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High-temperature stable and highly active/selective supported $NiCoMgCeO_x$ catalyst suitable for autothermal reforming of methane to syngas

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Abstract

Low-surface-area, macroporous, zirconia–haffnia-supported $NiCoMgO_x$ and $NiCoMgCeO_x$ (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 $NiCoMgCeO_x$, however, showed superior performance in the steam and CO_2 reforming reactions because of its much higher lattice oxygen mobility. Hence it is more suitable for the autothermal reforming of methane.

Keywords: Zirconia–haffnia-supported $NiCoMgO_x$ catalyst; Zirconia–haffnia-supported $NiCoMgCeO_x$ catalysts; Catalytic partial oxidation of methane; Autothermal reforming of methane; Steam reforming of methane; CO_2 reforming of methane; High-temperature stable supported $NiCoMgCeO_x$ catalyst

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_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 ($\geqslant 500,000\ cm^3\,g^{-1}\,h^{-1}$) leads to production of a large amount of heat in a small catalyst zone, even at very high selectivity (> 95%) for CO and H_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].

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Since the methane combustion reactions ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 191.8\ \text{kcal mol}^{-1}$ and $CH_4 + O_2 \rightarrow CO + 2H_2O + 124.1\ \text{kcal mol}^{-1}$) are much more exothermic than the partial oxidation of methane to syngas ($CH_4 + 0.5O_2 \rightarrow CO + 2H_2 + 5.4\ \text{kcal mol}^{-1}$), 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 ($\geqslant 1200\,°C$) 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 °C and subjected to oxyacetylene flame (about 2000 °C) or subjected to a number of high-temperature (about 2000 °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 ($\cong 0.1\ m^2\,g^{-1}$) 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 °C for 4 h and then at 900 or 1400 °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 °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 °C for 1 h. The gas hourly space velocity (GHSV) was measured at 0 °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 °C at a linear heating rate of $20\,°C\,min^{-1}$ 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 °C) or the injection at 900 °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 °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 °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 °C) shocks by direct exposure to an oxyacetylene flames for different periods, and their performance in the CPOM process was evaluated; the results