JOURNAL OF CATALYSIS **177,** 386–388 (1998)
ARTICLE NO. CA982051

RESEARCH NOTE

Design of Stable Ni Catalysts for Partial Oxidation of Methane to Synthesis Gas

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Received May 7, 1997; revised January 15, 1998; accepted February 23, 1998

The supported Ni catalysts with $CaAl_2O_4$ spinel compound layer existed between Ni and Al_2O_3 have been prepared, and the effect of the $CaAl_2O_4$ spinel layer on the stability of the catalysts for the partial oxidation of methane to syngas ($CO + H_2$) has been investigated at high space velocity ($250\ L \cdot g^{-1} \cdot h^{-1}$). Also, the catalysts have been characterized by XRD, TG/DTA. The Ni catalysts with $CaAl_2O_4$ spinel layer existed between Ni and Al_2O_3 show good stability for this process with the CH_4 conversion of ~83%, syngas selectivity of >90% and the coke deposit of <1 wt% during a long-time running at 873 K. The $CaAl_2O_4$ spinel layer can effectively suppress the phase transformation to form $NiAl_2O_4$ spinel phases and stabilize the Ni tiny crystallite, to which the good stability of the catalyst contributes. © 1998 Academic Press

The most effective utilization of the world's abundant resources of natural gas is to convert methane to more useful and easily transported chemicals. The first step in natural gas conversion is often the production of synthesis gas ($CO + H_2$). The synthesis gas can be used subsequently for the production of methanol and for the production of higher hydrocarbons by Fischer–Tropsch synthesis. For these two processes, the desired H_2/CO molar ratio is about 2.0. Steam/CH_4 reforming is the preferred commercial process for production of syngas with H_2/CO molar ratio of 3.0, which is a highly endothermic and costly process. Depending on the end use, the H_2/CO ratio of the reformer product gases is often modified in shift reactor by the water–gas shift reaction. However, interest has recently focused on CH_4/O_2-to-syngas reaction, which would directly give the desired H_2/CO ratio of about 2.0.

This process represents a promising alternative to steam/CH_4 reforming (1–11). In this way, it is possible to reach near equilibrium conversions more selectively while at the same time avoiding the need for external heat input, since the whole process of methane partial oxidation to synthesis gas is mildly exothermic. Several authors (12, 13), have offered economic analyses of these new developments and suggest that this new route to methanol requires 10–15% less energy, and approximately 25–30% less capital investment. The catalysts employed are mainly supported group VIII metals such as Ru, Rh, Pt, Pd, Ni, and Co (1–11). Among them, Rh and Ru are most efficient, but the availability of Rh and Ru (annual production: 4 tonnes Ru/year) (14) is too low to have a major impact on the total reforming catalyst market. Supported Ni catalysts exhibit the potential to replace noble metal catalysts (such as Rh, Ru, Pt) in CH_4/O_2-to-syngas reaction (Exxon process) (11). The major drawbacks with such catalysts are (i) their phase transformation (4, 5, 7), such as the formation of unreduciable $NiAl_2O_4$ spinel in the case of a Ni/Al_2O_3 because of very high local temperature; (ii) their tendency to form coke deposition (7, 15, 16). Al-Ubaid and Wolf (17) found a much greater stability for Ni supported on the aluminate than on other supports. Bhattacharyya and Chang (18) have recently proposed the use of a nickel aluminate spinel catalyst in order to reduce coke formation in CH_4/CO_2 reforming. Rostrup-Nielsen (19) shows that carbon nucleation requires nickel ensembles of a certain size, and its aggregation will be much slower and lower coking rates can be expected if the metal is stabilized.

The aim of this work is focused on developing stable Ni catalysts using $CaAl_2O_4$ spinel compounds layer modified Al_2O_3 as support. The performance of the catalysts in CH_4/O_2-to-syngas reaction and their resistance to phase transformation and to carbon deposition is investigated.

Catalyst supports employed were γ-Al_2O_3 (expressed as A), 8 wt% $CaAl_2O_4$–Al_2O_3 (B), and 8 wt% $CaAl_2O_4/Al_2O_3$ (C). Support B was prepared by co-precipitating the mixed solution of $Ca(NO_3)_2 \cdot 4H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ using ammonia as precipitant. The colloid was not filtered because Ca^{2+} could not be precipitated here and was

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0021-9517/98 $25.00

evaporated water at 343 K. Support C was prepared by impregnating Al_2O_3 using $Ca(NO_3)_2 \cdot 4H_2O$ as precursor. The samples B and C such formed were dried at 373 K and calcined in air at 1173 K for 10 h. The size of supports was 40–60 mesh. The catalysts prepared by impregnating supports with $Ni(NO_3)_2 \cdot 6H_2O$ solution, dried at 373 K and calcined in air at 973 K for 5 h. The structure of catalysts was confirmed by means of XRD (D-MAX-RB, Cu Kα). The patterns were recorded between 15 and 70° (2θ) using scanning velocity of 0.02°/s. The stability test of the catalysts (60 mg) was carried out in a conventional flow system at atmospheric pressure. All catalysts, packed in a reversed h-shaped quartz micro-reactor (ID, 6.0 mm) with a 2 mm (ID) outlet in the center, were reduced by H_2 at 973 K for 30 min before reaction. The feed and product gases were analyzed by a TCD using a Porapak N column. The exposed Ni metal surface area was measured by CO pulse adsorption at room temperature, assuming a stoichiometry of 1/1. The catalysts (0.3 g) were prereduced at 973 K for 1 h in flowing H_2 before CO adsorption measurements. The analysis of gases during the adsorption of CO at room temperature was conducted with an on-line ITD (ion trap detector, Finnigan MAT 700). An assessment of coke deposits and of the extent of coke formation in whiskers was examined by a JEM-1200EX/9100EDAX TEM. The total amount of coke deposit was measured by TG/DTA on Du Pont 1090, using highly pure N_2 (50 ml/min) as carrier gas with heating rate of 10 K/min.

Two Ni/A and Ni/B catalysts with 10 wt% Ni-loadings were employed for examining the differences in their high-temperature phase transformation and Ni-sintering. The data and assignments of the XRD patents of 10 wt% Ni/A and 10 wt% Ni/B catalysts are shown in Table 1. As may be seen, NiO phases are presented with almost equal particle size in both freshly calcined 10 wt% Ni/A and 10 wt% Ni/B catalysts, and there is also no significant amount of $NiAl_2O_4$ spinel phases. After high-temperature oxidation treatments in O_2 flow at 1123 K for 5 h, NiO phases have almost completely disappeared on 10 wt% Ni/A while $NiAl_2O_4$ spinel phases are clearly present. However, phase transformation of NiO to $NiAl_2O_4$ spinel compounds has not almost taken place on 10 wt% Ni/B in such case. It is believed that the layer of $CaAl_2O_4$ spinel, between NiO and Al_2O_3 support, can effectively suppress the high-temperature phase transformation of NiO to $NiAl_2O_4$ spinel. Additionally, after a long-time H_2-reduced treatment at 1023 K for 10 h, the Ni crystallite size is larger on 10 wt% Ni/A than that on 10 wt% Ni/B due to sintering while the structure of the $CaAl_2O_4$ spinel is not destroyed. The results reveal that Ni tiny crystals can also be stabilized by the $CaAl_2O_4$ spinel compounds.

In order to examine the stabilization of the $CaAl_2O_4$ spinel compounds on Ni/Al_2O_3 catalyst for $CH_4/O_2(2:1)$-to-syngas reaction, the stability tests were carried out over Ni/A, Ni/B, and Ni/C with Ni-loadinds of 2.9 wt% at 873 K and GHSV = 250 $L \cdot g^{-1} \cdot h^{-1}$. In catalyst stability tests, all catalysts would stay ignited to give hot spots in the reaction, implying the occurrence of the higher local temperature (20); 2.9 wt% Ni/A catalyst would completely lose its activity in about 10 min after the feed gas was introduced. The initially dark catalyst turned light green, which is $NiAl_2O_4$ compound (4, 5). Both 2.9 wt% Ni/B and 2.9 wt% Ni/C catalysts give the CH_4 conversion of ~83% and syngas selectivity of over 90% without any loss in catalytic activity and selectivity during a long-time running (see Fig. 1), and have the H_2 turnover number of 484 and 502 s^{-1}, respectively (see Table 2). The initially dark catalyst did not turn light green, indicating $NiAl_2O_4$ compound is not formed, which is identical with the results in Table 1. The above results propose that the stability of catalysts 2.9 wt% Ni/B and 2.9 wt% Ni/C is due to the effect of inhibition of $CaAl_2O_4$ spinel compound layer on the phase transformation to form $NiAl_2O_4$. Similarly, as long-time H_2-reduced 10 wt% Ni/C, the XRD analyses of 2.9 wt% Ni/B and 2.9 wt% Ni/C following a long-time CH_4/O_2-to-syngas reaction (not shown) also indicate that the structure of $CaAl_2O_4$ spinel compound

TABLE 1

Data and Assignments of XRD Patents of 10 wt% Ni/A and 10 wt% Ni/B Catalysts

Catalyst	Treating process	d (Å)	Assignments
Support A	Calcined at 873 K for 5 h	1.99, 1.40, 2.40	γ-Al_2O_3
10 wt% Ni/A	Fresh (calcined at 973 K for 10 h)	2.07, 2.42, 1.50	NiO (13 nm)[a]
	Calcined in O_2 flow at 1123 K for 5 h	2.42, 2.00, 1.41	$NiAl_2O_4$
	H_2-reduced at 1023 K for 10 h	2.04, 1.76	Ni (40.5 nm)[a]
Support B	Calcined at 1173 K for 10 h	1.99, 1.40, 2.40	Al_2O_3 (γ and δ)
		3.00 (weak)	$CaAl_2O_4$
10 wt% Ni/B	Fresh (calcined at 973 K for 10 h)	2.09, 2.40, 1.48	NiO (12.5 nm)[a]
	Calcined in O_2 flow at 1123 K for 5 h	2.09, 2.41, 1.48	NiO (14.5 nm)[a]
	H_2-Reduced at 1023 K for 10 h	2.04, 1.76	Ni (30.5 nm)[a]

[a] Crystallite size.

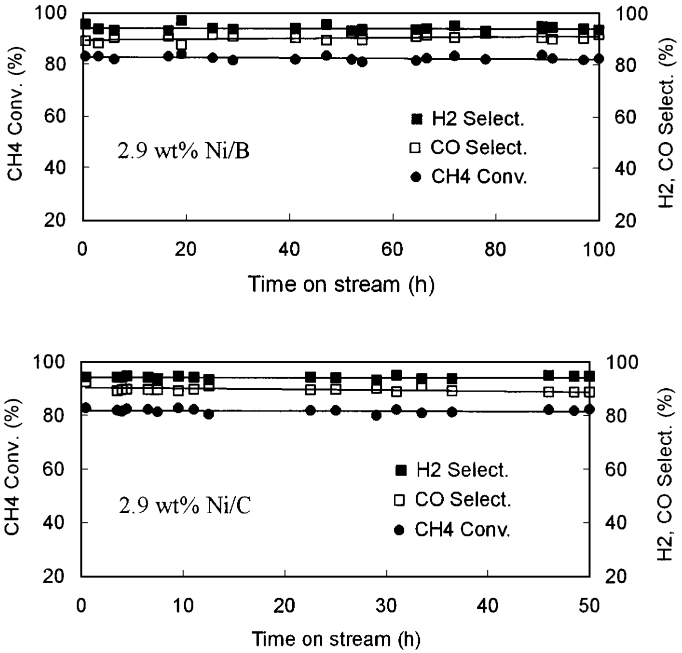

FIG. 1. CH_4 conversion and CO, H_2 selectivity as a function of time on stream over 2.9 wt% Ni/B and 2.9 wt% Ni/C catalysts (operating conditions: $T = 873$ K, $P = 1$ atm, GHSV $= 250\ L \cdot h^{-1} \cdot g^{-1}$, $CH_4/O_2 = 2:1$).

layer is not destroyed in the reaction. The TG/DTA analyses showed that the amount of coke deposit is 6×10^{-3} g/g_{cat} over 2.9 wt% Ni/B (after 100-h running) and 9×10^{-3} g/g_{cat} over 2.9 wt% Ni/C (after 50-h running) (see Table 2). As seen in TEM micrographs of both used catalysts, coke whiskers are always absent (not shown), which is completely different from other studies in the literature of coke formation on Ni catalysts during CH_4/O_2-to-syngas reaction (e.g., (15, 16)). To some extent, the high capacity of resistance to coke deposits can be attributed to the stabilization of $CaAl_2O_4$ spinel compounds to Ni tiny crystallites (see Table 1).

Considering the above results, supported Ni catalysts using $CaAl_2O_4$ spinel compounds modified Al_2O_3 support are stable for CH_4/O_2-to-syngas process. $CaAl_2O_4$ spinel compounds, existed between Ni and Al_2O_3, can effectively suppress the phase transformation to form $NiAl_2O_4$ spinel phases and stabilize the Ni tiny crystallites during the reaction.

TABLE 2

The Ni Surface Area, H_2 TON, and Amount of Coke Deposits of Various Catalysts

Catalyst	Ni surface area (m^2/g)	CH_4 initial conver. (%)	H_2 initial select. (%)	H_2 TON[a] (s^{-1})	Amount of coke deposits (g/g_{cat})
2.9 wt% Ni/A	0.45	84.4	96.2	449	ND[b]
2.9 wt% Ni/B	0.41	82.1	97.0	484	6×10^{-3}
2.9 wt% Ni/C	0.39	81.6	96.3	502	9×10^{-3}

[a] H_2 turnover number, which measured under the operating conditions: $T = 873$ K, $P = 1$ atm, GHSV $= 250\ L \cdot h^{-1} \cdot g^{-1}$, $CH_4/O_2 = 2:1$.
[b] Not detected.

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