A Single-Source Precursor Approach to Self-Supported Nickel–Manganese-Based Catalysts with Improved Stability for Effective Low-Temperature Dry Reforming of Methane

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Self-supported nickel-manganese-based catalysts were synthesized from heterobimetallic nickel manganese oxalate precursors via a versatile reverse micelle approach. The precursors were subjected to thermal degradation (400 °C) in the presence of synthetic air to form respective metal oxides, which were treated under hydrogen (500 °C) to form Ni₂MnO₄-O₂-H₂, Ni₆MnO₈-O₂-H₂ and NiO-O₂-H₂. Similarly, the precursors were also treated directly under hydrogen at the same temperature to form Ni₂MnO₄-H₂ and Ni₆MnO₈-H₂. The catalysts were ex-

Introduction

Sustainable use of global resources, especially conversion of unwanted or hazardous materials to industrially important products, is of special interest. In this respect, the conversion of greenhouse gases such as CO₂ into useful chemicals or fuels is an indispensable course of action.^[1-6] Dry reforming of methane (DRM) with carbon dioxide $(CH_4+CO_2\rightarrow 2CO+2H_2)$ mediated by a heterogeneous catalyst is an alternative approach to convert greenhouse gases into synthesis gas mixtures (CO+H₂), which has been used as the raw material in various well-established industrial processes such as the production of methanol and the Fischer-Tropsch synthesis.^[7,8] The DRM reaction is endothermic and therefore relatively high temperature is required.^[9-11] However, whilst most research is conducted at temperatures higher than 700 °C, benefits exist for lower-temperature DRM, for example in coupled reactor concepts.^[3] Precious-metal-based catalysts (Ru, Rh, Pt, Ir) have been used as efficient DRM catalysts for a long time due to high activities and resistance to carbon deposition, but they are considered to be too expensive for DRM.^[12-15] Moreover, cheaper nickel-

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 Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/ cplu.201600064. tensively investigated by PXRD, SEM, TEM, XPS and BET analyses. The resulting catalysts were applied for dry reforming of methane (DRM) and exhibit better stability and resistance to coking than coprecipitated catalysts. Further, we show that addition of manganese, which is not an active catalyst for DRM alone, to nickel has a significant promotion effect on both the activity and stability of DRM catalysts, and a Ni/Mn ratio lower than 6:1 enables optimized activity for this system.

based catalysts have also been studied in the last three decades. However, fast deactivation of the Ni catalyst through coking (carbon deposition) is a major problem for industrial application.^[10, 16–19] This problem is exacerbated at low temperatures, although comparatively little research has been conducted to address this directly. Therefore, the design of a more stable Ni-based catalyst system is of significant importance for utilization in industry.

Several Ni catalysts for DRM have been explored to minimize deactivation by coking. $^{\mbox{\tiny [20-23]}}$ Solid solutions of NiO-MgO were observed as promising catalysts where the alkaline-earth oxide acts as the promoter for DRM.^[24-29] Solid-supported Ni catalysts were studied extensively to find out the role of the support. Introduction of Ni into the perovskite structure $A^{2+}B^{4+}O_3^{2-}$ (where A and B represent the 12-coordinate and six-coordinate metal cations) is one of the alternative approaches to stabilize the system.^[30-33] Control over the reaction temperature to enable maximum activity with stability is also required, as carbon deposition can occur via different routes depending on the temperature. In the literature, the Ni-based catalysts have been reported to be active enough at relatively low temperature. $^{[34-37]}$ At 550 $^{\circ}\text{C},$ close to thermodynamic equilibrium with $38\,\%$ conversion of CH_4 was achieved with Ni supported on MgO along with 0.1% Pt doping.^[36, 37] Further lowering of the reaction temperature to 400 °C has also been reported involving Ni sites supported on mesoporous La₂O₃-ZrO₂.^[35] Stabilization of Ni⁰ in an oxide matrix was found to be operative at low temperature. Recently, a highly dispersed and anticoking Ni-La2O3/SiO2 catalyst as well as surface area yolk-shell Ni@Ni embedded in SiO have been reported with higher activity and enhanced stability.[35b-d] Ternary metal oxides have been used frequently to form the active catalyst in the highly reducing envi-

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ronment of DRM. Silica-supported nickel manganese oxides were used by Thomas et al. to form solid solutions of NiO-MnO.^{38a} It has been shown that addition of MnO to supported Ni DRM catalysts improves stability, at the cost of activity, by partially decorating the active Ni surface and also promoting CO_2 adsorption, both of which suppress deactivation resulting from carbon deposition on the catalyst surface.^[38b]

Because high temperature favours CH_4 and CO_2 conversion and can delay coke formation, the DRM reaction at low temperature (below 600 °C) has been rarely carried out. This is mainly due to the fact that at lower temperature the process thermodynamically favours coke formation and this could result in deactivation of the catalyst or damage to the reactor in a longer run. Therefore, it is essential to design catalysts that can show not only superior activity but also long-term stability at considerably lower temperatures if the DRM reaction is to be opened up to process integration concepts to address issues such as the high energy input required.

Herein, we present the facile formation of a stable self-supported Ni-MnO (or mixed) catalysts for effective low-temperature DRM, starting from well-defined heterobimetallic nickel manganese oxalates as single-source precursors (SSPs). The benefit of using the SSP approach has been demonstrated previously by our group.^[39-44] This route not only includes the low-temperature synthesis of a designed material but also enables definite control over its composition with maximum dispersion of the elements on the atomic level as well as control over the oxidation states of the metals through the molecular architecture of the precursor and the applied reaction conditions. In addition, the mixing at the molecular level assures product homogeneity. Furthermore, the anticipated degradation of such SSPs can lead to unusual and desirable structural features in the final products such as high surface area, low density, and the formation of metastable phases with the possibility of tuning their electronic properties. This method has already been well established for amorphous conducting oxides that have shown long-term stability along with high optoelectronic performance.[39,40]

The mixed nickel-manganese and nickel oxalate SSPs can be synthesized by the microemulsion approach through variation in the amount of nickel relative to the amount of manganese. The resulting NiMn oxalates and Ni oxalates were first subjected to thermal degradation in the presence of oxygen to form mixed nickel-manganese (Ni₂MnO₄ and Ni₆MnO₈) and nickel oxides (NiO) which were subsequently treated in H₂ to form mixed phases of Ni/NiO/MnO and Ni/NiO. These systems were found to be efficient DRM catalysts as well as stable at the reaction temperature for several hours. Increasing the Mn/Ni ratio in turn greatly increases the rate of the reaction providing higher stability to the system. This shows that a higher amount of Mn is required in the NiMn oxide system to carry out the reaction effectively with enhanced stability. On the other hand, thermal treatment of NiMn oxalates in H₂ also leads to the formation of catalysts that are efficient for the DRM reaction but with lower stability. Here we describe a new synthetic approach to produce very stable self-supported NiMn oxide mixed-phase catalysts through a SSP route which enable efficient DRM at considerably low temperatures.

Results and Discussion

First, the nickel manganese and nickel oxalates were synthesized via an inverse-micellar route through microemulsions containing cetyltrimethylammonium bromide (CTAB) as a surfactant, 1-hexanol as co-surfactant and hexane as the lipophilic phase and mixed with an aqueous solution containing Ni²⁺, Mn^{2+} and oxalate ions. $Ni_{0.85}Mn_{0.15}C_2O_4\cdot 2H_2O$ was precipitated when a 1:1 ratio of $Ni^{2+}{:}Mn^{2+}$ was used in solution, whereas Ni_{0.66}Mn_{0.34}C₂O₄·2H₂O was generated by changing the Ni:Mn ratio to 1:2. In the absence of Mn²⁺, NiC₂O₄·2H₂O was produced. The structure of oxalates comprises of one-dimensional chains with each manganese/nickel atom being coordinated to two bidentate oxalate ligands and two water molecules. Thus the formed oxalate SSPs were degraded in oxygen to produce nickel manganese oxide phase (see Experimental Section). Subsequently, the treatment of the nickel manganese oxides in H_2 produced $Ni_2MnO_4-O_2-H_2$ and $Ni_6MnO_8-O_2-H_2$ and the thermal treatment of the same SSPs directly in H₂ furnished Ni₂MnO₄- $\rm H_2$ and $\rm Ni_6MnO_8\text{--}H_2\text{,}$ respectively (Scheme 1). Similarly, NiO-O_2-H₂ was produced from nickel oxalate by heating in air followed



Scheme 1. Synthetic routes to the DRM catalysts from oxalate single-source precursors (SSPs).

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by treatment with hydrogen. All SSPs were characterized by powder X-ray diffraction (PXRD) and infrared spectroscopy (IR). The respective data are in good agreement with those reported for such metal oxalates (Figures S1–S4, Table S1). The rodlike morphology of NiMn oxalates and cubical microparticles of Ni oxalate were detected by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) as shown in Figures S5 and S6, respectively. The presence of corresponding elements and the Ni/Mn ratio were determined by energy-dispersive X-ray analysis (EDX; Figure S7). The Ni/Mn ratio was also confirmed by inductively coupled plasma atomic absorption spectroscopy (ICP-AES, Table S2).

The precursor morphology was changed when the SSPs were heated in air to form the respective mixed oxides (Figures S8 and S9). As shown by EDX and ICP analyses, the Ni/Mn ratio of the resulting oxides was invariable relative to the nature of the oxalate SSP (Figure S10 and Table S3). Also, the formation of monophasic Ni₂MnO₄, Ni₆MnO₈ and NiO from the respective precursors was also confirmed by PXRD analysis (Figures S11–13). Interestingly, the structure of Ni₆MnO₈ is considered to be the rock-salt structure where 6/8 of octahedral sites are occupied by Ni²⁺ atoms and 1/8 by Mn⁴⁺ atoms, and by vacancies (alternative (111) planes). Ni₂MnO₄ belongs to the spinel type (AB₂O₄) structures where the Mn^{4+} ions occupy the tetrahedral (B) sites and the octahedral (A) sites are preferred by $Ni^{2+/3+}$. However, NiO adopts a rock-salt structure. In addition, the PXRD patterns indicated that post-treatment of mixtures of NiMn oxides in H₂ furnished mixed-phase materials (Figure 1). A mixture of elemental Ni, NiO and MnO was detected in $Ni_2MnO_4-O_2-H_2$ and $Ni_6MnO_8-O_2-H_2$ as well as in the respective catalysts, which were only treated in H₂, and which did not have observably different crystallite sizes according to the diffraction patterns, whereas only Ni and NiO were present as components in NiO-O₂-H₂.



Figure 1. PXRD and Miller indices (*hkl*) of a) Ni₂MnO₄–O₂–H₂, b) Ni₂MnO₄–H₂, c) Ni₆MnO₈–O₂–H₂, d) Ni₆MnO₈–H₂ and e) NiO–O₂–H₂. The dotted lines represent the crystal phases of MnO (green, JCPDS 71-1177), Ni (red, JCPDS 4-850) and NiO (blue, JCPDS 47-1049).

Destruction of the morphology of the oxides after heating in H₂ is evident by SEM (Figure S14). TEM images also showed new morphological growth in Ni₂MnO₄–O₂–H₂ (Figure 2) and Ni₆MnO₈–O₂–H₂ (Figure S16). The reflections of the selected area diffraction pattern (SAED) of Ni₂MnO₄–O₂–H₂ (Figure 2)



Figure 2. TEM image (top, scale bar 50 nm) and the electron diffraction patterns (bottom) of $Ni_2MnO_4-O_2-H_2$ showing that the platelet-type particles consisted of pure crystal phases of metallic Ni, MnO and $Ni_xMn_{1-x}O$.

clearly displayed the presence of Ni, MnO and $\mathrm{Ni}_{0.75}$ Mn_{0.25}O.^[45,46] EDX analysis at different areas also indicated different Ni/Mn ratios (Figure S15). Interestingly, in the case of Ni₆MnO₈-O₂-H₂, spherical particles were observed (Figure S16) and the size of the particles varied to a large extent. The SAED pattern of these spherical particles clearly exhibited the rings corresponding to Ni and NiO.[45] In addition to particles of spherical morphology, plate-like particles were also observed containing only MnO as conferred by Fast Fourier Transform (FFT) of the lattices (Figure S17). A high amount of Ni was detected by EDX in the spherical particles, whereas the plates contain Mn-rich phase (Figure S18). Strikingly, in both cases $(Ni_2MnO_4-O_2-H_2 \text{ and } Ni_6MnO_8-O_2-H_2)$, the nickel particles were always found to be supported on the surface of MnO or NiO or mixed NiMn oxide to generate a self-supported system. Further, it was confirmed that this type of self-supported system provided additional stability to the system during DRM reaction. Temperature-programmed reduction (TPR) studies also showed essentially full reduction (\geq 93%) of precursor materials to both $Ni_2MnO_4-O_2-H_2$ and $Ni_6MnO_8-O_2-H_2$ via a major step related to reduction of the manganese oxide at 355 °C for Ni₆MnO₈ and 345 °C for Ni₂MnO₄; two shoulders also appear at lower temperatures of 180 and 240 °C for Ni₆MnO₈, and 150 and 213 °C for Ni₂MnO₄ which correspond to the reduction to NiMnO₃ and nickel (Figure S38). It is likely that any NiO detect-



ed by surface techniques after reduction is the result of reoxidation of metallic Ni upon contact with air at room temperature during transfer to the analysis chamber.

For Ni₂MnO₄–H₂ and Ni₆MnO₈–H₂, when NiMn oxalates were directly heated in an atmosphere of H₂, dropletlike morphology with wide range of sizes was observed by TEM (Figures S19–S22). The SAED pattern indicated the presence of Ni, NiO, MnO along with a Ni_xMn_{1-x}O phase.^[45,46] It was certain by comparing Ni₂MnO₄–O₂–H₂, Ni₂MnO₄–H₂, Ni₆MnO₈–O₂–H₂ and Ni₆MnO₈–H₂ that only Ni₆MnO₈–O₂–H₂ did not contain any Ni_xMn_{1-x}O oxide phase. In contrast to other catalysts, NiO–O₂–H₂ showed thick blocks and comprises Ni and NiO as detected by SAED (Figures S23 and S24). The reflections observed in the SAED pattern for all phases from catalysts are presented in Table S4.

X-ray photoelectron spectroscopic (XPS) studies of all catalysts have been performed. For Ni₂MnO₄–O₂–H₂, as shown in Figure 3, the two spin-orbit split $2p_{3/2}$ and $2p_{1/2}$ peaks of Mn 2p were very close to those of the $2p_{3/2}$ and $2p_{1/2}$ states of MnO ($2p_{3/2} \approx 642.2$ eV and $2p_{1/2} \approx 653.8$ eV).^[47–49] The XPS core level



Figure 3. High-resolution XPS spectra of $Ni_2MnO_4-O_2-H_2$ (see text for description).

spectrum of Ni 2p_{3/2} (middle) exhibited a peak at 854.5 eV that could be attributed to that of NiO.^[50-52] PXRD and TEM analysis revealed the presence of elemental nickel (Ni⁰) in the phases; however, no peak at 852.9 eV for metallic Ni could be detected in the XPS spectrum due to the existence of close binding energies of Ni²⁺/Ni⁰ and also because of the possible oxidation of the surface layer of the catalysts. The O 1s spectrum was deconvoluted into two peaks (O1 and O2). The first peak (O1) at 529.9 eV can be attributed to the oxygen atoms of the metal oxide. The peak (O2) at 531.5 eV corresponds to either oxygen in OH groups, indicating that the surface of the material is hydroxylated due to surface hydroxides or the substitution of oxygen atoms at the surface by hydroxyl groups, and the number of defect sites with low oxygen coordination in the

material with a small particle size.^[53–55] Similarly, the corresponding descriptions of XPS analysis for the catalysts $Ni_2MnO_4-H_2$, $Ni_6MnO_8-O_2-H_2$, $Ni_6MnO_8-H_2$ and $NiO-O_2-H_2$ are given in Figures S25–S28 (see the Supporting Information).

BET surface area measurements were performed for Ni₂MnO₄-O₂-H₂, Ni₂MnO₄-H₂, Ni₆MnO₈-O₂-H₂, Ni₆MnO₈-H₂ and nickel manganese oxalates and of the respective oxides which are shown in Figure S29. As expected, high-temperature treatment reduces the surface area of all catalysts. Oxidation of catalyst precursors to obtain Ni₆MnO₈ and Ni₂MnO₄ yielded materials with the highest surface areas, but subsequent reduction at 500 °C to form Ni₂MnO₄-O₂-H₂ and Ni₆MnO₈-O₂-H₂ caused a severe decrease in surface area, through destruction of the particle morphology as seen from SEM results. Ni₂MnO₄-H₂ and Ni₆MnO₈-H₂ which did not undergo oxidation showed significantly higher surface areas than Ni₂MnO₄-O₂-H₂ and Ni₆MnO₈-O₂-H₂.

To understand the possible advantages of the reverse-micelle synthesis route, synthesis of a standard Ni₂MnO₄ catalyst derived by the coprecipitation method was considered. However, it was not possible to control the ratio for Ni₂MnO_x (forming a catalyst with a Ni/Mn ratio of ca. 6:1) for comparison with Ni₂MnO₄–O₂–H₂. Therefore instead of Ni₂MnO₄, Ni₆MnO₈ catalyst was synthesized by coprecipitation (similar to Ni₆MnO₈–O₂–H₂) and was then reduced under similar conditions. PXRD analysis of this coprecipitated reduced standard catalyst confirmed the presence of Ni and MnO phases (Figure S31). Furthermore, a closer look at TEM analysis revealed platelike and irregular-type particles (Figures S32–S34) consisting of Ni, NiO, MnO with Ni_xMn_{1-x}O phase, and the material has a similar BET surface area to Ni₆MnO₈–O₂–H₂ of 3.69 m²g⁻¹.

The Ni₂MnO₄-O₂-H₂, Ni₂MnO₄-H₂, Ni₆MnO₈-O₂-H₂, Ni₆MnO₈-H₂ and NiO-O₂-H₂ catalysts have been tested for DRM and their activities (shown as conversion with time on stream at several temperatures) are presented in Figure 4. Conversions were by necessity (due to thermodynamic limits) lower than those of catalysts in the literature which had been tested at higher temperatures, but our values were comparable to those of catalysts tested at similar temperatures.[35-36,56] It should be mentioned here that the gas hourly space velocity (GHSV) for NiO-O₂-H₂ used as a standard in our experiments was 2.5 times lower than that of all other catalysts. NiO-O₂-H₂, nickel from nickel oxide nanoparticles, thus did not show high activity or stability. It deactivated faster than all manganesecontaining Ni₂MnO₄-O₂-H₂, Ni₂MnO₄-H₂, Ni₆MnO₈-O₂-H₂ and Ni₆MnO₈-H₂ and exhibited at best around half of the rate of reaction. The behavior as shown in the plot for all other catalysts was also similar to that of NiO-O2-H2, with a small gradual increase in activity up to roughly 10 h on stream. Catalytic activity was not improved with the presence of a greater amount of Ni. In fact, $Ni_2MnO_4-O_2-H_2$ produced from Ni_2MnO_4 showed the highest methane conversion followed by Ni₂MnO₄-H₂. This is striking, since addition of MnO (which is itself inactive for DRM) to Ni catalysts has previously been shown to improve only the catalytic stability whilst lowering activity, whereas this result clearly indicates that an optimum Ni/Mn ratio lower than 6:1 exists in terms of activity. To highlight this, Figure 5 shows



Figure 4. Activity and stability tests of Ni₂MnO₄-O₂-H₂, Ni₂MnO₄-H₂, Ni₆MnO₈-O₂-H₂, Ni₆MnO₈-H₂ and NiO-O₂-H₂ for the DRM reaction. CH₄/CO₂/He = 1:1:8, GHSV = 90 000 Lh⁻¹kg_{cat}⁻¹ (36 000 Lh⁻¹kg_{cat}⁻¹ for NiO-O₂-H₂, 18 000 Lh⁻¹kg_{cat}⁻¹ for MnO), atmospheric pressure. Equilibrium conversions for 500, 525 and 550 °C: 0.28, 0.36 and 0.45, respectively. Carbon dioxide conversions are presented in Figure S37.



Figure 5. Activity tests with Ni₂MnO₄–O₂–H₂ and Ni₆MnO₈–O₂–H₂ for the DRM reaction at 525 °C. 10 mg catalyst used, CH₄/CO₂/He = 1:1:8, GHSV = 180 000 Lh⁻¹kg_{cat}⁻¹, atmospheric pressure.

the activity test results for 10 mg of $Ni_2MnO_4-O_2-H_2$ and $\rm Ni_6MnO_8\text{-}O_2\text{-}H_2$ at 525 $^\circ\rm C.$ The catalyst with a higher Mn/Ni ratio was not only more active, but also exhibited a higher H₂/ CO ratio. It was also clear that direct degradation of the oxalate SSP Ni_{0.66}Mn_{0.34}C₂O₄·2H₂O in H₂ (Ni₂MnO₄-H₂) leads to samples that show lower activity than Ni₂MnO₄-O₂-H₂ that had been prepared by NiMn oxide formation and subsequent H₂ treatment. This difference is more prominent in the cases of Ni₆MnO₈-O₂-H₂ and Ni₆MnO₈-H₂, respectively. The results may also be explained by results from TEM studies due to the variable size and morphology in Ni₂MnO₄-H₂ and Ni₆MnO₈-H₂. The fact that the catalytic activity of $Ni_2MnO_4-O_2-H_2$ is better than that of Ni₆MnO₈-O₂-H₂ can be explained by the presence of a lower amount of Ni to generate a more diluted system, a higher BET surface area and a direct effect of Mn on the kinetics of the DRM reaction through promoting CO₂ adsorptivity.^[20] However, it should be noted that the number of different catalyst compositions studied means that these results are qualitative and activity is likely to also be strongly affected by other factors, such as total nickel surface area and particle morphology; this must be studied further to generalise these conclusions to other synthetic approaches.

The catalytic stability (for Ni₂MnO₄-O₂-H₂, Ni₂MnO₄-H₂, Ni₆MnO₈-O₂-H₂, Ni₆MnO₈-H₂) was significantly improved by the incorporation of Mn. The Ni particles generated in the H₂ stream were dispersed in the MnO support, which helps inhibit Ni particle sintering at the relatively high temperature of DRM. This is also reflected in the rate of the reaction. This is an interesting result, since the catalytically active species are nickelbased, and manganese and its oxides were currently not considered to be involved as catalysts for the DRM reaction. It is possible that a large amount of the active sites on the surface of the catalysts are rendered inactive within the first hour on stream and that the activity of higher-manganese-containing catalysts is apparently better stabilized. This would be attributable to a smaller nickel to manganese ratio on the catalyst surface, either preventing nanoparticle sintering or deactivating carbon formation through maintaining a smaller ensemble size.^[57] Post-reaction TPO experiments (Figure S35) showed a much higher rate of coking for the more active Ni₂MnO₄-O₂- H_2 (0.25 mg_cmg_{cat}⁻¹h⁻¹) than for the catalyst with a higher amount of nickel (0.028 mg_cmg_{cat}⁻¹ h⁻¹, Ni₆MnO₈–O₂–H₂), indicating that carbon deposition is not the primary cause of longterm deactivation but occurs to a greater extent on the moreactive surface. The effect of available surface area on the rate of carbon formation for the catalysts investigated was not clear due to the intimate situation of Ni and MnO in the selfsupported system, and the variance in overall particle size, and there was no correlation between carbon formation and overall particle size from TEM results (Figure S36).

The stability of the Ni₂MnO₄-O₂-H₂ and Ni₆MnO₈-O₂-H₂ was also compared with those of catalysts in which the precursors were directly reduced under H₂ atmosphere (Ni₂MnO₄-H₂, $Ni_6MnO_8-H_2$). As expected, the initial activities of $Ni_2MnO_4-H_2$ and Ni₆MnO₈-H₂ were equal to or higher than those of Ni₂MnO₄-O₂-H₂ and Ni₆MnO₈-O₂-H₂, because the calcination step inevitably causes some particle sintering. This is reflected in the higher BET surface areas of Ni₂MnO₄-H₂ and Ni₆MnO₈-H2. However, the long-term stability of such catalysts was poorer at higher temperature, presumably due to the lack of prior stabilization via calcination. The process of oxidation-reduction forms a self-supported system of nickel and manganese oxide particles which have already developed temperature-stable surface areas. In comparison, those only treated in hydrogen have higher initial surface areas but are highly susceptible to rapid deactivation by this loss of surface area, and as such undergo higher rates of deactivation at the start of the reaction; this can be seen more clearly by comparing the relative rates of similar catalysts at the beginning and end of the reaction. The chemical potentials for various sintering processes are affected by the reaction conditions; for example, significant coke deposits are likely to affect the resulting nickel particle size and nickel-support interactions. However, all catalysts



were deactivated gradually with time on stream. TEM images of post-reaction catalysts showed large carbon deposits (Figure S36) in both nanotubes and encapsulated graphite form, although no strong correlation could be found between the amount of carbon and the rate of deactivation across all catalysts. Therefore the main cause of deactivation was not attributed to the carbonization around the active metal centers.

 $Ni_6MnO_8-O_2-H_2$ was also compared to a co-precipitated standard catalyst of the same composition and showed superior stability under all conditions tested as shown in Figure 6. $Ni_6MnO_8-O_2-H_2$ formed solid carbon at a significantly lower



Figure 6. Activity tests with Ni₆MnO₈–O₂–H₂ and a co-precipitated standard catalyst with the same composition. CH₄/CO₂/He = 1:1:8, GHSV = 90 000 L h⁻¹kg_{cat}⁻¹, atmospheric pressure. Equilibrium conversions for 500, 525 and 550 °C:0.28, 0.36 and 0.45, respectively.

rate than the standard catalyst, which also rapidly deactivated under less aggressive conditions for carbon formation. This again indicates that coking may not be the primary cause of deactivation, although catalysts with higher initial activities appear to form carbon at a higher rate. The residual activity of $Ni_6MnO_8-O_2-H_2$ was consistently higher than that of the standard catalyst shown in Figure 7.

The higher activity and increased stability of Ni₂MnO₄–O₂–H₂ can be attributed to the platelets, which consist of Ni, MnO and Ni_xMn_yO, followed by Ni₂MnO₄–H₂, which has droplet-type particles of similar composition. It appears that the presence of a mixed nickel–manganese (Ni_xMn_yO) phase as well as the optimum Ni/Mn ratio is essential for effective low-temperature DRM. On the other hand, Ni₆MnO₈–O₂–H₂, prepared by the SSP approach, shows significantly superior activity and stability relative to the co-precipitated catalyst. This finding can be ascribed to the presence of spherical particles in Ni₆MnO₈–O₂–H₂ which exclusively contain a Ni-rich (Ni and NiO) phase supported by Mn-rich phases.

In comparison to known catalysts, the stabilities of the NiMnO catalysts tested herein are not high, as can be seen from Figures 4 and 7.^[58-61] Thermophysical stability appears to be the critical factor although the rate of carbon deposition is too high to solve the problems facing low-temperature DRM. This is potentially due to the high nickel contents of the mate-



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Figure 7. Results of stability testing (under aggressive conditions for carbon formation) for Ni₆MnO₈–O₂–H₂ and a co-precipitated standard catalyst, with the overall rate of carbon formation for both tests (inset). T=525 °C, CH₄/ CO₂/He = 1:1:3, GHSV=90000 L h⁻¹kg_{cat}⁻, atmospheric pressure.

Time on stream (h)

rials.^[31,38a] In order to develop materials intended for application, the approach of lowering the Ni/Mn ratio and using new synthesis techniques has clear benefits, but application of a thermally stable support or other means of preventing deactivation through thermal degradation is required to maintain the higher initial activity gained through particle morphology or lack of calcination.^[10,62]

Conclusion

In conclusion, self-supported active catalysts for low-temperature DRM reaction have been synthesized from heterobimetallic NiMn oxalates as SSPs. The new catalysts showed increased stability and high resistance to coke formation in comparison to coprecipitated catalyst. All catalysts exhibited slight deactivation behavior above 525 °C, although this was not attributable to surface carbon formation. However, it is clear from the screening results that the addition of manganese has a significant promotion effect on the DRM catalysts, in terms of stability, activity, and H₂/CO ratio. Considering that manganese alone is not an active DRM catalyst, we could now demonstrate that a Ni/Mn ratio lower than 6:1 leads to optimized activity for self-supported NiMn catalysts prepared by these methods.

Experimental Section

Synthesis of heterobimetallic nickel manganese and nickel oxalate precursors

For Ni_{0.85}Mn_{0.15}C₂O₄·2H₂O, three micro-emulsions containing cetyltrimethylammonium bromide (CTAB, 2.0 g) as a surfactant, 1-hexanol (20 mL) as a co-surfactant, and hexane (35 mL) as the lipophilic phase were prepared separately with an aqueous solution of 0.1 m nickel acetate, 0.1 m manganese acetate and 0.1 m ammonium oxalate. All three micro-emulsions were mixed slowly and stirred overnight at room temperature. The green precipitate then obtained was centrifuged, washed with a 1:1 mixture of chloroform and



methanol (200 mL) and subsequently dried at 60 $^{\circ}C$ for 12 h. Similarly, a mixture of 0.1 ${\rm M}$ nickel acetate, 0.05 ${\rm M}$ manganese acetate and 0.1 ${\rm M}$ ammonium oxalate produced Ni_{0.66}Mn_{0.34}C_2O_4·2\,H_2O. For NiC_2O_4·2\,H_2O, only 0.1 ${\rm M}$ nickel acetate and 0.1 ${\rm M}$ ammonium oxalate were used.

Synthesis of nickel manganese and nickel oxides

All oxalate precursors were heated to 400 °C at a rate of 2 °C min⁻¹ in dry synthetic air (20% O₂, 80% N₂), kept at 400 °C for 8 h in a tubular furnace and then cooled down to ambient temperature to form Ni₂MnO₄, Ni₆MnO₈ and NiO oxide phases from the Ni_{0.66}Mn_{0.34}C₂O₄·2 H₂O, Ni_{0.85}Mn_{0.15}C₂O₄·2 H₂O and NiC₂O₄·2 H₂O, respectively.

Synthesis of catalysts

As-obtained Ni₂MnO₄, Ni₆MnO₈, and NiO were heated in a pure hydrogen flow (100% H₂) of 15 mLmin⁻¹ for 15 °C min⁻¹ to 500 °C and held for 1 hour to form Ni₂MnO₄–O₂–H₂, Ni₆MnO₈–O₂–H₂ and NiO–O₂–H₂, The oxalate precursors Ni_{0.66}Mn_{0.34}C₂O₄·2H₂O and Ni_{0.85}Mn_{0.15}C₂O₄·2H₂O form Ni₂MnO₄–H₂ and Ni₆MnO₈–H₂, respectively.

Synthesis of the standard coprecipitated catalyst

0.1 \mbox{M} manganese acetate and 0.1 \mbox{M} nickel acetate was fist dissolved in water and an aqueous solution of 0.1 \mbox{M} ammonium oxalate was then added to form Ni_{0.85}Mn_{0.15}C_2O_4 2 H_2O. This co-precipitated oxalate precursor was heated at 400 °C for 8 h in a tubular furnace and cooled down to room temperature to form Ni_6MnO_8 which was subsequently reduced in a pure hydrogen flow (100 % H_2) of 15 mL min^{-1} by heating at 15 °C min^{-1} to 500 °C and holding for 1 hour.

Catalyst Characterization

Phase identification of the samples was conducted using PXRD on a Bruker AXS D8 advanced automatic diffractometer equipped with a position-sensitive detector (PSD) and a curved germanium(111) primary monochromator. The radiation used was Cu-K α ($\lambda =$ 1.5418 Å). The XRD profiles recorded were in the range of 5° < $2\theta < 80^{\circ}$ and the diffraction pattern fitting was carried out using the program WinxPow. The chemical composition of the precursors and oxides was confirmed by ICP-AES on a Thermo Jarrell Ash Trace Scan analyzer. The samples were dissolved in acid solutions (aqua regia) and the results of three independent measurements were averaged which showed good agreement with the chemical formulae. The quantification was also estimated by elemental analyses that were performed on a Flash EA 112 Thermo Finnigan elemental analyzer. The different vibrational modes of the precursor were studied using a BIORAD FTS 6000 FTIR spectrometer under attenuated total reflection (ATR) conditions. The data were recorded in the range of 400-4000 cm⁻¹ with an average of 32 scans and at 4 cm⁻¹ resolution. SEM was used to evaluate the size and morphology of the particles and EDX analyses were used to semiquantitatively determine the nickel and manganese present on the sample surfaces. The samples were placed on a silicon wafer and the measurements were carried on a LEO DSM 982 microscope integrated with EDX (EDAX, Appollo XPP). Data handling and analysis were carried out with the software package EDAX. The microstructure of the samples was investigated by TEM analysis. A small amount of the sample powder was placed on a TEM grid (carbon film on 300 mesh Cu grid, Plano GmbH, Wetzlar, Germany). The microstructure (morphology, particle size, phase composition, crystallinity) of the samples was studied with a FEI Tecnai G² 20 S-TWIN transmission electron microscope (FEI Company, Eindhoven, Netherlands) equipped with a LaB₆ source at 200 kV acceleration voltage. EDX analysis was carried out with an EDAX r-TEM SUTW Detector (Si (Li) detector). Images were recorded with a GATAN MS794 P CCD camera. Both SEM and TEM experiments were carried out at the Zentrum für Elektronenmikroskopie (ZELMI) of the TU Berlin. The XPS measurements were performed using a Kratos Axis Ultra X-ray photoelectron spectrometer (Karatos Analytical Ltd., Manchester, UK) using an Al-K α monochromatic radiation source (1486.7 eV) with 90° takeoff angle (normal to analyzer). The vacuum pressure in the analyzing chamber was maintained at $2 \times$ 10⁻⁹ Torr. The XPS spectra were collected for O 1s, Mn 2p and Ni 2p levels with pass energy 20 eV and step 0.1 eV. The binding energies were calibrated relative to C1s peak energy position as 285.0 eV. Data analyses were performed using Casa XPS (Casa Software Ltd.) and Vision data processing program (Kratos Analytical Ltd.). BET surface area measurements were carried out using a five-point N₂ adsorption analysis on a Micromeritics Gemini with VacPrep 061. It was not possible to avoid contact of samples with air at room temperature during transfer to analysis. Temperature -programmed reduction (TPR) conditions were chosen according to Monti-Baiker criteria, with approximately 20 mg of catalyst and 30 mLmin⁻¹ flow of roughly 15% hydrogen in nitrogen, with a heating rate of 10°C min⁻¹.

Catalytic Testing for DRM

All catalytic tests were carried out in a guartz fixed-bed tubular reactor, heated by an external electric furnace with a temperature probe in the catalyst bed. The catalyst was diluted with quartz sand or silica balls for post-reaction samples, with a total bed volume of 1.25 mL. Before each experiment, the catalyst was reduced in situ with a pure hydrogen flow of 15 NmLmin⁻¹ by heating at 15°Cmin⁻¹ to 500 C and holding for 1 hour. The reactor feed consisted of methane, carbon dioxide and helium (as diluent) in a ratio of 1:1:8 with a total flow of 30 mLmin⁻¹. All experiments were carried out at atmospheric pressure. The product gas was analyzed using a gas chromatograph (Agilent 7890A) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID). After reaction, temperature-programmed oxidation (TPO) was performed on the catalysts to quantify coke deposits. The reactor was heated at a rate of 5°C min⁻¹ to 800°C under a 60 mLmin⁻¹ flow of synthetic air, and the outlet gas was analyzed using a quadruple mass spectrometer (InProcess Instruments GAM 200).

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