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Rh-Ni/MgAl₂O₄ catalyst for steam reforming of methane: Effect of Rh doping, calcination temperature and its application on metal monoliths

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Graphical abstract



Highlights

- An optimum amount of Rh to be added to 15 wt.% Ni/MgAl₂O₄ is 0.5 weight percent
- Optimum amount of Rh is based on activity and stability tests at ambient and high pressure conditions
- Catalyst performance can be further improved by changing calcination temperatures
- Application of Rh-Ni/MgAl₂O₄ washcoated metal monolith further improves the process efficiency.

Abstract

The effect of adding small amounts Rh noble metal to 15wt.% Ni/MgAl₂O₄ catalyst were studied for the steam reforming of methane. For this purpose, two series of catalysts were prepared and then the most active catalyst from this study was selected for metal monolith application. Both series of catalysts were tested at ambient and high pressures conditions. The first series of

catalyst was used to determine the optimum Rh concentration by varying the Rh concentration from 0.1 to 1.0 wt.%. It was found that an optimum concentration of 0.5 wt.% Rh showed the highest activity and stability. The second series of catalysts containing 0.5wt.%Rh-15wt.% Ni/MgAl₂O₄ was used to study the effect of calcination temperature on the activity and stability. Studies on the second series of catalysts showed that the catalyst prepared by sequential impregnation and calcined at lower temperatures (600 °C after each Ni and Rh impregnation) showed the highest activity and stability. Among the several changes in factors detected due to Rh doping, the increase in catalytic activity for the catalyst calcined at lower temperatures was mainly attributed to its higher degree of reduction and higher abundance of Ni-Rh active sites. The most active Rh-Ni/MgAl₂O₄ catalyst was washcoated on FeCralloy metal monoliths and the performance compared with a packed bed and Ni/MgAl₂O₄ washcoated metal monolith. A significant increase of 24% in methane conversion was observed for Rh-Ni/MgAl₂O₄ washcoated metal monolith in comparison to NiMgAl₂O₄ washcoated metal monolith.

Keywords: Methane steam reforming; Rh-Ni/MgAl2O4 catalyst; Metal Monoliths

1. Introduction

Hydrogen has the highest energy content in comparison to other conventional fuels and offers a clean and environmentally friendly solution for future energy requirement [1]. Despite the continuous improvements in technologies for producing hydrogen, steam reforming of natural gas using conventional packed bed reactors is still widely used [2]. Several commercial catalysts with different active metal compositions and supports are used for this large scale steam reforming process and the details are available elsewhere [3]. Nickel, due to its low cost and availability, and MgAl₂O₄ spinel, due to its stability at elevated temperatures, is extensively used as the active metal and support, respectively. However, due to the propensity of nickel metal towards carbon formation and sintering at high temperatures, its application for longer run-time operations in conventional packed bed reactors, particularly at high pressures conditions, is a challenging task [4]. Furthermore, the conventional packed bed steam reforming process also suffers from other shortcomings, such as high pressure drop, lower catalyst utilization and heat transfer limitations.

Several studies have reported the application of noble metals for steam reforming of methane to address the shortcomings of conventional catalysts [5-7]. However, the high cost of noble metals precludes their use as supported monometallic catalysts in industrial reforming. Fortunately, several studies have also shown that introducing small amounts of noble metals, such as Pt, Rh, Ag, and Ru can significantly improve the activity and stability of the nickel-based bimetallic catalysts [8, 9]. In their work on reforming of n-butane, Ferrandon and co-workers found that for the same metal loading, Rh doped nickel catalyst performed even better than nickel and Rh alone [10]. Doping nickel catalysts with noble metals not only increases the resistance to carbon formation but also decreases the affinity of nickel towards sulfur poisoning during steam

reforming of hydrocarbons [11]. Studies have also reported that the introduction of small amounts of noble metals increases the self- activation and self- regeneration of the catalyst, which is particularly beneficial for operations involving frequent startup and shutdown [12, 13]. Addition of small amounts of these noble metals significantly changes the physicochemical properties of the catalyst, such as metal dispersion, crystallite size of active metal, and metal support interaction [14]. A study has shown that the enhanced properties of noble metal-doped Ni catalysts could be also be due to alloy formation, such as Pt-Ni or Rh-Ni alloys, resulting in enhanced electronic interaction between metal particles [15]. Furthermore, Garcia-Dieguez et al. found that on alumina supported Pt-Ni bimetallic catalysts, the addition of Pt also decreased the formation of nickel aluminate, which is a non-reducible inert species [16].

A few studies have been published on the effect of varying the amount of noble metal doped on the nickel-based catalysts [17, 18]. However, most of these studies were performed at atmospheric pressure and stability of the catalyst at high-pressure conditions was not reported. In our earlier work on Pt doped Ni/MgAl₂O₄ catalyst, it was found out that addition of 0.1wt.% of Pt to Ni/MgAl₂O₄ catalyst not only improved the activity of the catalyst but also its stability at high-pressures [19]. Furthermore, it was observed that testing of the catalysts at high-pressures was required for determining the stability of the catalyst.

In most of the earlier published studies on supported Rh-Ni bimetallic catalysts for steam reforming of methane, MgAl₂O₄ was not used as the support [8]. As mentioned above, MgAl₂O₄ is widely used as a support due to its stability under high-temperature operations. Moreover, most of the previous studies have been conducted at atmospheric pressure, whereas industrially the steam reforming of methane is conducted at higher pressures. Furthermore, the application of

metal monolith washcoated with Rh-Ni/MgAl₂O₄ catalyst for the SRM process has not been explored.

Besides the improvement in the catalyst effectiveness, application of noble metal doped Ni/MgAl₂O₄ washcoated on metal monolith can significantly improve the overall process efficiency in comparison to packed beds. Various studies have shown that due to their high thermal conductivity, better catalyst utilization and lower pressure drop, metal monoliths reactors can be an attractive alternative to conventional packed bed reactors for highly endothermic steam reforming process [20, 21].

Thus, the objective of this study was to investigate the promotional effect of Rh on Ni/MgAl₂O₄, determine the optimum doping of Rh, and examine the stability of the catalysts at ambient and high-pressure operations. To further enhance the catalytic activity and stability of Rh promoted nickel catalyst, the effect of calcination temperature for sequential impregnation was also studied. For comparison, a catalyst prepared by co-impregnation method was also synthesized, characterized and tested. After optimizing the amount of Rh and preparation method, the most active Rh doped Ni/MgAl₂O₄ catalyst was washcoated over a FeCralloy metal monolith. This washcoated metal monolith was then compared with a Ni/MgAl₂O₄ washcoated metal monolith and packed bed reactor containing the Ni/MgAl₂O₄ and Rh doped Ni/MgAl₂O₄ catalysts.

2. Experimental

2.1 Catalyst preparation

Two series of Rh noble metal-doped $Ni/MgAl_2O_4$ were prepared using impregnation method. The first series of catalysts were prepared to study the effect of Rh concentration, while the second series of the catalysts were prepared to study the effect of calcination temperature at

different stages of preparation. The catalyst support was prepared by calcining aluminum magnesium hydroxycarbonate powder, $Mg_{2x}Al_2(OH)_{4x+4}CO_3.nH_2O$, (Pural MG30, supplied by Sasol, Germany) at 900 °C for 4 h to ensure that magnesium aluminate spinel was formed. The MG30 sample contained about 30 wt.% MgO and 70 wt.% Al_2O_3 .

Before making the two series of catalysts, a large batch of 15 wt.% Ni/MgAl₂O₄ catalyst was prepared by wet impregnation. For this purpose, an aqueous solution of Ni(NO₃)₂.6H₂O (Loba Chemicals, India) was prepared. The previously prepared magnesium aluminate spinel powder (catalyst support) was then added to the aqueous solution of nickel nitrate solution. After stirring for 30 minutes, the prepared slurry was dried in a vacuum rotary evaporator at 90 °C. The nickel impregnated support from the vacuum evaporator was further air dried in an oven at 120 °C for 3 h. The dried sample was then separated into two batches.

For preparing the first series of catalysts, one batch of the 15 wt.% Ni/MgAl₂O₄ catalyst was calcined at 850 °C and then cooled to room temperature before sequential impregnation of the Rh precursor solution. The calcined catalyst was mixed with the required amount of rhodium(III) nitrate solution (10 wt.% Rh in HNO₃ solution, Alfa Aesar) using the incipient impregnation method. After Rh impregnation, the catalyst was dried in an oven at 120 °C for 3 h followed by calcination at 600 °C for 3 h. These catalysts are denoted as *x*Rh15Ni where *x* is the wt.% loading of Rh. The Rh loading was varied from 0.1 to 1.0 wt.%, whereas the nominal Ni loading was kept fixed at 15.0 wt.%.

A second series of catalysts containing 0.5 wt.% Rh doped 15wt.% Ni/MgAl₂O₄ were prepared by calcining the catalysts at either 600 °C or 850 °C after sequential impregnation of Ni and Rh. These catalysts were denoted as Cat T_1T_2 , where T_1 is the calcination temperature after Ni

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impregnation and T₂ is the calcination temperature after Rh impregnation. Thus, the catalyst calcined at 600 °C after Ni impregnation and 850 °C after Rh impregnation is denoted as Cat600850. In addition, one catalyst (0.5 wt.% Rh doped 15wt.% Ni/MgAl₂O₄) was also prepared by co-impregnation of rhodium mixed with nickel precursor solutions and calcined at 600 °C. This catalyst is denoted as RhNicoimp. Calcination for all the catalysts was done with a temperature ramp of 2 °C.min⁻¹.

2.2 Catalyst characterization

Several techniques were used to characterize the fresh and used catalysts. The BET (Brunauer– Emmett–Teller) surface area of the support and different catalysts were determined on AutosorbiQ (Quantachrome). The temperature-programmed reduction (TPR) profiles of the different catalysts were obtained on AMI200 instrument (Altamira). To remove the volatile impurities from the catalysts before TPR analysis, the samples were degassed for 30 minutes at 250 °C in an argon flow of 30 ml.min⁻¹. After degassing, the catalyst samples were reduced in a flow of 10 mol% hydrogen/argon mixture in the temperature range of 50 to 1000 °C. During the reduction step, the temperature was increased with a ramp of 10 °C.min⁻¹. The degree of reduction of each catalyst was calculated as follows:

$$Degree of reduction(f) = \frac{H_2 \ consumption \ from \ TPR \ experiment(U_{TPR})}{H_2 \ required \ for \ complete \ reduction}$$
(1)

The amount of H_2 consumed was calculated using the area obtained from the TPR profile of each catalyst, while the H_2 required for complete reduction was calculated from the total number of moles of Ni and Rh present in the catalyst. The following reduction reactions were considered for calculating the amount of H_2 required for complete reduction of Ni and Rh oxides:

$$NiO + H_2 \rightarrow Ni^o + H_2O \tag{2}$$

$$Rh^{3+} + 1.5H_2 \rightarrow Rh^o + 3H^+$$
 (3)

 H_2 chemisorption was measured using the same AutosorbiQ instrument (Quantachrome) as mentioned above. Before H_2 chemisorption, the samples were degassed at 350 °C for 3 h followed by reduction at 850 °C for 3 h. After reduction, the catalyst sample was cooled to 30 °C in a flow of helium. Two cycles of adsorption isotherm in the pressure range of 0.10 to 1.06 bar were measured to differentiate between the weak, strong and combined isotherms of adsorbed hydrogen over the metal. Based on the hydrogen uptake, the dispersion (**D**) was calculated, while the effective dispersion (**D**_{eff}) of the catalyst samples was calculated using the following equation:

$$D_{eff} = \frac{D}{\frac{f}{100}} \tag{4}$$

where f is the degree of reduction (%) of the catalyst as determined by temperature-programmed reduction.

X-ray diffraction (XRD) patterns of the magnesium aluminate spinel support and reduced catalyst samples were obtained from PAN analytical X'Pert instrument using Ni-filtered K α radiation from a Cu target ($\lambda = 1.541841$ Å). XRD data was recorded from 10° to 90° with a 4°min⁻¹ scanning rate. Crystallite sizes of the metal particle of the different catalysts were calculated using the Scherrer equation. For this purpose, the peak at 51.7°, due to the (200) crystal plane family of Ni, was used [22].

Transmission electron microscopy (TEM) analysis of 0Rh15Ni and Cat600600 was carried out using an FEI Titan G2 60-300 (300 kV) high-resolution transmission electron microscope to

determine the particle size change due to the addition of Rh. Before TEM imaging, the catalyst samples were reduced at 850 °C for 3 h, and the reduced catalyst was dispersed in ethanol. About 5 μ l of this dispersion was loaded on a carbon-coated copper grid, and then the loaded grid was dried at ambient conditions using a table lamp.

A Cary500 UV-vis (Agilent) instrument was used to obtain UV-vis spectra of the different samples. Spectra were recorded from 200 nm to 1800 nm under ambient conditions. Thermogravimetric analysis (TGA) of the as-received MG30 powder was obtained on a SDT Q600, TA Instruments. During TGA, the sample was heated from 25 °C to 1000 °C with a ramp of 10 °C/ min in a flow of air.

2.3 Washcoating of metal monolith

To compare the performance of metal monoliths with a packed bed reactor, 33 mm o.d. FeCralloy metal monoliths (supplied by Emitec Emission Control Tech. Pvt. Ltd, Pune) were cut into pieces of 30 mm length and the catalyst was deposited on these by washcoating.. Washcoating of metal monoliths using Ni/MgAl₂O₄ catalyst was done according to the procedure described in our earlier work [23]. Similar washcoating procedure was applied for Rh doped Ni/MgAl₂O₄ catalyst and Cat600600. Well-adhered homogeneous washcoat layer was obtained over FeCralloy metal monoliths for both the catalysts.

2.4 Activity tests

The activity tests of the two series of catalysts and metal monoliths were performed in two different Inconel600 reactor tubes. The effect of adding Rh to Ni/MgAl₂O₄ catalysts (Series I and II) was studied in a reactor tube of length 40 cm and diameter of 3.4 mm at 600 °C, and 1 or 10 bar pressure. In this study, internal mass transfer limitations were eliminated by keeping catalyst

particle size in the range of 0.25-0.30 mm. 100 mg of the catalyst was mixed with 100 mg of quartz particles of the same average size and placed at the centre of the tubular reactor. The temperature of the catalyst bed was measured with a Type K thermocouple placed just above the catalyst bed. The upper and lower parts of the reactor tube were filled with quartz chips for efficient mixing of reactants, preheating and supporting the catalyst bed.

As metal monoliths had a diameter of 33 mm, a different Inconel600 reactor tube of internal diameter 36mm and length 40 mm was used for the metal monoliths experiments. To avoid the bypassing, ceramic paper of thickness 1 mm was wrapped around the metal monolith before sliding it into the reactor tube. To investigate the SRM process near industrial conditions and to compare the performance of metal monoliths with a corresponding packed bed catalyst, packed bed experiments with average catalyst particle size of 1.5 mm were also performed in this reactor tube. Two Type K thermocouples were used to measure the tube outer wall temperature (T_{wall}) and the temperature at the centre of the catalyst bed (T_{center}). During these experiments, the total pressure was kept at 1 bar and the T_{wall} was maintained at 600 °C.

For both reactor configurations, methane and nitrogen (used as internal standard for GC analysis) were fed through mass flow controllers (Bronkhorst, Netherlands) while water was fed through a high pressure metering pump (Laballiance, USA). The reactant mixture was preheated to 400 °C. Excess water in the reactor effluent was condensed using a refrigerated circulator. Condensed water from the product gases was separated in a gas-liquid separator. To pressurize the reactor system at 1 or 10 bar, a Tescom back pressure regulator was installed after the gas-liquid separator. The reactor pressure was measured by a pressure gauge installed at the reactor inlet.

Analysis of product gases was achieved in a gas chromatograph (GC) equipped with a thermal conductivity detector. Separation of product gases in GC was performed using a Carbosphere

column (3 m long). Before the activity test, the catalyst samples and washcoated monoliths were reduced in-situ at 850 °C for 3 h in an H₂ flow of 60 ml.min⁻¹. The reduction temperature of 850 °C was reached with a ramp rate of 3 °C.min⁻¹. Activity tests were conducted for 8 h with a W/F_{A0} (ratio of weight of the catalyst to inlet molar flow rate of methane) of 0.34 gcat.h.mol⁻¹ and CH₄:H₂O:N₂ molar ratio of 1:5:1. Several runs were taken, and the reported values for the variation of CH₄ conversion with time-on-stream (TOS) were the average of these runs. Methane conversion and CO selectivity for each run were calculated as follows:

$$X_{CH_{4}} = \frac{F_{CO} + F_{CO_{2}}}{F_{CO} + F_{CO_{2}} + F_{CH_{4,out}}}$$
(5)
CO selectivity = $\frac{F_{CO}}{F_{CO} + F_{CO_{2}}}$
(6)

where F_{CO} , F_{CO_2} and $F_{CH_{4,OUT}}$ are the outlet molar flow rates of CO, CO₂, and CH₄, respectively. Hydrogen yield for each catalyst was calculated by dividing the molar fraction of hydrogen produced to the molar methane fed in the reactor.

3. Results and discussion

3.1 Catalyst characterization

Table 1 shows the surface area of the as-received MG30 powder, calcined MG30 and the different catalysts that were prepared. The surface area of the catalyst support decreased from 250.1 to 73.6 m².g⁻¹ after calcination at 900 °C. A TGA analysis showed a weight loss of 40% during calcination of the as-received MG30 powder. This decrease in surface area and weight loss was attributed to the change in pore structure and evolution of volatile substances present in the as-received MG30 powder during its transformation to the magnesium aluminate spinel

phase. The surface area of the support decreased further on addition of the metals. The surface area of the catalyst 0Rh15Ni decreased to 43.2 m².g⁻¹ after the calcined MG30 was impregnated with nickel metal and calcined at 850 °C. The surface area decreased once again for the Rh doped catalysts, which were prepared by sequential impregnation (Series 1 catalysts). Such a decrease in the surface area occurred probably due to two factors: re-calcination after metal impregnation, and blocking of support pores by metal particles [24]. Effect of re-calcination was confirmed by measuring the BET surface area of the Cat850 re-calcined at 600 °C. It was found that the surface area of this unpromoted re-calcined catalyst decreased from 43.2 m²/gm to 42.1 m^2/g . This observation indicates that re-calcination marginally affects the catalyst surface area and the decrease in surface area is mainly due to the addition of Rh metal. However, an increase in Rh concentration does not change the surface area significantly. For Series 2 catalysts, RhNicoimp had the highest surface area (60.7 m².g⁻¹) followed by Cat600600. It was observed that catalysts that had experienced a calcination temperature of 850 °C either after Ni or Rh impregnation had a lower surface area. The surface areas of these catalysts of Series 2 were similar to those catalysts of Series 1 since both series of catalysts experienced a calcination temperature of 850 °C. These results indicate that calcination temperature is the dominant factor for the decrease in surface area. Similar results have also been reported by Miyata and coworkers [25].

UV-vis spectroscopy was used to detect the presence of the nickel aluminate (NiAl₂O₄) phase. Studies have shown that nickel with alumina can form either tetrahedral or octahedral spinel structures in the oxygen lattice. Absorption bands for octahedral Ni(II) in a NiO lattice are observed at about 380, 430 and 720 nm, whereas the absorption bands for tetrahedral Ni(II) in the nickel aluminate lattice are observed at 550 nm and in the 600-650 nm region [26-29]. The

UV-vis spectra of catalysts of Series 1 and 2 are shown in Figs. 1(i) and 1(ii), respectively. As can be seen from Fig. 1(i) the spectra of 0Rh15Ni revealed the presence of bands corresponding to NiAl₂O₄ in addition to those due to NiO. The other Series 1 catalysts revealed no significant change in the peak due to NiAl₂O₄. It appears that NiAl₂O₄ was formed when the nickel impregnated catalyst was calcined at 850 °C. Furthermore, the presence of Rh did not affect the formation of NiAl₂O₄. For Series 2 catalysts shown in Fig. 1(ii), the formation of NiAl₂O₄ could be identified for the three catalysts (Cat600850, Cat850600, and Cat850850) that had experienced a calcination temperature of 850 °C during their synthesis. These results confirm that increasing the calcination temperature to 850 °C facilitates the formation of NiAl₂O₄ and that the presence of Rh does not have an effect on the formation of NiAl₂O₄. Furthermore, the support as previously reported [4, 26].

The TPR profiles of Series 1 and 2 catalysts are shown in Figs. 2(i) and 2(ii), respectively. The maximum of the peak in the TPR profiles of these samples (T_{max}) ranges from 745 to 806 °C. The presence of T_{max} at these high temperatures has usually been attributed to the reduction of NiAl₂O₄ [30]. Earlier studies have shown that metal oxide solid solutions are formed by NiO and MgO, and these solid solutions also reduce at high temperature [31, 32]. As suggested previously excess MgO is present on the surface of the MgAl₂O₄ spinel support [30]. The Ni impregnated can interact with this excess MgO to form NiO-MgO solid solutions, in addition to forming NiAl₂O₄. Thus, the T_{max} at these high temperatures is due to the reduction of NiAl₂O₄ and/or NiO-MgO solid solutions.

For the Series 1 catalysts, shown in Fig. 2(i), it can be observed that all Rh doped Ni/MgAl₂O₄ catalyst samples showed a slightly higher T_{max} temperature relative to Ni/MgAl₂O₄. This increase

in T_{max} can be attributed to the sequential impregnation method adopted during catalyst preparation. The sequential impregnation method adopted in this study involved two calcination steps, which facilitated the formation of strongly bonded Ni sites and NiAl₂O₄. The TPR profiles in Fig. 2(i) also revealed that with an increase in Rh content, T_{max} decreased. A peak attributed to the reduction of Rh-oxide was also observed between 300 and 400 °C, which became more intense with an increase in Rh content. Furthermore, the degree of reduction increased with Rh content as shown in Table 1. Earlier studies have also reported that addition of noble metals facilitates hydrogen spillover, which results in a decrease in reduction temperature and an increase in degree of reduction [33, 34]. It appears that with an increase in Rh content, the hydrogen spillover increases, which facilitates the reduction of the catalyst to occur at lower temperatures and increases the degree of reduction of the NiAl₂O₄ species and/or NiO-MgO solid solution.

The TPR profiles for the Series 2 catalysts and RhNicoimp are shown in Fig. 2(ii). In three of these catalysts (Cat600850, Cat850600, and Cat850850) NiAl₂O₄ was detected in the UV-vis spectra, whereas NiAl₂O₄ was not detected in RhNicoimp and Cat600600. As mentioned above, it appears that the lower T_{max} of Cat600600 and RhNicoimp catalysts was primarily due to the reduction of NiO-MgO solid solution [35]. Furthermore, the higher T_{max} temperature for all the Series 1 catalysts and Cat600850, Cat850600, and Cat850850 was due to the reduction of NiAl₂O₄ in addition to the reduction of the NiO-MgO solid solution. The change in T_{max} for Series 1 catalysts was related to the amount of Rh present on the catalyst surface, and a similar phenomenon might occur for the Series 2 catalysts. Furthermore, the presence of NiAl₂O₄ and NiO-MgO solid solution for Cat600850, Cat850600, and Cat850850 may also play a role in the change in T_{max} .

The degree of reduction of three catalysts of Series 2 (Cat600850, Cat850600, and Cat850850) and Series 1 catalysts that had experienced a calcination temperature of 850 °C was lower than the two catalysts (RhNicoimp and Cat600600) that were calcined at 600 °C. The lower degree of reduction for Cat600850, Cat850600, and Cat850850 can be readily attributed to the detectable amount of NiAl₂O₄ formed in these catalysts. Furthermore, the degree of reduction of NiO-MgO solid solution also decreases with increasing calcination temperature [32].

As active metal size and dispersion can significantly affect the catalytic activity, three characterization techniques (XRD, H₂ chemisorption and TEM) were used to determine these properties. Figs. 3(i) and 3(ii) show the XRD profiles of the Series 1 and 2 catalysts, respectively. In our earlier work, we have demonstrated that MG30 was converted to magnesium aluminate spinel after calcination at 900 °C for 4 h [4]. Peaks corresponding to MgAl₂O₄ spinel and Ni metal can be observed in both Figs. 3(i) and 3(ii). Peaks of Rh(111) and Rh(200) metal are expected at 41° and 47° [36]. However, such peaks were not detected in the XRD profiles either due to small amounts of Rh or the high dispersion of Rh or both. The peaks corresponding to NiAl₂O₄ could not be readily identified because these peaks overlap with those of MgAl₂O₄ spinel [37, 38]. It is interesting to note that even after reduction of the catalyst at 1000 °C, a small peak at 43.8° could be identified, which could be due to NiO and/or MgO [39]. In our earlier studies, this peak was attributed to NiO and the formation of metal oxide solid solutions. Some part of this metal oxide solid solution can migrate into the bulk support and remain inaccessible for reduction [4]. Presence of non reducible species or partial reduction of Series I and II catalysts also support this observation.

Ni metal peaks were identified at 51.8° and 76.3° , and the peak located at 51.8° was used to estimate the crystallite size using Scherrer equation. Table 1 shows the crystallite size (d_{Ni})

calculated for both series of catalysts. For Series 1 catalysts, on increasing the Rh loading from 0.0 to 1.0 wt.%, the crystallite size of Ni metal marginally decreased from 10.9 nm to 9.9 nm. Simultaneously, the dispersion of active metals increased from 5.4 to 6.3%. This marginal decrease in crystallite size was attributed to the high temperature (850 °C) calcination of the Ni/MgAl₂O₄ catalyst after nickel impregnation. Others have also reported that doping of small amount of noble metal increases the dispersion of nickel [40]. It appears that an inverse-correlation exists between the crystallite size and dispersion . Our earlier study had shown that for the Ni/MgAl₂O₄ catalyst calcined at 850 °C, the nickel active metal present on the surface of the support showed anchoring effect [4]. This anchoring of nickel appears to inhibit further dispersion of active metal on the support surface. Furthermore, the anchoring of nickel may be associated with the MgO present on the surface of the spinel support as discussed above.

Table 1 also lists the crystallite sizes of Series 2 catalysts. As can be seen from Table 1, the crystallite size of the catalyst prepared by co-impregnation (RhNicoimp) was smaller than Cat600600, which was prepared by sequential impregnation. This effect of preparation method on crystallite size can be attributed to two factors. Firstly, during the preparation of RhNicoimp, the spreading of NiO on the catalyst surface is more likely as both Rh₂O₃ and NiO are present during calcination of the catalyst. Secondly, Cat600600 was calcined twice at 600 °C instead of once for RhNicoimp. Similar observation have also been reported by Chantaravitoon and co-workers [41]. In their work, it was observed that co-impregnation of noble metal facilitates the dispersion of active metals on the support surface. The smallest crystallite size in Cat850850 can be attributed to the presence of rhodium oxide during the second calcination step, which further synergizes the dispersion of active metals on the support surface. Nagaoka et al. [40] suggested that the presence of Rh also enhances the anchoring of Ni particles, which results in a smaller

crystallite size. The nickel crystallite size of Cat600850 was smaller than that of Cat850600, which indicates that high calcination temperatures after addition of Rh give rise to a better dispersion of nickel.

To further investigate the effect of Rh on the particle size of the active metal, TEM imaging of reduced Cat600600 and 0Rh15Ni catalysts was carried out. These catalysts were selected for imaging because the highest activity was obtained with Cat600600 and the lowest with 0Rh15Ni (discussed later). The TEM images along with the particle size distribution are shown in Fig. 4. Addition of Rh resulted in a change in particle size distribution with a significant increase in the number of particles in the size range of 0-10 nm and a decrease in the number in the size range of 10-20 nm. The average particle size calculated from TEM analysis for 0Rh15Ni and Cat600600 catalysts was 11.7 and 8.6 nm, respectively. This observation further confirms the effect of Rh in decreasing the average particle size of the active metal, thereby increasing the dispersion of nickel on the support.

The dispersion data of Series 1 and 2 catalysts are also tabulated in Table 1. As discussed earlier, calcination at high temperature resulted in stronger metal oxide support interaction, which decreases the availability of nickel. To account for the loss of available nickel during catalyst calcination, the effective dispersion, D_{eff} , of the active metal particles was calculated using eqn. (1). However, the calcination temperatures used during catalyst preparation were different, and an appropriate degree of reduction needs to be considered. The D_{eff} of 0.1Rh15Ni, 0.5Rh15Ni and 1.0Rh15Ni catalysts was calculated using the degree of reduction of 0Rh15Ni catalyst, which was 46.3%. Such a choice was justified since these catalysts were calcined at 600 °C after Rh impregnation and no additional formation of NiAl₂O₄ relative to 0Rh15Ni was detected in the UV-vis spectra of these Rh doped catalysts as shown in Fig. 1(i). For the Series 1 catalysts, there

was a noticeable increase in D_{eff} when small amounts of Rh was added (comparing D_{eff} of 0Rh15Ni and 0.1Rh15Ni). This high value of D_{eff} was relatively constant for the 0.1Rh15Ni and 0.5Rh15Ni catalyst, whereas a marginal increase in D_{eff} was observed for the 1.0Rh15Ni catalyst. Various researchers have attributed this increase in the dispersion to the synergetic effect between Ni and the noble metal resulting in alloy formation [42, 43]. Earlier studies have also shown that although the addition of noble metal increases the dispersion, higher surface concentrations can result in the agglomeration of active metals [44].

For two of the Series 2 catalysts, Cat600600 and RhNicoimp, the D_{eff} was calculated using the degree of reduction of the catalyst that was calcined at 600 °C after nickel impregnation. The degree of reduction of such a catalyst was 56.4%, which is consistent with the data reported previously [39]. Based on this information, the D_{eff} for RhNicoimp was slightly more than Cat600600. Tomishige has also reported similar results for his work on sequential and co-impregnated Ni-Pt/ γ -Al₂O₃ catalyst [45]. The D_{eff} values for Cat600850, Cat850600 and Cat850850 were difficult to determine since the surface concentration of the Ni-Rh alloy, the formation of metal oxide support solid solution, and the formation of NiAl₂O₄ would have an effect on the degree of reduction and consequently D_{eff} .

3.2 Activity test

3.2.1 Promotional effect of Rh metal

The variation of methane conversion with time-on-stream for catalysts of Series 1 at a reactor pressure of 1 and 10 bar is shown in Figs. 5(i) and 5(ii), respectively. Table 2 shows the initial methane conversion and hydrogen yield (after 1h of time-on-stream) of all the catalyst. At both pressures, small amounts of rhodium (0.1 wt.% Rh) in the catalyst significantly increased the initial methane conversion and hydrogen yield. However, with a further increase in Rh content of

the catalyst, the methane conversion and hydrogen yield did not increase. Li and co-workers have also reported similar results for steam reforming of methane on Rh-Ni/Mg(Al)O catalyst [18]. Furthermore, at 1 bar pressure, the stability of the catalysts was high, and the presence of Rh resulted in only a marginal improvement in the stability of the catalyst of Series 1 (Table 2). Since the stability of catalyst is strongly affected by the reactor pressure, the stability of the catalyst was also checked at a reactor pressure of 10 bar. At 10 bar reactor pressure, the initial conversions achieved with 0.1Rh15Ni, 0.5Rh15Ni and 1.0Rh15Ni were similar and greater than the conversion achieved with 0Rh15Ni. However, the stability of the catalysts was different. As can be observed from Table 2 and Fig. 5(ii), compared to 0Rh15Ni the stability of 0.1Rh15Ni was lower, while the stability of 0.5Rh15Ni and 1.0Rh15Ni was similar.

Fig.6 shows the change in CO selectivity for Series 1 catalysts at 1 and 10 bar pressure. On increasing the Rh doping in the catalyst the CO selectivity increased at both reactor pressures. These results indicate that CO selectivity is directly related to the Rh concentration in the catalyst. To confirm these results, another experiment was conducted with 0.1%Rh/MgAl₂O₄ at similar conditions. A CO selectivity of 0.24 was observed for the 0.1%Rh/MgAl₂O₄ catalyst, which was significantly higher than the selectivity obtained with either 0Rh15Ni or 1.0Rh15Ni. Thus, the increase in CO selectivity can be attributed to the presence of Rh metal on the catalyst surface. In addition to the presence of Rh, the crystallite size of the active metals can also affect the CO selectivity [46]. Catalysts having a smaller crystallite size tend to form CO during reforming. As shown above, the addition of noble metal caused a decrease in the crystallite size of active metals. Thus, an increase in CO selectivity can also be attributed to this phenomenon.

Our earlier studies have shown that the calcination temperature can have a significantly effect on the activity and stability of the catalyst [4]. Consequently, the effect of calcination temperature

was investigated for 0.5wt.% Rh doped 15wt.%Ni/MgAl₂O₄ catalyst. For the Rh doped catalysts prepared by sequential impregnation there were two independent calcination temperatures. The two independent calcination temperatures gave rise to four catalysts, namely Cat600600, Cat600850, Cat850600 and Cat850850. A co-impregnated catalyst, RhNicoimp, that was calcined at 600 °C was also included in the comparison to see the effect of preparation method. Figs. 7(i) and 7(ii) show the variation of conversion with time-on-stream for Series 2 catalysts at 1 and 10 bar pressure, respectively. As can be seen from these figures Cat600600 showed the highest activity among the Series 2 catalysts, while Cat850600 had the lowest activity. As observed for the activity of the Series 2 catalyst, the hydrogen yield also followed a similar trend. At both pressures (1 and 10 bar), the trend in activity was as follows:

Cat600600 > RhNicoimp > Cat600850 ~ Cat850850 > Cat850600.

The higher activity of Cat600600 and RhNicoimp catalyst calcined at a relatively lower temperature of 600 °C can be attributed to the relative abundance of surface Ni and Ni-Rh sites. Moreover, the catalytic activity of Cat600600 was higher than RhNicoimp catalyst. This increase in catalytic activity of sequentially impregnated Cat600600 catalyst in comparison to co-impregnated RhNicoimp catalyst was attributed to a higher surface concentration of Rh species in the sequentially impregnated catalyst. A higher surface concentration of Rh would facilitate the formation of Ni-Rh alloy. Such a proposal is consistent with the work on oxidative reforming of methane on Pt-doped Ni/Al₂O₃ by Li et al.[47]. In their study the FTIR spectra of adsorbed CO revealed that the catalyst prepared by sequential impregnation had a higher surface concentration of Pt metal than the co-impregnated catalyst, which resulted in a higher catalytic activity.

The activity of Series 2 catalysts shown in Figs. 7(i) and 7(ii) reveals that the intermediate and final calcination temperature used during synthesis also affects the activity and stability of the catalyst. Comparing the activity of Cat600600 with the catalysts that have experienced a calcination temperature of 850 °C during their synthesis suggests that the decrease in activity of the latter was due to the loss of Ni metal caused by the formation of NiAl₂O₄ and/or NiO-MgO solid solution. An increase in calcination temperature may also cause a decrease in activity of the NiO-MgO solid solution as reported previously [31, 32]. However, the trend in the catalytic activity of Cat600850, Cat850850, and Cat850600 is difficult to reconcile and may be related to the surface abundance of the Ni-Rh sites, the amount of NiAl₂O₄ formed and the availability of Ni in the NiO-MgO solid solution. Comparing the catalytic activity of Cat850600 and Cat850850 suggests that an increase in the surface concentration of Rh is facilitated at 850 °C. For these catalysts attempts to correlate the catalytic activity with D_{eff} were ineffective since, as discussed above, the basis for the calculation of D_{eff} was difficult to ascertain.

Table 2 shows the stability data for Series 2 catalyst at 1 and 10 bar pressure. Stability of Series 2 catalysts varied in the order of

Cat600600 > RhNicoimp > Cat600850 ~ Cat850850 > Cat850600.

In our earlier work, we have shown that the main cause of deactivation of catalyst in steam reforming of methane was carbon formation on the catalyst surface [4]. This carbon formation over the active metal surface is affected by several factors. These factors include the crystallite size of active metal particles, the formation of metal support complexes such as NiAl₂O₄, metal oxide support interaction, nature and surface concentration of active metal species present on the catalyst surface, e.g., Ni-Ni, Ni-Rh and Rh-Rh [40, 46, 48, 49]. The higher stability of

Cat600600 and RhNicoimp catalyst was attributed to the higher abundance of Ni-Rh sites on the catalyst surface, which also gave rise to a higher activity of these catalysts. Among the catalysts that experienced high calcination temperatures, Cat 600850 and Cat850850 showed higher stability relative to Cat850600. Higher stability of these two catalysts was attributed to the high surface concentration of Rh, which is known to improve the stability [50, 51].

Fig.8 shows the CO selectivity of Series 2 catalysts at 1 and 10 bar pressure. Similar to the observation for Series 1 catalysts, a decrease in CO selectivity was observed when the pressure was increased to 10 bar pressure. Similar to the trend observed for catalytic activity, Cat600600 had the highest CO selectivity while Cat850600 had the lowest. It would appear that the increase in conversion is directly related to the increase in CO selectivity. To further confirm the observation of an increase in CO selectivity due to the presence of Rh metal, CO selectivity of Cat600600 and 0Rh15Ni were compared at iso-conversions, which can be achieved by changing the contact time. It was found that the CO selectivity of Cat600600 was 0.12 and of 0Rh15Ni was 0.10 at ~49% methane conversion, which confirms that Rh gives rise to these changes. Similar observations have also been by reported by Kusakabe and co-workers [52]. As discussed earlier for the CO selectivity of Series 1 catalysts, the availability of Rh metal on the catalyst surface, as well as the particle size of active metals, can significantly affect the CO selectivity of the catalyst. Due to its highest degree of reduction, Cat600600 showed the highest selectivity. Similar CO selectivities were observed for RhNicoimp, Cat600850, and Cat850850, while the CO selectivity was lower for Cat850600. As discussed earlier, lower CO selectivity of Cat850600 can be attributed to lower active metal dispersion on the catalyst surface.

3.2.2 Application of washcoated metal monolith

To further improve the performance of Rh-Ni/MgAl₂O₄ catalyst for the steam reforming reaction, the most active catalyst and base catalyst, Cat600600 and 0Rh15Ni, were washcoated on separate metal monoliths and compared with the corresponding catalysts in packed bed reactors. Fig. 9 shows the comparison of metal monoliths and packed bed reactor for both Ni/MgAl₂O₄ and Rh-Ni/MgAl₂O₄ catalysts at 600 °C reactor wall temperature and atmospheric pressure. Negligible pressure drop was detected across both metal monolith reactor and packed bed reactor. Figure 9 reveals that Rh-Ni/MgAl₂O₄ catalyst was more active than Ni/MgAl₂O₄ catalyst in both packed bed and metal monolith reactors. Moreover, for both catalysts, the performance of the metal monolith was significantly better than that of the packed bed reactor. Lower methane conversion in the packed bed reactor was attributed to the presence of heat and mass transfer limitations. Our previous studies have shown that catalyst with an average particle size above 0.275 mm show internal mass transfer limitations [23]. Since in this study the average size of catalyst particle was kept as 1.5 mm, the presence of strong internal mass transfer limitations was expected. In contrast, the washcoat thickness in the metal monolith reactor was about 17 µm and the internal mass transfer limitation was eliminated. Furthermore, the T_{center} in the monolith reactor was 570 °C due to higher thermal conductivity, in comparison to 530 °C observed in the packed bed reactors, which suggest the presence of heat transfer limitations.

Apart from heat and mass transfer limitations, our previous study revealed that the activity of the catalyst also increased after the washcoat preparation step [22]. To deposit a well- adhered and homogeneous washcoat on the monoliths, the washcoating preparation step required the particle size of the catalyst slurry to be decreased in a ball mill for 48 h. This milling process not only reduces the catalyst particle size but also redistributes the active metal present on the catalyst surface. This active metal redistribution increased the active metal dispersion which also

contributed to the higher conversion obtained in the monolith reactor. Furthermore, it was also noticed from Fig. 9 that there was an increase of ~9% in methane conversion for the two metal monoliths compared to ~ 4% for the two packed bed reactors. Higher increase in methane conversion in metal monoliths in comparison to packed bed reactor for both catalysts was attributed to higher geometrical surface area in case of metal monolith reactors. Earlier studies have shown that an increase in geometrical surface area significantly increases the availability of active metal over the catalyst surface, which results in a higher catalytic activity of the washcoated metal monolith in comparison to catalyst pellets [41].

The change in product distribution due to change in reactor system for both Ni/MgAl₂O₄ and Rh-Ni/MgAl₂O₄ catalysts is presented in Table 3. CO selectivity of both catalysts was calculated using equation (6). It was found that for both catalysts the H₂/CO ratio was higher in case of packed bed reactors compared to monolith reactor. However, higher H₂/CO₂ ratio and CO selectivity was observed in metal monolith reactors for both the catalysts. Decrease in H₂/CO ratio, and increase in H₂/CO₂ ratio and CO selectivity was attributed to higher methane conversion in metal monolith reactors.

Conclusions

Addition of Rh noble metal has a significant effect on the physicochemical properties of the Ni/MgAl₂O₄ catalyst, and these changes result in an increase in catalytic activity, hydrogen yield and stability. Addition of 0.1wt.% Rh to Ni/MgAl₂O₄ was sufficient to significantly increase the catalytic activity. Further addition of Rh did not have an appreciable effect on the initial catalytic activity. However, the stability of the catalyst increased till the addition of 0.5 wt.% Rh and further Rh addition did not affect catalyst stability. The increase in activity and stability of the

Rh doped catalyst was attributed to an increase in degree of reduction, increase in dispersion of active metals and formation of Ni-Rh alloy. A change in intermediate or final calcination temperature after impregnation of either Ni or Rh also had an effect on the physicochemical properties of the catalyst. The catalysts calcined at 600 °C had a smaller active metal particle size compared to catalysts calcined at 850 °C after either Ni or Rh impregnation. TPR results also revealed that the catalysts calcined at 600 °C have a higher degree of reduction. Activity test also shows that the 0.5wt.%Rh modified Ni/MgAl₂O₄ catalyst calcined at 600 °C both after Ni and Rh impregnation, i.e. Cat600600, had the highest activity, hydrogen yield and stability amongst those studied. Furthermore, the sequentially impregnated catalyst Cat600600 showed better activity than co-impregnated method catalyst calcined at 600 °C. Washcoating of this Cat600600 catalyst on metal monoliths further improves its performance. Furthermore, the higher activity of this Rh-Ni/MgAl₂O₄ washcoated metal monolith was attributed to the absence of heat and mass transfer limitations and increase in active metal dispersion of washcoat catalyst.

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Fig. 1. UV-vis spectroscopic patterns of (i) Series1 catalysts and (ii) Series 2 catalysts (a) RhNicoimp,(b) Cat600600, (c) Cat600850, (d) Cat850600 and (e) Cat850850

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Fig.2. TPR patterns of Rh-Ni/MgAl₂O₄(i) Series 1 and (ii) Series 2 catalysts



Fig.3. XRD patterns of reduced Rh doped Ni/MgAl₂O₄ catalysts (i) Series 1 and (ii) Series 2 catalysts where (\Box) denotes NiO+MgO, (\circ) denotes MgAl₂O₄ and (Δ) Ni metal.



Fig. 4. TEM image and particle size distribution of (a) 0Rh15Ni and (b) Cat600600 catalyst



Fig.5. Effect of Rh concentration on activity of Rh-Ni/MgAl₂O₄ catalyst(Series 1) at pressure (i) 1 bar and (ii) 10 bar(Temperature: 600 °C, Steam/CH₄:5 mol/mol, GHSV: 2.0*10⁶ h⁻¹and W/F_{ao}: 0.34 gcat-h/gmol)



Fig.6. Effect of Rh concentration on CO selectivity of Rh-Ni/MgAl₂O₄ catalyst after 1h of time-onstream(Temperature: 600 °C, Pressure: 1 and 10 bar, Steam/CH₄:5 mol/mol, GHSV: 2.0*10⁶ h⁻¹ and W/F_{a0}: 0.34 gcat-h/gmol)



Fig.7. Effect of calcination temperature on the activity of 0.5%Rh15%Ni/MgAl₂O₄ catalysts (Series 2) at pressure (i) 1 bar and (ii) 10 bar(Temperature: 600 °C, Steam/CH₄:5 mol/mol, GHSV: 2.0*10⁶ h⁻¹ and W/F_{ao}: 0.34 gcat-h/gmol)



Fig. 8. Effect of calcination temperature on CO selectivity of Rh-Ni/MgAl₂O₄ catalyst after 1h of timeon-stream(Temperature: 600 °C, Pressure: 1 and 10 bar, Steam/CH₄:5 mol/mol, GHSV: 2.0*10⁶ h⁻¹ and

W/Fao: 0.34 gcat-h/gmol)



Fig.9. Comparison of Rh-Ni/MgAl₂O₄ (Cat600600) and Rh-Ni/MgAl₂O₄ (Cat850) washcoated metal monolith (T_{wall} : 600 °C, Pressure: 1 bar, Steam/CH₄:5 mol/mol, GHSV= 6000 h⁻¹and W/F_{ao}: 0.34 gcat-

h/gmol)

Catalyst		BET Surface area, m ² /g	Degree of reduction, %	Dispersion ^ψ , %	Effective Dispersion ^ξ , %	d _{Ni} a, nm
MG30 as-received		250.1	-	-	-	-
MG30 calcined		73.6				-
Series 1	0Rh15Ni	43.2	46.3	2.5	5.4	10.9
	0.1Rh15Ni	32.1	50.2	2.8	6.1	10.3
	0.5Rh15Ni	31.9	51.1	2.8	6.1	10.1
	1.0Rh15Ni	34.5	52.6	2.9	6.3	9.9
Series 2	RhNicoimp	60.7	63.4	3.6	6.4	9.1
	Cat600600	42.3	65.5	3.5	6.2	9.4
	Cat850600	31.9	51.1	2.8	-	10.1
	Cat850850	36.5	50.2	3.3	-	9.3
	Cat600850	35.5	52.7	3.2	-	9.8

Table 1 Physico-chemical properties of the different catalysts

 ψ :Dispersion calculated from H₂ chemisorption

 ξ :Effective dispersion was calculated using equation (4)

a : crystallite size of the active metal was calculated using Scherrer equation

	Catalyst	Methane		Stability of the		Hydrogen yield ^γ x 10 ²	
		Conversion ⁷ , %		catalyst [#] , %			
	_	1 bar	10 bar	1 bar	10 bar	1 bar	10 bar
	0Rh15Ni	49.4	40.0	96.6	82.4	188.3	163.9
Series	0.1Rh15Ni	58.1	47.0	97.8	71.1	207.2	180.3
1	0.5Rh15Ni	59.2	47.1	98.4	80.7	213.5	178.4
	1.0Rh15Ni	59.2	47.6	99.0	83.7	224.3	178.7
	RhNicoimp	66.0	52.2	98.6	86.7	238.4	201.9
	Cat600600	68.2	50.2	98.8	88.9	239.6	213.7
Series	Cat600850	62.9	48.6	98.5	85.4	232.2	201.4
2	Cat850600	59.2	47.1	98.4	80.7	213.5	177.4
	Cat850850	60.8	47.0	99.3	85.7	229.5	188.0

Table 2Activity, stability and hydrogen yield of the catalysts at 1 bar and 10 bar reactor pressure

: stability of the catalyst is defined as percentage change in methane conversion between 1h and 8h time-on-stream

 γ :after 1h of the time-on-stream

	Ni/MgA	l ₂ O ₄ catalyst	Rh-Ni/MgAl ₂ O ₄ catalyst		
	Packed bed reactor	Metal monolith reactor	Packed bed reactor	Metal monolith reactor	
H ₂ /CO	68.1	46.6	45.4	37.0	
H_2/CO_2	3.9	4.2	4.2	4.6	
CO selectivity	5.3*10 ⁻²	8.2*10 ⁻²	7.9*10 ⁻²	11.0*10 ⁻²	

Table 3: Comparison of product distribution of packed bed reactor and metal monolith reactor $(S/C=5; P = 1bar; W/F_{ao} of 0.34g_{cat}-h/gmol)$