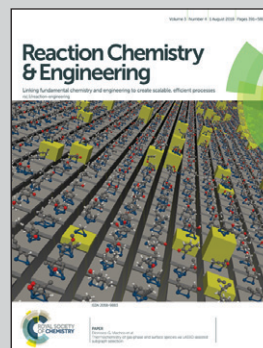


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Robust mesoporous bimetallic yolk–shell catalysts for chemical CO₂ upgrading *via* dry reforming of methane

Ni/ZnO cores were successfully encapsulated utilising a porous silica shell in an effort to prevent the sintering and coking that occurs at high temperatures and thus prolonging the catalyst's lifetime.

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Robust mesoporous bimetallic yolk–shell catalysts for chemical CO₂ upgrading *via* dry reforming of methane†

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Here, we report the synthesis of mesoporous ZnO/Ni@m-SiO₂ yolk–shell particles. The unique ZnO/Ni@m-SiO₂ catalysts demonstrate impressive resistance to sintering and coking for dry reforming of methane (DRM). They also display long term stability with high levels of conversion and selectivity, making this catalyst promising for chemical CO₂ upgrading.

The use of supported nanoparticulate materials as catalysts is a long-standing practice as they demonstrate impressive catalytic properties when applied to numerous reactions.^{1–5} However, these materials are plagued by numerous drawbacks, some of which are associated with the harsh environments that reactions often demand, causing them to lose activity over time. This poses a significant cost to all industries that use supported catalysts in the form of unplanned shutdowns and material replacement every year. Although the time period over which a catalytic material remains active is highly variable; iron catalysts for ammonia synthesis lasting several years and cracking catalysts sometimes lasting only seconds,⁶ deactivation is unavoidable.

Although deactivation is certain for all catalysts, it can be postponed. Through the careful design and development of resistant materials, the active lifetime of these catalysts can be extended. This area of research has attracted significant interest for a number of years, being the topic of a considerable amount of research^{7–13} and review.^{14–17} The goal of this research being to develop an economically viable material, ideally not containing noble metals, that are resistant to

these forms of deactivation that continue to produce high levels of conversion and reaction performance.

The yolk@shell materials detailed in this paper were designed to tackle two well-known areas of catalytic deactivation: coking and sintering. Where supported metal catalysts are concerned, coking can occur in a number of ways: adsorption to the surface through a “monolayer-multilayer” mechanism,^{13,18,19} total encapsulation of the material that completely deactivates the catalyst^{19,20} or fill micro- and meso-pores to prevent or at least limit access of the reactants to the active sites.^{19,20}

Where sintering is concerned, it occurs in several ways: reduction in active surface area due to the growth of the catalytic phase, reduction in the amount of support area due to the collapse of the support phase in addition to the collapse of the porous structure. To prevent these problems, the shell within which our active Ni/ZnO core is held, provides a physical shield to mitigate sintering and also acts as a barrier to prevent the blocking of the active sites through coke formation.

The resultant catalysts were used in the dry reforming of methane (DRM) reaction due to renewed interest in the “green” chemistry approach to produce added value products through chemical recycling CO₂, building on the research of other groups^{21–25} as well as our own.^{26–28} The chemical recycling of CO₂ through the DRM reaction, represented by eqn (1) is a highly endothermic reaction that requires temperatures high enough to favour the process. The later also triggers sintering of active phases and the formation of coke. In fact, given the relatively hard conditions of DRM, it constitutes an excellent “proof-of concept” reaction to validate the yolk–shell approach.



In this scenario we aim to demonstrate the effectiveness of *m*-SiO₂ as a shell material for ZnO–Ni cores within the DRM reaction in the unique “yolk@shell” morphology as a method

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for preventing the thermal degradation of the active nickel species that does not prevent high levels of conversion.

The schematic preparation method of our encapsulated catalysts along with representative scanning electron microscopy (SEM) image is depicted in Fig. 1 and further explained in the ESI.† The SEM image illustrates a broken yolk shell particle with the core clearly visible through the hole in the shell. This provides not only visual confirmation of the successful encapsulation process but also shows the size of these particles to be approximately 400 nm in diameter with a 200 nm core.

The yolk@shell material as well as reference Ni based catalysts were tested in the DRM reaction using a continuous flow reactor at different temperatures (Fig. 2A), details of the procedure for catalytic testing can be found in the ESI.† As seen in Fig. 2, the increasing reactant conversion and product ratio can be tracked against increasing temperature for all the studied samples. As expected within an endothermic reaction, it can be seen that the material performs best at higher temperatures, with conversion of CO₂ reaching 98% at 850 °C. In a similar way, the H₂/CO ratio also increases for all the studied catalysts and in the case of the yolk-shell materials it goes from 0.6 at 550 °C to 0.97 at 850 °C. From Fig. 2 it can be inferred that our advanced yolk-shell catalysts present a comparable performance than that exhibited by the standard DRM catalysts. Ni/SiO₂-Al₂O₃ seems to be slightly more active in the low temperature range however the stability of this solid is very poor in comparison to that displayed

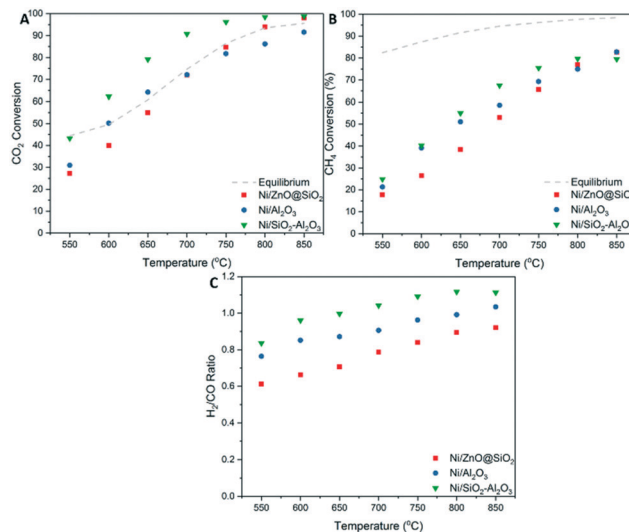


Fig. 2 Shows the comparative temperature screening results of our reported material against Ni/Al₂O₃ and Ni/SiO₂-Al₂O₃ concerning A) CH₄ conversion B) CO₂ conversion and C) H₂/CO ratio.

by the encapsulated catalyst as shown in Fig. S1 (ESI†). Indeed, this stability test reveals the superiority of the yolk-shell catalyst in comparison to benchmark materials which show a rapid deactivation.

Fig. 3 represents a longer term stability test and shows that our ZnO/Ni@m-SiO₂ particles can be applied for continuous operations displaying good levels of CO₂ and CH₄ conversion. The long term catalytic performance of this material in the DRM reaction, was examined at a temperature of 850 °C, due to the extraordinary performance achieved under these conditions. The material demonstrated considerable long-term stability and high levels of CO₂/CH₄ conversion when compared to recent DRM studies (Table S1, ESI†), albeit with some deactivation (96% to 78% for CO₂, 89% to 61% for CH₄) after 143 hours of continuous operation. Additionally the catalyst produces an excellent syngas stream with a H₂/

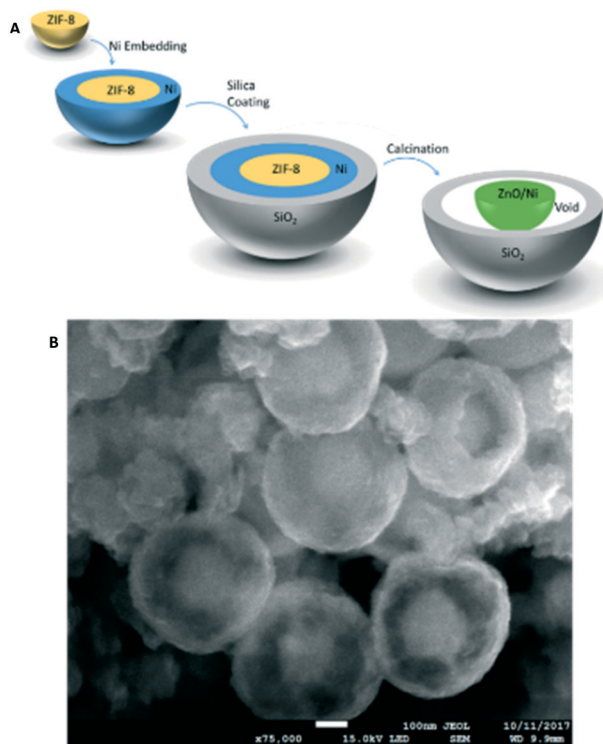


Fig. 1 A) A schematic illustration of the synthetic procedure of yolk-shell catalysts. B) SEM image of the resultant ZnO/Ni@m-SiO₂ yolk-shell particles, confirming successful encapsulation.

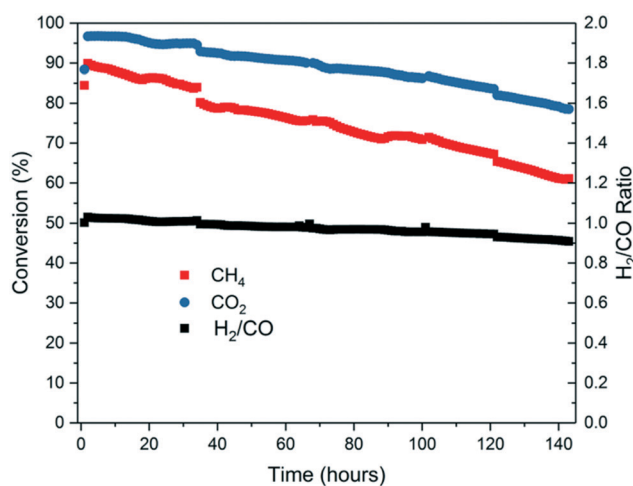


Fig. 3 Shows the long term stability reactant conversion and H₂/CO ratio data of our reported material at 850 °C.



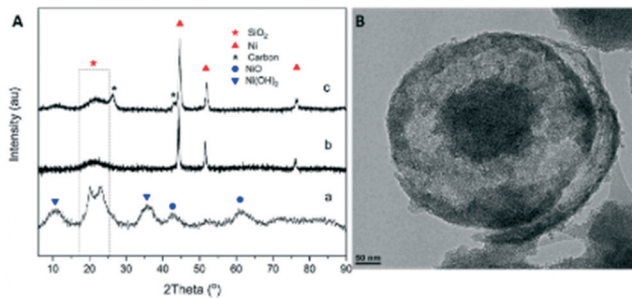


Fig. 4 A) XRD patterns of the calcined material, a, the activated material, b, and the post reaction sample, c. B) TEM image showing the successful encapsulation of the ZnO/Ni core within the *m*-SiO₂ shell.

CO ratio close to 1 (the maximum allowed by the nature of the reaction). Such syngas is a highly valuable product for chemical synthesis and can be used to produce fuels (*via* Fischer-Tropsch), methanol or could be directly utilised to power a solid oxide fuel cell (SOFC).

It can be seen however that carbon peaks appear on the post-reaction XRD pattern in Fig. 4A. This coking can be observed on the TEM images (Fig. S2, ESI[†]) to be taking place on the small amount of unencapsulated nickel/zinc oxide cores that are present throughout the sample. In the same images, it is apparent that the encapsulated cores remain uncoked and thus can be assumed to be successfully resistant.

Furthermore, when the post-reaction sample underwent Raman Spectroscopy (Fig. S3, ESI[†]), the carbon deposits were found to be very graphitic in nature, adding to the notion that the formation of such unreactive graphitic carbon filaments are responsible for the deactivation of this material. Carbon deposition above 650 °C is caused by the decomposition of methane and is a common occurrence within the DRM, especially with bulk nickel catalysts that have minimal support interaction.^{29–31} Similar phenomena have been noted in several papers involving the use of Ni catalysts in the DRM reaction,^{29,32–34} demonstrating that this method of deactivation is highly probable for our material in particular for the fraction of unencapsulated Ni particles.

The XRD patterns **b** and **c** in Fig. 4A, represent the activated and post-reaction catalyst samples, respectively. There is little difference between the two, with the exception of the appearance of carbon peaks in pattern **c**, the formation of which is in good agreement with Raman spectra.

Ni crystallite size was estimated using the Scherrer equation on the most intense reflections in Fig. 4A. It was found that the Ni crystallite size increased by 2 nm, from 21.5 to 23.5 nm respectively. It can be assumed then that the nickel crystallite size did not increase significantly after the reaction and that the *m*-SiO₂ shell successfully prevented the cores (active phase) from sintering.

This is of particular interest as the operating temperature of the DRM reaction undertaken in this study is significantly above the Tamman and Hüttig temperatures for nickel as shown in the work by Moulijn *et al.*,³⁵ meaning

that sintering should have been observed in the post-reaction sample. The fact that it has not been observed, shows the *m*-SiO₂ shell is providing effective protection to the active particles in the core despite the harsh reaction conditions (high reaction temperature and relatively high space velocities).

All the characterisation data obtained from these samples, including the visual confirmation *via* TEM (Fig. 4B) and SEM (Fig. 1B), supports the successful synthesis of the yolk-shell particles and the ability of nano-encapsulated catalysts to tolerate metallic sintering.

However, we are aware of the presence of a small amount of unencapsulated nickel/ZnO cores after detailed analysis of the SEM and transition electron microscope (TEM) images (Fig. S2 and S4, ESI[†]) that are seen as black spots contained in the carbon nanotubes. Here we observe carbon filaments barring access to reactants for both ZnO/Ni cores without shells and our encapsulated material (Fig. S4, ESI[†]). The presence of unencapsulated cores that are prone to sintering and coking, explains the activity drop observed in Fig. 3.

In any case, this work documents the successful synthesis and effective application of ZnO/Ni@*m*-SiO₂ yolk-shell particles towards the DRM reaction, showing also the benefits of the mesoporous silica shell to prevent the sintering of the active metal cores. Also this work demonstrates the superiority of Ni based yolk-shell catalysts over standard Ni catalysts which are traditionally used in reforming units. Despite still suffering from coking, we postulate that a variation to the shell composition would solve this and allow to, at the very least, maintain the significant performance this material displayed within the DRM, perhaps even improving it.

Efforts are currently ongoing in our lab to improve the synthetic method to ensure fully encapsulated yolk@shell materials as well as fine tune physicochemical properties to improve catalytic performance.

Nevertheless, this seminal work demonstrates the robustness of Ni based yolk@shell catalysts towards sintering and their potential to combat coking. Overall, this new family of encapsulated catalysts display excellent skills for environmental catalysis applications as for example CO₂ upgrading *via* dry reforming.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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