

REFORMANCE-WGSTM
NON-PYROPHORIC WATER GAS SHIFT CATALYST

Richard Q. Long, PhD.
Senior Research Engineer
Nexceris, LLC

ABSTRACT:

Over 90 percent hydrogen today is manufactured through steam reforming of natural gas, followed by water gas shift (WGS) and hydrogen purification. The industrial WGS process today uses two-step WGS reactors, i.e., high-temperature $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalyst and low-temperature $\text{CuO-ZnO-Al}_2\text{O}_3$ catalyst, with heat removal between them. This makes the water-gas-shift system complicated and large, which is suitable within their original design intent—large centralized hydrogen production systems.

In contrast, numerous new business models and product technologies require water-gas-shift performance in a compact, lightweight reactors. Examples of these opportunities include on-site hydrogen generation for chemicals, semiconductors, and glass, where the cost and complexity of hydrogen transport can be eliminated. New energy applications, like fuel cells, require compact reforming and hydrogen delivery at modest flows and high efficiency. Current technologies are cumbersome and have design concerns (e.g., pyrophoricity) that limit their application.

To solve this problem, Nexceris engineers have developed *Reformance-WGSTM*, a highly active precious metal based water-gas-shift catalyst. The catalyst is based on nanoscale mixtures of ceria-based oxides and uniformly incorporated precious metal. The catalyst exhibits equilibrium CO conversions at high gas space velocities ($\geq 60,000$ ml/g-hr) and more active than both $\text{CuO-ZnO-Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalysts at 300-400°C. Consequently, the reactor size can be shrunk to 5-10 percent of current two-stage WGS system. This catalyst is also non-pyrophoric and does not need to pre-activation prior to use.



INTRODUCTION:

Hydrogen is used commercially for ammonia synthesis, hydro-treating of petroleum feedstocks (to remove sulfur and nitrogen), hydrogenation of unsaturated organic compounds, and as a fuel for PEM fuel cells. Over 90 percent hydrogen today is manufactured via steam reforming of natural gas and hydrocarbons. The produced syngas (CO + H₂) then goes through high-temperature water gas shift (WGS) and low-temperature WGS reactions to further convert carbon monoxide to hydrogen, followed by hydrogen purification.

The commercial high-temperature WGS catalyst used is Fe₂O₃-Cr₂O₃, while the low-temperature WGS catalyst is CuO-ZnO-Al₂O₃. Although these two catalysts are suitable in large hydrogen plants, they are not appropriate in the applications where compact reactors are required. Their low activities create systems that are large and heavy, poorly suited for distributed (or mobile) hydrogen generation. These two catalysts also need pre-reduction and suffer from pyrophoric problems when exposed to air, causing safety concerns.

To solve these problems, Nexceris engineers have developed a new precious metal based WGS catalyst. The catalyst is based on nanoscale mixtures of ceria-based oxides and uniformly incorporated precious metals.

REFORMANCE-WGS™ PERFORMANCE

To demonstrate the performance of *Reformance-WGS™* catalyst, Nexceris performed a number of tests compared to various high- and low-temperature shift catalyst formulations. The results demonstrate the performance advantage of the catalyst for intermediate temperature operation, and the opportunity for reactor size reduction in distributed reforming applications. Testing was performed on granules and washcoated monoliths at Nexceris.

The catalyst granules with 35-60 mesh size were loaded in a tubular reactor for WGS performance testing. The testing conditions were 1 atm, 6.9%CO, 31.0%H₂O, 10.3%CO₂, 50.3%H₂, 1.4%N₂ and GHSV = 60,000 and 300,000 ml/g-h. The gas compositions were analyzed with a GC.

The catalyst was washcoated on a cordierite monolith with 400 CSPI channel density for activity testing. The catalyst powders were ball milled and then washcoated on the monolith by dip-coating, followed by drying and calcination at high temperatures. The testing conditions were 1 atm, 6.9%CO, 31.0%H₂O, 10.3%CO₂, 50.3%H₂, 1.4%N₂ and GHSV = 20,000 h⁻¹.

The results have demonstrated several advantages of Nexceris catalyst compared to existing commercial WGS catalysts: (1) superior activities at high temperatures (where kinetics are more favorable), (2) no need for activation prior to use, (3) non-pyrophoric characteristics when exposure to air, and (4) availability of conventional washcoating technologies for ceria-based catalysts (reduced size and weight, improved ruggedness). Some testing results are shown in Figures 1-3. Nexceris catalyst clearly exhibits higher CO conversion than commercial Fe-Cr oxides at 200-375°C (Figure 1) and Cu-Zn-Al oxides when the temperature is above 280°C (Figure 2). Also when the catalyst was washcoated onto a cordierite monolith (400 CPSI), it exhibited equilibrium CO conversions when the temperature was above 290°C (Figure 3).



TARGET™ Tar Reforming Catalyst for Gasification Process Streams

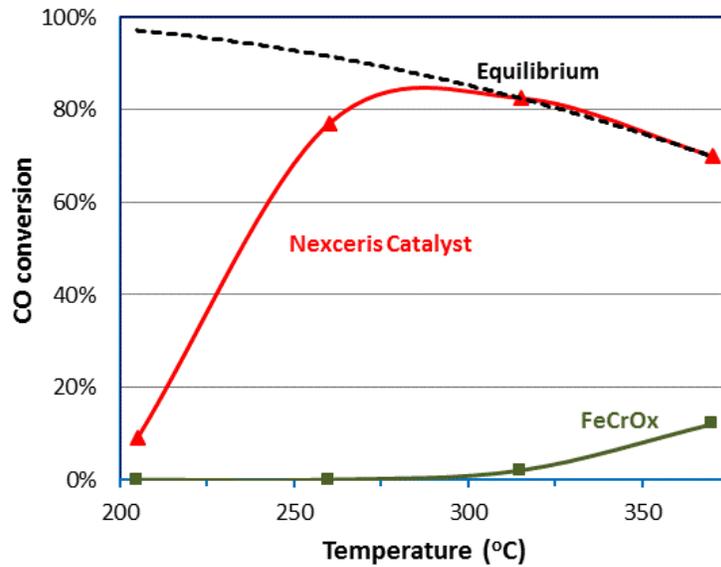


Figure 1. Water gas shift activities on Nexceris catalyst and a commercial FeCrOx catalyst under the conditions of 1 atm, 6.9%CO, 31.0%H₂O, 10.3%CO₂, 50.3%H₂, 1.4%N₂ and GHSV = 60,000 ml/g-hr.

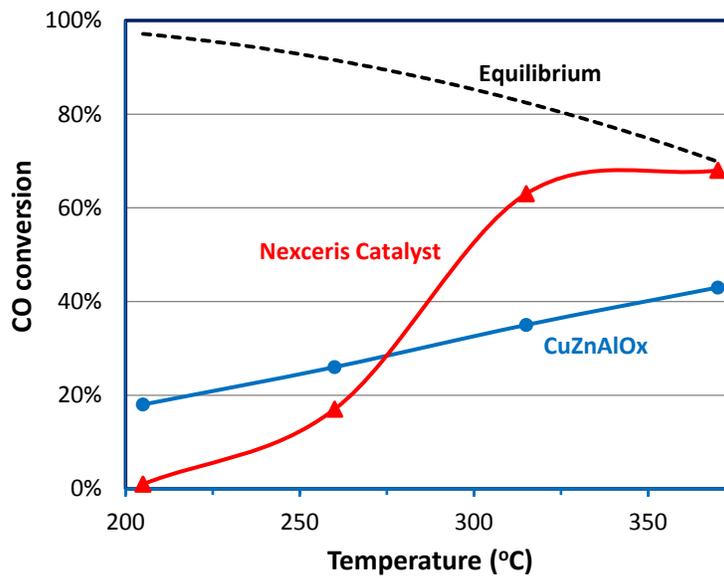


Figure 2. Water gas shift activities on Nexceris catalyst and a commercial CuZnAlOx catalyst under the conditions of 1 atm, 6.9%CO, 31.0%H₂O, 10.3%CO₂, 50.3%H₂, 1.4%N₂ and GHSV = 300,000 ml/g-hr.



TARGET™ Tar Reforming Catalyst for Gasification Process Streams

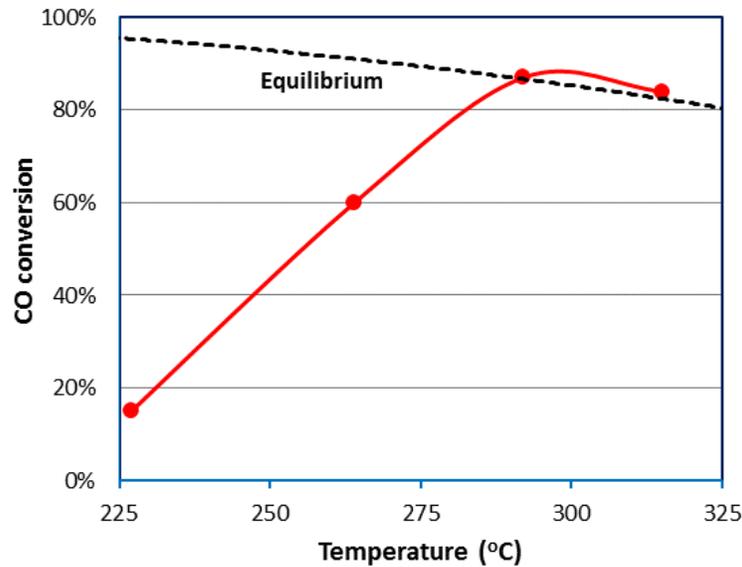


Figure 3. Water gas shift activities on Nexceris catalyst washcoated monolith under the conditions of 1 atm, 6.9%CO, 31.0%H₂O, 10.3%CO₂, 50.3%H₂, 1.4%N₂ and GHSV = 20,000 h⁻¹.

COMMERCIAL IMPLICATIONS:

Because of the high WGS activity, Nexceris' catalyst can be used in fixed bed reactors to convert CO to H₂ at 300-400°C when compact reactors are needed for hydrogen production. The reactor size can be shrunk to 5-10 percent of current two-stage WGS system. The Nexceris' shift catalyst can be manufactured in the forms of pellets and washcoated monoliths.

CONCLUSIONS:

Based on the above results, it can be concluded that Nexceris catalyst shows excellent WGS activity at medium to high temperatures. It is available as pellets or as washcoated ceramic and metallic monoliths to reduce pressure drop and minimize hot spots at high gas flow rates to convert CO to hydrogen, improving catalyst selectivity and lifetime.