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Influence of the Ni/Co ratio in bimetallic NiCo catalysts on methane conversion into synthesis gas

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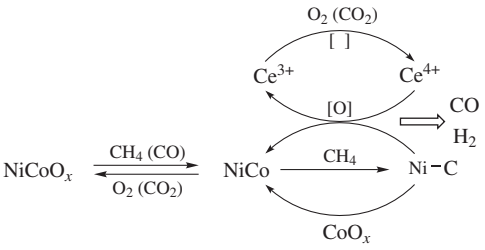
Mesoporous NiCo–$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$ catalysts with a variable Ni/Co ratio were synthesized by co-precipitation with sonication. The catalysts exhibited high activity and selectivity for synthesis gas production by CH_4–O_2 and CH_4–CO_2 reforming at 850–950 °C. The catalyst with 80Ni/20Co demonstrated the best results in the partial oxidation and dry reforming of methane.



The conversion of methane into various products[1,2] including synthesis gas[3] is of considerable importance for industrial applications. The dry reforming of methane (DRM) and the partial oxidation of methane (POM) are the most promising, environmentally favorable, and cost effective processes,[4,5] especially, for the Fischer–Tropsch synthesis, biogas utilization, and the conversion of greenhouse gases. The Ni-based catalysts for these reactions are inexpensive and highly active,[6–9] but the rapid deactivation of the catalysts is a problem[10,11] related to the sintering of active sites (Ni particles) and carbon formation due to CH_4 and CO decomposition on these sites.

To overcome this problem, a support with improved characteristics should be prepared.[12,13] The deactivation occurs very fast without noticeable oxygen mobility and reactivity.[14] Previously,[15,16] stable $Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$ support was developed for this goal. The addition of a second metal is a method for developing the carbon resistance of Ni-containing catalysts. A small amount of precious metals (Pt, Pd, Rh, and Ru) promotes the reducibility of Ni and stabilizes its degree of reduction in a catalytic process;[17–22] however, it is advisable to add non-noble metals to Ni-containing catalysts to enhance catalytic activity and carbon resistance. The Ni–M (M = Co, Mn, Cu, Fe and Mo) catalysts were investigated, and it was found that a Ni–Co bimetallic catalyst was superior to the others.[18,23–25] The Ni–Co catalyst showed both high catalytic activity, comparable to the systems with noble metals, and resistance to coke formation in the reaction.[16,26]

Catalyst deactivation remains a serious problem for methane reforming; however, the high surface area and mesoporous structure of a support, the high metal dispersion of an active component and strong metal–support interaction are assumed to solve this problem. Therefore, this work was focused on developing stable noble metal-free catalysts for POM and DRM based on a mesoporous support of ceria solid solution containing a low-cost Ni–Co bimetallic active component with different Ni/Co ratios to find an optimal composition.

Table 1 gives the main characteristics of the catalysts. All fresh catalysts possess a mesoporous structure. The samples have a IV type isotherm and an H2 hysteresis loop (not shown) indicating that the catalysts are solids consisting of particles crossed by cylindrical channels and/or the aggregates and agglomerates of nearly spherical particles. The range of pore sizes is narrow (2–10 nm, Table 1).

Table 1 Main characteristics of fresh catalysts (composition, 5 wt% NiCo–$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$).

Catalyst	Ni/Co molar ratio	d_{XRD}/nm (support)	S_{BET}/m^2 g^{-1}	D_{pore}/nm
20Ni/80Co	20 : 80	6	101	2–6
30Ni/70Co	30 : 70	8	79	2–20
40Ni/60Co	40 : 60	9	81	2–10
50Ni/50Co	50 : 50	7	54	2–5
60Ni/40Co	60 : 40	8	85	2–10
70Ni/30Co	70 : 30	9	79	2–10
80Ni/20Co	80 : 20	9	72	2–8

The XRD patterns of the catalysts before and after reaction are shown in Figure S1 (see Online Supplementary Materials). In all of the catalysts, the support remained as a solid solution of ceria without changes. In fresh catalysts [Figure 1(*a*)], the formation of cubic Co_3O_4 and cubic NiO was detected. The XRD pattern of used catalysts after POM [Figure 1(*b*)] indicates that Co_3O_4 and NiO were present in smaller amounts, and the formation of cubic CoO occurred (Co_3O_4 was partially reduced by CH_4 and/or CO). The formation of NiCo alloy was detected after DRM [Figure S1(*c*)] because only one peak was identified between monometallic Ni and Co to indicate alloy formation between Ni and Co under the reducing conditions of DRM. The formation of other phases (carbides, Ni–Co–O spinel[27] or solid solution[28]) was not observed.

The TEM images of fresh and used catalysts are shown in Figure S2. The average particle sizes of the fresh system are about 10 nm or 20–30 nm in used catalysts. The formation of cubic solid solution (support) and secondary phases with cubic structure [NiO–Co_3O_4 (POM) or NiCo (DRM)] was confirmed by

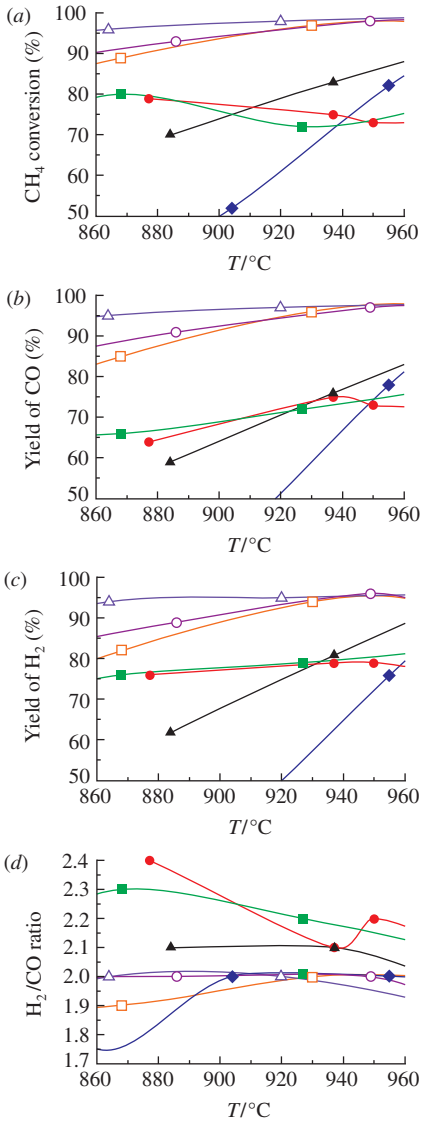


Figure 1 Catalytic activity of samples with the following compositions: (△) 80Ni/20Co, (○) 70Ni/30Co, (□) 60Ni/40Co, (▲) 50Ni/50Co, (■) 40Ni/60Co, (●) 30Ni/70Co (◆) 20Ni/80Co in POM.

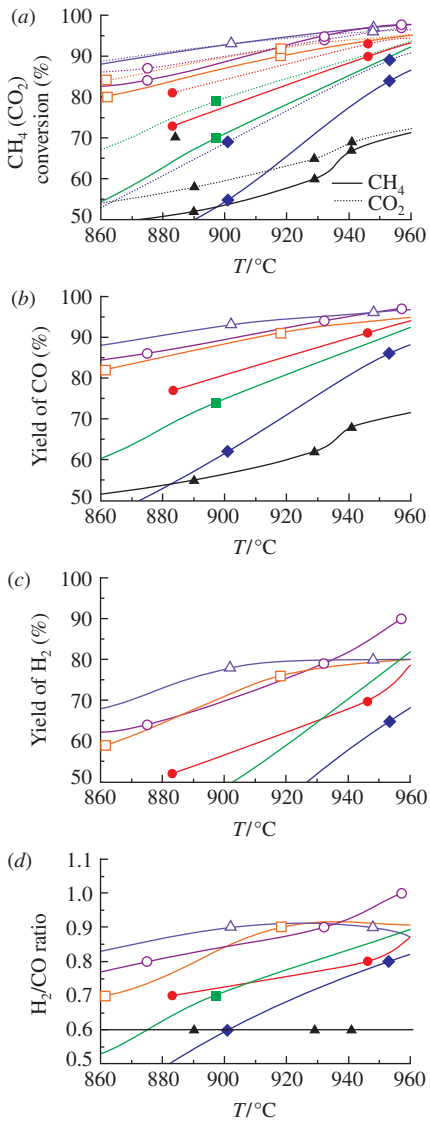


Figure 2 Catalytic activity of samples with the following compositions: (△) 80Ni/20Co, (○) 70Ni/30Co, (□) 60Ni/40Co, (▲) 50Ni/50Co, (■) 40Ni/60Co, (●) 30Ni/70Co (◆) 20Ni/80Co in DRM.

SAED. Carbon deposition (nanotubes, nanofibers, whiskers or amorphous carbon) was observed only after DRM, and no coke formation was found after POM; in the SEM images (Figure S3), the deposition was not observed in both cases. For this reason, the amount of carbon deposited on used catalyst was analyzed by TG-DSC. No traces of carbon deposits were detected in the catalyst used after POM. Two distinctive peaks were revealed in 80Ni/20Co after DRM, indicating two different types of carbon formation. The oxidation temperatures were 200–350 °C (amorphous carbon) and 350–550 °C (single-walled carbon nanotubes).[29] It is known that monometallic catalysts (Ni, Co, Fe, *etc.*) act ineffectively on the resistance of carbon formation The rate of carbon deposition on the catalyst 80Ni/20Co was estimated at 0.15 $mg_{carbon}\ g_{cat}^{-1}\ h^{-1}$. This catalyst was more stable than that developed previously.[23]

The activity of the catalysts increases with the reaction temperature (Figures 1 and 2). The O_2 conversion in POM was 100% for all samples. Ni and Co ions in complex oxide catalysts can be reduced during POM or DRM processes to give metallic nanoparticles,[16,30] as evidenced from the XRD data (Figure S1). Figures 1 and 2 demonstrate that catalysts containing a low amount of cobalt (the samples 60Ni/40Co, 70Ni/30Co and 80Ni/20Co) were more active in POM and DRM than those with high cobalt content. The most active catalyst in both of the reactions was 80Ni/20Co.

In conclusion, the NiCo–$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$ catalysts were synthesized by co-precipitation and investigated in the partial oxidation and dry reforming of methane. The NiCo-containing catalysts demonstrated high activity and selectivity in synthesis gas production by CH_4–O_2 and CH_4–CO_2 reforming at 850–950 °C. According to TEM, SEM, and TG-DSC data, no coke formation occurred after POM, while the formation of amorphous carbon and single-walled carbon nanotubes in small amounts was observed after DRM to indicate high stability in DRM. The XRD data confirmed Ni–Co alloys formed upon DRM, while only Ni and Co oxides were present after POM. The catalyst 80Ni/20Co demonstrated the best results and stability in the partial oxidation and dry reforming of methane since the active component (Ni) is not carbonized so quickly, purified by oxidation of various forms of carbon by cobalt. The balance of two processes, conversion of methane and purification of active sites, is responsible for the high performance properties of this catalyst. The 80Ni/20Co rather than 70Ni/30Co ratio was an optimum for DRM and POM processes.[26] The developed catalyst was more active and stable than industrial catalysts, for example, Katalco 57–4 (16% Ni/Al_2O_3).[31]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.09.027.

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