

REFORMANCE-SMRTM CATALYSTS FOR STEAM METHANE REFORMING TO SYNGAS

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ABSTRACT:

Reformance-SMRTM catalysts are designed to improve syngas productivity in steam methane reformers and significantly reduce system capital cost for plants of all sizes. *Reformance-SMRTM* catalysts achieve equilibrium conversion of methane over a broad temperature range, allowing reactor designs and materials to be considered. Alternatively, the high activity of the catalyst can be leveraged to reduce reactor size and complexity. With either design approach, the cost of converting natural gas to valuable chemicals through syngas can be decreased when *Reformance-SMRTM* catalysts are adopted.

Reformance-SMRTM catalysts are uniquely designed to achieve excellent steam methane reforming (SMR) performance. Nexceris uses proprietary synthesis routes to create high surface area catalysts with optimized metal dispersion in *Reformance-SMRTM* catalysts. H₂ chemisorption indicates that the metal dispersion and surface area on Nexceris catalyst are 2.5 times that of the catalyst prepared *via* impregnation, which translates to SMR activity that is seven times higher than a commercial Ni catalyst. The catalysts also demonstrate good stability in preliminary lifetime testing.

In addition to the excellent SMR activity and stability, *Reformance-SMRTM* is resistant to coke formation under severe testing conditions at low steam to carbon ratios. Further, with the demonstrated support approach, the *Reformance-SMRTM* can provide high thermal conductivity, low pressure drop, large exterior surface area and high mechanical robustness.



INTRODUCTION:

The worldwide chemicals market is experiencing a fundamental shift from processes that rely upon petroleum and naphtha feedstocks to a natural gas driven supply chain. Hydraulic fracturing technology has unlocked a wealth of natural gas; chemical manufacturers who can most effectively capitalize on this resource will capture market share. To date, natural gas is often used to generate low value products like electricity and process heat, but if more active and energy efficient catalysts are used, the same methane resource can be used to produce low-cost, high value chemicals. In developing its *Reformance-SMR™* catalysts, Nexceris has sought to increase process efficiency through control of surface area, composition and the dispersion of catalytic sites. The resulting catalysts can allow process designers to reduce reactor size and/or operating temperatures, expanding the design envelope for cost effective reforming systems. The technology creates new opportunities to capture the value of methane near natural gas point-of-extraction gas to liquid systems, or in point-of-use applications.

In the steam methane reforming (SMR) reaction, methane is reacted with steam to form syngas (a mixture of H₂, CO, CO₂ and H₂O), which is further converted to H₂, ammonia, methanol and liquid fuels. Conventional SMR catalysts (Ni/Al₂O₃ promoted with MgO and/or CaO) are typically formed into large rings, pellets and cylinders with holes to reduce pressure drop. Heat transfer in the pellet/ring beds is poor due to the low thermal conductivity of these ceramic forms. Because SMR is highly endothermic ($\Delta H^\circ = 206$ kJ/mol), cold spots form in the catalyst beds at high gas flow rates, resulting in poor conversion.

The resulting packed-bed reactors that use these catalysts are massive, consisting of arrays of multi-story packed bed tubular reactors, with similarly huge direct-fire burners providing process heat. The poor thermal conductivity of the catalysts drive the need for the high aspect (small diameter, long length) tubular reactors, as well as the tremendous energy input to manage thermal cool spots. The high temperatures require expensive materials of construction (typically high-cost specialty nickel alloys) driving conventional technology toward the economies of scale of large, centralized plants.

In order to improve SMR efficiency, Nexceris engineers have developed new structured catalysts to convert methane to syngas. The catalysts are prepared with a unique synthesis method, and then washcoated on metallic substrates with excellent thermal conductivity. Unlike conventional synthesis methods, Nexceris' approach generates catalysts with unique, high performance characteristics. The selected metallic substrates provide low pressure drop, very good mechanical strength and high heat transfer. Consequently the syngas productivity is increased significantly, allowing significant reduction in reactor size and materials requirement. These features allow new system designs, where decentralized syngas production near stranded gases or even portable power systems, becomes economically feasible.

REFORMANCE-SMR™ PERFORMANCE:

To provide a comparison of catalyst performance, conventional and *Reformance-SMR™* catalyst granules of 35-60 mesh size were mixed with α -Al₂O₃ at a 1:20 weight ratio and loaded in a tubular reactor for performance testing. The testing conditions were 1 atm, H₂O/CH₄ = 3/1 and GHSV = 200,000-1,200,000 h⁻¹. The gas compositions were analyzed with a gas chromatograph.

Reformance-SMR™ catalyst was also washcoated on two types of metal foams with 1.2 mm pore size for the SMR testing. The foams have 90 percent porosity and 4.3 m²/liter geometric surface area. The foams were aluminized with *Alumi-Lok™* aluminization process, developed at Nexceris. The catalyst powders were ball milled and then washcoated on the foams by dip-coating, followed by drying and calcination at high temperatures. The testing conditions were 1 atm, H₂O/CH₄ = 3/1 and GHSV = 30,000 h⁻¹.



Reformance-SMR™ Catalysts for Steam Methane Reforming to Syngas

The testing data showed that the SMR activity on *Reformance-SMR™* catalyst was much higher than a commercial Ni catalyst under the testing conditions. At a GHSV of 400,000 h⁻¹, 88-98 percent methane conversions were obtained at 650-750°C on *Reformance-SMR™*. In comparison, only 10-33 percent methane conversions were achieved on the commercial catalyst (Figure 1). Also, CO selectivity on the *Reformance-SMR™* catalyst was higher than that on the commercial catalyst.

Because methane conversions were close to thermal equilibrium at GHSV = 400,000 h⁻¹ on the *Reformance-SMR™* catalyst, we further increased gas flow rate to reach a GHSV of 1,200,000 h⁻¹. Under this condition, 69 percent methane conversion was achieved on the *Reformance-SMR™* catalyst (Figure 2). The conversion was slightly decreased to 68 percent in 6 hours and then stabilized. By comparison, 15 percent methane conversion was achieved in the beginning on the conventional catalyst. It was slightly decreased to 9 percent in 14 hours (Figure 2). The above results have demonstrated that the *Reformance-SMR™* catalyst is seven times more active than the conventional Ni catalysts and also more stable under the testing conditions.

Moreover, during a preliminary lifetime testing, no deactivation was observed in 500 hours on stream. In addition to the excellent SMR activity and stability, the catalyst was resistant to coke formation under severe testing conditions with a low steam to carbon ratio, i.e., H₂O : CH₄ = 1.2:1.

To assess mass and heat transfer effects, *Reformance-SMR™* catalyst was washcoated on two metal foams. The metallic substrates provide high thermal conductivity, low pressure drop, high geometric surface area and high mechanical robustness. Nexceris' *Alumi-Lok™* aluminization process was used to create a porous Al₂O₃ layer on exterior surfaces, improving catalyst adhesion at high loading. A photo of a representative foam structure and a micrograph of the support prior to catalyst application is shown in Figure 3.

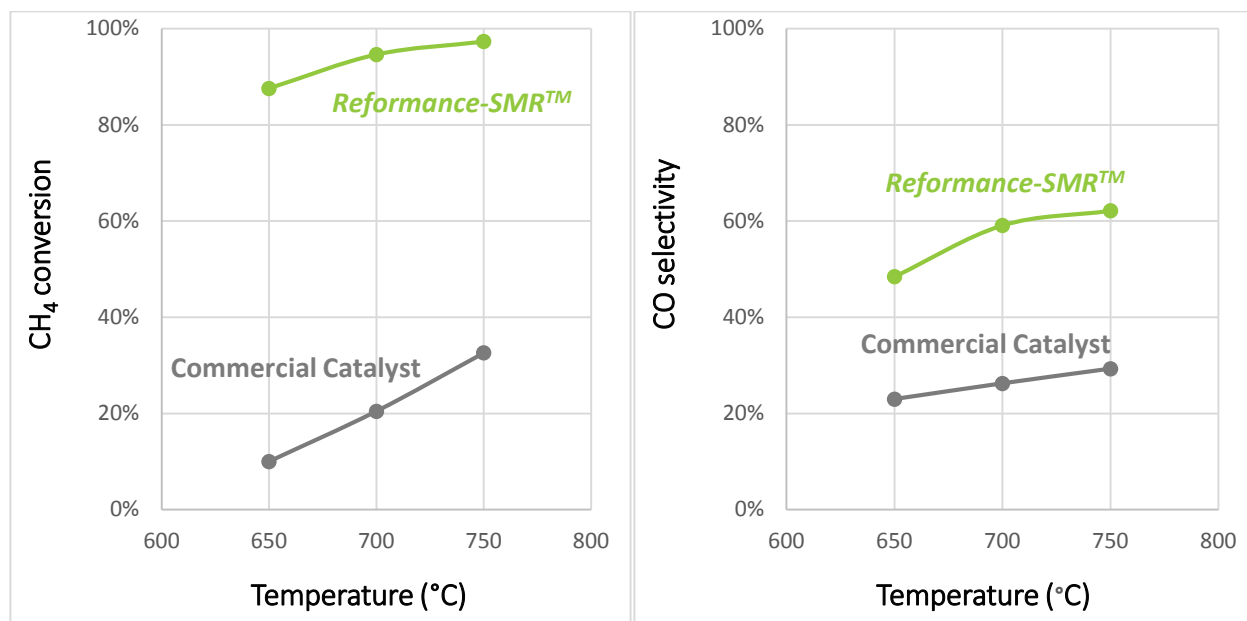


Figure 1. SMR performance on Nexceris granular catalyst and a commercial Ni catalyst under the conditions of 1 atm, 750°C, H₂O/CH₄ = 3/1 and GHSV = 400,000 h⁻¹.

The resulting structured catalyst samples also exhibited excellent SMR performance. Equilibrium methane conversion was achieved on the catalyst coated foams at a GHSV of 30,000 h⁻¹ (see Figure 4), ten times that of commercial operation conditions (i.e., 3,000 h⁻¹). This suggests that, by using *Reformance-SMR™* structured catalyst, reactor volume could be reduced tenfold with the same syngas production.



Reformance-SMR™ Catalysts for Steam Methane Reforming to Syngas

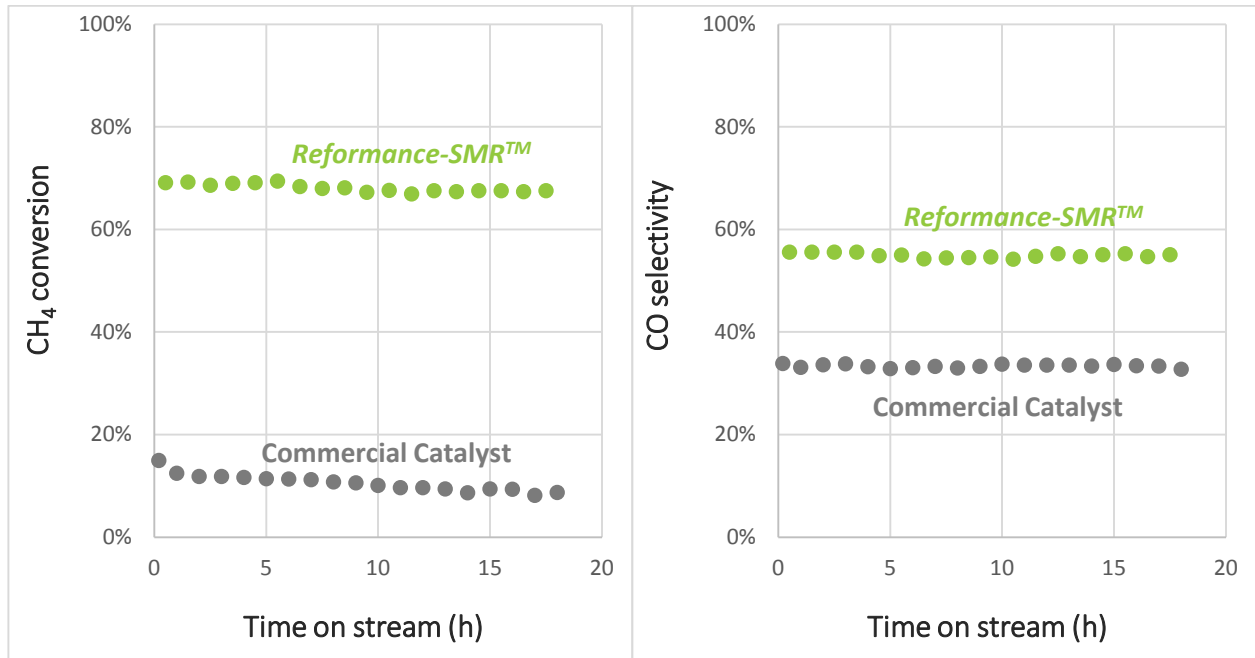


Figure 2. SMR performance on Nexceris granular catalyst and a commercial Ni catalyst under the conditions of 1 atm, 750°C, H₂O/CH₄ = 3/1 and GHSV = 1,200,000 h⁻¹.

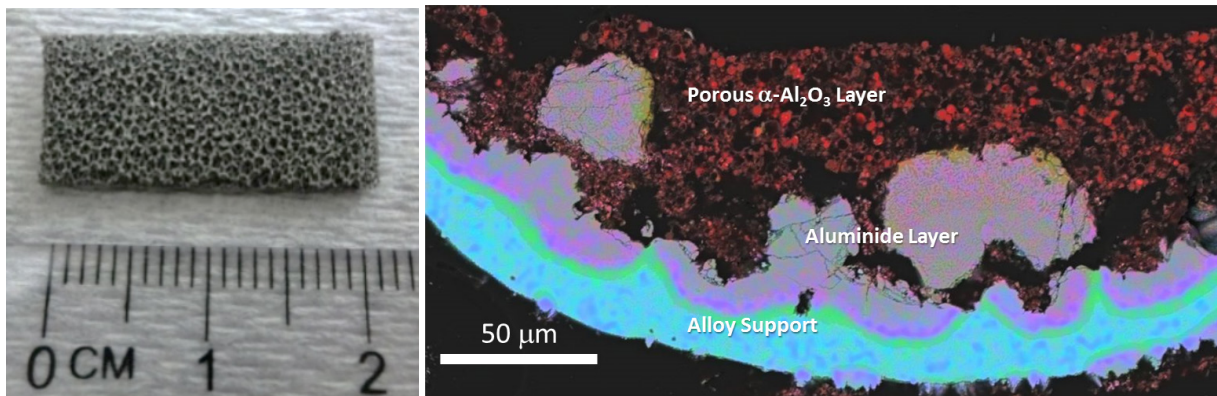


Figure 3. Photo (left) and SEM micrograph (left) of Alumi-Lok™ coated alloy foams. The process simultaneously provides corrosion protection via aluminide formation, and a porous α -Al₂O₃ layer that improves catalyst washcoating and adhesion.



Reformance-SMRTM Catalysts for Steam Methane Reforming to Syngas

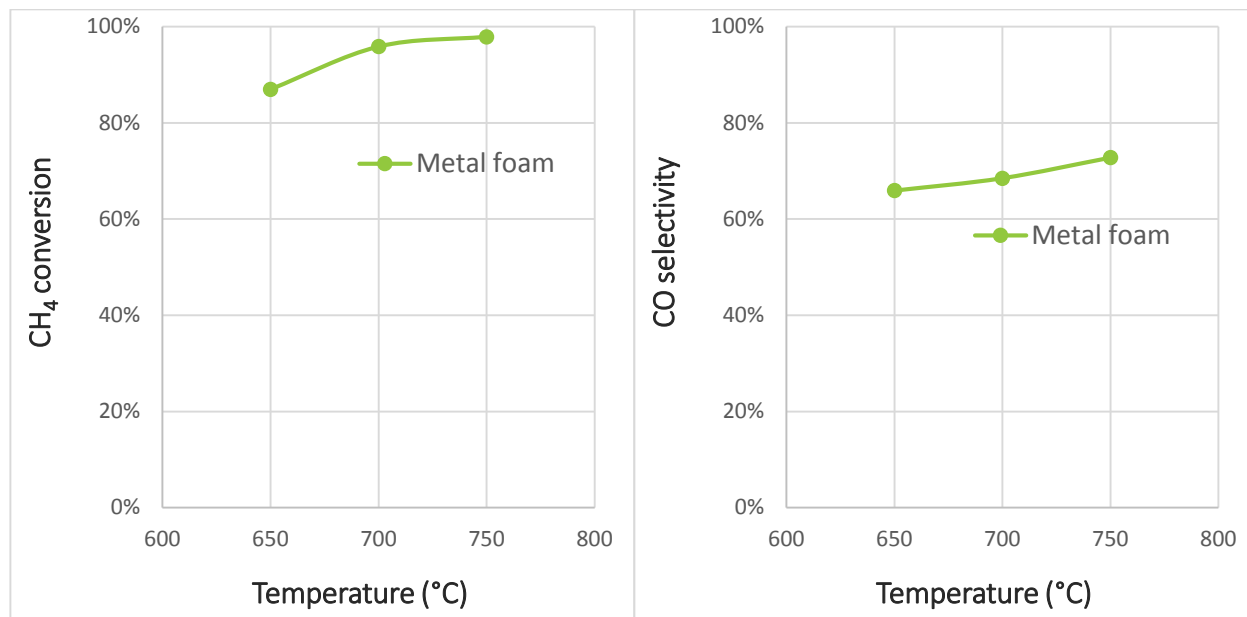


Figure 4. SMR performance on aluminized metal foams coated with Nexceris catalyst under the conditions of 1 atm, H₂O/CH₄ = 3/1 and GHSV = 30,000 h⁻¹.

COMMERCIAL IMPLICATIONS:

Reformance-SMRTM catalysts are suitable any application requiring syngas and hydrogen from methane. For existing reactors, we Reformance-SMRTM structured catalysts could replace conventional Ni/Al₂O₃ pellets/rings to multiply the volume production of an existing facility; alternatively, the system could be modified to significantly reduce the number of active tubes in a system and the heat input required to maintain targeted levels of production. In retrofit scenarios, the substrate can be tailored to fit the existing reactor, improving packing uniformity and reducing pressure drop, a key consideration in SMR system performance and life.

The opportunity for new-build reactors include those listed above, along with the ability to design more compact reformers for flow rates that would prove uneconomic for conventional SMR catalysts. Whether designed to generate syngas from stranded natural gas in remote locations, or to provide reformat at point of use hydrogen generators, the size and efficiency benefits afforded by Reformance-SMRTM catalysts are enabling for reducing capital and operating costs.

CONCLUSIONS:

The combination of high intrinsic catalyst activity and excellent thermal conductivity of the substrate brings an advanced SMR catalyst that significantly improves syngas productivity. As compared to conventional Ni pellets/rings, the improved syngas productivity using Nexceris' catalyst technology will shrink reactor systems with the same syngas output or increase syngas output with the same reactor size. Both of these will result in significant reduction in capital cost and energy inputs for the same syngas production. Consequently, the cost of converting natural gas to valuable chemicals through syngas will be decreased when Nexceris catalyst technology is adopted, improving the economics of existing systems and enabling the deployment of next-generation distributed reforming technology.