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Partial oxidation of methane to synthesis gas over (Ca,Sr)(Ti,Ni) oxides

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Abstract

Ni catalysts supported on perovskite were in situ prepared from $Ca_{1-x}Sr_xTi_{1-y}Ni_yO$ precursors and were tested in the oxidation of CH_4 by increasing reaction temperature from room temperature to 800°C. NiO originally separated from the perovskite structure under sol–gel preparation conditions was reduced to Ni metal during the CH_4 oxidation and thus formed Ni metal supported on perovskite showed high activity for synthesis gas production at 800°C. This process involves first the oxidation of a part of CH_4 to H_2O and CO_2 followed by the reforming reaction of CH_4 with H_2O and CO_2. When the catalyst of $y = 0.2$ was used, high Sr contents afforded high activity for the CH_4 oxidation and the highest activity to synthesis gas was obtained with $x = 0.2$. In the catalysts of $x = 0.2$, those of $y \geq 0.1$ showed high activity for the synthesis gas production, that of $y = 0.05$ required pretreatment with CH_4 for acquiring the activity and a further decrease in the Ni content resulted in no activity. Ni catalyst prepared by impregnation over the perovskite carrier showed a high activity, while those prepared by mixing metal oxides were not active. It is thus most likely that perovskite structure possesses an important role as the carrier in Ni catalysts.

1. Introduction

The partial oxidation of CH_4 to synthesis gas is an established industrial process [1] but operates at high temperature (>1200°C) and high pressures (150 atm). Recently, several papers have been published on the catalytic partial oxidation of CH_4 to synthesis gas [2,3]. This process has advantages over the conventional steam reforming of CH_4 to make synthesis gas, because the latter process is also highly endothermic; it also produces synthesis gas having a H_2/CO ratio ≥ 3. The direct partial oxidation of CH_4, expected to afford synthesis gas having a H_2/CO ratio of about 2, makes methanol synthesis an ideal follow-up process. Ashcroft et al. [2] reported that transition metals, Ni, Ru, Rh, Pd, Ir, and Pt supported on alumina were active in this oxidation at a temperature of 775°C. Ni/Al_2O_3, a typical catalyst for the steam reforming, was studied for the partial oxidation of CH_4 at temperatures >700°C [3]. Schmidt et al. reported that platinum and rhodium surfaces in metal-coated ceramic monolith afforded mostly H_2 and CO with almost complete conversion of CH_4 and O_2 [3].

We found that, in the oxidation of CH_4, $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}-$ or $La_{0.8}Sr_{0.2}Co_{0.8}Ni_{0.2}$-oxides catalysts in situ produced Ni metal and showed the activity for the production of synthesis gas [4]. In both cases, Ni catalysts were in situ prepared from the perovskite-like precursors

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obtained by the sol–gel method. It is likely that an important feature in these catalyst systems was perovskite structure as the carrier of Ni metal. In situ formation and high activity of metal species for synthesis gas production have also been reported in the La–Rh–O perovskite system, however perovskite structure was not kept during the oxidation reaction [5]. This paper deals with the details of the activity of (Ca,Sr)(Ti,Ni) oxide catalysts for the synthesis gas production from CH_4.

2. Experimental

$Ca_{1-x}Sr_xTi_{1-y}Ni_y$ oxides, Ni metal supported on $(Ca,Sr)TiO_3$, and mechanical mixtures of metal oxide components were used as the catalyst. $Ca_{1-x}Sr_xTi_{1-y}Ni_y$ oxides were prepared by the citrate process [6] as follows: an aqueous solution of reagent grade nickel nitrate, alkaline earth carbonate and titanium isopropoxide was treated with an equimolar amount of citric acid and ethylene glycol, evaporated at 80–90°C to make a sol of organic metal complex, followed by two-step decomposition by heating at 200°C for 5 h and 500°C for 5 h in air and finally calcining at 850°C for 10 h. Ni catalyst supported on $(Ca,Sr)TiO_3$ was prepared by the impregnation method, as follows: the calculated amount of aqueous nickel nitrate was treated with an equimolar amount of citric acid and ethylene glycol, evaporated at 80–90°C to make a viscous liquid, and then diluted with distilled water. The solution was added into a suspension of the perovskite $Ca_{0.8}Sr_{0.2}TiO_3$ in distilled water, which was previously prepared by the citrate method. The suspension was again evaporated at 80–90°C, and calcined at 850°C in air for 5 h. The mechanical mixture was prepared as follows: mixtures of metal oxides were well ground and calcined at 850 or 1100°C in air for 5 h.

The structure of the catalysts was studied as follows: the powder X-ray diffraction pattern (XRD) diagrams were recorded by using MXP-18 (MAC Science Co.) with Cu Kα radiation. X-ray photoelectron spectra (XPS) were obtained with a PHI-5000 spectrometer employing Al Kα radiation (1486.6 eV) and an electron flood gun to provide charge neutralization of the non-conducting samples. The surface area of the catalyst was measured by the BET method with a Micromeritics model 2200.

All the catalysts have been tested in a mixture of air (2.4 l/h) and CH_4 (1.0 l/h) by increasing the reaction temperature from room temperature to 800°C at the rate of 2.5°C·min^{-1}. The quartz reactor used was U-shaped, with the catalyst bed near the bottom. 300 mg of catalyst was dispersed in 2 ml of quartz wool to avoid sintering and clogging of the reactor. Above and below the catalyst bed the reactor was filled with quartz sand. The thermocouple was introduced from the top of the reactor, and placed in the middle of the catalyst bed. Product gases were sampled immediately after the reactor and injected into a gas chromatography for analysis. The selectivities to C_2 compounds, CO_2, CO and H_2 were calculated based on the atom numbers of carbon and hydrogen in CH_4.

3. Results and discussion

The reactor filled with quartz sand and quartz wool, i.e. without catalyst, was tested with the same gas mixture as used in the catalytic reactions. The CH_4 oxidation occurred above 750°C and the conversions of O_2 and CH_4 reached 57% and 28%, respectively, at 800°C. Product distributions in selectivity are as follows: CO (63%), C_2 compounds (28%, ethene/ethane ratio = 2.6) and CO_2 (9%), and a production of H_2 (16% based on reacted CH_4) was observed.

3.1. Oxidation of CH_4 over $Ca_{1-x}Sr_xTi_{1-y}Ni_y$ oxides

XRD measurements of $Ca_{0.8}Sr_{0.2}Ti_{1-y}Ni_y$ oxides also clearly showed the peaks of NiO together with $Ca_{0.8}Sr_{0.2}TiO_3$ perovskite, revealing NiO separated from the perovskite structure even

Table 1. CH_4 Oxidation over $Ca_{0.8}Sr_{0.2}Ti_{1-y}Ni_y$ oxide[a]

Catalyst y	Conversion/% CH_4	O_2	Selectivity/% C_2	CO_2	CO	H_2	ΣC mmol•h^{-1}
0	34.0	84.4	10.2	47.0	42.8	21.8	41.2
0.01	30.7	94.5	12.3	83.8	3.9	2.2	40.8
0.025	33.7	94.3	21.0	75.1	3.9	3.3	41.3
0.05	36.3	92.3	18.1	68.0	3.9	4.8	40.9
0.1	92.5	94.9	0.1	5.2	94.7	98.5	41.8
0.2	98.7	94.5		1.8	98.2	99.0	42.4
0.4	97.4	94.8		2.2	97.8	98.0	41.6

[a] just after increasing reaction temperature to 800°C (2.5°C•min^{-1}).

in a small nickel content of y = 0.1. No shift in the diffraction lines of $Ca_{0.8}Sr_{0.2}TiO_3$ perovskite when nickel content increased also suggests the phase separation, i.e., no substitution of the Ti sites with Ni. Oxidation of CH_4 with air over $Ca_{0.8}Sr_{0.2}Ti_{1-y}Ni_y$ oxide was carried out using 300 mg of each catalyst (Table 1). $Ca_{0.8}Sr_{0.2}TiO_3$ showed a low activity above 700°C and a similar products distribution to the reaction in the absence of catalyst. The addition of a small amount of Ni resulted in a substantial increase in the activity as well as a decrease in the productions of CO and H_2. This might be due to the oxidation activity of NiO. The catalysts of $y \geq 0.1$ showed the activities for CH_4 combustion above 500°C, where a small amount of C_2 compounds was produced at 700–750°C and then almost complete conversion to synthesis gas was observed at 800°C. The catalyst of y = 0.05 showed the activity for synthesis gas production after the reduction with CH_4. When the Ni content was low, i.e., y = 0–0.025, no reforming occurred even after the reduction of the catalysts with CH_4. The selectivity to synthesis gas increased with increasing Ni content and reached almost constant value above y = 0.2 and the Ti/Ni ratio was thus fixed at 0.2/0.8 in the present study. It is likely that the reaction proceeds by the following mechanism: first the oxidation of a part of CH_4 to H_2O and CO_2 (1) followed by the reforming reaction of CH_4 with H_2O (2) and CO_2 (3). The reaction (1) is highly endothermic and, therefore, a large increase in the temperature of the catalyst bed is frequently observed when using Ni catalyst [3]. In the present study, the reaction temperature was measured and controlled by the thermocouple in a quartz tube introduced at the center of the catalyst bed. Therefore, the real temperature must be much higher than the measured value and a large temperature gradient may take place in the catalyst bed. The reactions (2) and (3) are controlled by the thermodynamic equilibrium because of their highly endothermic character. Over the catalyst of $y \geq 0.1$, the reaction might almost reached the equilibrium state. The exact evaluation of the equilibrium composition of the products must be done after measuring the correct temperature.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (2)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (3)$$

In the CH_4 oxidation over $Ca_{1-x}Sr_xTi_{0.8}Ni_{0.2}$ oxides, higher oxidation activity was observed with higher Sr content, while higher selectivity to synthesis gas was observed with rather lower Sr content; the highest value was with $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ oxide. XRD measurements

clearly showed the peaks of NiO together with $Ca_{1-x}Sr_xTiO_3$ perovskite; NiO was separated from the perovskite structure. It is likely that NiO in $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ oxide catalyst can be rapidly reduced to Ni metal during the reaction; the activity for synthesis gas production suddenly appeared when the reaction temperature reached 800°C. Ni metal is reasonably the active species for the synthesis gas production in the present catalyst system (vide infra). The other $Ca_{1-x}Sr_xTi_{0.8}Ni_{0.2}$ oxides did not produce the synthesis gas but substantially catalyzed the CH_4 combustion just after reaching 800°C. 10–30 min of the reactions were required for modifying all these catalysts to be active for synthesis gas production. The highest selectivity to synthesis gas was also observed with $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ oxide. It is thus concluded that the most efficient catalyst for the synthesis gas production is $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ oxide.

After the oxidation of CH_4 at 800°C, all the catalysts in the $Ca_{1-x}Sr_xTi_{0.8}Ni_{0.2}$ series and the catalysts containing Ni of $y \geq 0.05$ in the $Ca_{0.8}Sr_{0.2}Ti_{1-y}Ni_y$ series showed the lines of Ni metal as well as of $Ca_{0.8}Sr_{0.2}TiO_3$ perovskite in XRD measurements. $Ca_{1-x}Sr_xTiO_3$ perovskite structure was still well maintained after the reaction and only NiO was reduced to Ni metal. The total amount of carbon in the effluent gas (ΣC) coincided well with that of the feed gas in all the reactions in Table 1, suggesting no occurrence of carbon deposition over the catalysts. A clear decrease in ΣC was observed over the Ni catalyst prepared from $(La,Sr)NiO_{3-\delta}$ on which carbon deposition substantially occurred. It was thus confirmed that Ni catalyst prepared from $Ca_{1-x}Sr_xTi_{1-y}Ni_y$ series showed a stable and high activity for the synthesis gas production from CH_4 without carbon deposition.

3.2. *Effects of the preparation method of the Ni catalysts*

It seems that the high activity of the Ni catalyst for the synthesis gas production strongly depends on a combination of Ni metal and the perovskite structure. $Ca_{0.8}Sr_{0.2}Ti_{1.0}Ni_{0.2}$ oxide catalysts were prepared by three different methods, i.e., the citrate method, the impregnation method, and by the mechanical mixing method. In the last method, two calcination conditions, 850°C for 5 h and 1100°C for 5 h, were applied in order to see the effect of growing the perovskite structure during the calcination. The results of the CH_4 oxidation over these catalysts are shown in Table 2. The highest activity for synthesis gas production was obtained over the catalyst prepared by the citrate method, followed by the impregnation method. After the reduction with CH_4 flow ($1.01 \cdot h^{-1}$) for 2 h, the activity of the latter increased to almost the same value to that of the former. The mixing method afforded a very low activity for synthesis gas production even after the calcination at 850°C

Table 2. CH_4 oxidation over $Ca_{0.8}Sr_{0.2}Ti_{1.0}Ni_{0.2}$ oxides.

Catalyst preparn.	Temp. °C	Conversion/% CH_4	O_2	Selectivity/% C_2	CO_2	CO	H_2	ΣC mmol•h^{-1}
Sol-gel.	800	97.0	94.9		2.2	97.7	101.9	42.4
Impreg.	800	90.7	95.0		6.4	93.6	99.9	41.7
Mech. mix. 850°C	800	30.7	94.9	8.6	86.5	4.8	9.8	42.1
Mech. mix. 1100°C	800	36.2	90.7	25.5	70.8	3.7	7.6	39.6

for 5 h. Calcination at 1100°C rather resulted in an increase in the activity for C_2 compounds production together with a decrease in that for the synthesis gas production. In all the reactions, ΣC was maintained at almost constant value except for the case using the catalyst prepared by the mixing method and calcined at 1100°C, which showed a low ΣC value together with a low activity for synthesis gas production.

XRD measurement of the catalyst prepared by the impregnation method showed that orthorhombic $Ca_{0.8}Sr_{0.2}TiO_3$ perovskite structure was kept and NiO was reduced to Ni metal during the reaction. The catalyst prepared by the mixing method and calcined at 850°C showed the peaks of CaO, TiO_2 (Rutile) and NiO as well as the weak peaks of $CaTiO_3$ and Sr_2TiO_4 before the catalytic test, suggesting no substantial formation of perovskite structure. After the catalytic test, the peaks of CaO and NiO were weakened, that of Sr_2TiO_4 disappeared and new peaks of Ni metal and $CaCO_3$ appeared, suggesting that NiO was partially reduced to Ni metal, the unstable structure was decomposed, and CaO was converted to $CaCO_3$ during the reaction. The partial reduction of NiO to Ni metal is in marked contrast to the results obtained with the citrate and the impregnation methods, where NiO was completely reduced to Ni metal. When calcined at 1100°C, $CaTiO_3$ perovskite structure was more clearly observed compared to that calcined at 850°C. After testing, CaO and NiO were weakened and Ni metal appeared, showing the partial reduction of NiO to Ni metal similarly to the catalyst calcined at 850°C. The particle sizes of Ni metal calculated from X-ray line broadening measurements were as follows: $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ (citrate), 20 nm; $Ca_{0.8}Sr_{0.2}Ti_{1.0}Ni_{0.2}$ (impreg.), 33 nm and $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ (mech. mix.), 40 nm. Thus, the citrate method clearly afforded the finest particles of Ni metal in the catalyst.

XPS measurements of the catalysts showed that Ni 2d spectra appeared at 852.7 eV (Ni^0) and around 855.6 eV (Ni^{2+} or Ni^{3+}) and the former peak was clearly enhanced after the test. The composition of each metal was calculated from the XPS spectra by using the method reported by Penn [7] (Table 3). The amount of Ni was obtained by summarizing Ni^0, Ni^{2+} and Ni^{3+}. The citrate method ($Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ and $Ca_{0.8}Sr_{0.2}Ti_{0.95}Ni_{0.05}$) afforded metal compositions rather close to the calculated value, suggesting a homogeneous distribution of the metal components through the surface to the bulk. The

Table 3. Surface composition of the catalyst observed by XPS[a]

Catalyst		Relative concentration			
		Ca	Sr	Ti	Ni
$Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$	fresh	39.7	11.1	39.0	10.3
(Citrate)	used	42.2	11.0	36.1	10.7
$Ca_{0.8}Sr_{0.2}Ti_{0.95}Ni_{0.05}$	fresh	38.0	11.2	46.1	4.8
(Citrate)	used	41.0	10.8	43.1	5.0
$Ca_{0.8}Sr_{0.2}Ti_{1.0}Ni_{0.2}$					
Citrate, used		29.3	10.8	46.0	14.0
Impreg., used		31.8	9.9	46.6	11.6
Mech. mix. (850°C), used		77.6	6.2	10.6	5.7
Mech. mix. (1100°C), used		69.0	7.2	14.2	9.6

impregnation method ($Ca_{0.8}Sr_{0.2}Ti_{1.0}Ni_{0.2}$) showed a similar distribution to the citrate method. However, the mixing method revealed a sharp increase in the Ca content as well as a decrease in the B site atom content on the surface. By calcining at 1100°C, the Ca content decreased with increasing in the B site atom content. These results agree well with the partial reduction of NiO to Ni metal and the growth of perovskite structure at the high temperature observed in the XRD analyses. These suggest that Ni species homogeneously distributes through the surface to the bulk of the catalyst particles prepared by the citrate and the impregnation method, while the mixing method affords a catalyst containing Ni species in the bulk. NiO in the bulk of the catalyst cannot be reduced so easily, resulting in the partial reduction of NiO to Ni metal. It is interesting that the citrate method afforded the highest concentration of Ni of the preparation methods tested. The catalytic activity for the CH_4 conversion strongly depends on the amount of Ni metal on the surface of the catalyst as well as the surface properties.

It seems that Ni migrates to the surface of the catalyst particle during the preparation of the catalyst by the citrate method. In the catalyst prepared by the mechanical mixing method, however, the Ni concentration on the catalyst surface was not so high because NiO in the catalyst bulk cannot be reduced so easily as the other two catalysts. SEM images of the catalyst prepared by the citrate method showed that the particle size of 5 μm in diameter before testing became very small (1 μm) after test, suggesting that the catalyst particles were pulverized during the CH_4 oxidation. This may be due to the reduction of NiO to Ni metal: NiO was separated from the perovskite structure and might be at the grain boundaries as the binder of the catalyst crystals before the test, and the catalyst grains might be dispersed to fine particles due to the disappearance of NiO as the binder after the test. On the other hand, the catalyst prepared by the mixing method might be composed of tight agglomerates formed by the sintering of small particles of the metal oxides crystals, in which NiO cannot be easily reduced during the CH_4 oxidation. Only the surface morphology was changed by calcination. It is most likely that these different behaviors of Ni species strongly affected the catalytic activity.

4. References

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