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Nickel-Calcium Phosphate/Hydroxyapatite Catalysts for Partial Oxidation of Methane to Syngas: Effect of Composition

Jin Hyuk Jun, Kyeong Sook Jeong, Tae-Jin Lee*, Sang Jun Kong, Tae Hoon Lim**,
Suk-Woo Nam**, Seong-Ahn Hong** and Ki June Yoon†**

Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, South Korea
*School of Chemical Engineering & Technology, Yeungnam University, Kyongsan 712-749, South Korea
**Battery and Fuel Cell Research Center, Korea Institute of Science and Technology, Seoul 136-791, South Korea

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Abstract−Nickel-calcium phosphate/hydroxyapatite catalysts have recently been reported to exhibit high activity and selectivity in partial oxidation of methane (POM). In this work the optimum composition was determined. The optimum mole ratio of Ca/PO_4 was around 10/6 and that of Ni/PO_4 was in a range from 1.0/6 to 3.0/6 with the optimum Ca/PO_4, and the activity could be related with the amount of metallic nickel. In a temperature range from ca. 400 to 700 K, an apparent autothermal reaction was observed to occur in some cases. This is due to the fact that the actual catalyst temperature is higher than the measured temperature, which comes from the exothermic nature of the reaction. The mixing sequence of the precursors during the catalyst preparation does little affect the catalyst activity and characteristics. Deactivation of the catalyst occurred slowly, but the catalyst could easily be regenerated. Moreover, the nickel-calcium phosphate/hydroxyapatite catalyst showed higher activity than the nickel-strontium phosphate catalyst.

Key words: Calcium Hydroxyapatite, Calcium Phosphate, Nickel, Optimum Composition, Partial Oxidation of Methane

INTRODUCTION

Catalytic partial oxidation of methane (POM) for synthesis gas (syngas) and hydrogen production has been an active research subject in recent years because it is currently more economical and feasible than other methods such as water electrolysis and photodecomposition. This process arouses an interest when compared with the well-established steam reforming of methane since POM is mildly exothermic and does not require high operating pressures and hence is more energy efficient [Au and Wang, 1997; Chen et al., 2000; Choudhary et al., 1997; Diskin and Ormerod, 2000; Dissanayake et al., 1991, 1993; Hayakawa et al., 1997; Liu et al., 2000, 2002a, b; Takehira et al., 2000; Takehira, 2002; Torniainen et al., 1994; van Looij and Geus, 1997]. In reality, autothermal reforming for the production of syngas, which is a combination of the partial oxidation and steam reforming of methane, has been in operation for many years [Hydrocarbon Processing, 2002].

There have been numerous studies on POM over various metal catalysts such as Ni, Rh, Pt and Pd. Although Rh is known to be the most active for POM [Au and Wang, 1997; Torniainen et al., 1994], Ni is the most extensively studied catalyst because it is effective as well as cheap. Ni is usually supported on alumina and silica, but it is susceptible to the formation of inactive nickel aluminate and silicate. Sintering of Ni and the supports and coke formation are other problems. Several attempts have been reported to overcome these problems as described in earlier works, such as precoating of alumina with MgO or $Ce\text{-}ZrO_2$ [Choudhary et al., 1997; Liu et al., 2002a, b], use of perovskite [Hayakawa et al., 1997; Takehira et al., 2000] and Al-Mg oxide supports [Takehira, 2002]. In recent works from our laboratory, it has been reported that another type of new catalyst, nickel-strontium phosphate, exhibits high activity and selectivity in POM [Jun et al., 2003; Lee and Yoon, 2001; Lee et al., 2002]. No refractory oxide support was used in this catalyst. It was found that this catalyst could be activated by the reacting gases only (methane+oxygen) at around 850 K.

In a more recent work, a similar type of catalyst, nickel-calcium phosphate/hydroxyapatite, was studied [Jun et al., 2004]. It was found that this type of catalyst also showed high catalytic performance. In addition, this catalyst could also be activated by the reacting gases only at a lower temperature (ca. 723 K) after re-oxidation of the catalyst surface, once it had been reduced before. Characterizations of nickel-calcium phosphate/hydroxyapatite catalysts had been performed with high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), hydrogen chemisorption and O_2 sorption. In these catalysts, very fine nickel particles of several nanometers were observed from HRTEM, and these are believed to come out from the calcium nickel phosphate and hydroxyapatite structure under reducing environment during the reaction, which is supported by TPR and XRD. Over this catalyst, methane conversion and H_2 and CO concentrations close to those predicted by the thermodynamic equilibrium were observed.

In this work, investigation of the nickel-calcium phosphate/hydroxyapatite catalysts was continued for POM as a complement of the previous work. To find the optimum composition, the Ca/PO_4 and Ni/PO_4 mole ratios were varied to wider ranges than before and the catalytic performance was tested. In catalyst preparation, the effects of different sequences of the precursor mixing were investigated. Catalyst stability was also studied by a long-term test. In ad-

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† To whom correspondence should be addressed.
E-mail: kijyoon@skku.edu

‡ This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

dition, the activities of the nickel-calcium phosphate/hydroxyapatite and the nickel-strontium phosphate were compared.

EXPERIMENTAL

1. Catalyst Preparation

The catalysts were prepared by following the same procedure as described in the previous work [Jun et al., 2004]. The pH of each of the aqueous solutions of calcium nitrate, nickel nitrate and dibasic ammonium phosphate was adjusted to 10-11 by adding ammonia water, and predetermined amounts of the solutions were mixed at room temperature with vigorous stirring for 1 h. The water was evaporated to get a thick paste and the mixture was dried at 383 K overnight and finally heat-treated in air at 1,073 K for 2 h to obtain the catalyst. The solid catalyst was crushed and sieved, and the particles of 40- to 80-mesh size were used for the test.

The mole ratio of Ca/PO_4 employed was varied from 8.0/6 to 13.0/6 and Ni/PO_4 mole ratio was varied from 0.5/6 to 3.5/6. The catalysts were designated to be Ca*NiP(a), where * being 60 times of the Ca/PO_4 mole ratio and a being 60 times of the Ni/PO_4 mole ratio employed. For example, Ca95NiP(25) has the composition ratio of $Ca_{9.5}Ni_{2.5}(PO_4)_6$. The multiplication by 60 was taken for convenience sake in order to express the composition by integers, since calcium phosphate ($Ca_3(PO_4)_2$) and calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) have the least common multiple of 6 between the subscript numbers of the phosphate group. In addition, -f or -u was affixed when necessary, where f and u denote fresh (before-reaction) and used (after-reaction) catalyst, respectively.

2. Performance Test and XRD Analysis

The catalyst performance was tested by a conventional method using an 8 mm i.d. quartz-tube flow reactor as described in the previous work [Jun et al., 2004]. The reaction temperature was measured by a thermocouple inserted from the top of the reactor and contacting directly the catalyst particles. Unless specified otherwise, the following standard experimental conditions were employed. The catalyst charge was 0.2 g. The partial pressures of methane and oxygen were 16.2 and 8.1 kPa (0.16 and 0.08 atm), respectively. Ar was used as the diluent gas and the total flow rate was 100 cm^3 (STP)/min. For each catalyst, the first run was performed at the reaction temperature of 1,023 K without employing the hydrogen pretreatment since this temperature had been found to be sufficiently high for the activation [Jun et al., 2003, 2004; Lee and Yoon, 2001; Lee et al., 2002], and then the temperature was raised to 1,073 K and then lowered with 50-degree intervals until the activity became practically zero. The product gas was analyzed by two gas chromatographs using Carboxen 1004 columns (Supelco); one used Ar as the carrier gas and the other used He. The latter was needed especially when the concentration of produced CO_2 was too low to detect by using the Ar carrier gas. Since several other characterizations had been made in the previous work [Jun et al., 2004], only XRD (M18xHF-SRA, Mao Science) was used.

The CO selectivity is defined here as (moles of CO produced)/(moles of CH_4 consumed). The CO_2 selectivity is defined likewise. No other carbon-containing products were detected. The H_2 yield is defined as (moles of H_2 produced)/[2×(moles of CH_4 fed)].

RESULTS AND DISCUSSION

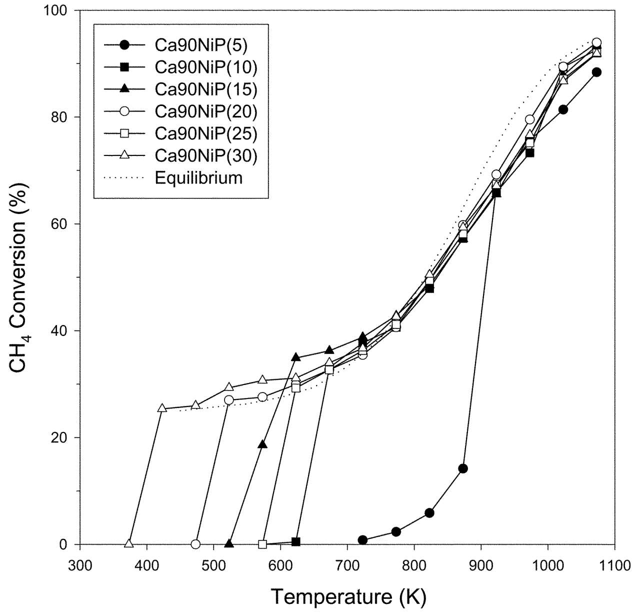

Fig. 1. CH_4 conversion vs. temperature over Ca90NiP(a) catalysts with different nickel content.

1. Effect of Nickel Content

The performances of the catalysts with different Ni content but with a fixed Ca/PO_4 ratio were compared in this section. The methane conversions over Ca90NiP(a) catalysts are shown in Fig. 1. In the catalyst with a low content of Ni such as Ca90NiP(5), the activity was low below ca. 900 K, and this is probably due to the low content of Ni. The performances of the catalysts from Ca90NiP(10) to Ca90NiP(30) were excellent. Above ca. 700 K, the methane conversions can be considered to be almost the same within the experimental error. The phenomena observed below 700 K will be discussed later.

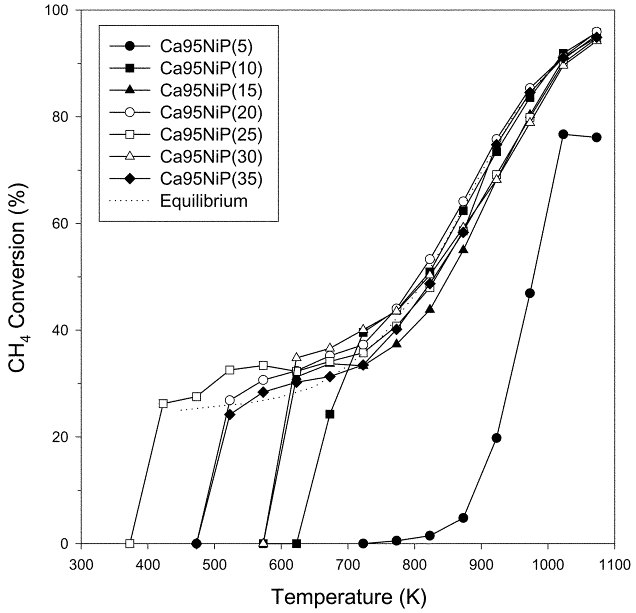

Fig. 2. CH_4 conversion vs. temperature over Ca95NiP(a) catalysts with different nickel content.

Fig. 2 shows the methane conversions over Ca95NiP(a) catalysts with different Ni content. Ca95NiP(5) also exhibited poor performance. Ca95NiP(10) and other catalysts with higher contents of Ni exhibited excellent performances. Above 723 K, the differences in the conversion were again small. Especially above 973 K, the differences were much smaller, and this is probably due to the closeness to the chemical equilibrium.

For other catalysts with different Ca/PO_4 ratios, such as Ca80NiP (a), Ca85NiP(a) and Ca100NiP(a), a similar trend was observed (not shown here for brevity's sake). From these results, it may be said that the catalysts having a between 10 and 30 exhibit similar activities to each other. Therefore, the effect of Ca/PO_4 ratio was investigated with a fixed Ni/PO_4 ratio of 2.5/6 in the next section.

2. Effect of Ca/PO_4 Ratio

The XRD patterns for the catalysts with different Ca/PO_4 ratios and a fixed Ni/PO_4 ratio of 2.5/6 (or a=25) are shown in Figs. 3 and 4. Fig. 3 is the summarized results of the previous work [Jun et al., 2004]. For the catalyst with a low Ca/PO_4 ratios such as Ca85NiP(25), the calcium phosphate was the dominant phase and only a small amount of the apatite was observed. As the Ca/PO_4 ratio increased, the calcium phosphate phase became smaller and the calcium hydroxyapatite phase became dominant. This is certainly due to the higher Ca/PO_4 ratio, which is favorable for the formation of the apatite phase. In the fresh catalysts, as the Ca/PO_4 ratio increased, the amount of NiO increased gradually up to the Ca/PO_4 ratio of 10/6, and it appeared to be similar in the fresh catalysts with the higher Ca/PO_4 ratios. In the used catalysts, the amount of metallic nickel also increased up to Ca/PO_4 ratio of 10/6 with the decrease of the NiO, and then the amount of the metallic nickel decreased as the Ca/PO_4 ratio increased further. In Ca130NiP(25) having the highest Ca/PO_4 ratio among the catalysts investigated, the metallic nickel was not observed. It would be suggested that the NiO could not easily be reduced since NiO particles might be covered with excess calcium in the form of CaO or $CaCO_3$.

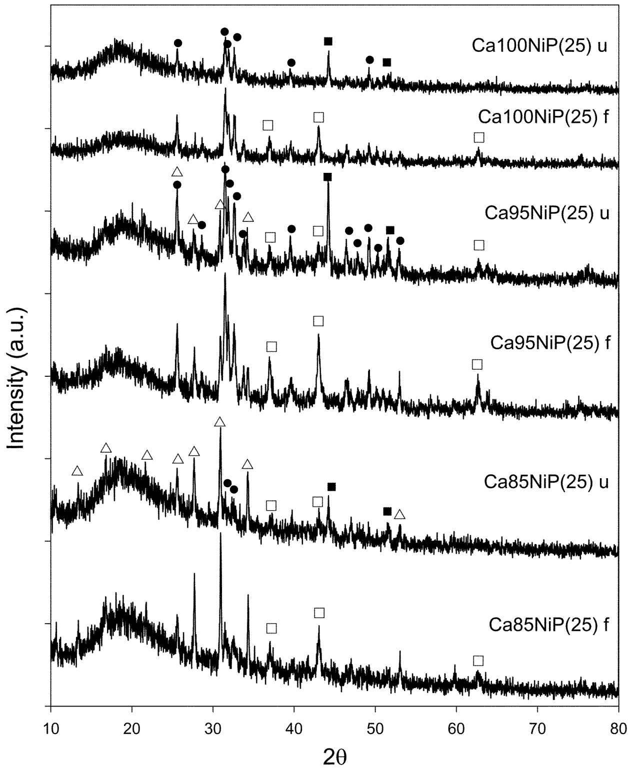

Fig. 3. X-ray diffractograms for Ca85NiP(25), Ca95NiP(25) and Ca100NiP(25) (△: β-$Ca_3(PO_4)_2$; ●: $Ca_{10}(PO_4)_6(OH)_2$; □: NiO; ■: Ni).

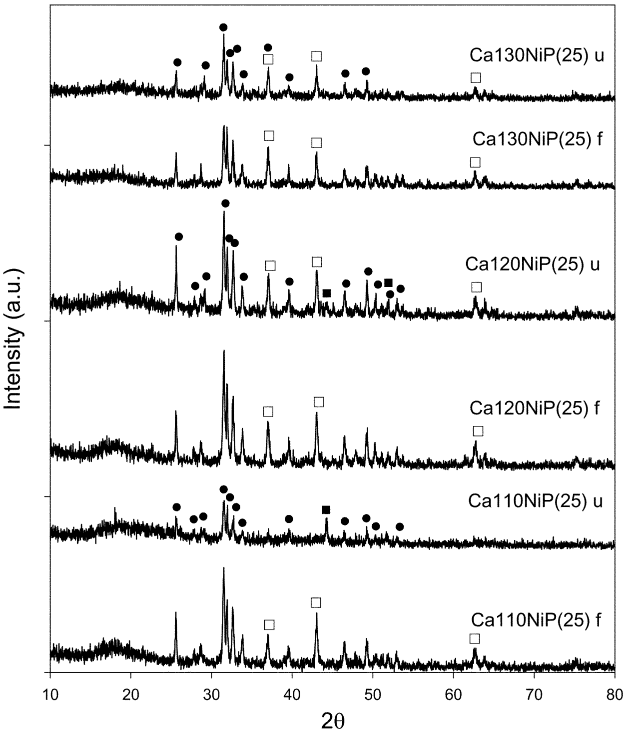

Fig. 4. X-ray diffractograms for Ca110NiP(25), Ca120NiP(25) and Ca130NiP(25) (△: β-$Ca_3(PO_4)_2$; ●: $Ca_{10}(PO_4)_6(OH)_2$; □: NiO; ■: Ni).

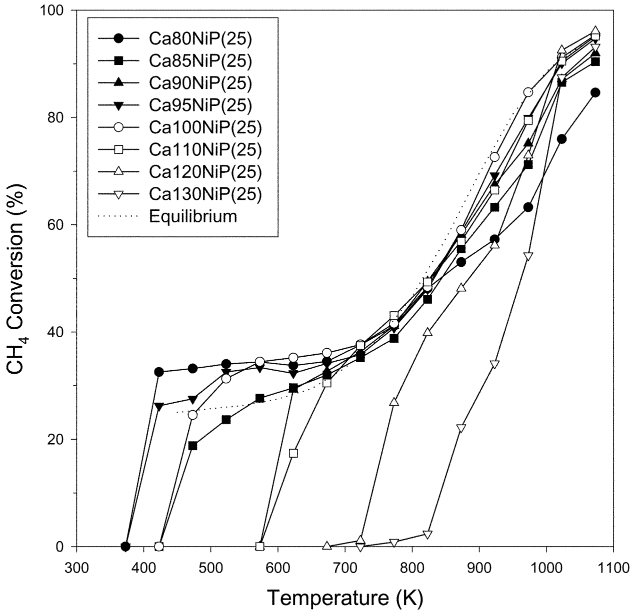

Fig. 5. CH_4 conversion vs. temperature over Ca*NiP(25) catalysts with different Ca/PO_4 ratios.

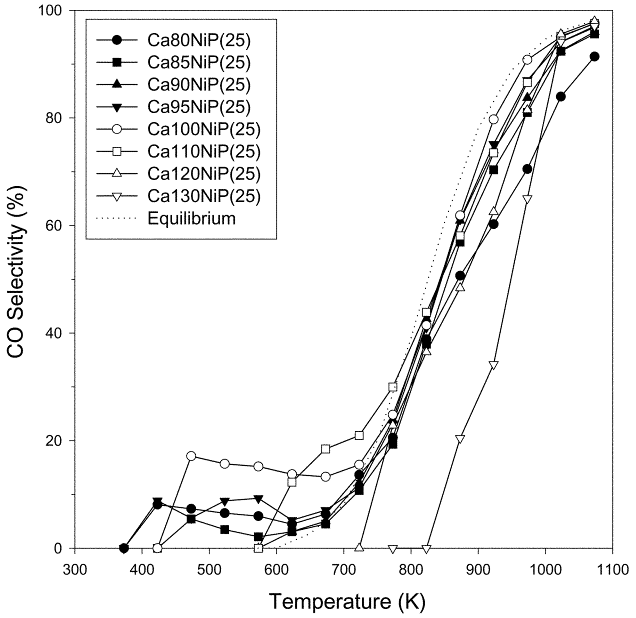

Fig. 6. CO selectivity vs. temperature over Ca*NiP(25) catalysts with different Ca/PO$_4$ ratios.

Figs. 5 and 6 show a comparison of the activity and CO selectivity for the catalysts with different Ca/PO$_4$ ratios and a fixed Ni/PO$_4$ ratio of 2.5/6 (or a=25). The H_2 yield was not shown here because its trend was the same as that of CO selectivity and the H_2/CO ratio was mostly close to 2. Above 723 K, as the Ca/PO$_4$ ratio increased up to 10/6, the catalytic performance appeared to become higher. Ca100NiP(25) exhibited the highest activity and CO selectivity, which were very close to or in excess of the equilibrium. As the Ca/PO$_4$ ratio increased further, the performance became poorer.

The methane conversions against Ca/PO$_4$ ratios obtained over Ca*NiP(25) catalysts at 923 K are shown in Fig. 7. This temperature was chosen for the comparison since the differences in the conversion above 973 K were relatively small. From this figure, the optimum Ca/PO$_4$ mole ratio can be said to be near 10.0/6. The catalysts with the Ca/PO$_4$ mole ratio from 9.0/6 to 11.0/6 also showed excellent performance. The XRD peak intensity ratios, $[I_{Ni}/(I_{AP}+I_{CP})]_u$, are also shown in Fig. 7, similarly to the previous work [Jun et al., 2004]. I_{Ni} is the intensity of the most intense peak of metallic Ni (111) peak in the used sample. I_{AP} and I_{CP} are the intensities of the highest peak of calcium hydroxyapatite, (211) peak, and that of calcium phosphate, (0.2.$\underline{10}$+217) peak, respectively. This ratio and the catalyst activity appeared to be well correlated. Therefore, the amount of metallic Ni is an essential factor of the catalytic activity. Since the reduction of nickel in the phosphate structure requires a temperature higher by about 100 K than that in the apatite structure, as observed by TPR in the previous work [Jun et al., 2004], the degree of reduction of nickel in the catalysts with the Ca/PO$_4$ ratio lower than 10.0/6, which predominantly have the phosphate phase, may become smaller. The reason for the lower amounts of metallic Ni in the catalysts with a Ca/PO$_4$ ratio higher than 10.0/6 is that the surplus calcium compounds (such as CaO and/or $CaCO_3$), which are not participating in the formation of the phosphate and the apatite, cover the catalyst surface and thus suppress the reduction of Ni^{2+} in NiO as well as the nickel in the phosphate and apatite structures. The methane conversions against the Ni content at 923 K are shown in Fig. 8. For the Ca100NiP(a) catalysts, the activities were nearly the same in the range of a from 5 to 30. For the Ca95NiP(a) catalysts, however, the activity of Ca95NiP(5) was considerably lower than the other catalysts. Although the catalyst with a higher than 35 was not investigated, common sense indicates that too high nickel content may not be beneficial for the activity. Therefore, it is concluded that the optimum Ca/PO$_4$ ratio is near 10/6 and the optimum range of Ni/PO$_4$ is from 1.0/6 to 3.0/6, if safely speaking based on the ranges investigated in this work.

3. Autothermal Reaction

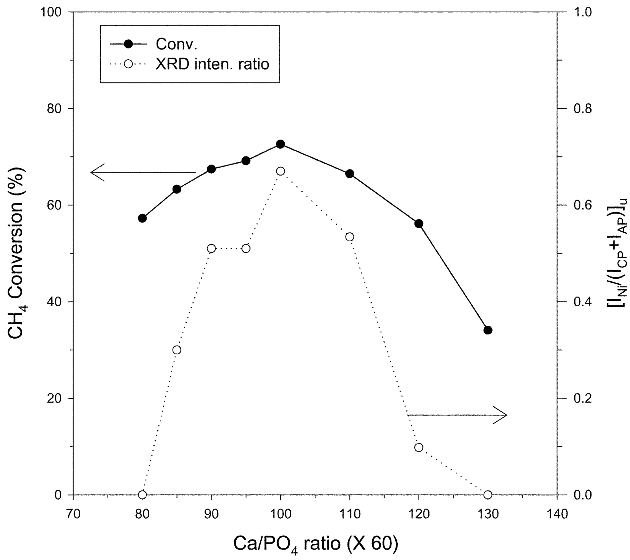

Fig. 7. CH$_4$ conversion at 923 K and relative amount of metallic nickel in the used samples against Ca/PO$_4$ ratio for Ca*NiP (25) catalysts.

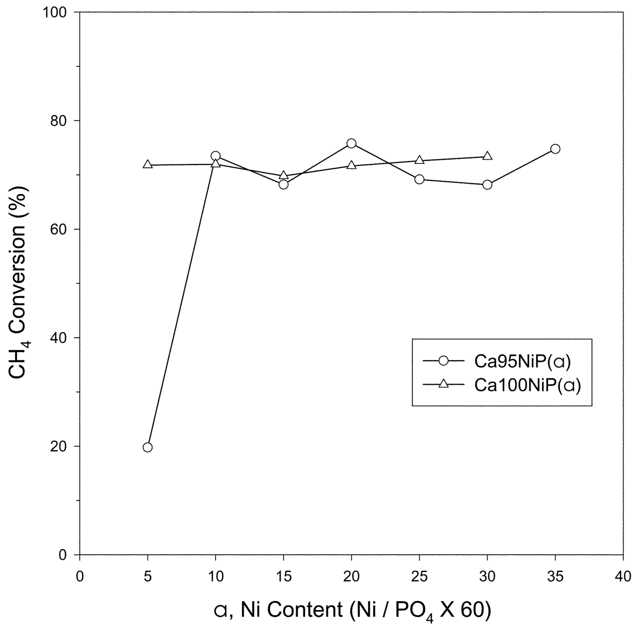

Fig. 8. CH$_4$ conversion at 923 K against Ni content.

An interesting feature was observed in Figs. 5 and 6 as well as in Figs. 1 and 2. In the temperature range from ca. 400 to 700 K, the methane conversion did not always drop to zero at 673 K but remained quite high. The CO selectivities were several percent and the H_2 yields amounted to about 5-15%. These are higher than the equilibrium. One thing to be considered here is that the reaction temperature measured by the thermocouple may not reflect the actual catalyst temperature due to the limitations of the measuring device, especially for such a case of high heat of reaction. During the experiments in this temperature range, the furnace temperature was lower by more than 100 degrees than the catalyst bed temperature measured by the inserted thermocouple. In some cases, the furnace was removed but the temperature was maintained. This is certainly due to the heat liberated by the exothermic reactions, apparently resulting in the behavior of an autothermal reaction [Torniainen et al., 1994]. However, this phenomenon was not reproducible and the measured temperature at which the activity became zero was irregular case by case. In addition, the CO selectivity and H_2 yield also irregularly varied with the measured reaction temperature. Thus, it is thought that the maintenance of the catalyst temperature and activity in this temperature range is unstable, or it may be a problem of reactor stability. In addition, it is thought that the actual catalyst temperature may be considerably higher than the measured temperature and/or may not be uniform throughout the bed. A more careful study, such as measurement of temperature along the catalyst bed (which is difficult in this reactor system of powder catalyst), will be needed to better understand this phenomenon.

4. Effect of Different Mixing Sequence of the Precursors

Effects of the different mixing sequence of the precursors in the catalyst preparation were investigated. The composition of Ca95NiP(25) was chosen as a representative sample. The precursors of the catalyst were calcium nitrate (A), dibasic ammonium phosphate (B) and nickel nitrate (C). As described in the Experimental section for the catalyst preparation under standard conditions, C solution was first mixed to B solution, and then (B+C) solution was mixed to A solution continuously. In another different mixing sequence, C solution was mixed to A, and then (A+C) was mixed to B continuously (Ca95NiP(25)-1). In the next different mixing sequence, A solution was mixed to B, and then C was mixed to (A+B) continuously (Ca95NiP(25)-2).

The crystalline phases and intensities observed by XRD were nearly the same among the fresh samples. Likewise, they were also nearly the same among the used samples. Fig. 9 shows the results of reaction experiments over Ca95NiP(25) catalysts with the different mixing sequence. For all cases, methane conversion, CO selectivity and H_2 yield exhibited similar results, almost in the error range of experiment. Below 600 K, each catalyst has some different total re-oxidation temperature, where the activity drops zero. But this does not mean that the catalysts have different intrinsic properties, as discussed in Section 3. These results tell us that the mixing sequence of the precursors has negligible effects on the catalyst activity and characteristics.

5. Durability Test

Literature survey tells us that nickel-based catalysts in POM could be deactivated by the carbon deposition and sintering of nickel, and hence the catalyst stability is important. Therefore, a long-term test was carried out for Ca95NiP(25) (Fig. 10). The test was performed at 1,023 K.

The initial methane conversion was 90%, CO selectivity 94% and H_2 yield 87%, but the methane conversion and CO selectivity slowly decreased with time on-stream. After 84 hour, the conversion and CO selectivity decreased to 80 and 88%, respectively. At this moment, the methane flow was stopped and only oxygen and argon flowed for about 1 h. When the reaction experiment resumed, it was found that the catalyst activity was restored to the initial value

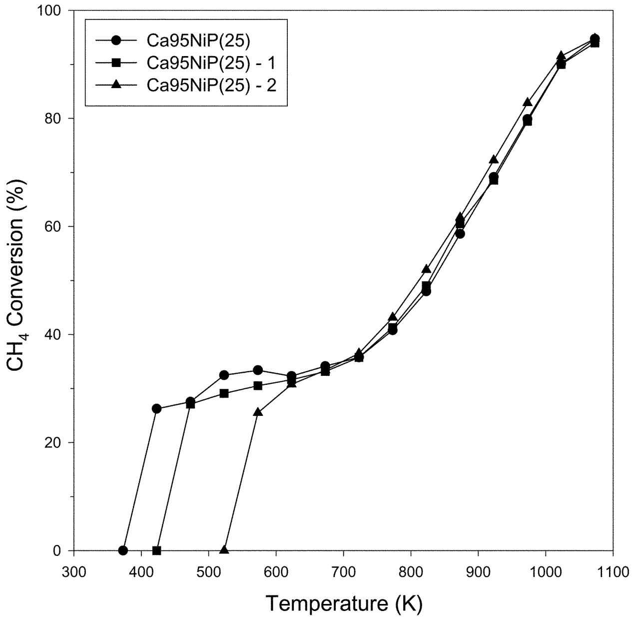

Fig. 9. CH_4 conversion vs. temperature over Ca95NiP(25) catalysts with different mixing sequence of the precursors.

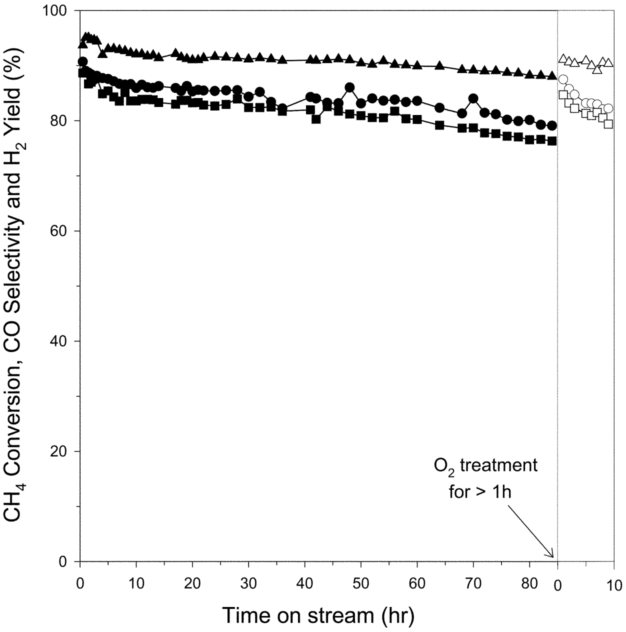

Fig. 10. Durability test of Ca95NiP(25) catalyst at 1,023 K. ●: CH_4 conversion, ▲: CO selectivity, ■: H_2 yield (open symbols: after oxidation for 1 hour).

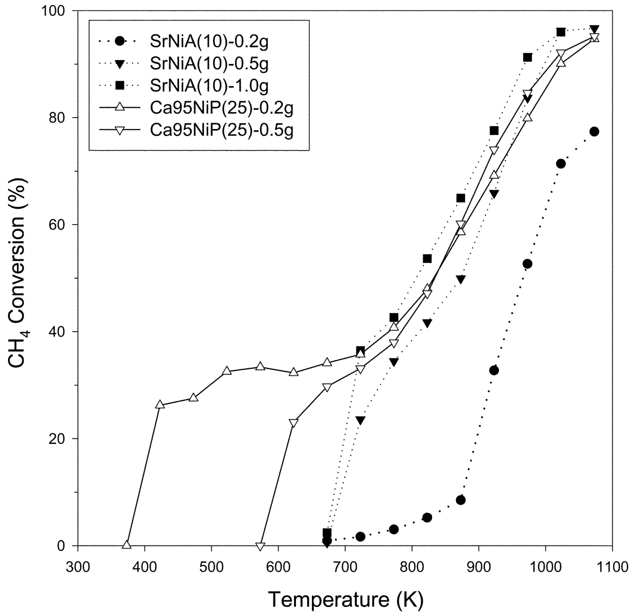

Fig. 11. Comparison of the CH_4 conversion over Ca95NiP(25) with that over SrNiA(10) (P_{CH_4}=0.16 atm, CH_4/O_2=2, total flow rate=100 cm^3/min).

(Fig. 10, open symbols). But the deactivation appeared to occur somewhat more rapidly than before. After 9 h, the conversion decreased to 82%. The main cause of the deactivation is considered to be coke deposition. A small amount of carbon fibers and nanotubes, diameters of several tens of nanometers, was observed by HRTEM. Restoring of the activity by oxygen treatment also support this. Anyway, the activity of catalyst could relatively easily be regenerated. Another factor of the catalyst deactivation may be the sintering, but it is difficult to confirm for the present since an appropriate characterization method is not available due to suppression of hydrogen chemisorption on Ni in this kind of catalyst [Jun et al., 2004].

6. Comparison of Activity with Ni-Strontium Phosphate

In this section, the activities of Ca95NiP(25) and another same type of catalyst $Sr_{9.0}Ni_{1.0}(PO_4)_6$ (designated as SrNiA(10)) [Jun et al., 2003, 2004; Lee et al., 2002] were compared. SrNiA(10) had been found to be the optimum catalyst among Ni-strontium phosphate catalysts [Lee et al., 2002]. Fig. 11 shows the conversions of the two catalysts. Under the same reaction conditions (the amount of catalyst, space velocity, partial pressure, etc.), the conversions obtained by the two catalysts were considerably different. When the catalyst charge was 0.2 g, the conversion was 90% over Ca95NiP(25) at 1,023 K while it was significantly lower over SrNiA(10) (about 71%). For SrNiA(10) with relatively lower space velocity, the activities were similar to Ca95NiP(25) or a little larger. Above 773 K, the conversion obtained over 0.2 g of Ca95NiP(25) was similar to that over 0.5 g of SrNiA(10), and that over 0.5 g of Ca95NiP(25) was also similar to that over 1.0 g of SrNiA(10). This indicates that Ca95NiP(25) catalyst has considerably higher activity than SrNiA(10) in POM. One reason for this may be the fact that the Ca-Ni-PO_4 system is easy to form the apatite phase, while the Sr-Ni-PO_4 system is liable to form the phosphate phase [Lee et al., 2002]. That is, the nickel in the former phase is easier to be reduced than the latter, as mentioned in Section 2, which results in a higher amount of the metallic nickel.

CONCLUSIONS

Nickel-calcium phosphate/hydroxyapatite, a new type of catalyst with no oxide support, exhibited very high activity and selectivity for the partial oxidation of methane. The optimum ranges of Ni/PO_4 and Ca/PO_4 ratios were determined. The optimum mole ratio of Ca/PO_4 was near 10/6 and that of Ni/PO_4 was in a range from 1.0/6 to 3.0/6 with the optimum Ca/PO_4. Over the optimum catalysts, methane conversions and CO and H_2 concentrations in excess of, or close to, those predicted by the thermodynamic equilibrium were observed. The amount of metallic nickel was found to be an important factor for the activity. When the nickel content was too small, the activity was poor. When the Ca/PO_4 ratio was low, the activity became low due to the dominant formation of the phosphate phase, the nickel in which is more difficult to be reduced than that in the hydroxyapatite phase. When the Ca/PO_4 ratio was too high, surplus calcium compounds seemed to suppress the reduction of nickel. For the catalyst preparation, the mixing sequence of the precursors has negligible effects on the catalyst activity and characteristics. For the durability test, deactivation of the catalyst occurred slowly, but it could easily be regenerated. Moreover, the nickel-calcium phosphate/hydroxyapatite catalyst exhibited superior performance to the nickel-strontium phosphate catalysts, another similar type of catalyst. Therefore, the hydroxyapatite phase is more beneficial to the activity than the phosphate phase.

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