H₂O or Fe(NO₃)₃·9H₂O in required amounts in de-ionized water; heating the solution to boiling; adding water when precipitation begins (about 30 min after boiling); aging the precipitate in boiling water with constant stirring and addition of water for 8 hours; filtering and washing the precipitate twice in 50-70°C water with constant stirring for 30 min each time; and drying the precipitate at about 100°C for 8 h. The dried lump was crushed into particles smaller than 150 μm in diameter and calcined in air by heating slowly (2°C/min) to 650°C and keeping it at this temperature for 4 h.

Many formulations of the catalyst were prepared. La or Zr was used as dopant in ceria in small amounts (from 10 to 30 at %). These dopants were added to improve the surface area and thermal stability of ceria. Copper or iron oxide was a minor component in ceria. All formulations are written with the atomic amounts of the additive indicated. As an example, the formulation 5at%Cu-Ce(10at%La)O_x means:

$\text{Cu}/(\text{Cu}+\text{Ce}+\text{La}) = 0.05$, $\text{Ce}/(\text{Cu}+\text{Ce}+\text{La}) = 0.95 \times 0.90$, and $\text{La}/(\text{Cu}+\text{Ce}+\text{La}) = 0.95 \times 0.10$.

C12-4-02, a commercial catalyst containing 80-95 wt% Fe₂O₃, 5-10 wt% Cr₂O₃, <5 wt% CrO₃, 1-5 wt% CuO and 1-5 wt% graphite, was provided by United Catalysts, Inc. in pellet form, and used after crushing it to <150μm size powder.

5wt%CeO₂/C12-4-02 was prepared by deposition/precipitation of cerium hydroxide onto the C12-4-02 particles through the following steps: adding Ce(NO₃)₃ solution dropwise into a slurry of the particles held at a constant pH=7 in a (NH₄)₂CO₃ solution and under constant stirring; aging the precipitate for 1 hour at 70°C; filtering it and washing with 70°C water for 30 min; drying the precipitate at about 100°C overnight; calcining the resultant powder at 400°C for 10 hours using a heating rate 2°C/min. to reach this temperature.

A leached sample was prepared by immersing a 10%Cu-Ce(10%La)O_x sample in 70% HNO₃ solution for 8 h, filtering and washing it twice with de-ionized water, drying it at about 100°C overnight and calcining it at 400°C for 4 h.

2. Catalyst characterization

The elemental composition of each sample was analyzed by inductively coupled plasma (ICP) spectroscopy. Hydrogen peroxide and nitric acid were used to dissolve the solids at room temperature. The BET surface area of each sample was measured by single- point nitrogen adsorption/ desorption cycles in a Micromeritics Pulse Chemisorb 2705 instrument, using a 30%N₂/He gas mixture.

Temperature programmed reduction (TPR) tests with H₂ were run in the Micromeritics instrument according to the following procedure: about 1 gram sample was heated to 350°C (10°C/min) in 50ml/min (NTP) 20%O₂/He and kept at this temperature for 30 min to fully oxidize the sample. Heating was then stopped and when the temperature dropped to 200°C, purge gas, 50 ml/min N₂ (99.999%), was switched in. TPR began after the sample had been cooled to room temperature. The reduction gas was 20%H₂/N₂ (50 ml/min) and the heating rate was 5°C/min.

Temperature programmed oxidation (TPO) tests were run according to the following procedure: the sample was heated to 350°C (10°C/min) in He (99.999%, 50ml/min) and kept at 350°C for 30 min to remove any CO₂ adsorbed. After the sample was cooled down to room temperature, it was heated in a 20%O₂/He (50ml/min) gas mixture to 650°C at a heating rate of 5°C/min. A mass spectrometer (MKS-model RS-1) was used for detection of CO₂.

X-ray powder diffraction (XRD) analysis was performed on a Rigaku 300 X-ray Diffractometer with rotating anode generators and a monochromatic detector. Cu K_α radiation was used. Samples in fine powder form were directly pressed onto a 3/4 by 5/8 inch frosted area etched on a glass holder. A small amount of tungsten powder was added to the sample to calibrate the peak position. The crystal size of ceria was determined by the Scherrer equation, and the lattice constant of ceria was determined from Bragg's law.

X-ray photoelectron spectroscopy (XPS) was performed using a Perkin Elmer 5200C instrument with a 300 W (15kV by 20mA) aluminum K_α anode as X-ray source. Samples used in XPS analysis were in powder form pressed on a double-sided adhesive copper tape. The tape with the sample was mounted on a sample holder and introduced into the XPS vacuum chamber. Analysis was performed after a desired low pressure in the vacuum chamber had been reached.

3. Activity tests in a packed-bed microreactor

CO conversion tests were performed at atmospheric pressure with 150 mg catalyst load on a quartz frit at the center of a flow quartz-tube microreactor (1.0 cm ID, 50cm long), which was heated inside an electric furnace. The contact time was 0.09g·s/cc, with the total gas flow rate of 100ml/min (STP). This corresponds to a gas hourly space velocity of 80,000 h⁻¹. All samples were used without activation. Initial screening tests were run in mixtures of CO and H₂O in He gas. The gases used were helium (grade 5.0), 10%CO/He or 50%CO/He, 50%CO₂/He or pure CO₂ (grade 4.0), and 50%H₂/He or pure H₂ (ultra high purity). All gas mixtures were certified calibration gases. A hydrocarbon trap was connected at the outlet of the CO/He gas cylinder to remove any iron carbonyl from the CO/He mixture. Water was injected into the flowing gas stream by a calibrated water pump and vaporized in the heated gas feed line before entering the reactor. A condenser filled with ice was installed at the reactor exit to collect water. The exit gas was analyzed by a Carle gas chromatograph, equipped with a thermal conductivity detector and a 1/4-inch dia. x 6 ft long Carbosphere column for CO and CO₂ separation. The CO conversion was calculated from the concentration of CO and CO₂ detected. There was no methane formation even when H₂ and CO₂ were included in the feed gas mixture.

Rate measurements were performed at atmospheric pressure. Catalyst samples (< 150 μm- size particles) were diluted with quartz salt and loaded on a quartz frit at the center of the flow quartz-tube microreactor described above. Tests were run at very short contact times to ensure operation in the

kinetic regime. The activation energies were calculated from the reaction rates at CO conversions $< \sim 15\%$.

The reaction rate was calculated by:

$$\text{Rate} = N_{\text{CO}} X_{\text{CO}} / W_{\text{cat}} (\text{mol g}^{-1} \text{s}^{-1}) \quad (1)$$

where N_{CO} is the molar flow rate of CO in the feed gas in mol/s, X_{CO} is the conversion of CO to CO_2 , and W_{cat} is the catalyst weight in grams.

4. Membrane Reactors and Testing Procedure

A stainless steel membrane holder with copper gaskets was constructed and used for hydrogen permeability tests. Hydrogen (99.97% purity) pressure was measured with an Omega PX880 pressure transducer with $\pm 0.25\%$ accuracy. The bleed flow rate was varied using an outlet valve. Bleed and permeate flow rates were measured by a bubble flow-meter and had a deviation of $\pm 3\text{-}5\%$. The temperature was measured by a thermocouple at the outer edge of the membrane holder. The flow rate of each gas was controlled by a mass flow meter. When water was used, it was injected into the flowing gas stream by a calibrated syringe pump and vaporized in the heated gas feed line before entering the furnace.

Reduced thickness, free-standing Pd-Cu membranes were prepared by wet etching of 25- μm thick foils according to methods disclosed in US Patent 6,103,028⁶. Each $\text{Pd}_{60}\text{-Cu}_{40}$ membrane (diameter 9/16 inch, disk area 1.6 cm^2) was punched out, washed with acetone using ultrasound and cleaned with fine blotting paper. Fresh membranes were heated to 400°C at a hydrogen upstream pressure of 4.4 atm (50 psig) and hydrogen downstream pressure 1 atm (0 psig). After the permeation in pure hydrogen was stable, hydrogen permeation was measured at the desired temperatures and pressures in either pure H_2 or a gas mixture. After about 20 min of stabilization, the H_2 flux was measured over a period of 30-40 min at each temperature to ensure steady-state operation.

A large flat- membrane (5 cm x 10 cm oval) reactor was used during the last year of the project. The Pd-Cu membranes were thinned to 10 μm using the etching procedure described above. Initially, the decision was made to deposit the catalyst on fine mesh aluminum screens. Various procedures were evaluated to prepare the catalyst and washcoat the screens with a uniform adherent layer. The successful procedure involved using a sonicator to break the catalyst powders suspended in alcohol solution into very fine particles. Etched and oxidized aluminum screens were dipped into the slurry many times with intermittent drying in a stream of air to a desired catalyst loading. A total of 1.1 g catalyst was thus coated on the aluminum screen corresponding to ~ 40 wt% loading. In later tests, to achieve higher loadings, we eliminated the screens and directly packed the catalyst (in granular form) onto the Pd-Cu membrane. Tests were run with simulated coal-gas mixtures over a wide range of space velocities and at temperatures in the range 350 – 500 °C. Long-term performance stability tests were conducted at 450 °C.

Results and Discussion

1. Catalyst Characterization

Table 1 shows the bulk compositions, BET surface areas, ceria crystallite sizes, and ceria lattice constants of the catalyst samples prepared and tested in this work. The bulk compositions are almost the same as in the preparation. The samples containing up to 15 at. % Cu or Fe, after calcination at 650°C, have surface areas around 90 m²/g. At higher than 15 at. % content, addition of Cu or Fe decreases the surface area of La-doped ceria.

It has been reported by Li et al.⁵ that in the Cu-ceria system, Cu or CuO clusters are non-detectable by XRD up to ~15 at. % copper content. Similarly, we did not see reflections of Cu compounds in all the samples listed in Table 1. Also, crystallites of Fe or its oxides in our Fe-ceria samples are also too small to detect by XRD. In the Zr-doped samples and the 8 at. % La-doped samples, there was no reflection of lanthana or zirconia because both of them go into solid solution with ceria, and the only XRD-detectable phase was ceria. In the samples with 30 at. % La, small amounts of hexagonal, tetragonal, and monoclinic crystals of lanthanum oxide carbonate (La₂CO₅) were identified in addition to ceria (Table 1); only hexagonal La₂CO₅ still existed after use in the WGS reaction. The lattice parameter of ceria (5.41 Å) increases with La³⁺ doping and decreases with Zr⁴⁺ doping, as a result of the difference of the ionic radii (La³⁺ > Ce⁴⁺ > Zr⁴⁺). Used samples (either after 32 h or 20 h) lost about 20% of their surface area (Table 1). Concomitantly, the crystal size of ceria increased by about 20% as measured by XRD.

2. Identification of most active and stable catalyst composition

Cu or Fe-Ce(8%La)O_x catalysts (with different contents of Cu or Fe) were evaluated in WGS tests with a 2%CO-10%H₂O-He gas mixture. The catalyst amount was 0.15 grams and the contact time was 0.09 g*s/cc. The space velocity was 80,000 h⁻¹ (NTP) except for the commercial iron-chrome catalyst, C12-4-02 (48,000 h⁻¹) due to its different density. Steady-state CO conversion plots are shown in Figure 1. The Fe-Ce(8%La)O_x samples have higher activities than Ce(8%La)O_x, showing that addition of Fe increases the activity of ceria. The commercial catalyst C12-4-02 is more active than the Fe-Ce(8%La)O_x samples, but all the Cu-Ce(8%La)O_x samples are much more active than C12-4-02. The CuO contained in C12-4-02 may be the reason that C12-4-02 is more active than the Fe-Ce(8%La)O_x samples. Among the Cu-ceria samples, 10%Cu-Ce(8%La)O_x and 15%Cu-Ce(8%La)O_x were the most active. The 13%Fe-Ce(8%La)O_x was the most active among the Fe-ceria samples.²

H₂-TPR of various catalyst compositions are shown in Figures 2 and 3, and Table 2. These help us understand the differences in WGS activity among the catalysts shown in Figure 1. The low-temperature peak (surface oxygen reduction) of ceria shifts to lower temperatures with addition of Cu. As shown in Figure 2, the presence of even 1 at. % Cu shifts the peak reduction temperature by more than 100°C. With higher copper contents, the effect is much more pronounced. Thus, Cu dramatically increases the reducibility of ceria, as has been amply documented in the literature.^{5, 7, 8} As shown in Table 2, the normalized hydrogen consumption does not change much with addition of copper above ~ 1 at. %. There is no need to use ceria catalysts containing more than ~ 10 at% copper, in agreement with the activity data of Figure 1. Figure 1 shows that the sample containing 40 at% Cu was inferior, probably due the lower surface area and further sintering during reaction. Addition of Fe increases the reducibility of ceria, but to a lesser extent than Cu, as shown in Figure 3 and Table 2. Promotion of iron-based shift catalysts by ceria has been reported in the literature and attributed to enhancement of reducibility^{19, 20}. The activity tests of the iron oxide-ceria catalysts performed in the present work correlate well with the H₂-TPR results of Figure 3. The best Fe-ceria catalyst shown in Figure 1 was the one containing 13 at.

% Fe. Interestingly, as shown in Figure 3, for the sample containing 13 at. % Fe, the iron oxide reduction begins and peaks at lower temperatures. The reduction of the bulk oxygen of ceria is not affected by the presence of either iron (Figure 3) or copper oxide (not included in Figure 2).

In many practical cases, hydrogen will be obtained from coal gasification. As mentioned above, CO₂ enrichment of the gas occurs when the WGS reaction is integrated with hydrogen permeation through a dense membrane. Therefore, the WGS activities of the 10%Cu-Ce(8%La)O_x and 13%Fe-Ce(8%La)O_x catalysts were tested and compared with the commercial catalyst C12-4-02 in a simulated coal gas mixture with a molar composition 10%CO-34%H₂O-10%CO₂-15%H₂-He (here helium is used instead of N₂) and in a CO₂-rich gas containing 2%CO-10%H₂O-35%CO₂-He, both at contact time 0.09 g*s/cc. In both gas mixtures (Figure 4 and Figure 5), the ranking of the catalysts is the same as that in Figure 1, i.e. the 10%Cu-Ce(8%La)O_x is more active than C12-4-02, which is superior to 13%Fe-Ce(8%La)O_x. Lund et al.³ have reported a dramatic poisoning effect of CO₂ on iron oxide-based catalysts, whereby the reaction rate decreased by several orders of magnitude in CO₂-rich gas. Cu-ceria, on the other hand, shows very good activity, reaching equilibrium CO conversions above 450 °C, in the simulated coal gas mixture and at high space velocity (80,000 h⁻¹, NTP), Figure 4. After all the measurements from 300°C to 600°C (50°C interval, 1.5 h at each temperature), the CO conversions over both 10%Cu-Ce(8%La)O_x and C12-4-02 were checked again at 400°C, as shown by a single filled triangle and a single circle in Figure 4. The CO conversions over both catalysts dropped, but both were still higher than that over the 13%Fe-Ce(8%La)O_x sample at 400°C before exposure to high temperatures; the conversion over 10%Cu-Ce(8%La)O_x was still higher than that over C12-4-02. The activity of Cu-ceria is stable in the artificially high CO₂-content gas mixture, Figure 5. Thus, only the Cu-ceria catalyst merits further development for high-temperature water-gas shift reaction carried out in a membrane reactor.

Dopant effect. Steady-state conversions of CO in WGS over the 10%Cu-Ce(dopant)O_x samples with dopants 8%La, 30%La and 24%Zr were measured in the microreactor in a gas mixture of 10%CO-30%H₂O-10%CO₂-15%H₂-He, with a catalyst amount of 0.05 g and at contact time 0.012 g*s/cc. The activity was in the order of 30%La > 24%Zr > 8%La. Because the surface areas of these samples are all similar (Table 1), we conclude that the effect is chemical, and not scalable with the surface area. Figure 6 shows the stability of 10%Cu-Ce(30%La)O_x and 10%Cu-Ce(24%Zr)O_x with time-on-stream at 450°C. The contact time was 0.0303 g*s/cc. Higher conversions of CO were measured over the La-doped sample throughout the 40 hour-long test period. Both catalysts lost some activity fast at the beginning, but their activities became stable after 20 hours on-stream.

No carbon deposition was found on either of the two used samples, as checked by temperature-programmed oxidation (TPO). The BET surface areas of both catalysts decreased by about 20% after use for either 32 h or 20 h (Table 1), and the increase of ceria crystal size of both samples (Table 1) was also around 20%. The drop of CO conversion over both catalysts (after 32 h or 20 h) was more than 20%. Over both catalysts, the CO conversion after 2 hours was around 1.6 times of the conversion after 20 hours. Therefore, loss of surface area (together with increase of ceria crystal size) was not the only reason for the observed activity loss. XPS analysis of the 10%Cu-Ce(30%La)O_x sample (Table 3) showed that, after reaction under similar conditions (10%CO-30%H₂O-10%CO₂-15%H₂, 450°C, 34 h), Cu enrichment of the surface from 13 to 21 at. % took place, while the surface concentration of La did not change. It is possible that copper enrichment of the ceria surface contributed to the activity loss.

On the basis of these findings, the 10%Cu-Ce(30%La)O_x formulation was selected for further study in this project.

3. WGS reaction rate measurements

The kinetics of the WGS reaction were investigated over the selected catalyst composition. The results were summarized in our second annual report to DOE.⁹ Additional kinetics work was performed during the last year of the project.

The WGS reaction rate was measured over the 10%Cu-Ce(30%La)O_x catalyst in the simulated coal gas mixture used in Figure 6. The apparent activation energy of the reaction was calculated from the following equations:

$$\text{Rate} = R_f (1-\beta) \quad (2)$$

$$R_f = R_{f0} \exp(-E_a/RT) \quad (3)$$

where β is the approach to equilibrium,

$$\beta = P_{\text{CO}_2}P_{\text{H}_2} / (K_{\text{eq}}P_{\text{CO}}P_{\text{H}_2\text{O}}) \quad (4)$$

R_f is the forward reaction rate, K_{eq} is the WGS reaction equilibrium constant, E_a is the apparent activation energy in J mol^{-1} , $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$ is the ideal gas constant, and T is temperature in degrees Kelvin. The factor $(1-\beta)$ represents the effect of the reverse reaction. If the feed gas does not include CO_2 and H_2 , $\beta = 0$, and equation (3) is used to calculate the activation energy.

Figure 7 shows Arrhenius-type plots for the WGS reaction rates measured over the 10%Cu-Ce(30%La)O_x and the copper-free Ce(30%La)O_x catalysts. The apparent activation energy of the reaction over these catalysts is 70.4 kJ/mol and 98.5 kJ/mol, respectively. This large difference is attributed to the modification of the surface of ceria by the addition of copper. As discussed before, copper greatly increases the reducibility of the surface oxygen of ceria. This modified site is the active site for the WGS reaction. The reaction pathway on copper-free ceria is different, and of larger activation energy.

At high temperatures, such as 450°C, the fresh 10%Cu-Ce(30%La)O_x sample deactivates fast in the initial time-on-stream (Figure 6). To obtain a stable conversion and reaction rate, and an accurate measurement of the activation energy, we measured the reaction rate over the 10%Cu-Ce(30%La)O_x sample after it had been used in the reaction gas mixture at 450°C for 20 h. The same activation energy was measured over the used sample (from 300 to 450°C) and the fresh one (from 250 to 350°C). The Ce(30%La)O_x catalyst does not deactivate that fast, so the fresh sample was used in all tests.

Comparison of reaction rates with other Cu-ceria catalysts^{10, 11} is also shown in Figure 7. The values of reaction rate on the 10%Cu-Ce(8%La)O_x catalyst prepared by the same UGC procedure, but calcined at 400°C, and tested in a slightly different gas composition¹⁰, are very close to the rates reported here. If extrapolated to our gas composition, the rates in ref. 10 would drop a little, and cross ours at 250°C. The difference in activation energy is not much, and may be due to the different gas composition used. Another comparison was made with the rates on an 8wt%Cu-ceria sample, reported recently by

Koryabkina et al.¹¹ This is shown by a dashed line in Figure 7, calculated using the reported reaction orders, activation energy, and rate at 200°C in 7%CO-22%H₂O-8.5%CO₂-37%H₂-bal. inert gas. While not exposed to high temperatures, this Cu-ceria sample is comparable to our 450°C-used sample, but less active than our fresh Cu-ceria catalyst, which contains only ~ 5 wt% Cu. A possible explanation for the higher activity of our sample is the presence of lanthana and the different preparation method, which leads to better dispersion of Cu in ceria.

Figure 8 shows WGS reaction rates measured over the 10%Cu-Ce(30%La)O_x and Ce(30%La)O_x samples in a gas mixture free of H₂ and CO₂: 11%CO-23%H₂O-He. Under this condition, both samples showed better stability than in the product-containing gas. The fresh 10%Cu-Ce(30%La)O_x sample was first tested at 450°C for 1 hour and then at each temperature of 400°C, 350°C, 300°C and 250°C for 40 minutes. After the catalyst was tested for 20 h at 450°C the activation energy did not change. The apparent activation energy is 54 kJ/mol over 10%Cu-Ce(30%La)O_x and 75 kJ/mol over Ce(30%La)O_x, i.e. considerably lower than the values measured in the simulated coal gas mixture in Figure 7, and the reaction rates were higher than the those in Figure 7. Therefore, there is inhibition of the reaction by at least one of the two reaction products (H₂ or CO₂), but the total inhibition effect of H₂ and CO₂ decreases with temperature.

The WGS reaction orders in CO, H₂O, CO₂ and H₂ were evaluated at 450°C (Figure 9). The catalyst sample was pretreated in 10%CO-30%H₂O-He at 450°C for 30 h to avoid deactivation during the kinetics measurements. The rate data were fitted with a power law equation:

$$\text{Rate} = k_f P_{\text{CO}}^a P_{\text{H}_2\text{O}}^b P_{\text{CO}_2}^c P_{\text{H}_2}^d (1-\beta) \quad (5)$$

where the rate is in mol/g/s, P_i is the partial pressure of component i in atm, k_f is the forward reaction rate constant, a, b, c, d are forward reaction orders, and β is the approach to equilibrium as described by equation (4).

The reaction orders in CO, H₂O, CO₂ and H₂ were found to be 0.8, 0.2, -0.3, and -0.3, respectively. This shows that H₂O has very little effect on the reaction rate, and that both CO₂ and H₂ weakly inhibit the reaction.

A comparison of reaction orders and apparent activation energies with those over other catalysts¹⁰⁻¹³, is shown in Table 4. The gas composition used in our work was not significantly different from that of Koryabkina et al.¹¹ Comparing to their data over Cu-ceria, the reaction order in CO over our catalyst is similar, but the order in H₂O is lower, and the inhibition by either CO₂ or H₂ is less. We attribute these differences to temperature difference; our tests were run at 450°C, a temperature much higher than the 240°C examined in ref. 11.

The almost first order dependence of the WGS reaction rate in P_{CO} and almost zeroth order in P_{H₂O} is interesting, and indicative of a surface saturated with hydroxyls. Whether CO adsorbs on neutral or charged copper clusters or copper ions embedded in the ceria lattice is of fundamental interest and will be explored in future work. The important finding is that the Cu-O-Ce species are stable under WGS conditions at 450°C. Thus, this catalyst is a good alternative to the iron-chrome catalyst for any WGS application, and the only choice for membrane reactor applications.

4. Hydrogen permeation tests

Hydrogen permeation through 10 μ m-thick Pd₆₀Cu₄₀ alloy membranes was investigated in pure hydrogen in the membrane reactor system. To study the effects of CO, CO₂ and H₂O, hydrogen permeation was also measured in the following gas mixtures: 53%CO-H₂, 53%CO₂-H₂, 53%H₂O-H₂ and 10%CO-23%H₂O-10%CO₂-10%He-47%H₂, and, for comparison, also in 53%He-H₂ (or 53%Ar-H₂) at the same flow rate and temperature conditions.

Figure 10 shows the hydrogen flux (hydrogen permeation) through the 10 μ m-thick membrane in the temperature range from 80°C to 450°C at upstream pressure 50 psig (4.4 atm absolute) and permeate hydrogen pressure 0 psig (1 atm absolute). Our data of hydrogen permeation through the 25 μ m-Pd₆₀Cu₄₀ membranes² and data in the literature¹⁴ are also shown in this figure for comparison. The superiority of the thin membrane is clearly depicted in this figure.

Figure 11 shows the effect of CO and CO₂ on H₂ permeation through the 10 μ m-thick membrane in the temperature range 350-450°C. In the 53%CO-H₂ and the 53%CO₂-H₂ gas mixtures, the permeation was less than in the 53%He-H₂ mixture or the 53%Ar-H₂ gas mixture. This shows that both CO and CO₂ decrease H₂ permeation. The lower the temperature, the more pronounced the inhibition. Because the diffusion coefficient of the Ar-H₂ system is close to that of the CO-H₂ or CO₂-H₂ gas mixture, the effect of CO and CO₂ is not due to mass transfer limitation. Overall, the inhibitory effects are minor above 400 °C.

Figure 12 shows that H₂O vapor has a negligible effect on hydrogen permeation through the Pd-Cu membrane. Finally, the overall effect of the simulated coal-gas mixture on the permeation was evaluated. The results are shown in Figure 13 in a mixture of 10%CO-23%H₂O-10%CO₂-10%He-47%H₂; minor inhibition of hydrogen permeation is observed. From this study, we concluded that operation of the coupled catalyst/membrane system at 450 °C would be almost free of inhibitory effects on hydrogen permeation.

To examine how fast the WGS reaction would be on the blank Pd-Cu membrane (without catalyst), a test was run with a feed gas of 20%CO-60%H₂O-20%CO₂ at 450°C in the same system with the permeation path blocked. The total gas flow was 100 ml/min and the conversion of CO was about 1.7%. Since the flowrate of each mixture was 800 ml/min, and at 450°C the reverse WGS reaction is slower than WGS reaction, both the WGS and reverse WGS reaction would be too slow to change the composition of mixture.

A larger (38 cm² oval) flat Pd-Cu membrane reactor was used next with the catalyst close coupled with the membrane. A schematic of this reactor is shown in Figure 14. Testing of the washcoated aluminum screen containing 1.1 g catalyst took place at 430 °C and 150 psi pressure. Equilibrium conversion of CO was attained with screen-membrane assembly at flow rates for which the catalyst screen alone gave 50-60 % of the equilibrium CO conversion. At this point, we decided to use a packed bed of fine granules of catalyst directly resting on the Pd-Cu membrane. At the same time, a smaller water pump was installed to better control low water flow rates. The new configuration with ~ 4.5 g catalyst loading allowed for a broader parametric study.

Figure 15 shows the effect of space velocity on the distance from equilibrium of the CO conversion to CO₂ over the 10%Cu-Ce(La)O_x catalyst- membrane assembly at 400 °C. At medium high space velocities, the effect of the membrane is ‘felt’ by the catalyst. Above about 30,000 h⁻¹, the catalyst

activity is too low to match the flux through the membrane. Only a small area of the membrane is still covered with catalyst granules at the end of these tests. A large fraction of the granules is pushed to one corner of the membrane by the flowing gas stream. The space velocity calculation takes this into consideration.

Figure 16 shows the stability of the selected catalysts in the membrane reactor with time-on stream. At 400 C and a space velocity of 22,000 h⁻¹(NTP), the CO conversion in the reaction gas remained constant at the equilibrium value over a 27 –hr period. No carbon deposition was found on the catalyst or the membrane after this test. Therefore, Cu-ceria catalyst is suitable for high-temperature shift reaction with hydrogen separation through the Pd-Cu membrane. Operation in the temperature range 400- 430 °C is stable. Therefore, reactor modules of 10 µm-thick Pd-Cu membrane with the Cu-ceria WGS catalyst properly washcoated on screens close-coupled to the membrane are suitable for efficient hydrogen generation at high temperatures.

Conclusions

In this project, high temperature water-gas shift catalysts based on Cu-ceria were developed and studied in detail for applications in hydrogen separation by Pd-Cu membrane reactors operating at high temperatures (> 350 °C). A small amount (~ 5 wt%) of copper in ceria is enough to create a very active and stable catalyst. We showed that this type catalyst is superior to iron-based catalysts, such as the commercial iron-chromia materials, which deactivate fast in CO₂ – rich gases. The formulation 10%Cu-Ce(30%La)Ox was the best; this was evaluated in kinetic and structural studies. WGS reaction rates were measured in a simulated coal-gas mixture, and long-term stability of catalyst performance was established. A series of hydrogen permeation tests were conducted in a flat-membrane reactor using 10 µm -thick Pd₆₀Cu₄₀ alloy membranes (produced from thinning of 25 µm- thick foils). Small inhibitory effects of CO and CO₂ were found at temperatures above 350 °C, while H₂O vapor had no effect on hydrogen permeation through the Pd-Cu membrane. No carbon deposition took place during many hours of membrane operation. Washcoating of catalysts on screens close-coupled with the membrane was shown to be feasible. Further development of catalytic Pd-Cu membrane reactors using Cu-ceria as HTS catalyst is recommended operating at temperatures in the range 400-430 °C.

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Table 1. Physical properties of catalyst samples ^a

Sample	Metal Composition (by ICP)		BET surface area	XRD		
	Cu/(Cu+Ce+La)	La/(La+Ce)		Crystalline phase	CeO ₂ particle size ^b	CeO ₂ lattice constant ^c
	Fe/(Fe+Ce+La)	Zr/(Zr+Ce)	(m ² /g)		(nm)	(Å)
	(%)	(%)				
Ce(8%La)O _x	-	7.12	98	CeO ₂ ⁵	7.1 ¹⁵	NM
5%Cu-Ce(8%La)O _x	5.21	7.45	107	CeO ₂ ⁵	5.2 ¹⁵	NM
10%Cu-Ce(8%La)O _x	10.2	7.55	112	CeO ₂	5.1	5.44
10%Cu-Ce(8%La)O _x used ^d	-	-	NM	CeO ₂	6.0	5.44
15%Cu-Ce(8%La)O _x	15.5	7.64	85	CeO ₂ , CuO ⁵	NM	NM
40%Cu-Ce(8%La)O _x	41.7	7.93	66	CeO ₂ , CuO ⁵	NM	NM
6.2%Fe-Ce(8%La)O _x	6.71	7.87	109	NM	NM	NM
13%Fe-Ce(8%La)O _x	12.6	7.57	98	CeO ₂	5.2	5.42
29%Fe-Ce(8%La)O _x	28.4	8.31	80	NM	NM	NM
Ce(30%La)O _x	-	28.8	103	CeO ₂ , La ₂ CO ₅	4.7	5.45
Ce(30%La)O _x used ^e	-	-	72	CeO ₂ , La ₂ CO ₅	5.0	5.45
10%Cu-Ce(30%La)O _x	9.4	28.6	81	CeO ₂ , La ₂ CO ₅	5.1	5.44
10%Cu-Ce(30%La)O _x used ^f	-	-	65	CeO ₂ , La ₂ CO ₅	5.8	5.44
10%Cu-Ce(24%Zr)O _x	10.2	24.2	92	CeO ₂	5.0	5.36
10%Cu-Ce(24%Zr)O _x used ^e	-	-	74	CeO ₂	5.3	5.35
C12-4-02 ^g	-	-	96	NM	NM	NM

^a All catalysts except C12-4-02 were prepared by the UGC method; calcined in air at 650°C, 4h

^b Calculated based on the peak width of crystal plane (111), using the Scherrer equation.

^c Average of values calculated from crystal planes (111), (200), (220), (311), (222), using Bragg's law.

^d Used in 10%CO-34%H₂O-10%CO₂-15%H₂-He at 300-600°C with a 50°C interval, then 400°C, 1.5 h at each temperature.

^e Used in 11%CO-23%H₂O-11%CO₂-17%H₂-He at 450 °C, 20 h.

^f Used in 11%CO-23%H₂O-11%CO₂-17%H₂-He at 450 °C, 32 h.

^g 80-95 wt% Fe₂O₃, 5-10 wt% Cr₂O₃, <5 wt% CrO₃, 1-5 wt% CuO, 1-5 wt% graphite, supplied by United Catalysts, Inc. and tested after crushing to < 150 μm -size particles

NM: Not measured.

Table 2. H₂-TPR peak temperatures and areas (H₂ consumption)

Sample	Peaks below 500°C		
	Temperature (°C)	Total H ₂ consumption (mmol H ₂ /g)	H ₂ consumption by ceria only ^a (mol H ₂ /mol CeO ₂)
C8L ^b	408	0.560	0.106
1%Cu-C8L	135, 302	0.539	0.092
5%Cu-C8L	126, 132, 145(small)	0.737	0.085
10%Cu-C8L	96, 103, 129(small), 164(small)	1.156	0.108
40%Cu-C8L	94, 154(shoulder), 195	3.414	0.078
6.2%Fe-C8L	123, 367		
13%Fe-C8L	119, 359		
29%Fe-C8L	362		

^a after subtraction of the H₂ consumed by CuO

^b Ce(8%La)O_x is denoted as C8L

Table 3. XPS analysis of 10%Cu-Ce(30%La)O_x before and after reaction

Atomic metal ratio	Before reaction	After reaction ^a
Cu/(Cu+Ce+La)	0.133	0.208
La/(Ce+La)	0.330	0.340

^a Used in 10%CO-30%H₂O-10%CO₂-15%H₂-He at 450°C for 34 h.

Table 4. Comparison of Reaction Orders and Apparent Activation Energies

Catalyst	Ref.	Activation Energy, E_a (kJ/mol)	Temp. ^a (°C)	Reaction orders (and range)			
				CO	H ₂ O	CO ₂	H ₂
10at%Cu-Ce(30at%La)O _x ^b	This work	70.4	450	0.8 1-10%	0.2 11-50%	-0.3 5-35%	-0.3 5-40%
8wt%CuO-CeO ₂ ^c	14	56	240	0.9 5-25%	0.4 10-46%	-0.6 5-30%	-0.6 25-60%
10at%Cu-Ce(8at%La)O _x ^d (prepared by UGC method, calcined at 400°C)	12	60	300	0.8 3.4-25%	0.5 2.7-16%	-0.5 13-44%	-0.4 13-44%
Fe ₂ O ₃ -Cr ₂ O ₃	1	-		0.9	0.25	-0.6	0
Promoted Fe ₂ O ₃ -Cr ₂ O ₃	2	95	300-350	1.1	0.53	0	0

^a Temperature at which the reaction rates were measured

^b Varying CO, H₂O, CO₂ or H₂ in 10%CO-30%H₂O-10%CO₂-15%H₂-bal.He

^c Varying CO, H₂O, CO₂ or H₂ in 7%CO-22%H₂O-8.5%CO₂-37%H₂-bal.Ar

^d Varying CO, H₂O, CO₂ or H₂ in 11%CO-26%H₂O-7%CO₂-26%H₂-bal.He

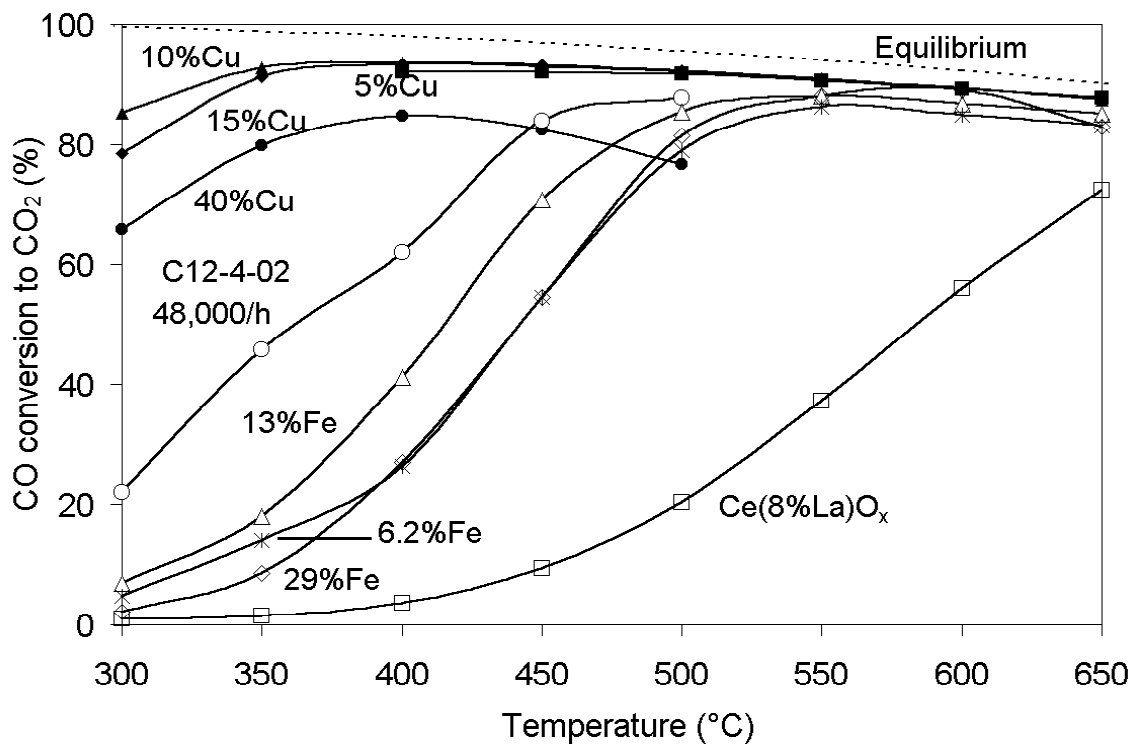


Figure 1. Steady-state WGS performance of Cu- and Fe-Ce(8%La)O_x in 2%CO-10%H₂O-He, 0.09g*s/cc, S.V.=80,000 h⁻¹ (except C12-4-02).

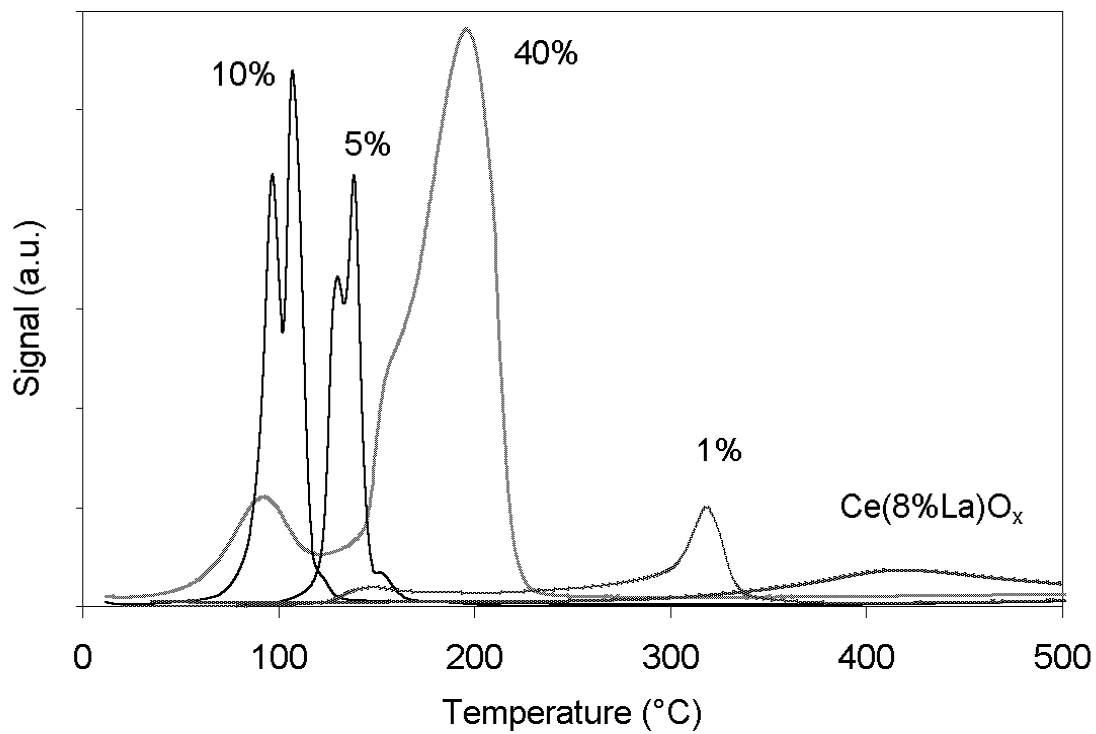


Figure 2. H₂-TPR of x%Cu-Ce(8%La)O_x samples.

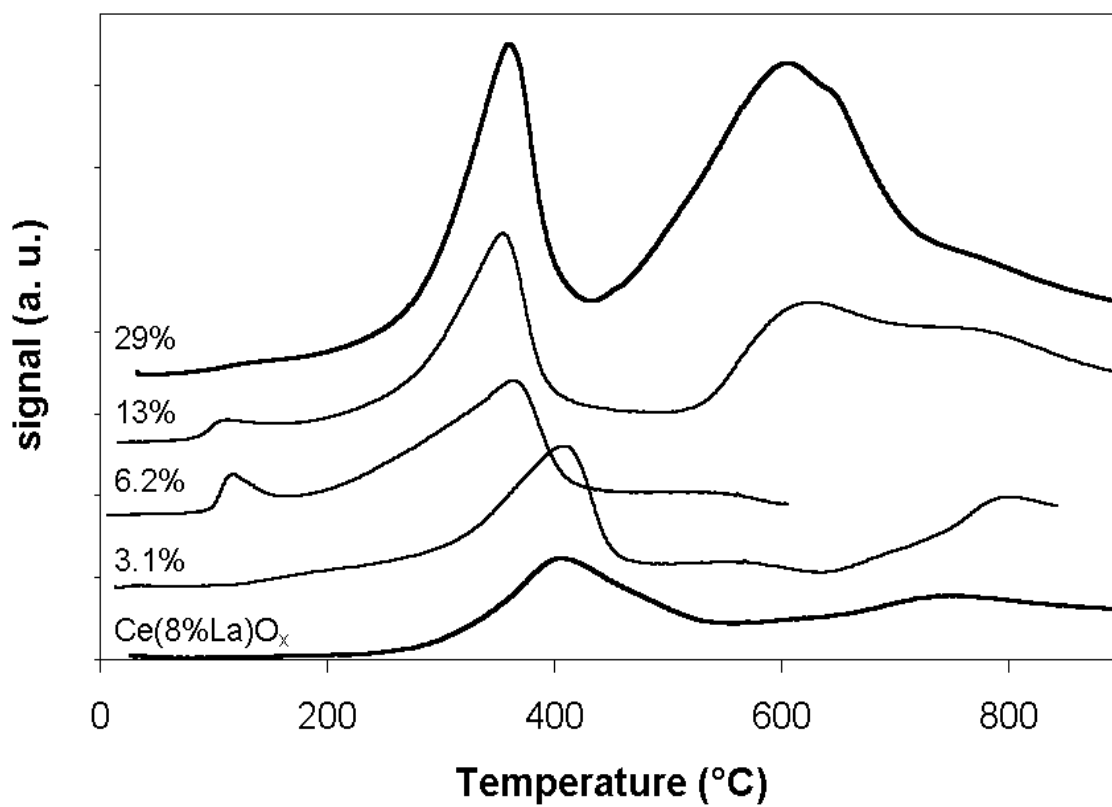


Figure 3. H₂-TPR of x%Fe-Ce(8%La)O_x samples.

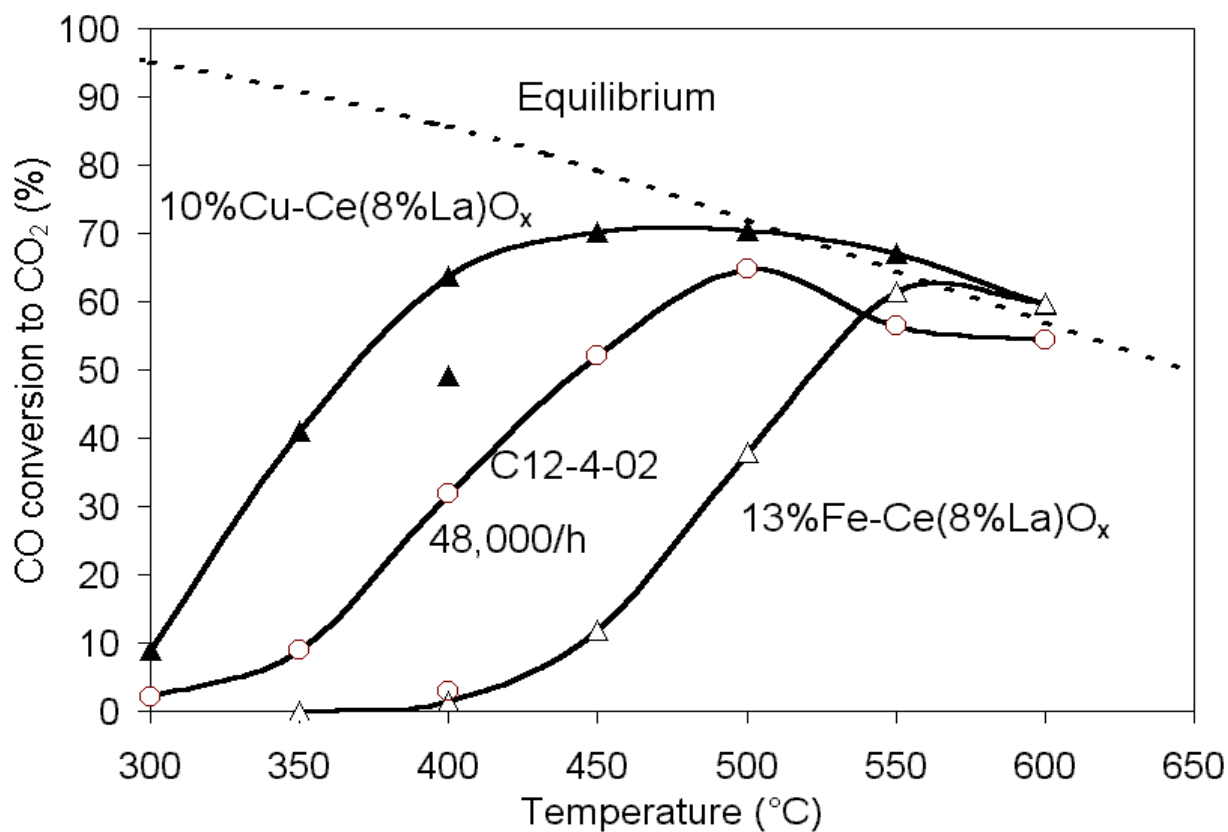


Figure 4. Steady-state WGS activity in a simulated coal-gas composition, 10%CO-34%H₂O-10%CO₂-15%H₂-He, 0.09g*s/cc, S.V.= 80,000 h⁻¹ (except C12-4-02).

Single filled triangle: conversion at 400°C after the 300-600°C measurement over 10%Cu-Ce(8%La)O_x;
 single circle: conversion at 400°C after the 300-600°C measurement over C12-4-02.

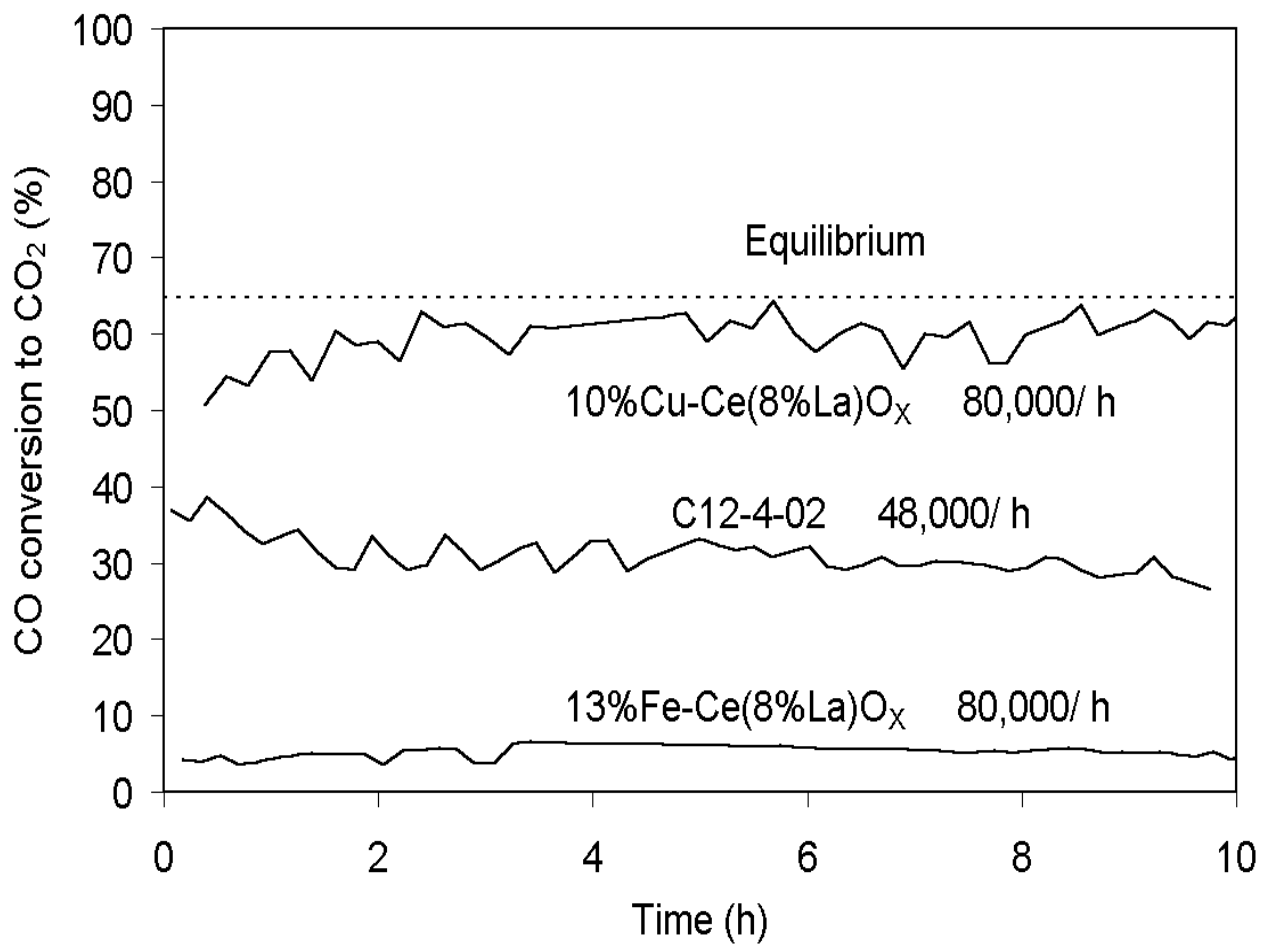


Figure 5. Catalyst activity/stability in 2%CO-10%H₂O-35%CO₂-He, 450°C, 0.09g*s/cc, SV.= 80,000 h⁻¹

¹ (except C12-4-02).

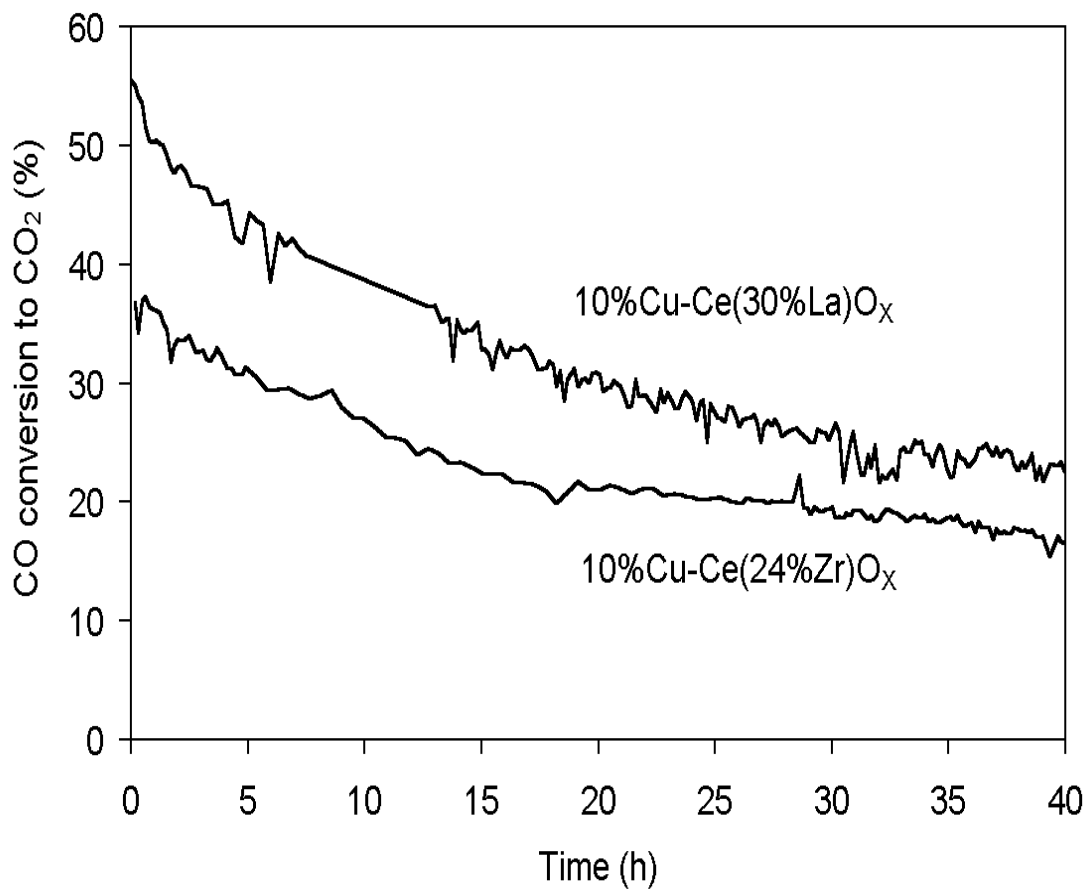


Figure 6. Long-term stability of 10%Cu-Ce(30%La)O_x and 10%Cu-Ce(24%Zr)O_x in 11%CO-23%H₂O-11%CO₂-17%H₂-He, 0.0303g*s/cc, 450°C.

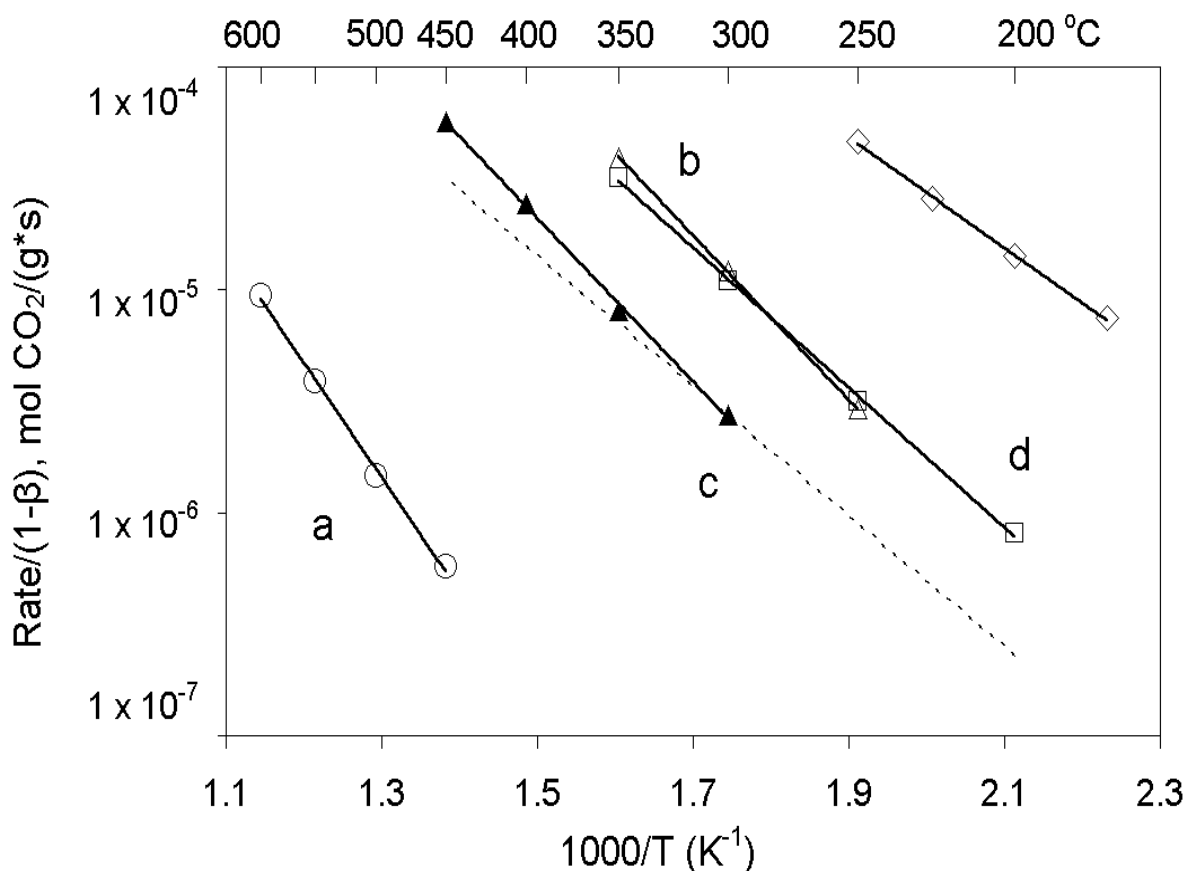


Figure 7. Steady-state WGS reaction rates over 10%Cu-Ce(30%La)O_x and Ce(30%La)O_x in 11%CO-23%H₂O-11%CO₂-17%H₂-He and comparison with other catalysts. $\beta = P_{\text{CO}_2}P_{\text{H}_2} / (K_{\text{eq}}P_{\text{CO}}P_{\text{H}_2\text{O}})$.

a: Ce(30%La)O_x, $E_a = 98.5$ kJ/mol;

b (Δ): 10%Cu-Ce(30%La)O_x, $E_a = 70.6$ kJ/mol;

c: 10%Cu-Ce(30%La)O_x used at 450°C for 20 h, $E_a = 70.2$ kJ/mol;

d (\square): 10%Cu-Ce(8%La)O_x (calcined at 400°C, S.A. = 200 m²/g) in 11%CO-26%H₂O-7%CO₂-26%H₂-He, data from ref. 10, $E_a = 60$ kJ/mol;

e: G-66A (supplied by United Catalysts, Inc., 42wt%CuO, 47wt%ZnO, 10wt%Al₂O₃, S.A. = 49 m²/g), 11%CO-26%H₂O-7%CO₂-26%H₂-He, data from ref. 10, $E_a = 47$ kJ/mol;

dashed line: 8wt%Cu-ceria, extrapolated to 11%CO-23%H₂O-11%CO₂-17%H₂-bal. inert using the reaction orders, activation energy, and rate at 200°C in 7%CO-22%H₂O-8.5%CO₂-37%H₂-bal. inert reported ref. 11.

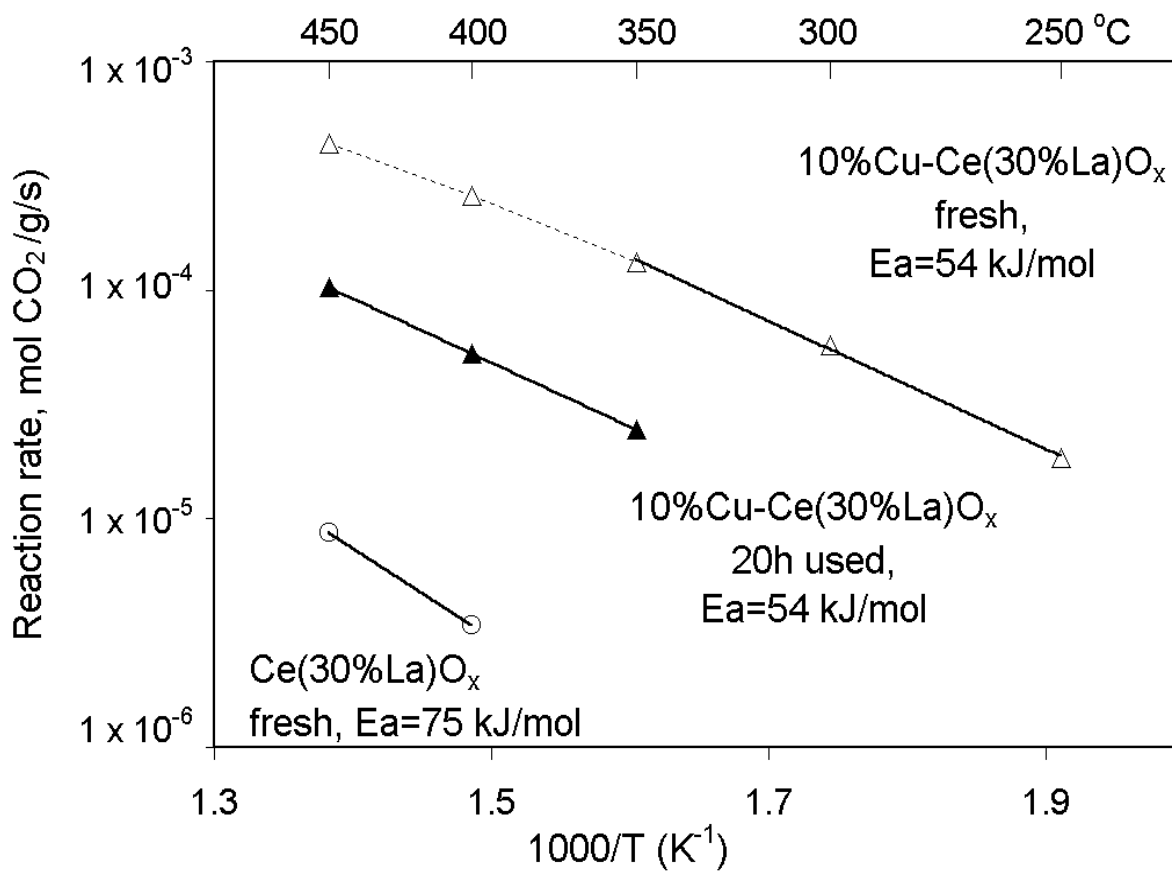


Figure 8. Steady-state WGS reaction rates over 10%Cu-Ce(30%La)O_x and Ce(30%La)O_x in 11%CO-23%H₂O-He.

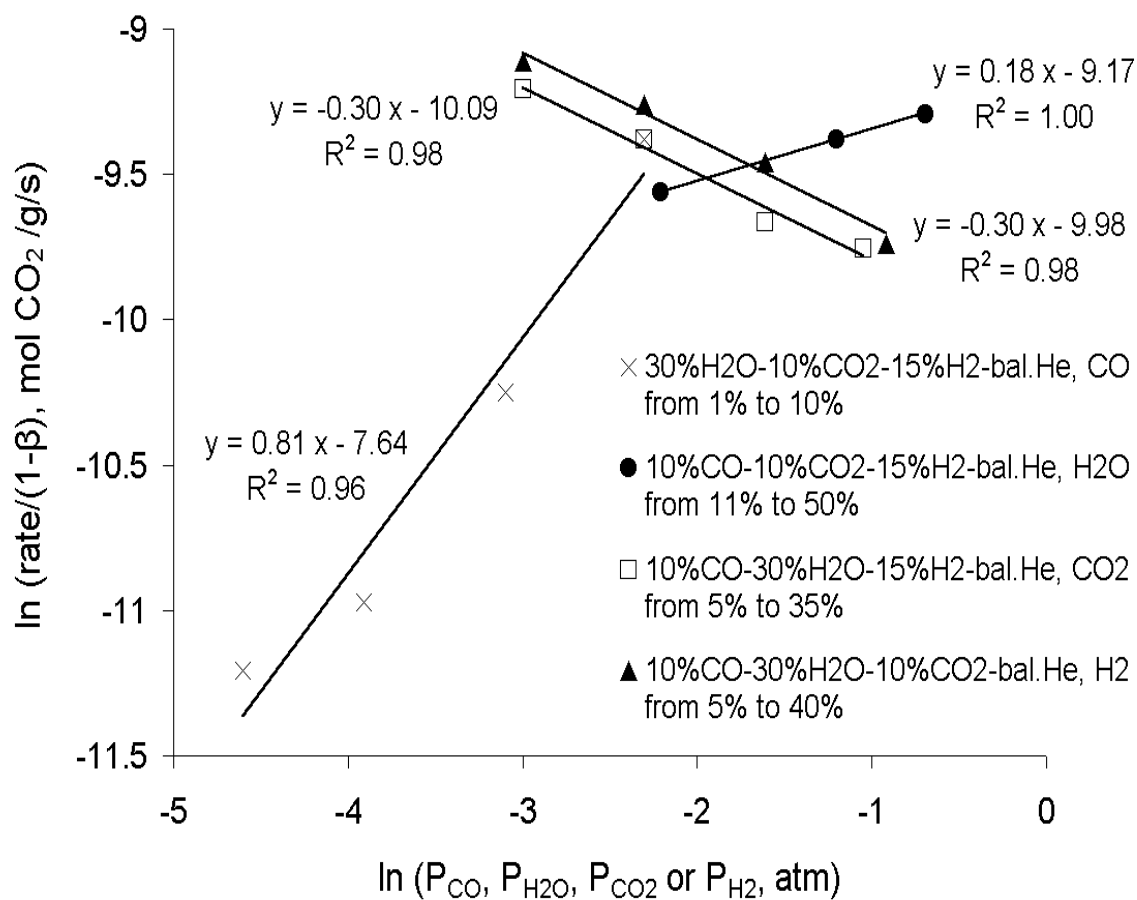


Figure 9. Effect of CO, H₂O, CO₂ and H₂ on WGS rates over 10%Cu-Ce(30%La)O_x (30 h used in 10%CO-30%H₂O-He), 450°C, 10%CO-30%H₂O-10%CO₂-15%H₂-He, varying CO from 1% to 10%, H₂O from 11% to 50%, CO₂ from 5% to 35% or H₂ from 5% to 40%, $\beta = P_{CO_2}P_{H_2} / (K_{eq}P_{CO}P_{H_2O})$.

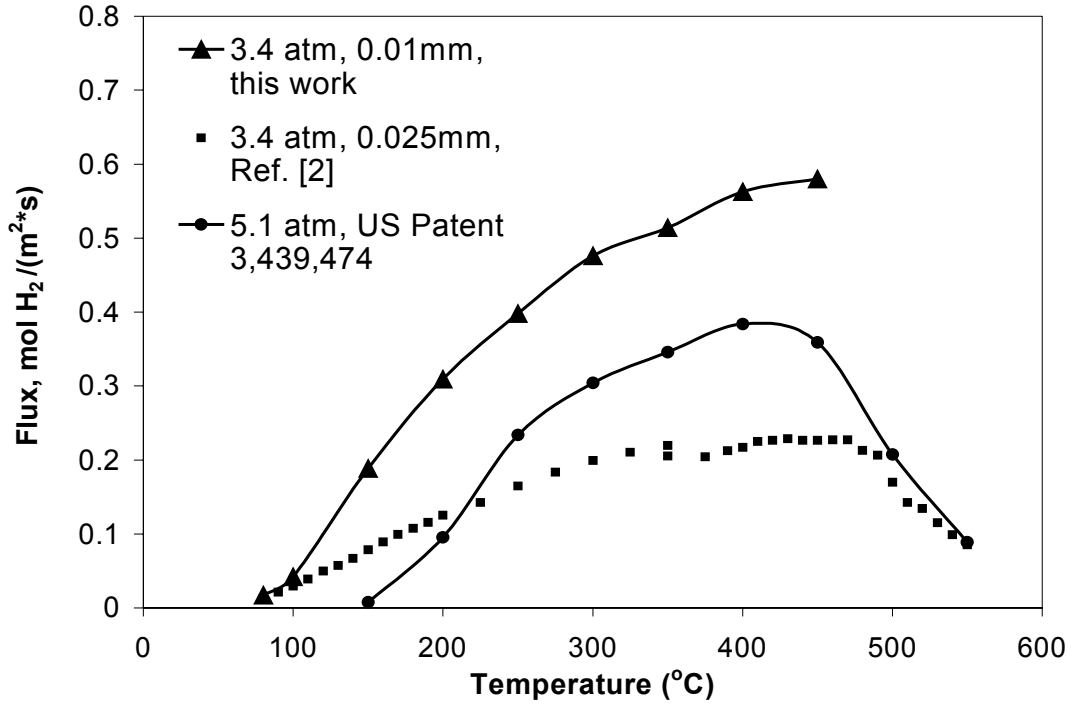


Figure 10. H₂ permeation through Pd-Cu membranes, 10 μm –thick compared with the 25 μm membrane in ref.2 and in the literature; P1= 50 psig, P2 = 0 psig.

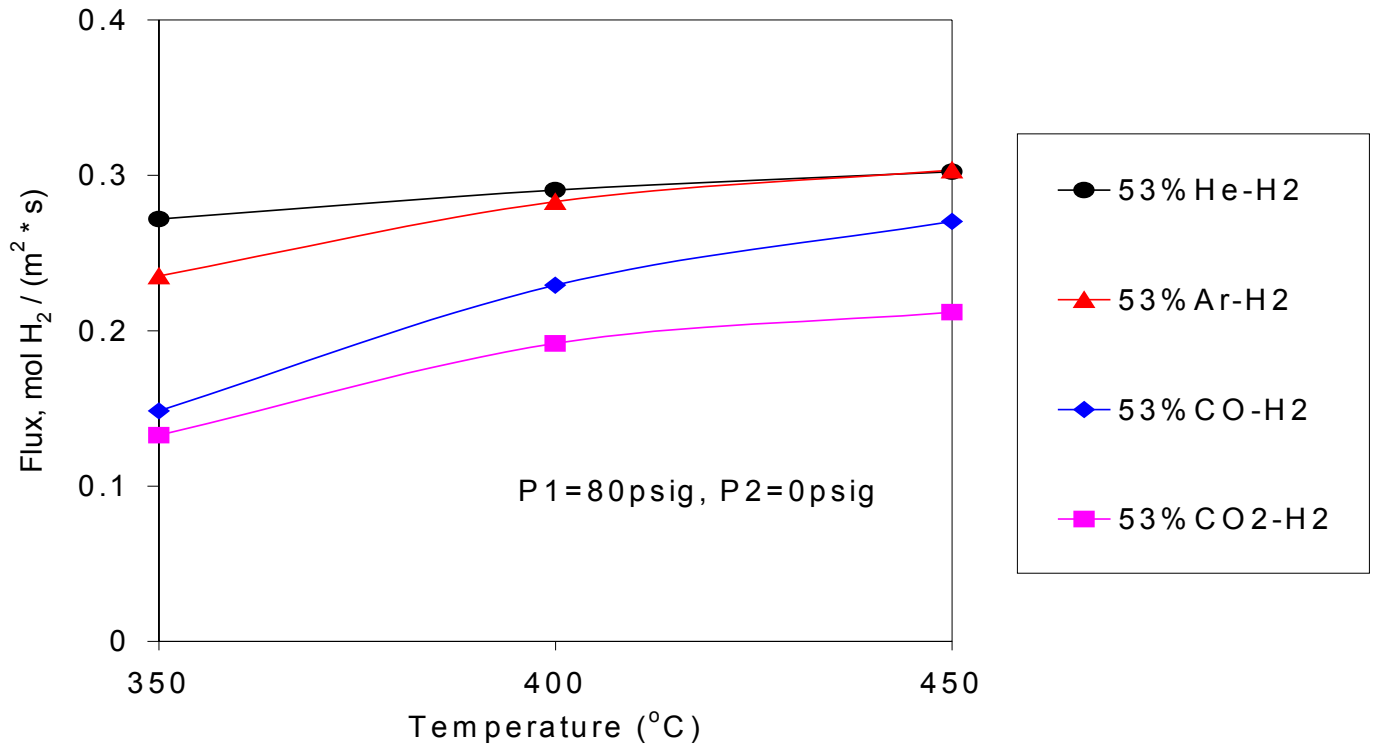


Figure 11. H₂ permeation through 10µm-thick Pd-Cu membrane in 53%CO-H₂, 53%CO₂-H₂, 53%He-H₂ and 53%Ar-H₂, P1=80psig, P2 =0psig

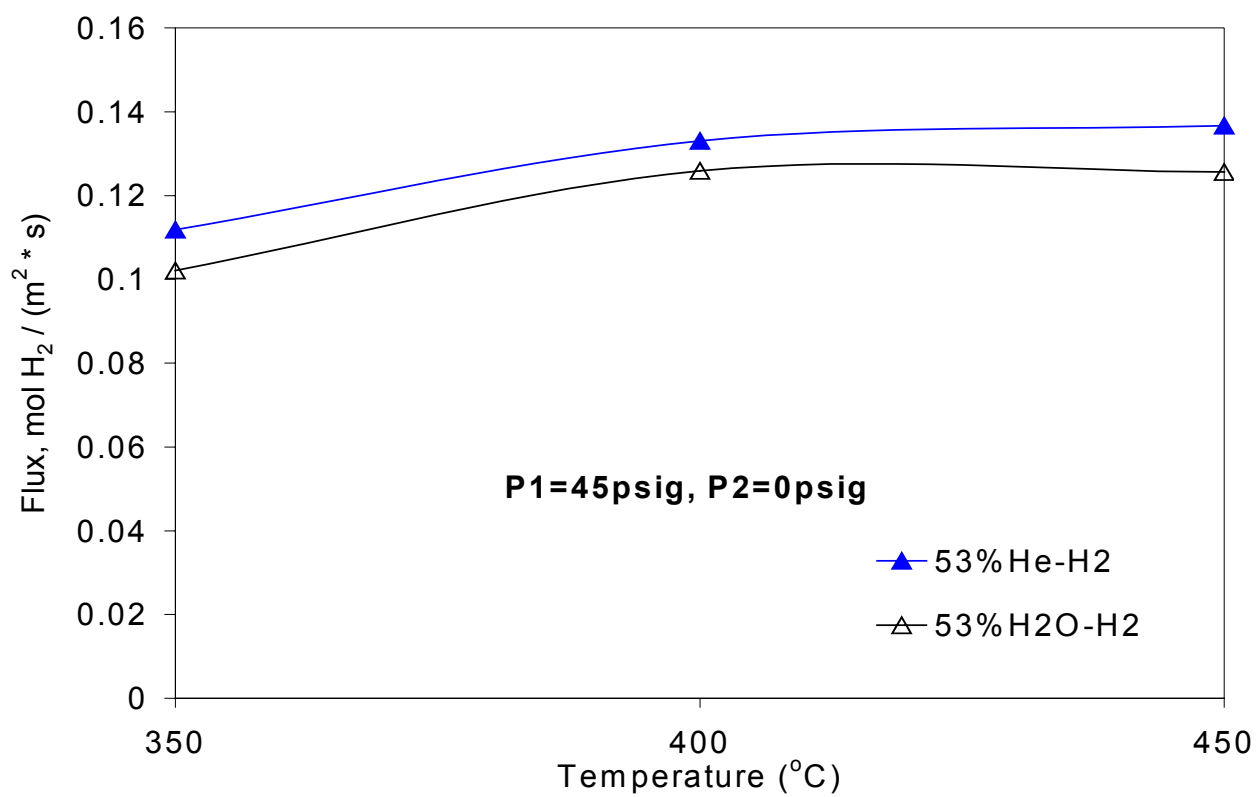


Figure 12. H₂ permeation through a 10 μm-thick Pd-Cu membrane in 53% H₂O-H₂ and 53% He-H₂, P₁=45psig, P₂=0psig

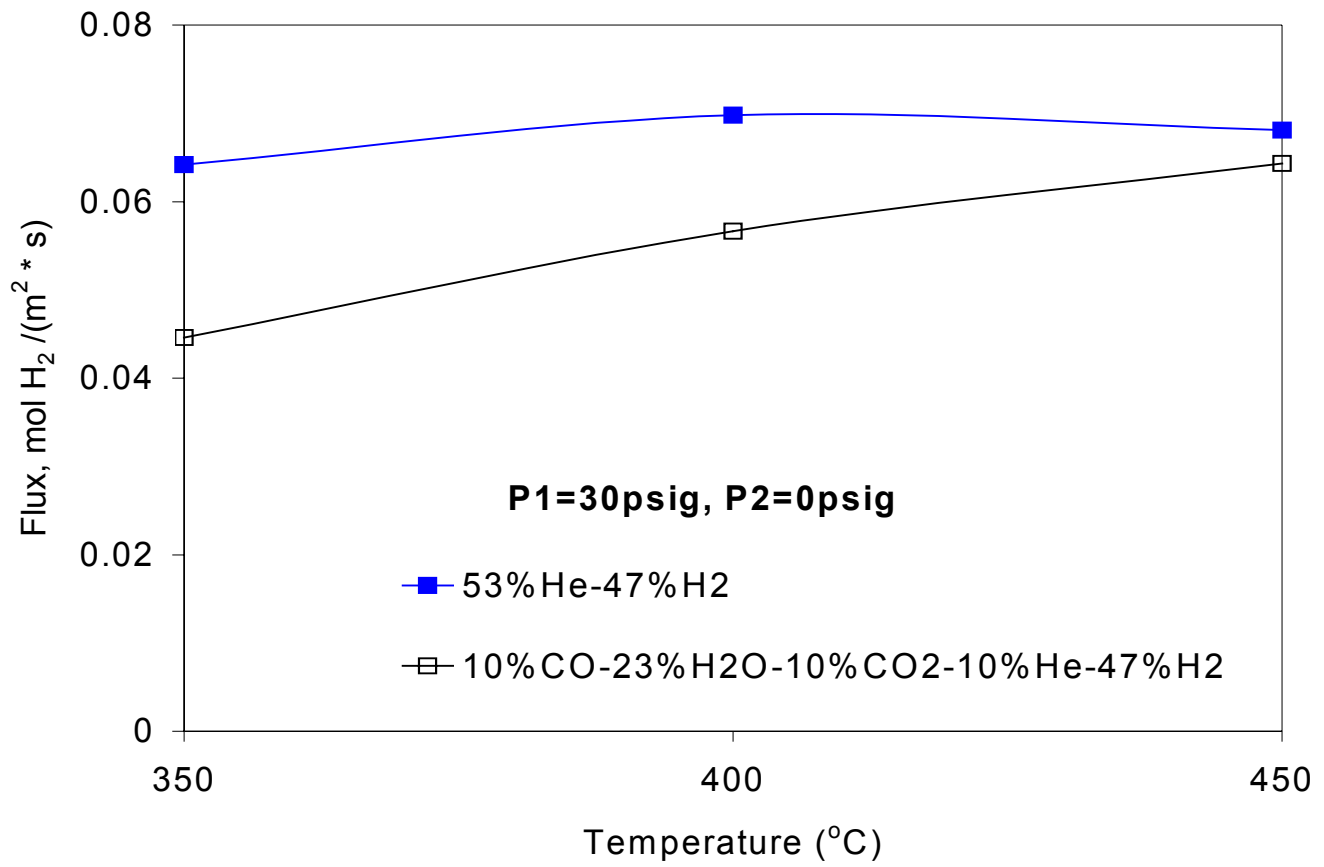


Figure 13. H₂ permeation through a 10 μ m- thick Pd-Cu membrane in 10%CO-23%H₂O-10%CO₂-10%He-47%H₂ and 53%He-47%H₂, P1=30psig, P2=0psig

Laboratory Membrane Reactor

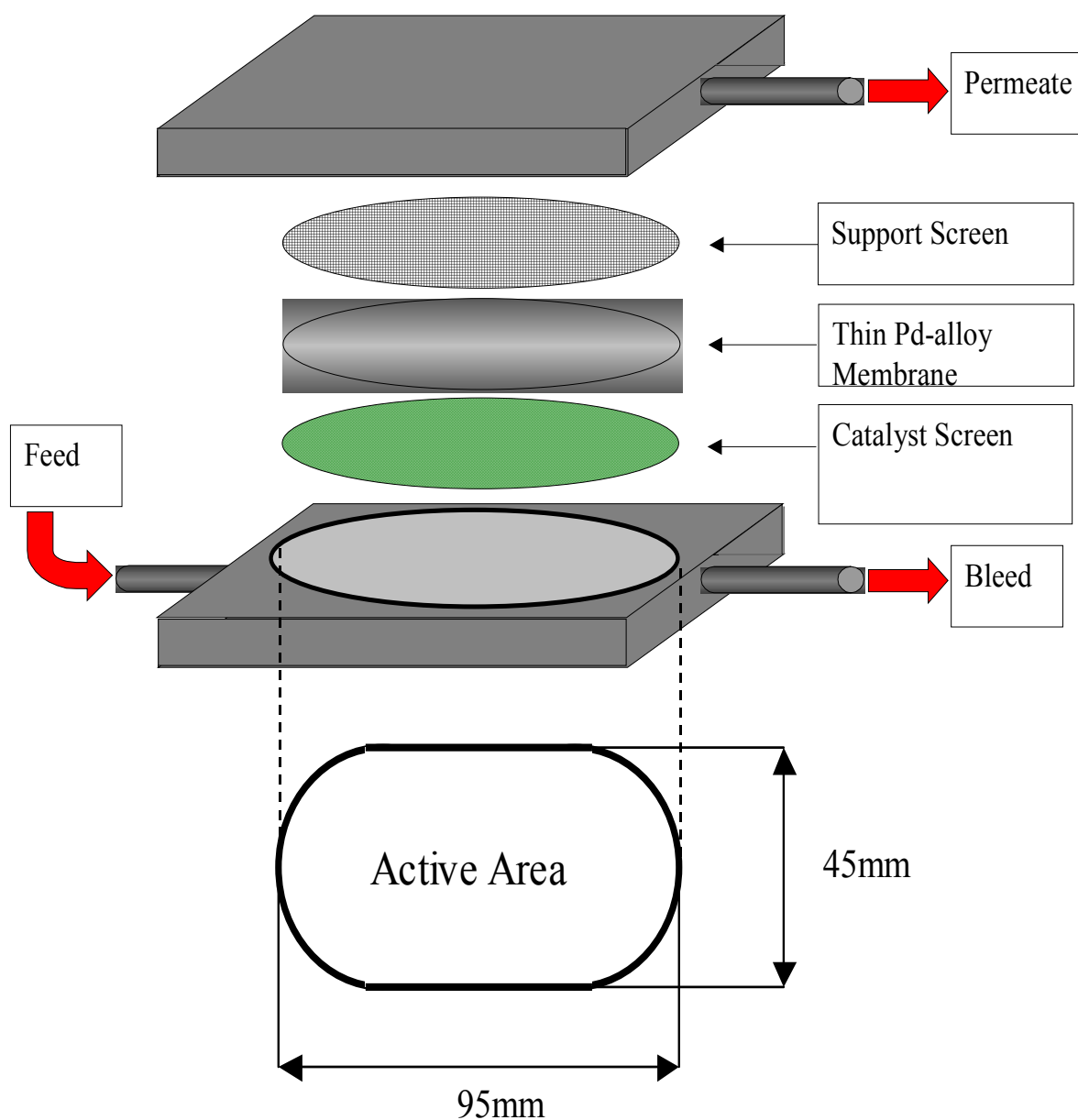


Figure 14. Schematic of the flat (38 cm^2 oval) Pd-Cu membrane reactor

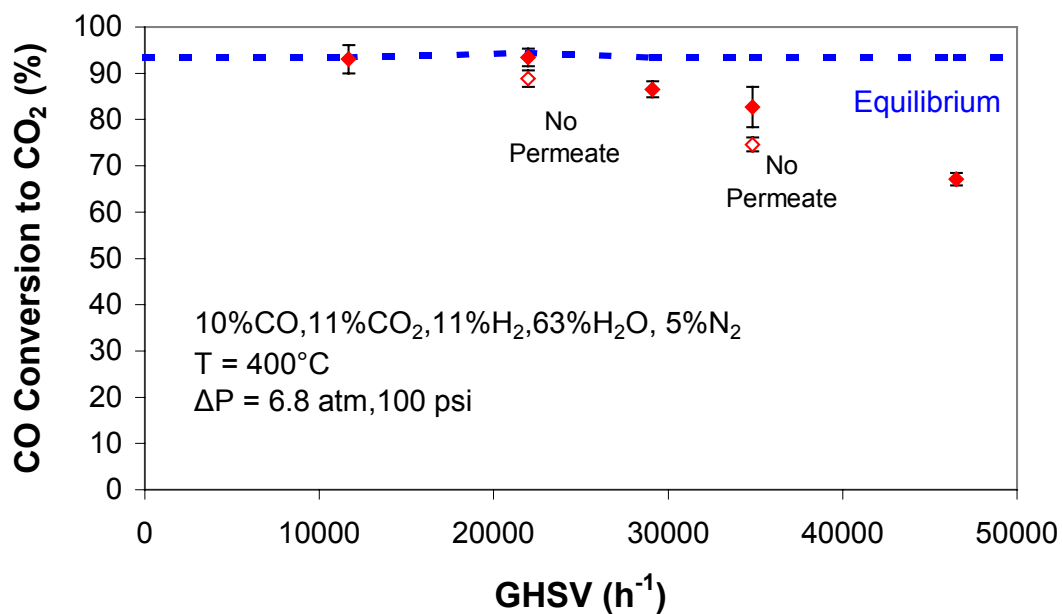


Figure 15. Space velocity effect on the equilibrium approach of the CO conversion to CO₂ in the membrane reactor of Fig. 14; 10 at % Cu-Ce(30 % La)O_x catalyst granules (150-1000 μm size) directly loaded on the 10 μm-thick Pd-Cu membrane.

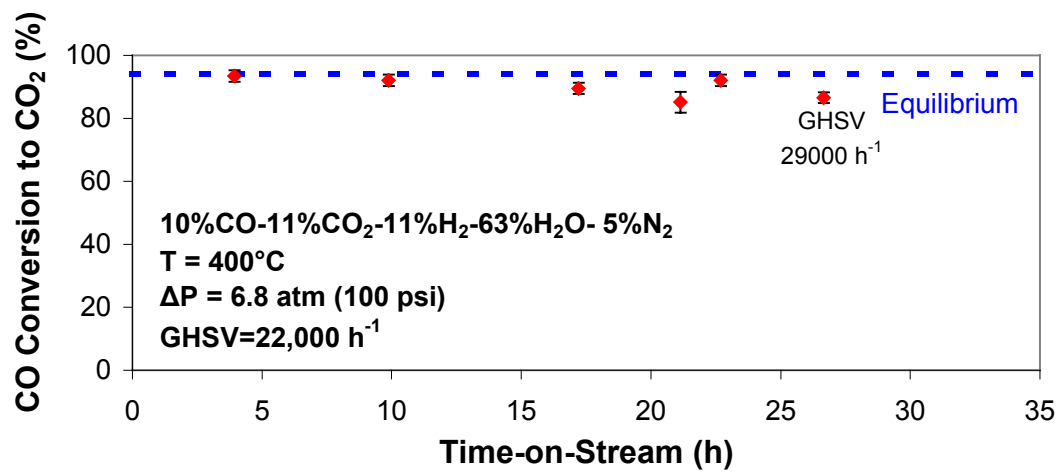


Figure 16. Long-term stability of 10at%Cu-Ce(30%La)O_x catalyst (granules 150-1000 μm) and Pd-Cu membrane assembly at 400 °C.