High-temperature stable and highly active/selective supported NiCoMgCeO\textsubscript{x} catalyst suitable for autothermal reforming of methane to syngas

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Abstract

Low-surface-area, macroporous, zirconia–hafnia-supported NiCoMgO\textsubscript{x} and NiCoMgCeO\textsubscript{x} (Ni/Co/Mg/Ce = 1/0.2/1.2/0.0 or 1.2) catalysts, precalcined at high temperature (1400 °C for 4 h), showed both high activity (> 98% conversion) and selectivity (> 95%) in the catalytic partial oxidation of methane (CPOM) to syngas. Their performance remained unchanged even after they were subjected to higher temperature (> 2000 °C for 30 min) or a number of high-temperature (> 2000 °C) shocks, due to their direct exposure to an oxyacetylene flame. The supported NiCoMgCeO\textsubscript{x}, however, showed superior performance in the steam and CO\textsubscript{2} reforming reactions because of its much higher lattice oxygen mobility. Hence it is more suitable for the autothermal reforming of methane.

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1. Introduction

Methane autothermal reforming (MATR) is carried out in two separate reaction zones—in the first zone, a part of the methane from feed is combusted in a flame or catalytic burner, producing a hot (about 1400 °C) product stream, and, in the second zone, the unconverted methane from the product stream is reformed to syngas by the methane combustion products (steam and CO\textsubscript{2}) over a steam-reforming catalyst [1]. The MATR process requires no external energy, and yet its use is limited, mainly because of the catalyst fouling (deactivation by sintering and formation of inactive mixed-metal oxides and degradation/disintegration) resulting from the high-temperature (about 1400 °C) treatment and thermal shocks received by the catalyst, particularly during the process start-up and closedown periods.

In the last decade or two, extensive efforts have been made on the catalytic partial oxidation of methane (CPOM) to syngas, which is covered in a number of recent reviews [2–5]. The CPOM process, operating at a very low contact time (about a millisecond) [6–10], is of great practical importance. However, in this process a high methane conversion (> 90%) coupled with very high space velocity (≥ 500,000 cm\textsuperscript{3} g\textsuperscript{-1} h\textsuperscript{-1}) leads to production of a large amount of heat in a small catalyst zone, even at very high selectivity (> 95%) for CO and H\textsubscript{2}, causing a large adiabatic temperature rise (which is difficult to control) and ultimately resulting in the deactivation of a thermally unstable catalyst. Our earlier studies showed that a highly active/selective supported Ni-containing catalyst (prepared by deposition of NiO on a MgO-precoated low-surface-area macroporous silica-alumina) is thermally stable when calcined only up to about 1000 °C; at the higher calcination temperature (1200 °C), it is completely deactivated, mostly because of the formation of catalytically inactive mixed-metal oxides [11].
Since the methane combustion reactions (\(\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 191.8 \text{ kcal mol}^{-1}\)) and \(\text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O} + 124.1 \text{ kcal mol}^{-1}\) are much more exothermic than the partial oxidation of methane to syngas (\(\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 + 5.4 \text{ kcal mol}^{-1}\)), even a small loss in the selectivity due to catalyst deactivation is expected to make the CPOM process highly hazardous, or even render it out of control. It is therefore of great practical interest to overcome the major limitation of the MATR and CPOM processes by developing a high-temperature-stable catalyst that demonstrates desirable activity and selectivity in the methane-to-syngas conversion reactions and has a high mechanical strength, even when the catalyst is subjected to a very high temperature (\(\geq 1200 ^\circ \text{C}\)) and thermal shocks.

This has been accomplished in this investigation. We report here that a NiCoMgCeO\(_x\) deposited on a low-surface-area macroporous zirconia–haffnia catalyst carrier, even when calcined at 1400 \(^\circ\)C and subjected to oxyacetylene flame (about 2000 \(^\circ\)C) or subjected to a number of high-temperature (about 2000 \(^\circ\)C) thermal shocks, shows high catalytic activity, selectivity, and stability in the CPOM and in the steam reforming and CO\(_2\) reforming reactions, without losing its mechanical strength. These highly desirable qualities are of great practical importance for use of the catalyst in the MATR process and in the high-temperature CPOM process.

2. Experimental

The supported NiCoO\(_x\) (Ni/Co = 1:0.2), NiCoCeO\(_x\) (Ni/Co/Ce = 1:0.2:1.2), NiCoMgO\(_x\) (Ni/Co/Mg = 1:0.2:1.2), and NiCoMgCeO\(_x\) (Ni/Co/Mg/Ce = 1:0.2:1.2:1.2) catalysts were prepared by the impregnation of respective metal nitrates from their mixed aqueous solution on a commercial low-surface-area (\(\equiv 0.1 \text{ m}^2 \text{g}^{-1}\)) macroporous (porosity = 45% and pore volume = 0.15 cm\(^3\) g\(^{-1}\)) sintered zirconia–haffnia (94.1% ZrO\(_2\)–HfO\(_2\)) catalyst carrier (SZ-5564, obtained from M/S Norton Co., USA) by the incipient wetness technique and calcination first at 600 \(^\circ\)C for 4 h and then at 900 or 1400 \(^\circ\)C for 4 h. The loading of Ni and Co with or without CeO\(_2\) and/or MgO on the support was as follows: 8.5% Ni and 1.7% Co for the NiCoO\(_x\)/SZ-5564; 8.5% Ni, 1.7% Co, and 30.1% CeO\(_2\) for the NiCoCeO\(_x\)/SZ-5564; 8.5% Ni, 1.7% Co, and 7.0% MgO for the NiCoMgO\(_x\)/SZ-5564; and 8.5% Ni, 1.7% Co, 7.0% MgO, and 30.1% CeO\(_2\) for the NiCoMgCeO\(_x\)/SZ-5564. To ascertain the presence of different metal oxides and/or mixed-metal oxide phases, we characterized the catalysts by XRD.

The high-temperature (about 2000 \(^\circ\)C) treatment of the catalysts and the temperature shocks were accomplished by the application of an oxyacetylene flame (oxidizing portion of the flame) directly to the catalyst (0.3 g), which was kept in a zirconia boat once for 30 min or repeatedly (six times) for 30 s at intervals of 10 min.

The CPOM and steam and CO\(_2\) reforming reactions over the catalysts were carried out at atmospheric pressure in a continuous-flow quartz reactor (i.d. = 9 mm) packed with 0.2 g catalyst (22–30 mesh size) by the procedure described earlier [11–13]. Before use, in the reaction, the catalyst was reduced by 50% H\(_2\) in N\(_2\) at 900 \(^\circ\)C for 1 h. The gas hourly space velocity (GHSV) was measured at 0 \(^\circ\)C and 1 atm pressure.

The TPR over the catalysts was carried out in a quartz reactor containing 0.15 g catalyst in a flow of 5 mol% H\(_2\) in Ar (30 cm\(^3\) min\(^{-1}\)) from 50 to 1100 \(^\circ\)C at a linear heating rate of 20 \(^\circ\)C min\(^{-1}\) by the procedure described earlier [11]. The H\(_2\) pulse reaction over the catalysts was carried out in a quartz pulse microreactor (containing 0.1 g catalyst) connected to a gas chromatograph [14] (with a porapak-Q column and thermal conductivity detector) by injection of a pulse of pure H\(_2\) (0.2 cm\(^3\)) in the reactor, with Ar as the carrier gas, at different temperatures (200–900 \(^\circ\)C) or the injection at 900 \(^\circ\)C of a number of H\(_2\) pulses, one after another, at an intervals of 10 min or 1 h, after which the conversion of H\(_2\) in each pulse experiment was determined.

3. Results and discussion

Results for the CPOM over the zirconia–haffnia-supported NiCoO\(_x\), NiCoCeO\(_x\), NiCoZrO\(_x\), NiCoMgO\(_x\), NiCoMgCeO\(_x\), and NiCoMgZrO\(_x\) catalysts are listed in Table 1. The crystalline metal oxides and/or mixed-metal oxide phases present on the support for the supported catalysts are also included in Table 1. The results indicate that the catalyst containing MgO with or without cerium oxide showed very high methane conversion activity (\(> 98\%\) methane conversion) and high selectivity for both CO and H\(_2\) (\(> 96\%\)) in the CPOM process at a low contact time (GHSV = 62,000 cm\(^3\) g\(^{-1}\) h\(^{-1}\)), even when the catalysts were precalcined at a very high temperature (1400 \(^\circ\)C). It is interesting to note that when all of these catalysts were supported on alumina, silica, or silica-alumina support and calcined at the high temperature, they showed little or no activity in the CPOM process because of the formation of catalytically inactive mixed-metal oxide phases by the solid–solid reaction between the catalytically active components (viz., Ni and Co) with silica and/or alumina [11, 15]. In the present case, even the supported NiCoO\(_x\) catalyst with or without CeO\(_2\) or ZrO\(_2\), calcined at a temperature as high as 1400 \(^\circ\)C, shows high activity and selectivity in the CPOM process. This is attributed to the fact that the support (zirconia–haffnia) does not react with the catalytically active components during the high-temperature catalyst calcination. Among the supported catalysts (Table 1), the supported NiCoMgO\(_x\) and NiCoMgCeO\(_x\) catalysts are highly promising.

To further confirm their high-temperature stability, the two promising catalysts (NiCoMgO\(_x\)/SZ-5564 and NiCoMgCeO\(_x\)/SZ-5564) were further subjected to very high temperature (\(> 2000 \(^\circ\)C\)) shocks by direct exposure to an oxyacetylene flames for different periods, and their performance in the CPOM process was evaluated; the results
Performance of the supported Ni–Co catalysts (with or without MgO and/or CeO₂) calcined at 1400 °C (for 4 h) in the partial oxidation of methane to syngas (feed = a mixture of 64.3 mol% CH₄ and 35.7 mol% O₂, GHSV = 62,000 cm³ g⁻¹ h⁻¹ and temperature = 900 °C)

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>XRD phases</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
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<tr>
<td>NiCoO₂/SZ-5564</td>
<td>NiO, CoO, Co₂O₃ and Co₃O₄</td>
<td>87.7</td>
<td>100</td>
</tr>
<tr>
<td>NiCoZrO₂/SZ-5564</td>
<td>–</td>
<td>90.6</td>
<td>100</td>
</tr>
<tr>
<td>NiCoCeO₂/SZ-5564</td>
<td>–</td>
<td>92.5</td>
<td>100</td>
</tr>
<tr>
<td>NiCoMgO₂/SZ-5564</td>
<td>NiO–MgO and CoO–MgO solid solutions and MgCo₂O₄</td>
<td>98.2</td>
<td>100</td>
</tr>
<tr>
<td>NiCoMgCeO₂/SZ-5564</td>
<td>NiO–MgO and CoO–MgO solid solutions, MgCo₂O₄, MgCeO₃ and CeO₂</td>
<td>98.5</td>
<td>100</td>
</tr>
<tr>
<td>NiCoMgZrO₂/SZ-5564</td>
<td>–</td>
<td>92.6</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2

Performance of the NiCoMgO₂/SZ-5564 and NiCoMgCeO₂/SZ-5564 catalysts (precalcined at 900 or 1400 °C), subjected to high temperature shocks by directly exposing them to acetylene-oxygen flame, in the partial oxidation of methane to syngas at 850 °C (feed = a mixture of 64.3 mol% CH₄ and 35.7 mol% O₂)

Table 3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Methane conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCoMgO₂/SZ-5564</td>
<td>78.8</td>
<td>100</td>
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<tr>
<td>NiCoMgCeO₂/SZ-5564</td>
<td>94.2</td>
<td>100</td>
</tr>
<tr>
<td>NiCoO₂/SZ-5564</td>
<td>29.4</td>
<td>90.7</td>
</tr>
<tr>
<td>NiCoMgCeO₂/SZ-5564</td>
<td>74.7</td>
<td>97.3</td>
</tr>
</tbody>
</table>

The above results clearly indicate that both the supported NiCoMgO₂ and NiCoMgCeO₂ catalysts have very high-thermal stability against the high-temperature treatments/thermal shocks, and both show high activity and selectivity in the CPOM process. Both catalysts also showed stable activity and selectivity when their performance in the CPOM process was tested for 50 h. Because of their high-thermal stability, the formation of hot spots in the catalyst bed and/or high temperatures prevailing at the catalyst sur-
face during the CPOM process would cause little or no effect on the catalytic activity and selectivity of the two catalysts, making them suitable for the CPOM process, even under adiabatic conditions. These results also indicate that there is little or no formation of catalytically inactive mixed-metal oxide phases during the high-temperature treatments of both catalysts. However, for the MATR process, the supported NiCoMgCeOₓ catalyst is more suitable than the supported NiCoMgOₓ catalyst, because of the much higher performance of the former catalyst in both the steam and CO₂ reforming reactions. However, neither catalyst showed deactivation due to coking for 20 h, even for CO₂ reforming. This is consistent with our earlier studies indicating that the presence of cobalt in the nickel-containing catalysts causes a drastic reduction in the coke formation in the oxidative conversion [12,15,16], oxy-CO₂ reforming [17], and CO₂ reforming [13,17] of methane to syngas.

The much higher activity observed in both the steam and CO₂ reforming reactions of the supported NiCoMgCeOₓ catalyst (Table 3) is attributed mostly to its higher oxygen storage capacity and/or oxygen mobility because of the presence of cerium oxide in the catalyst, as indicated by the temperature-programmed reduction (TPR) by H₂ in Fig. 1 and also by the H₂ pulse reaction (Fig. 2) over the two catalysts.

The TPR curve for the supported NiCoMgOₓ catalyst shows two TPR peaks (with maxima at 456 and 1045 °C), whereas that for the supported NiCoMgCeOₓ catalyst shows three peaks (with peak maxima at 413, 670, and 1027 °C) (Fig. 1). For both catalysts, the first low-temperature peak (between 300 and 500 °C) is due to the reduction of free nickel and/or cobalt oxides and that at the high temperatures (above 800 °C) corresponds to the reduction of nickel–cobalt oxides dissolved in the MgO and doped in the ZrO₂ (from the support). The peak between 500 and 700 °C for the supported NiCoMgCeOₓ catalyst is expected mostly because of the reduction of cerium oxide (2CeO₂ + H₂ → Ce₂O₃ + H₂O) present at the catalyst surface [18]. The XPS of this catalyst showed that the surface concentration of cerium is much lower than that of the magnesium in the catalyst (at the surface Ce/Mg = 0.02). This is expected because of the formation of CeO₂–ZrO₂ (from the support) solid solution at the high calcination temperature. The degree of reduction of the nickel and cobalt oxides (estimated from the H₂ consumed in the TPR) is found to be 32.8 and < 55.2%, respectively, for the supported NiCoMgOₓ and NiCoMgCeOₓ catalysts.

The very significant shift observed in the TPR curve for the supported NiCoMgCeOₓ catalyst toward the lower temperature side (Fig. 1) and the higher degree of reduction clearly show that the reduction of the nickel and cobalt oxides of the supported catalyst becomes easier because of the presence of cerium oxide in the catalyst. This is expected mostly because of an increase in the mobility of lattice oxygen in the catalyst in the presence of cerium oxide, particularly in the form of MgCeO₃ (observed by XRD) and CeO₂–ZrO₂ solid solution.

**Fig. 1.** Temperature programmed reduction (TPR) by H₂ of NiCoMgCeOₓ/SZ-5564 (a) and NiCoMgOₓ/SZ-5564 (b).

**Fig. 2.** H₂ conversion (X_H₂) in the pulse reaction of pure H₂ over the NiCoMgCeOₓ/SZ-5564 (a₁, a₂) and NiCoMgOₓ/SZ-5564 (b₁, b₂) catalysts (both precalcined at 1400 °C) as a function of reaction temperature (T) or pulse number (N) at 900 °C. For studying the influence of pulse number on the H₂ conversion, each of the H₂ pulses numbered 1, 2, 4, 5, 7, 8, 10, 11, 13 and 14 was injected in the reactor at 900 °C after an interval of 10 min, whereas each of the H₂ pulses numbered 3, 6, 9 and 12 was injected after an interval of 1.0 h.
Results of the H2 pulse reaction over both catalysts at different temperatures and as a function of pulse number (at 900 °C) (Fig. 2) further confirm the above conclusion/prediction. In the case of the supported NiCoMgCeOx catalyst, the H2 conversion (at the same temperature) in the pulse reaction is much higher (Fig. 2a1, b1) and the observed increase in the H2 conversion for the H2 pulse injected after a much longer period (1 h) is also much higher (Fig. 2a2, b2). The increase in the H2 conversion (by about 10 and 20% for the supported NiCoMgOx and NiCoMgCeOx, respectively) due to the increase in the interval for the H2 pulse injection (from 10 min to 1 h) is attributed to the migration of subsurface oxygen to the catalyst surface. These results clearly showed that the lattice oxygen in the catalyst in the presence of cerium oxide is more mobile. Thus the presence of cerium oxide in the catalyst not only provides an oxygen storage capacity, but also greatly enhances the mobility of lattice oxygen in the catalyst. Hence, the supported NiCoMgCeOx catalyst, even when calcined at 1400 °C, shows excellent performance not only in the CPOM but also in the steam and CO2 reforming reactions, with high stability against deactivation due to coking, even in the CO2 reforming. The appreciable oxygen mobility observed in the supported NiCoMgOx catalyst is expected, however, because of the doping of a part of the nickel and cobalt in the ZrO2 [19,20].

4. Conclusions

Low-surface-area, macroporous, zirconia–hafnia-supported NiCoMgCeOx (Ni/Co/Mg/Ce = 1/0.2/1.2/1.2) catalyst shows high catalytic activity, selectivity, and mechanical stability when it is calcined at a very high temperature (at 1400 °C for 4 h or > 2000 °C for 0.5 h) or even when it is subjected to a number of high-temperature (> 2000 °C) shocks. Because of its high catalytic activity and selectivity and excellent thermal stability, this catalyst is particularly suitable for the autothermal reforming of methane to syngas, involving the exposure of catalyst to high temperatures and/or high-temperature thermal shocks. In the absence of CeO2 the catalyst also shows similar high-temperature stability and a comparable activity and selectivity in the CPOM process, but it shows a markedly inferior performance in the steam and CO2 reforming reactions. The better performance of the former catalyst in the steam and CO2 reforming reactions is due to the presence of cerium oxide, which not only provides an oxygen storage capacity, but also greatly enhances the mobility of lattice oxygen in the catalyst.

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