

Characterization of a Nickel-Strontium Phosphate Catalyst for Partial Oxidation of Methane

Jin Hyuk Jun, Sang Jin Lee, Seung-Hwan Lee, 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, Korea

*School of Chemical Engineering & Technology, Yeungnam University, Kyongsan 712-749, Korea

**Battery and Fuel Cell Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

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Abstract—A nickel-strontium phosphate catalyst was recently reported to exhibit high activity and selectivity in partial oxidation of methane (POM). Further characterizations have been performed in the present work in order to better understand the characteristics of this catalyst. TEM showed that very fine nickel particles of a few nanometers of the size were present in the needle shape in the sample after the reaction. TPR showed the presence of three nickel species, confirming that the nickel in the strontium hydroxyapatite and phosphate structures comes out as fine particles and is reduced during the reaction. As the calcination time during the preparation increased, the total re-oxidation temperature became higher. This is considered due to larger crystallite size owing to the longer calcination, which results in a smaller amount of nickel coming out of the matrix to the surface.

Key words: Calcination, Nickel, Partial Oxidation of Methane, Strontium Nickel Hydroxyapatite, Strontium Nickel Phosphate

INTRODUCTION

Catalytic partial oxidation of methane (POM) for synthesis gas production has been an active subject in recent years. The process arouses renewed interest as a promising alternative to the steam reforming of methane [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; Takehira et al., 2000; Tornaiainen et al., 1994; van Looij and Geus, 1997]. Compared with highly endothermic steam reforming, POM is mildly exothermic and does not require high operating pressures, and hence is more energy efficient. The reaction can be carried out with lower investment and will produce a smaller amount of CO₂. Recently, POM has been of particular interest in fuel processing applications such as in fuel cells for start-up from cold, owing to its exothermic nature [Tornaiainen et al., 1994; Diskin and Ormerod, 2000].

There have been numerous studies on POM over various metal catalysts. Rh is known to be the most active for POM [Tornaiainen et al., 1994]. However, 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 metallic nickel and coke formation are other problems that cause catalyst deactivation. Several attempts have been reported to overcome these problems. Choudhary et al. [1997] have shown that in supported Ni catalysts prepared by depositing NiO on alumina and silica precoated with MgO, chemical interactions of NiO with the support could be prevented by providing a stable protective layer of magnesium aluminate and silicate. Hayakawa et al. [1997] and Takehira et al. [2000] have reported that Ni supported on perovskite-type oxides prepared by the

solid phase crystallization, such as Ni_{0.2}/ATiO₃ (A: Ca, Sr or Ba), shows good activity and selectivity as well as very low coke formation. They explained that this would be due to highly dispersed and stable Ni metal particles on the perovskite, where the nickel species thermally evolve during the reaction from the cations homogeneously distributed in an inert perovskite matrix as the precursor. Takehira [2002] also reported that a Ni/Al-Mg oxide catalyst prepared by the solid phase crystallization had very fine Ni particles and showed high activity, selectivity and stability. Such studies suggest that high dispersion of metal species and/or use of alkaline earth metals may be beneficial to improve the catalytic performance for the POM. Liu et al. [2002a, b] have recently reported that Ni/Ce-ZrO₂/θ-Al₂O₃ shows high activity and stability and that a protective layer of Ce-ZrO₂ suppresses the formation of inactive NiAl₂O₄.

From the work in our laboratory, it has recently been reported that another type of new catalyst, nickel-strontium phosphate, exhibits high activity and selectivity in POM [Lee and Yoon, 2001; Lee et al., 2002]. Over this catalyst, methane conversion and H₂ and CO concentrations close to or sometimes in excess of those predicted by the thermodynamic equilibrium were observed. No refractory oxide support is used in this catalyst. It is considered that the presence of Sr imparts some alkalinity to the catalyst and might be beneficial for the suppression of coke formation. However, many still remain to resolve for the characteristics of this catalyst. The presence of fine nickel particles, which were evolved from the strontium phosphate or the strontium hydroxyapatite structure, was suggested but no direct evidence was given. Another question is that under what conditions the nickel evolves from the structure. This work is a continuation of the previous work to better understand the characteristics of the catalyst. Transmission electron microscopy (TEM) will give the direct evidence of the presence of fine particles. Temperature programmed reduction (TPR), X-ray dif-

†To whom correspondence should be addressed.

E-mail: kijyoon@skku.edu

fraction (XRD) and variation of calcinations time will give us more information of coming-out and reduction of the nickel.

EXPERIMENTAL

The catalysts were prepared from nearly saturated aqueous solutions of strontium nitrate, nickel nitrate and dibasic ammonium phosphate. The solutions were mixed with vigorous stirring and the mixture was dried at 383 K overnight and finally calcined in air at 1,073 K for 2, 15 and 24 h to obtain the catalyst. The molar ratios of Sr/PO₄ and Ni/PO₄ were 9/6 and 1/6, respectively, since this had been found to be the optimum composition in the previous work [Lee et al., 2002]. The Ni content in this catalyst is about 4 wt%. The catalyst was designated to be SrNiA(10/t)-f or u, where t denotes the calcination time in hour and f and u denote fresh (before-reaction) and used (after-reaction) catalyst, respectively.

The catalyst performance was tested by a conventional method using an 8 mm ID quartz-tube flow reactor. The reaction temperature was measured by a thermocouple directly contacting the catalyst particles and controlled by an electric furnace. Unless specified otherwise, the following experimental conditions were employed. The catalyst charge was 1.0 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 cm³ (NTP)/min. 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 CO₂ produced was too low to detect by using the Ar carrier gas. The first reaction experiment for each catalyst was carried out at 1,023 K by flowing the reaction gas mixture only, since this temperature was sufficiently high for the activation of the catalyst [Lee and Yoon, 2001; Lee et al., 2002].

The catalysts were characterized with XRD by using Ni-filtered Cu-K α (M18xHF-SRA, Mao Science) and high-resolution transmission electron microscopy (HRTEM, JEM3011, JEOL). The TPR was carried out by using 5% H₂/Ar with the total flow rate of 100 cm³/min for 1.0 g of the catalyst and the ramp rate of 10 K/min.

RESULTS AND DISCUSSION

Let us begin with the summary of the previous work on SrNiA(10/2) [Lee et al., 2002]. For the fresh SrNiA(10/2), three crystalline phases were observed. The two were identified as strontium phosphate [Sr₃(PO₄)₂; this will be called as the phosphate hereafter] and strontium hydroxyapatite [Sr₁₀(PO₄)₆(OH)₂; this will be called as the apatite hereafter]. The third phase could not be identified from the JCPDS powder diffraction files, but it was suggested to be Sr_{3-x}Ni_x(PO₄)₂, a part of the Sr²⁺ (ionic radius: 126 pm) being substituted with Ni²⁺ (ionic radius: 69 pm), since the contraction of d spacing for the major peaks was about 3–4 pm when compared with the d spacing for the major peaks of strontium phosphate. This suggestion could be strongly supported by a recent work on strontium iron phosphate [Belik et al., 2001]. Belik et al. also showed that Ni, Co, Cu, Zn, Mn and Cd could substitute the Sr²⁺. The third phase, however, disappeared after the reaction experiment, and it was confirmed that the third phase also disappeared after hydrogen treatment. Another conclusion was that the catalyst could be activated

by only the reaction gas mixture at 823–873 K without hydrogen treatment usually employed for the activation of Ni catalysts. After the activation the third phase disappeared. In addition, the apatite almost disappeared and the phosphate became the dominant constituent. Therefore, it was suggested that the Ni in the third phase came out of the apatite and/or the phosphate structure under reducing environment and was transformed to metallic Ni. Contrary to the expectation, NiO and metallic Ni as well as nickel phosphate phases were not observed by XRD in either the fresh or the used

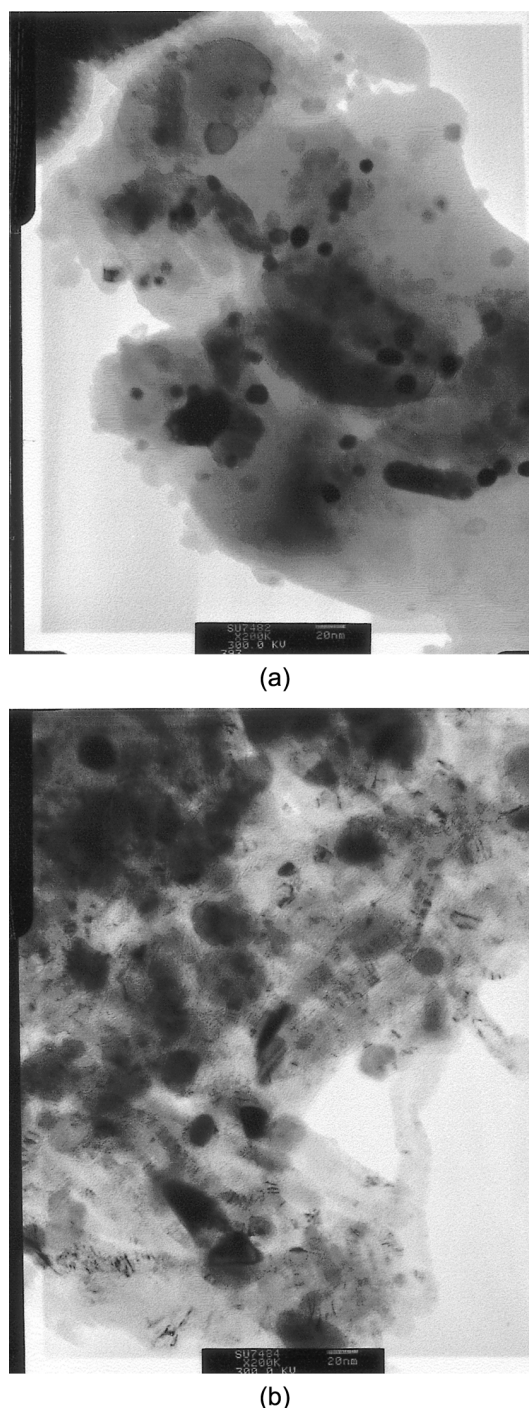


Fig. 1. TEM pictures for SrNiA(10/2).
(a) fresh catalyst, (b) used catalyst

catalyst.

1. TEM Results

Fig. 1 shows the TEM pictures for SrNiA(10/2)-f and SrNiA(10/2)-u. In the fresh catalyst, round particles of 5–20 nm size were observed. These particles were identified as NiO by energy-dispersive X-ray spectroscopy (EDS) equipped in the TEM apparatus, since the major elements in the particles, when irradiated with about 10 nm size beam, were found to be Ni and O. At the other part of the catalyst, the major elements were Sr, P and O, together with a small amount of Ni. In the used catalyst, very fine particles were observed; they had not been seen in the fresh catalyst. Many of them were needle shaped, with a width of about 1 nm and length of several nm. Round particles of a few nm diameters were also observed. For these particles a major element was found to be Ni by EDS. Therefore, it is certain that these are Ni particles, and the suggestion in the previous work that the Ni comes out of the matrix during the activation is pertinent. This phenomenon for the Ni coming out from the matrix appears similar to the solid phase crystallization mentioned in the introduction.

Failure of observation of NiO and Ni phases by XRD can be elucidated from these outcomes. One reason is surely that the particle size was too small to detect by XRD. Another reason may be due to the small amount of Ni, amounting to less than a few wt %.

2. TPR Results

Fig. 2 shows the TPR result for SrNiA(10/2). Hydrogen consumption started at around 560 K and there appeared at least four peaks (the fast decrease up to about 550 K for SrNiA(10/2) is the baseline drifting).

For SrNiA(10/2), the first peak at 645 K is considered due to reduction of free NiO, according to earlier works [Dong et al., 2002; Liu et al., 2002b; Roh et al., 2001a, b]. The second and third peaks

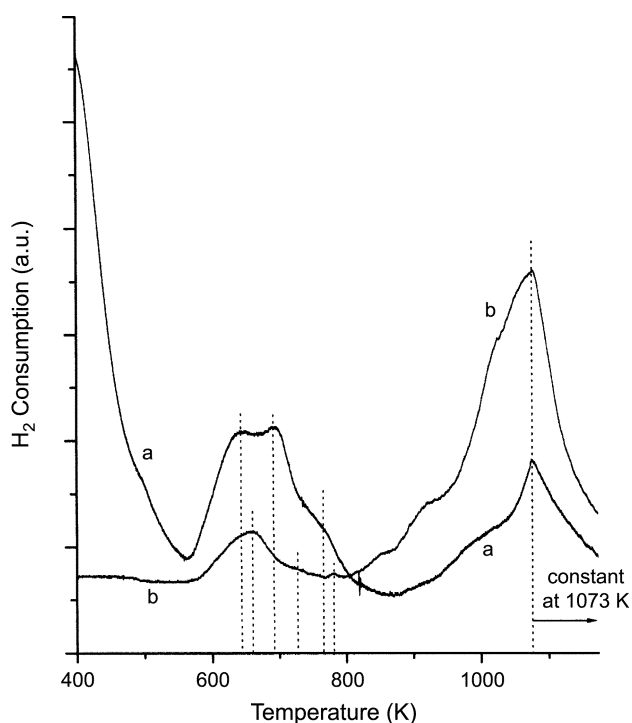


Fig. 2. TPR patterns for (a) SrNiA(10/2) and (b) SrNiA(10/24).

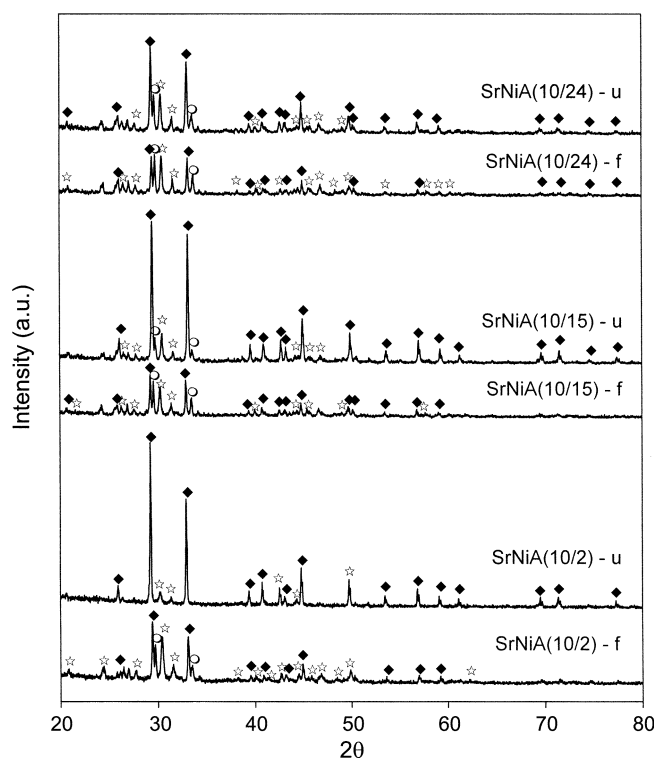


Fig. 3. XRD patterns of fresh and used SrNiA(10/t) catalysts (☆: the apatite $[\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2 + \text{Sr}_{10-y}\text{Ni}_y(\text{PO}_4)_6(\text{OH})_2]$; ◆: $\text{Sr}_3(\text{PO}_4)_2$; ○: $\text{Sr}_{3-x}\text{Ni}_x(\text{PO}_4)_2$).

at around 690 and 765 K are attributable to nickel species that are less easily reducible than the above NiO. One might think that the second peak would be attributable to very fine NiO particles that have a stronger interaction with the substrate (strontium hydroxyapatite and strontium phosphate) than the larger NiO particles. However, since the presence of very fine particles of a few nanometers, especially of needle shape, in the fresh sample was not observed by HRTEM, this is not considered to be the case. Instead, they may be assigned to the nickel ions substituting Sr^{2+} in the strontium hydroxyapatite and phosphate structures. Although presence of a strontium nickel hydroxyapatite phase, in which a part of Sr^{2+} was substituted with Ni^{2+} , could not be identified by XRD (Fig. 3), this does not necessarily rule out its presence if the XRD patterns of strontium hydroxyapatite and strontium nickel hydroxyapatite are almost the same (note: there are no diffraction files for strontium nickel hydroxyapatite in JCPDS). Rather, the presence of strontium nickel phosphate strongly supports the possible presence of the strontium nickel hydroxyapatite because the substituting chemistry would be the same (Sr and Ni have the same oxidation number of +2) [Belik et al., 2001]. Therefore, it would be more accurate to consider that the apatite phase actually consists of strontium hydroxyapatite and strontium nickel hydroxyapatite. The OH-Ni-O-PO_3^- structure in the apatite is considered to be chemically less stable than the $-\text{PO}_3-\text{O-Ni-O-PO}_3^-$ structure in the phosphate when comparing the OH-Ni- and $-\text{PO}_3-\text{O-Ni-}$ structures, and hence the second peak is attributable to the Ni in the former structure. The amount of the nickel in the apatite structure is at least two times larger than that in the phosphate structure. This seems to be in agreement with the disap-

pearance of the apatite phase after the POM reaction, since the initial amount of the apatite appears larger than that of the strontium nickel phosphate as seen by the XRD results [Fig. 3, for SrNiA(10/2)]. Hence, this strongly supports the above suggestion that the fine nickel particles are formed from the Ni species coming out of the apatite and phosphate structures.

When only methane and oxygen were flowing, the catalyst activation temperature was around 850 K [Lee et al., 2002]. When considering the difference in the reducing ability between hydrogen and methane-oxygen, this activation temperature is not considered to be so higher than those reduction temperatures observed in the TPR.

The peak at 1,073 K is attributed surely to a species that is much more difficult to reduce. One plausible explanation is that this is due to reduction of phosphate, for instance transformation of orthophosphate (PO_4^{3-}) to pyrophosphate ($\text{P}_2\text{O}_7^{4-}$, or $\text{PO}_3\text{-O-PO}_3$), or reduction of SrO.

3. Effect of Calcination Time

Fig. 2 also shows the TPR result for SrNiA(10/24), which experienced a longer calcination time. The first peak became broader and its highest point appeared at around 660 K, which was about 15 degrees higher than the corresponding one for SrNiA(10/2). This peak is also due to the reduction of free NiO. The reason for the higher temperature and broader peak is considered to be because of the enlarged particles (or sintering) owing to the longer calcination. That is, it will take more time for the larger particles, especially NiO in the core, to be reduced completely. There might be a stronger interaction between NiO and the substrate owing to the longer calcination, but it did not seem to happen because the interaction would instead be weakened if the particle size increased. It is noteworthy that the second and third peaks became much smaller and appeared at the temperatures higher by 35 and 15 degrees, respectively, than the corresponding ones for SrNiA(10/2). This reflects that the crystallites of strontium nickel hydroxyapatite and phosphate would have become larger or more crystalline due to the longer calcination. This argument will be further discussed and verified below by employing the XRD and reaction results. The larger amount of what was reduced at around 1,073 K is consistent with the suggestion in the above paragraph. That is, due to the longer calcination, more phosphate (including the apatite) would have been crystallized, or more SrO would have been formed (note: when strontium nickel phosphate is formed, there may be surplus Sr which is not combined with the phosphate group).

Fig. 3 shows the XRD patterns of SrNiA(10/*t*) catalysts prepared with different calcination time *t*. It is certain that the apatite phase is transformed, to a more or less extent depending on the calcination time, to strontium phosphate under reducing environment during the reaction. Fig. 4 compares the relative amount of the third phase, $\text{Sr}_{3-x}\text{Ni}_x(\text{PO}_4)_2$, in the three SrNiA(10/*t*) catalysts. The relative amount was presented by the ratio of the intensity of the most intense XRD peak of the strontium nickel phosphate phase [I_3 for (015) plane] to the intensity sum of the most intense peaks of the phosphate and the apatite phases [I_1 for (015) plane + I_2 for (211) plane].

The strontium nickel phosphate phase was present in all the fresh catalysts. The relative amount of this phase became larger as the calcination time increased. After the POM reaction, the third phase

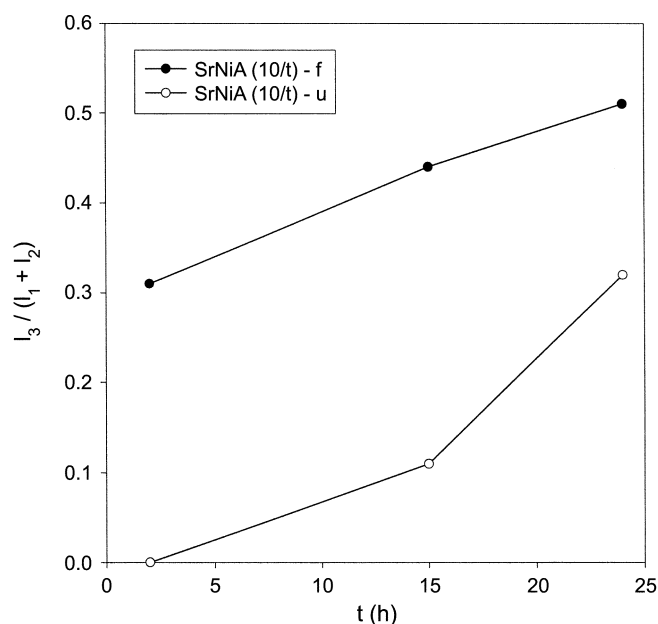


Fig. 4. Relative peak intensities of $\text{Sr}_{3-x}\text{Ni}_x(\text{PO}_4)_2$ with respect to the sum of $\text{Sr}_3(\text{PO}_4)_2$ and the apatite phases in the fresh and used catalysts with different calcination time.

almost entirely disappeared in SrNiA(10/2)-u. In SrNiA(10/15)-u and SrNiA(10/24)-u, however, significant amounts of this phase were still remaining, and the amount in the latter sample was larger than that in the former sample. The same trend was observed for the apatite phase. These results indicate that the amounts of the strontium nickel phosphate and the apatite become larger with the calcination time or the grain size of the crystallites becomes larger or the crystallization is achieved to a greater extent. As a consequence, the Ni ions in the matrix of larger or more crystalline crystallites

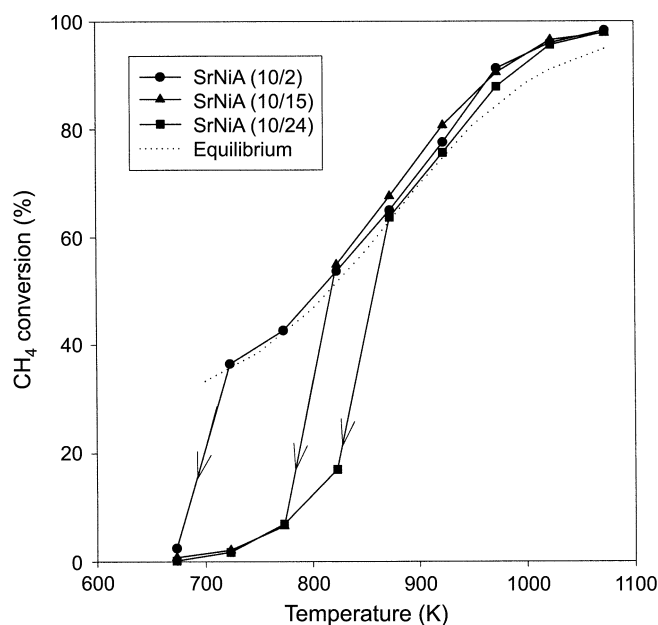


Fig. 5. CH_4 conversion vs. temperature over SrNiA(10/*t*) catalysts with different calcination time *t*.

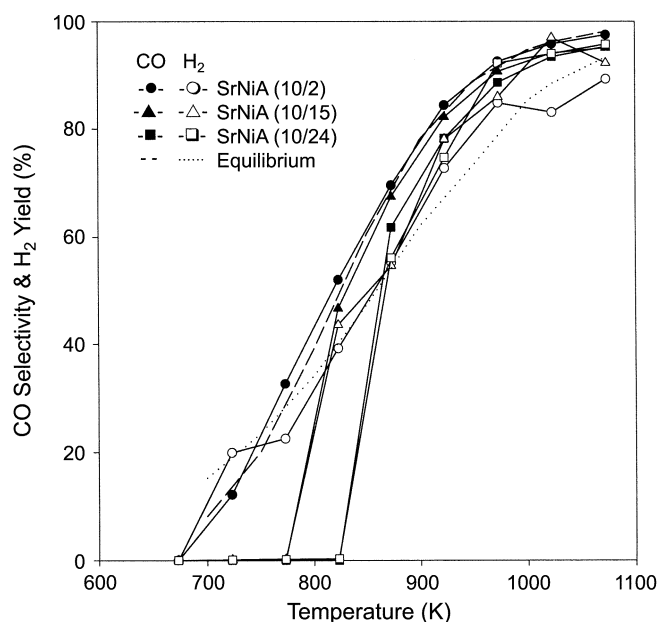


Fig. 6. CO selectivity (closed symbols) and H_2 yield (open symbols) vs. temperature over $SrNiA(10/t)$ catalysts with different calcination time.

will have a greater difficulty in coming out of the matrix, at least due to the physical reason. Hence, it is expected that the amount of Ni at the surface of the catalyst becomes smaller as the calcination time increases.

Figs. 5 and 6 show the results of the POM reaction experiments. The CO selectivity is defined here as (moles of CO produced)/(moles of CH_4 consumed). The H_2 yield is defined as (moles of H_2 produced)/[2×(moles of CH_4 fed)]. Above 873 K, the differences between the catalysts were negligible or quite small because the values were close to the equilibrium values. However, the temperature at which the activity dropped abruptly became higher as the calcination time increased. The abrupt decrease is due to total re-oxidation of metallic Ni surfaces, resulting in loss of POM selectivity and only the complete oxidation occurring. This has been observed in the previous work [Lee et al., 2002] as well as by several investigators [Dissanayake et al., 1991, 1993; van Looij and Geus, 1997]. The reason why the total re-oxidation temperature becomes higher with the calcination time is certainly because the amount of Ni at the surface becomes smaller with the calcination time. This again proves that the discussion in the above paragraph is valid.

CONCLUSIONS

Ni-strontium phosphate exhibited excellent activity and selectivity in POM. Likewise to the presence of both the strontium phosphate and strontium nickel phosphate phases, the hydroxyapatite phase in the fresh sample was considered to consist of strontium hydroxyapatite and strontium nickel hydroxyapatite. The catalytic activity was attributed to the fine Ni metal particles, which were formed from the Ni ions coming out of the strontium nickel phosphate and strontium nickel hydroxyapatite and being reduced during the reaction. TEM, TPR and XRD results verified this conclusion. TEM showed that many fine particles of a few nanometers in

needle and round shapes were present in the used sample while they were not observed in the fresh sample. As the calcination time increased, the crystallite size or the extent of crystallization seemed to become greater, resulting in a smaller amount of Ni at the surface and thus poorer catalytic performance, that is, higher total re-oxidation temperature.

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