Ni/(Rare Earth Phosphate) as a New Effective Catalyst for Autothermal Reforming of Methane

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The stability of metal phosphate during H_2 reduction is one of the critical factors that determine the catalytic behavior of Ni/(metal phosphate) in CH_4 autothermal reforming. Ni/(rare earth phosphate), particularly Ni/(Gd, Ce, or $ErPO_4$), has been found to be a new family of effective catalysts.

Hydrogen-based fuel cells are an attractive alternative to conventional combustion engines because of their higher efficiency, which in turn leads to a reduction of CO_2 emissions. Further, fuel cells generate lower atmospheric emissions such as CO, NO*x*, and SO*x*. Owing to the advances in fuel-cell technology, the demand for new catalysts for the production of hydrogen has increased. CH_4 autothermal reforming with H_2O and air is an effective alternative for steam reforming of the fuel for fuel-cell feeds.[1] This is because it does not require the supply of a large amount of external heat. Further, the cost involved in the oxygen/nitrogen separation can be avoided for this application.

Usually, Ni, which is an active species for hydrocarbon reforming, is supported on metal oxides. Recently, a few reports revealed the availability of non-oxide supports, i.e., metal phosphate/hydroxyapatite.[1–3] However, only limited types of metal phosphates—Al, Ca, and Sr—were used in these reports; and the SV values were extremely low from the viewpoint of application to fuel cells. Therefore, Ni was supported on various types of metal phosphates and their availability for CH_4 autothermal reforming was investigated at a high SV of 204 L/(h·g).

Metal phosphates were prepared by the precipitation of the corresponding nitrates by 85% orthophosphoric acid.[4] The metal phosphates were calcined at 1073 K in static air before impregnation with $Ni(NO_3)_2 \cdot 6H_2O$ by incipient wetness methods. Nickel loading was set to 20 wt %. The samples were dried at room temperature and at 373 K, followed by calcination at 673 K in flowing air. The catalyst weighing 50 mg was loaded into a tubular inconel reactor passivated with an aluminum diffusion coating and held between quartz wool plugs. After the catalysts were reduced in H_2 at 1073 K for 1 h followed by Ar purge, a $CH_4/O_2/Ar/H_2O$ mixture ($CH_4/O_2/Ar/H_2O = 2/1/4/2$, SV = 204 L/(h·g)) was passed over the catalyst. Note that the feed composition was determined by assuming the total conversion of CO to CO_2 in the entire set of catalytic reactions ($CH_4 + 0.5O_2 + H_2O \rightarrow CO_2 + 3H_2$). A thermocouple was placed at the outside of the reactor and was used to control the oven temperature. The reaction products were analyzed by two gas chromatographs with a thermal conductivity detector (TCD) equipped with a Porapak Q column and Molecular sieve 13X. The catalysts were characterized by XRD and the amounts of carbonaceous species were quantified by temperature-programmed oxidation (TPO).

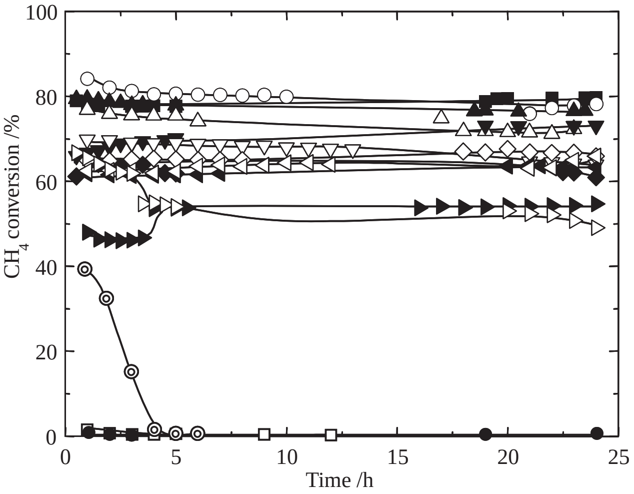

Figure 1. CH_4 conversion vs time on stream for 20 wt % Ni/(metal phosphate) catalysts at 1073 K. (■) Gd; (○) Ce; (▲) Er; (△) Pr; (▼) Sm; (▽) Sr; (◆) Y; (◇) Nd; (◀) Dy; (◁) La; (▶) Mg; (▷) Al; (◎) Zr; (□) Ca; (●) Ga.

Activities and stabilities of Ni/(metal phosphate) catalysts were tested and the results are presented in Figure 1. At the condition, equilibrium CH_4 conversion is >99%. Note that the H_2 yields of the catalysts also displayed the same tendencies as the CH_4 conversions (not shown). In the figure, a marked difference in the catalytic behavior was observed. All the catalysts including rare earth or Sr exhibited high initial CH_4 conversions (above 60%) and high stabilities for 24 h. In addition, note that only $Ni/Sr_3(PO_4)_2$ exhibited a relatively good performance as a support among the alkaline earth metal phosphates, whereas all Ni/(rare earth phosphate) catalysts studied showed a good performance. In particular, it was observed that Ni/(Gd, Ce, or $ErPO_4$) maintained a high CH_4 conversion (above 75%) during the reaction for 24 h. Additionally, it must be emphasized that $Ni/CePO_4$ maintained the high activity for 50 h, and maximal H_2 formation rate reached 85.6 L/(h·g). These results reveal Ni/(Rare earth phosphate) to be a new family of effective catalysts for CH_4 autothermal reforming. On the other hand, $Ni/AlPO_4$ gradually deactivated up to 74% of the initial value, and the catalysts including Zr, Ca, and Ga were deactivated/inactive and did not show any activity eventually.

In order to understand the characteristics critical to catalytic behavior, XRD measurements were performed for selected catalysts after different treatments (Figure 2). After the calcination at 673 K, the peaks for NiO and each metal phosphate of the supporting material were observed (not shown). It must be mentioned that the catalyst support phase for $Ni/Ca_2P_2O_7$ was pyro-

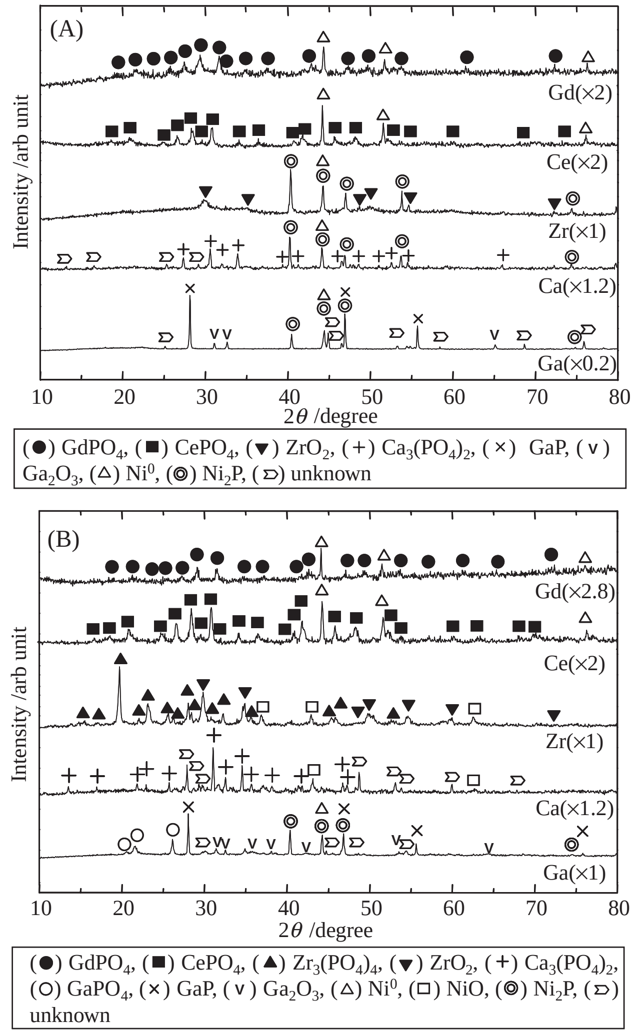

Figure 2. XRD patterns for selected 20 wt % Ni/(metal phosphate) catalyst after H_2 reduction at 1073 K (A), and the subsequent reaction (B).

phosphate and not orthophosphate; however, only the orthophosphate support phase was visible in the remaining catalysts. H_2 reduction and the subsequent CH_4 autothermal reforming brought about various influences on the Ni species and support materials of these catalysts. In the case where Ni/(Gd or $CePO_4$) displayed high and stable activities in the reaction, NiO was reduced to metallic Ni by the H_2 reduction. Further, the state remained unchanged during the reaction, and orthophosphates were retained until the end of the reaction. On the other hand, in the case of the remaining catalysts, which were inactive or completely deactivated during the reaction, Ni phosphide species (Ni_2P or Ni_3P) were formed in addition to trace amounts of Ni^0 during the H_2 reduction. Formation of Ni phosphide species must have been induced by the loss of phosphorous from the support materials during H_2 reduction; this was identified by the observation of oxides (ZrO_2 or Ga_2O_3) consisting of support materials or orthophosphate ($Ca_3(PO_4)_2$) (Figure 2a). After the following reaction, NiO was the only Ni species observed by XRD measurements for the Ni/($Zr_3(PO_4)_4$ or $Ca_2P_2O_7$), whereas only Ni_2P was visible for the Ni/$GaPO_4$. It is possible that O_2 or H_2O in the reactant converted Ni phosphide species to NiO. However, it is still unknown why Ni phosphide species on $Zr_3(PO_4)_4$ and $Ca_2P_2O_7$ were converted to NiO, whereas Ni_2P on $GaPO_4$ did not induce such a change. Further research is necessary in order to clarify this point. Usually, the deactivation of a reforming catalyst occurs owing to coking on the active sites, oxidation of metal, and/or sintering of metal. Hence, TPO was carried out for these catalysts after the reaction. The amounts of carbonaceous species on the catalysts were less than 0.25 wt %; this revealed that the main cause of the low activities was not coking. Therefore, we concluded that the inactive/deactivation nature was attributed to the formation of inactive Ni phosphide species and occasionally that of NiO under the reaction condition. Since it was apparent that the formation of Ni phosphide species was brought about by the destruction of support phosphate (loss of phosphorous) during H_2 reduction, it has been suggested that the stability of metal phosphate against the reduction treatment at high temperature is a crucial factor for the determination of catalytic behavior.

TPO was also carried out for the Ni/(Gd or $CePO_4$) after the reaction for 24 h. The amounts of carbonaceous species were 0.13 and 0.16 wt % for Ni/$GdPO_4$ and Ni/$CePO_4$, respectively. These results revealed a strong coking resistant nature of these catalysts.

We have revealed that the stability of the metal phosphate under H_2 reduction is one of the critical factors that determine the catalytic behavior of Ni/(metal phosphate) in CH_4 autothermal reforming. It has been found that Ni/(rare earth phosphate), particularly Gd, Ce, or $ErPO_4$, is a promising catalyst with high and stable activities. The catalysts also exhibited an extremely strong resistant nature against coking. Potential advantage of rare earth phosphates is their low reactivity with Ni under oxidative condition, where the catalysts were exposed for shutdown and restart of the fuel-cell system. In general, metal oxides react with Ni, and results in complex oxide or solid solution which is difficult to be reduced by reductive, CH_4, in the reactant. However, NiO was the only species detected in case of Ni/(rare earth phosphate) catalysts after O_2/N_2 treatment at 1073 K following to H_2 reduction at the same temperature (not shown). Since the preparation method of metal catalysts supported on metal phosphate is yet to be established, the research on optimizing the preparation method is in progress. The knowledge obtained in the current study can be applied to the design of various rare-earth-phosphate-supported non-noble metal catalysts for the reforming reactions of hydrocarbons.

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