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SUPIRCAT^{TM} INTERNAL REFORMING CATALYSTS FOR SOLID OXIDE FUEL CELLS (SOFC) APPLICATIONS

ABSTRACT:

Nexceris has developed a family of steam reforming catalysts (*Supircat*^{TM}), geared towards internal reforming in Solid Oxide Fuel Cells (SOFC) applications. *Supircat*^{TM} catalysts immediately achieve equilibrium conversion when heated to reaction temperature and do not require a pre-reaction activation step for activation. This allows SOFC developers to integrate a high performing internal reforming catalyst into their systems without the operational costs and manufacturing complexity associated with pre-reducing the stack. Careful catalyst optimization has ensured equilibrium level activity is achieved with the minimum precious metal loading to provide a low-cost high-performance catalyst. S*upircat*^{TM}'s activity has been examined with particular attention to factors such as coke formation (encountered in low S/C feedstocks), sulfur tolerance (encountered in typical natural gas feedstocks), and thermal cycling. *Supircat*^{TM}'s performance under these conditions has shown that if operated in typical SOFC regimes, the performance will not be affected. *Supircat*^{TM}'s performance has been probed both in pellet form as well as a coating on pre-aluminized stainless-steel plates and the performance has been exemplary in both cases.

INTRODUCTION:

A solid oxide fuel cell (SOFC) generates electricity directly from oxidizing a hydrocarbon fuel. SOFCs are more efficient, generate less emissions, require low maintenance costs, and have low to no noise pollution. These features have made SOFCs attractive as energy generators in applications requiring stationary (e.g. Power plants), or portable (e.g. power generators and auxiliary power units) uses. In its basic design (Figure 1), an SOFC is powered by both Hydrogen (H_2) and carbon monoxide (CO), which are generated through steam reforming of natural gas.[1, 2]

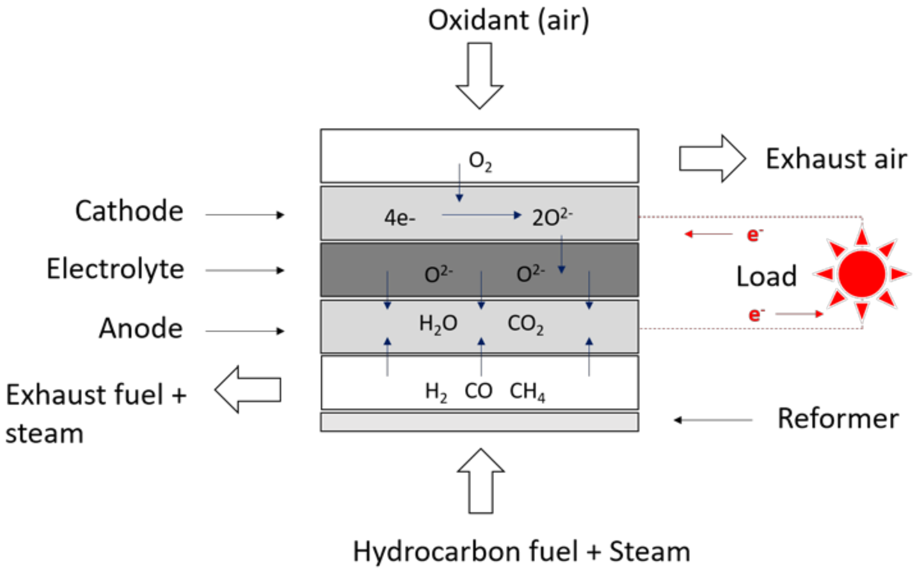

Figure 1. Schematic diagram of an internal reforming solid oxide fuel cell (SOFC)

Methane reforming can be accomplished either externally (in a separate reformer unit) or internally (in a thermally integrated reformer). In an integrated reformer, reforming can be achieved directly or indirectly. Directly (DIR-SOFC) on the anode (typically Ni/YSZ) and indirectly (IIR-SOFC) in a separate unit close to the anode.

The integrated internal reformer has advantages not enjoyed by the external reformer such as the efficient utilization of the heat generated from electrochemical cell to power the reforming reaction. SOFCs typically operate at high temperature of 600°C to 1000°C, and during operation can generate sufficient heat for endothermic reforming reaction. An integrated reformer operated in the IIR mode is less susceptible to failure mechanisms associated with DIR integrated reformers such as coking of the anode and fouling of the anode due to sulfur poisoning. Sulfur cannot be avoided as it is found in natural gas at between 5 and 500ppm depending on the source.[3] The need for active catalysts that can withstand the operating conditions and the environment encountered in IIRs cannot be understated.

Nexceris has developed a family of high performing internal reforming catalysts. Called *Supircat^{TM}*; these catalysts have been designed for use in IIR-SOFC units. In developing *Supircat*^{TM}, attention was paid to the following parameters needed to be met or exceeded: (i) cost element, (ii) achieves equilibrium conversion at high space velocities, (iii) immediate activity without the need for reduction of the active metals, (iv) is resistant to coke and sulfur, (v) has a long lifetime. For steam reforming applications, Ni, or noble metals Ru, Rh, Pd, Ir, and Pt are used as the active metal. Due to its low cost, Ni is preferred, however, it has a lower relative activity to all the noble metals except for Pd and Pt.[4] Coincidentally, both Pt and Pd are the highest cost drivers in an internal reforming catalyst system. A combination of these elements can also be used with cost and activity as guiding parameters. For instance, Rh-promoted Ni/α-Al_2O_3 has been found to exhibit higher activity than either Ni/α-Al_2O_3 or Rh/α-Al_2O_3 alone.[5]

The immediate high activity is a key design parameter that avoids a lengthy activation procedure, reducing operational costs. The choice of active metal as well as support material are important design parameters as well. A good support offers good metal-support interaction which enhances the metal's activity in steam reforming. Generally, high surface area supports offer better dispersion of the active metal and hence higher activity. α- and γ-Al_2O_3, $MgAl_2O_4$, MgO, ZrO, and TiO_2 are the commonly used supports for reforming catalysts. Finally, the catalyst must show resistance to coking, be tolerant to a given level of sulfur, as well as have a long lifetime under different conditions as evaluated by a series of thermal cycling tests. In addition to the above, *Supircat*^{TM} has been designed to retain high activity both in pellet form as well as when applied as a coating on stainless steel substrates.

SUPIRCAT^{TM} CHACRACTERIZATION AND PERFORMANCE:

Supircat^{TM} has been designed by supporting steam reforming-active metals on a support containing a mixture of oxides. A commercial mixed oxide support having the ratio of the dominant oxide 1 varied between 60% and 80%, was compared to an in-house support having the ratio close to the 80% commercial oxide. Down-selected reforming metals were deposited onto these supports to yield *Supircat*^{TM} *A*, *B*, and *C*. The resultant catalysts retained the native surface areas of the bare support materials as can be seen in Table 1. Crystal structure analyses of both commercial and in-house supports showed a close match in phases and crystal structures.

Table 1 Brunauer-Emmett-Teller (BET) surface are (SA) measurements of commercial and in-house oxide supports and with catalysts deposited onto the supports

Entry	ID	Support Oxides ratio	Support Surface Area (m^2/g)	Catalyst Surface Area (m^2/g)
1	*Supircat A*	20/80	82	80
2	*Supircat A*	40/60	113	101
3	*Supircat A*	20/80	96	110
4	*Supircat B*	20/80	82	80
5	*Supircat C*	20/80	82	79

Catalysts identified by entries 1, 4, and 5 were prepared on a commercial support (with oxides ratio 20/80), entry 2 was prepared on a commercial support with oxides ratio 40/60, while entry 3 was prepared on *Nexceris* support with oxides ratio 20/80.

The performance of *Supircat*^{TM} catalysts has been analyzed both in pellet form and as a coat on stainless steel plates. In pellet form, the powder was pressed into pellets of approximately 3 mm, and packed in the middle of a ½ inch high temperature *Inconel* tube made of a nickel alloy to a volume of 5cc supported on either side with 1 cc of 3 mm α-Al_2O_3 pellets. The tube was placed in a horizontal programmable temperature furnace and heated to reaction temperature in a stream of 100 sccm air. In control reactions, the tubes were heated under a stream of nitrogen or a successive switching between nitrogen and hydrogen. Once steady-state temperature was achieved, steam and methane were introduced and testing initiated. The water was converted into steam by passing it through a vaporization chamber. The testing conditions were 1 atmosphere, $H_2O/CH_4 = 3/1$ and GHSV = 3000 - 8000 h^{-1}. Methane conversion was calculated from calibrated GC data by establishing the methane slip, as well as by checking the reaction volume expansion (flow rate increase) and validating using equilibrium data generated using HSC 9.0 chemistry thermochemical software.

From pellets testing, *Supircat™ A* (deposited either on commercial or *Nexceris* support) was chosen, formulated into slurry using *Nexceris's* proprietary methods and deposited onto stainless-steel plates containing a porous alumina layer prior-deposited using *Nexceris' AlumiLok™* technology. The *AlumiLok'd* catalyst-coated plate was welded in a stainless-steel manifold, and placed in a horizontal programmable temperature furnace then heated to reaction temperature in either a stream of air or nitrogen. Once steady-state temperature was achieved, steam and methane were introduced, while air or nitrogen was cut off. Testing was initiated. The testing conditions were 1 atmosphere, H_2O/CH_4 = 2.5/1 and GHSV = 5000 - 14000 h^{-1}. Figure 4 shows a graphical representation of the stainless steel coated plate and the welded manifold used in the testing.

Figure 2 shows the results obtained from pellet testing of the three different formulations of *Supircat™*. Results indicate that there is very little difference between non-reduced and reduced catalysts as both achieve equilibrium conversion. Figure 2 also shows that all catalysts showed high methane conversions with all candidates meeting the threshold of equilibrium conversion at a space velocity of 3000 h^{-1} as a design parameter. When space velocity was increased to 8000 h^{-1}, there was a break-through in equilibrium conversion. The most active catalyst was 10% off-equilibrium while the least active was 18%. Once the as-loaded pellets had reacted with continuous monitoring for about 2 h, pure hydrogen (H_2) was introduced and CH_4/H_2O switched off. The catalysts were reduced for 1 h, H_2 switched off and testing resumed. Reduction had no significant effect on conversion at 3000 h^{-1}. When these catalysts were prepared on supports with a ratio of dominant oxide at 60%, the conversion fell drastically. This implied that an intimate compositional level is critical to achieve the above high performance of *Supircat™* catalysts.

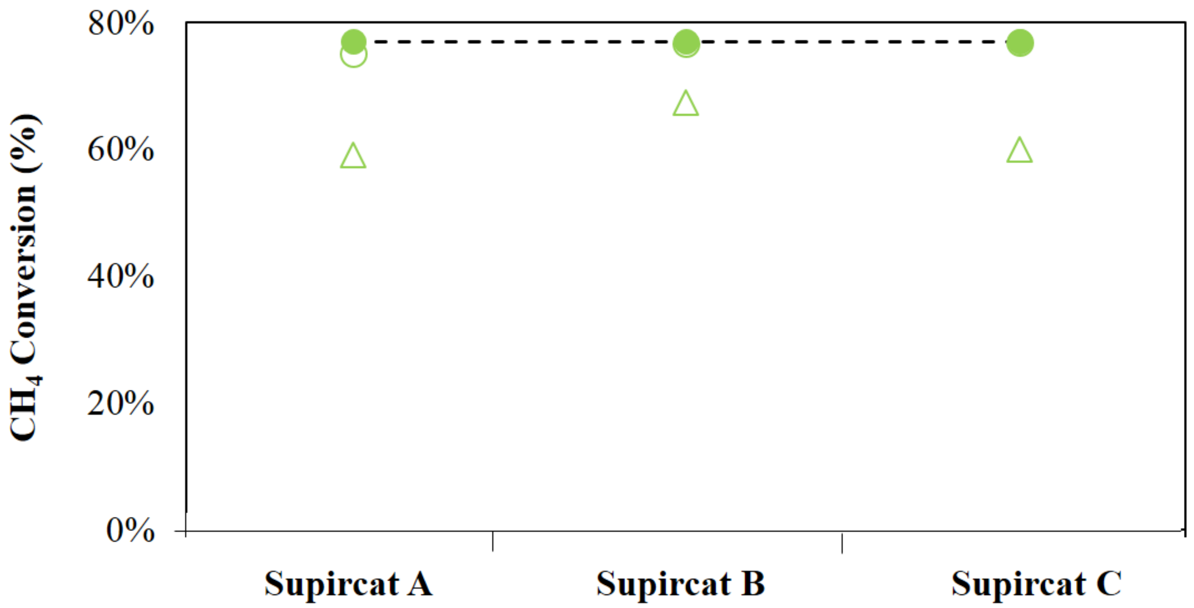

Figure 2. Performance of the three formulations of Supircat™ (supported on commercial support 1) at space velocities of 3,000 h-1 on non-reduced (○) and reduced (●) as well as 8,000 h-1 on non-reduced catalyst (Δ), a steam/carbon ratio of 3, and temperature of the coking test. Supircats A and B showed a slight increase in weight of about 0.15% which Supircat C had a weight increase of 0.5%. A temperature programmed oxidation (TPO) study also confirmed coke combustion.

Coking resistance tests have been performed by flowing a reforming mixture with a steam to carbon ratio of 2:1 on a 5-cc bed of catalyst for a period of 12 h. Figure 3 shows the results of

Preliminary studies (not reported here) on the effect of Sulfur on *Supircat™* indicate that there is some loss of activity at accelerated poisoning using hydrogen sulfide (H_2S) as the poisoning gas. Current studies are looking into mitigating this effect as well as designing a more tolerant catalyst.

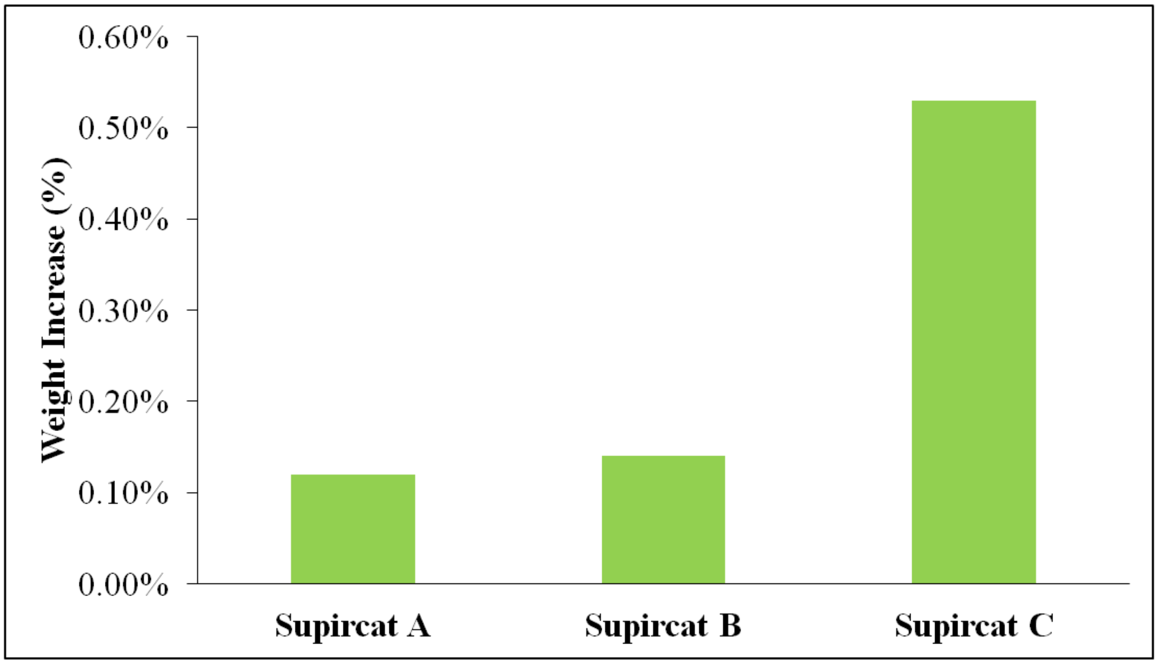

Figure 3. Weight changes of *Supircat™* catalysts after a 12 h coke resistance test.

The performance of *Supircat™* as a coating is shown in Figure 5 and Figure 6. In Figure 5, *Supircat™ A* was deposited on a pre-aluminized stainless-steel plate using Nexceris' proprietary *AlumiLok™* technology. The plate was then welded to a manifold for application-relevant testing. Both commercial as well as *Nexceris* supports were used in making this catalyst and results were compared. Both catalysts showed equilibrium conversion at both low (5,000 h^{-1}), and high (14,000 h^{-1}) space velocities. The activity of these catalysts has been investigated at even much higher space velocities (up-to 24,000 h^{-1}) with only a slight decrease in activity. When contrasted with testing in pellet form that showed an equilibrium break-through at only 8,000 h^{-1}, it can be seen that when *Supircat™* is deposited on a planar surface, there is increased exposure of active sites, which require very high space velocities to before encountering mass transfer limitations. These catalysts have been shown to retain high activity even under a series of thermal cycles. The lifetime studies on *Supircat™ A* (Figure 6) show that the performance is stable for the duration of the study (250 h). The gradual decrease in performance after 250 h is suspected to be due to deposition of alloy metals (found in the manifold cover and stainless-steel tubing). This has been corroborated by elemental analyses of the surfaces of the catalysts after studies. *Nexceris* is in the process of protecting the manifold covers by applying an *AlumiLok™* coating on the top cover of the manifold to mitigate this.

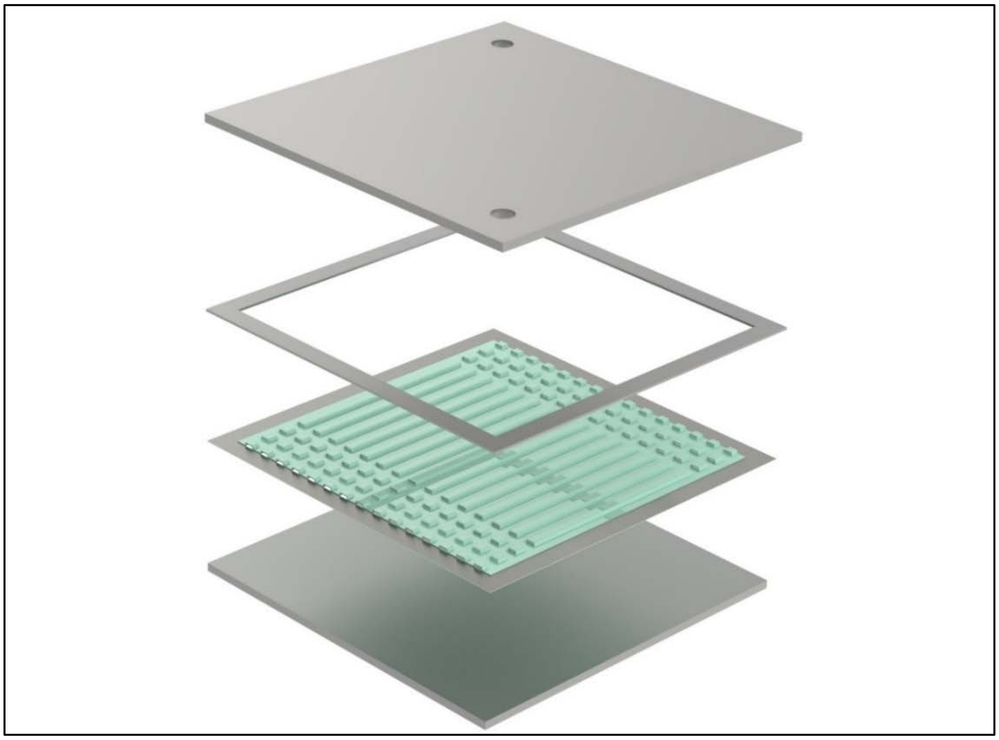

Figure 4. Rendered schematic of the catalyst-coated stainless-steel plate (441S, green color, 4.25"× 3.875"), in-between the Crofer 22APU manifold covers.

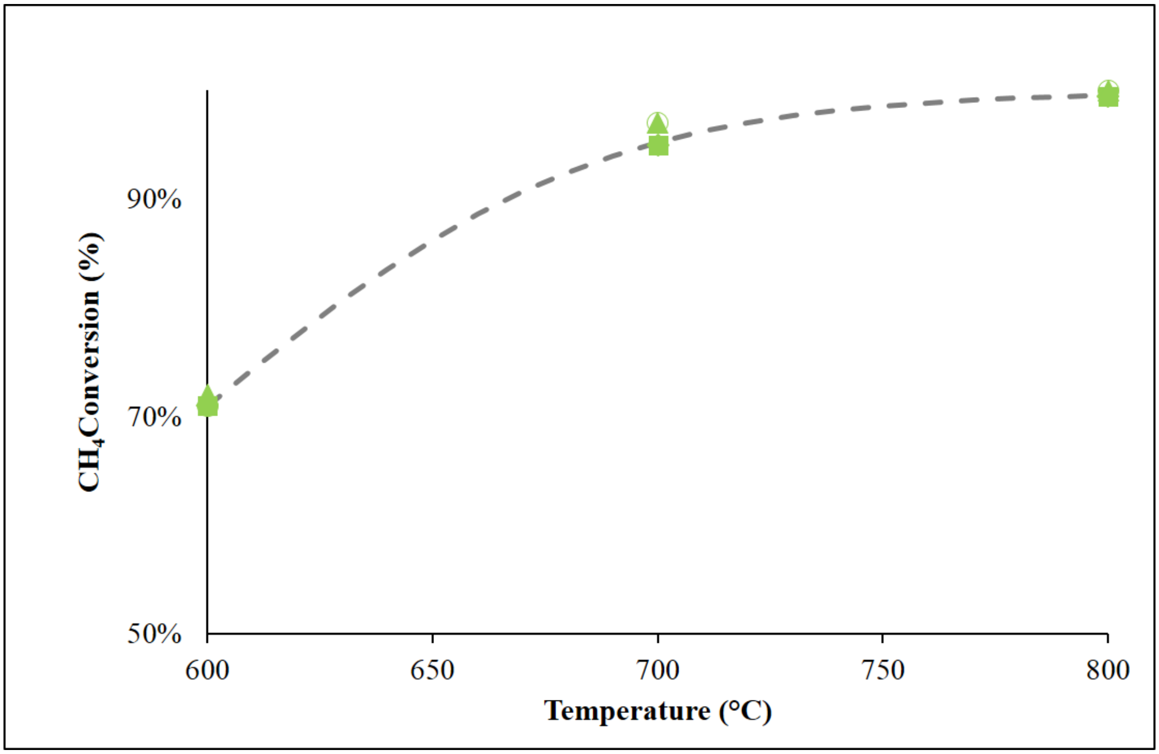

Figure 5. Performance of *Supircat^{TM}* supported on commercial (◊,□) and well as in-house supports (○,Δ) internal reforming catalyst in steam methane reforming reaction. Reaction conditions are space velocity 5,000 h^{-1} (◊,○) and 14,000 h^{-1} (□,Δ), steam/carbon ratio

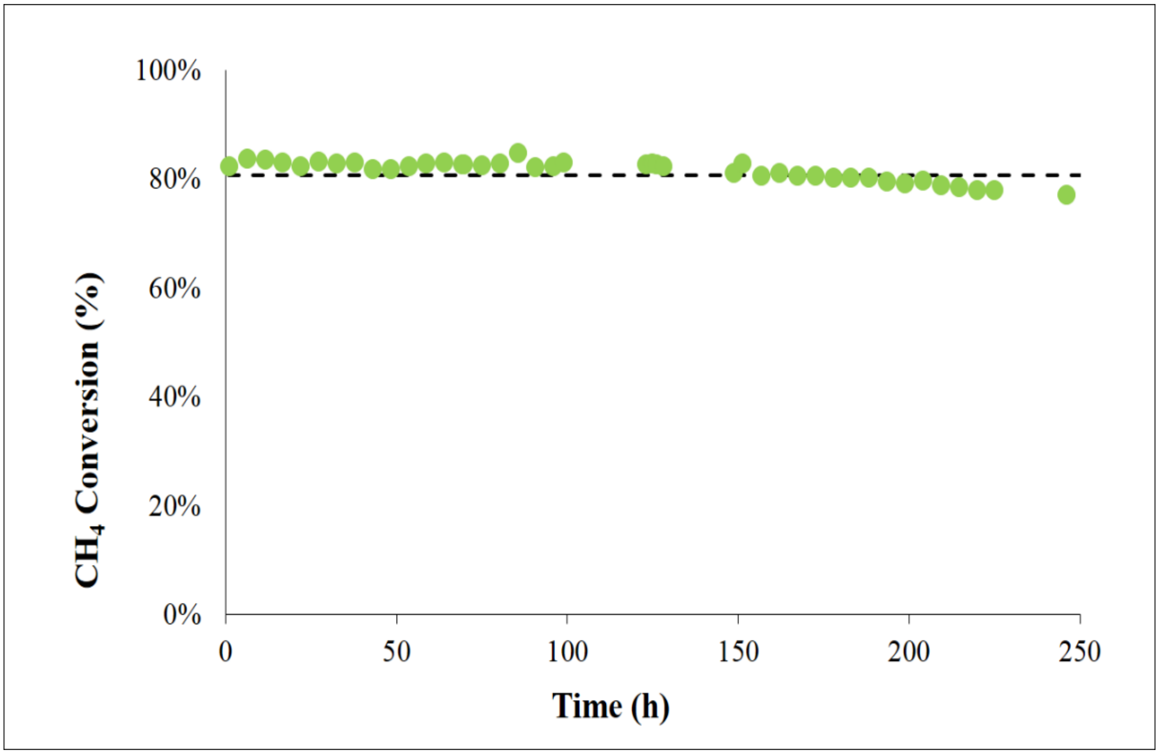

Figure 6. Long term stability study of *Supircat^{TM}* A at 5,000 h^{-1} space velocity and a steam-to-carbon ratio of 2.5, operating at 630°C.

COMMERCIAL IMPLICATIONS:

The high activity displayed by *Supircat^{TM}* catalysts without a prior activation step both in pellet as well as on planar substrates makes these catalysts ideal for internal reforming in SOFC applications. Importantly, the design of these catalysts has considered the cost of the active metals, ensuring that the resultant materials are cost competitive. The competitive cost of *Supircat^{TM}* coupled with its immediate high activity implies that its adoption as an internal reforming catalyst in SOFC systems will lead to savings in both capital and operational costs by stationary as well as portable power generators.

CONCLUSIONS:

Supircat^{TM} internal reforming catalysts offer developers the opportunity to directly integrate high performance catalysts into SOFC stacks, as electrical interconnects, gas distribution plates, or dedicated reforming inserts. The coatings require no pre-reduction, have demonstrated high activity and stability during operation, and are produced by high volume aerosol spray deposition approaches, compatible with other coating processes commercialized by *Nexceris*.

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