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Catalytic autothermal reforming of propane over the noble metal-doped hydrotalcite-type catalysts

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ABSTRACT

This study examined the propane reforming performance of noble metal-doped hydrotalcite-type catalysts in a continuous flow fixed-bed catalytic reactor for autothermal reforming. Hydrotalcite-type catalysts were prepared by co-precipitation and were modified by the addition of noble metals, such as Pt, Pd, and Ru. The noble metal-doped hydrotalcite-type catalysts showed better propane reforming performances than the Ni/MgAl catalyst due to the more abundant distribution of Ni catalyst particles and the lower level of carbon deposition. In the case of the hydrotalcite-type catalyst prepared using a mixed solvent of water and alcohol, the reforming activity increased due to an increase in the degree of dispersion and better thermal stability. Propane autothermal reforming over the noble metal-doped hydrotalcite-type catalysts showed higher reforming performance, better stability and less carbon deposition, which highlights their feasibility for hydrogen production from hydrocarbons.

1. Introduction

Hydrogen is one of the major feedstocks in many chemical and petrochemical industries, and is considered as one of the pollution-free primary energy carriers and electricity generation sources for future transportation fuels. It has the highest energy density among non-nuclear fuels and can be easily converted to electrical and thermal energy [1–5]. Hydrogen can either be generated on-site or provided in storage tanks through liquefaction, gas compression, or other storage technologies. The on-site production of hydrogen requires the development of cost-effective technologies, which are affected by the hydrogen efficiency, system size, weight, start-up time, and life time.

The reforming via fuel processes utilizing different hydrocarbons is considered one of the solutions for the hydrogen production [6–9]. Steam reforming (SR), partial oxidation reforming (POX), and autothermal reforming (ATR) are currently used for hydrocarbon reforming. SR is a highly endothermic process that demands an efficient heat supply to the system, which is usually operated at 850–950 °C on Ni-based catalysts. The present SR technology approaches 90% of the maximum thermodynamic efficiency. However, SR is an economically unattractive option for the low-volume and low-pressure production of hydrogen. POX has the greatest fuel-type flexibility with an exothermal reaction using pure oxygen. However, it has disadvantages due to the lowest H_2 yield and high level of pollutant emission [10,11].

Among the hydrocarbon reforming processes, ATR has attracted considerable attentions in recent years as a potential viable process for hydrogen generation of fuel cell systems due to the lower operation temperature, easier start-up, and wider choice of materials. Moreover, it has a higher energy efficiency than SR or POX due to the low energy requirement, high GHSV (gas-hourly space velocity), lower process temperature, and easily regulated H_2/CO ratio [12,13].

Current research efforts on ATR have focused on the development of catalysts to improve the activity, yield, and stability under a realistic range of operating conditions [14]. The use of mixed oxides derived from hydrotalcite-type catalysts has potential applications in hydrocarbon reforming because the highly dispersed and homogeneously distributed metal particles provide higher catalytic stability [15–17]. Hydrotalcites, a family of anionic clays, are lamellar compounds of magnesium and aluminum hydroxides with interlayer spaces containing exchangeable anions. In addition, they have advantages in that the active site properties, catalyst structure and stability can be controlled through various ion exchanges. The large surface area, acid–base and redox properties are the most interesting properties of these materials, which depend on the nature of incorporated cations, thermal stability, and homogeneous inter-dispersion of elements. Hydrotalcite-type catalysts can be applied to a variety of reactions

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including reforming, NO_x reduction, methylamine production, etc. [18–20].

The hydrocarbon reforming results were rarely reported in the noble metal-doped hydrotalcite-type catalysts at high temperature up to 700 °C. Also, the mixed solvent effect on the characteristic and reforming performances was not found in the noble metal-doped hydrotalcite catalysts as far as we know. In this study, the influence of noble metal (Pt, Rh, and Pd) doping on the properties of the hydrotalcite-type catalysts and reforming performance was investigated. In addition, the properties of the noble metal-doped hydrotalcite-type catalysts prepared by a mixture of water and alcohol were characterized in terms of the degree of dispersion and thermal stability. The propane ATR performances of the hydrotalcite-type catalysts were evaluated by measuring the propane conversion and H_2 yield in a continuous fixed-bed reactor at higher temperatures ranging from 300 to 700 °C.

2. Experimental

2.1. Preparation of catalysts

The tertiary metal hydrotalcite-type catalyst, Ni(15%)/MgAl, was prepared by co-precipitation. A mixed aqueous solution of Mg and Al nitrates was stirred for 1 h at a constant temperature of 60 °C, and then dropped into an aqueous solution of Na_2CO_3. The solution pH was adjusted to 10 with 1 N NaOH. The solution containing the precipitates was aged at 60 °C for 18 h. The precipitates were then dried in a rotary evaporator at 100 °C after washing with distilled water and filtration. The resulting precipitates were calcined at 600 °C for 3 h in air to form powders of the catalyst precursors for noble metal-doping. The noble metal-doped hydrotalcites were prepared by co-precipitation using mixed aqueous solutions of the respective noble metals salts (Pt, Pd, and Ru) in the solution dissolved with the precursor for Ni/MgAl. $Ni(NO_3)_2{\cdot}6H_2O$ (Aldrich), $Mg(NO_3)_2{\cdot}6H_2O$ (Junsei), and $Al(NO_3)_2{\cdot}9H_2O$ (Wako Pure) were used as metal precursors. And, $Pt(NH_3)_4{\cdot}(NO_3)_2$ (Aldrich), $Pd(NO_3)_2$ (Kanto), and $RuCl_3{\cdot}3H_2O$ (Kojima) were used as precursors for Pt, Pd, and Ru, respectively.

2.2. Characterization of the catalysts

The chemical structures of the catalysts were examined by the powder X-ray diffraction (XRD, Rigaku powder diffraction unit, DMAX 100) with mono-chromatized Cu Kα radiation. The diffraction pattern was identified by comparison with those supplied from the JCPDS (Joint Committee of Powder Diffraction Standards) data base. The level of carbon deposition on the catalyst surface was analyzed using a thermal gravimetric analyzer (TGA/SDTA 851^e, Mettler Toledo). The SEM measurements were performed using a field emission scanning electron microscope (S-4700, Hitachi, Japan) at an accelerating voltage of 200 kV. The metal particle distribution of the catalysts was determined by analyzing the TEM images (JEN-2000FXII, JEOL, Japan) at an accelerating voltage of 200 kV.

2.3. Catalytic activity

The activity measurements were performed in a continuous flow fixed-bed catalytic reactor at atmospheric pressure. Five hundred milligrams of the catalyst was placed in a quartz glass tube with a 16 mm i.d. The temperature of the catalytic reactor was measured using Cr–Al thermocouples. Steam was supplied by heating distilled water in a pre-heater. Fig. 1 shows the experimental setup for the catalytic reaction. The reaction tests were carried out using a feed of $H_2O/C = 3.0$ and $C/O_2 = 2.7$ at a GHSV of 9600 $ml/g_{cat}h$. The reaction temperatures were varied from 300 to 700 °C. The reaction products were analyzed on-line using a DS 6200 gas chromatograph (Donam, Korea) with Ar carrier gas, a thermal conductivity detector, and Porapak Q column (2 m, 1/8 in. i.d.) and 5A molecular sieves.

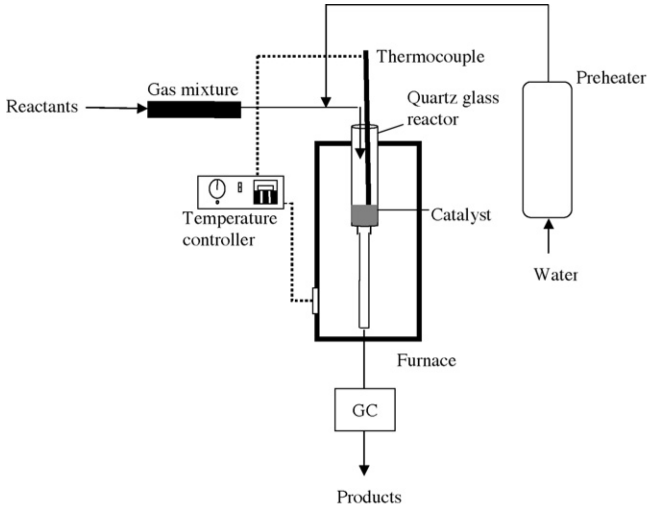


Fig. 1. Schematic diagram of the experimental setup for propane reforming.

3. Results and discussion

3.1. Characterization of the hydrotalcite catalysts

Fig. 2 shows the XRD patterns of the hydrotalcites. The diffraction peaks for the MgAl hydrotalcite-type precursor were observed after drying. The intensity of some of the characteristic hydrotalcite peaks decreased due to water extraction after calcination, while peaks for spinel structures (NiO or MgNiO) were observed in the figure. In the case of the noble metal-doped hydrotalcite, the XRD patterns were similar to those of the calcined Ni/MgAl.

Fig. 3 shows SEM images of the Ni/MgAl and Pt-Ni/MgAl catalysts co-precipitated at pH 10. The Pt-Ni/MgAl catalyst, which consists of hydrotalcite according to the XRD, had a plate-like morphology, as expected from its layered structure in Fig. 3(b). On the other

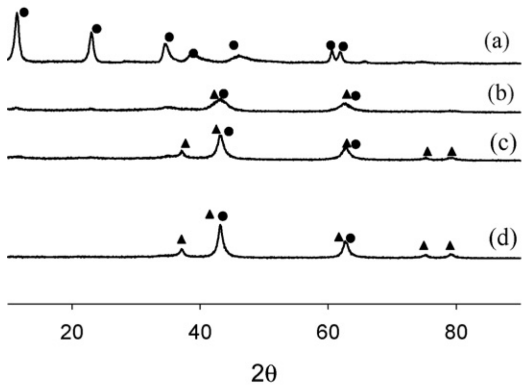
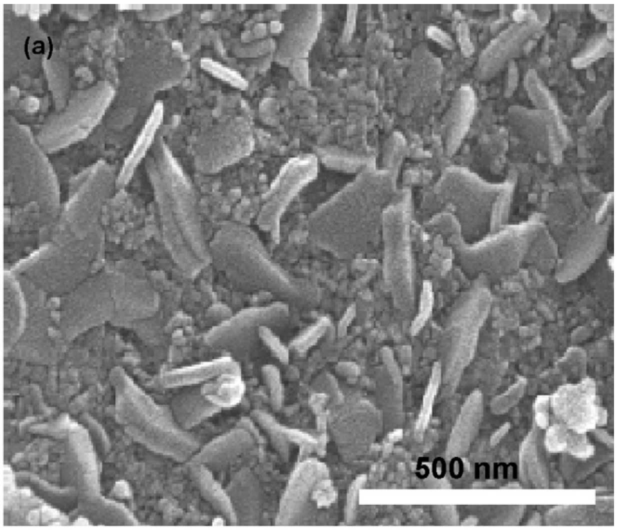


Fig. 2. XRD patterns of the hydrotalcite-type catalysts (Mg–Al after drying (a), Mg–Al after calcinations (b), Ni/MgAl after calcinations (c), and Pd/Ni/MgAl after calcinations (d)). Hydrotalcite (●) and MgNiO or NiO (▲).



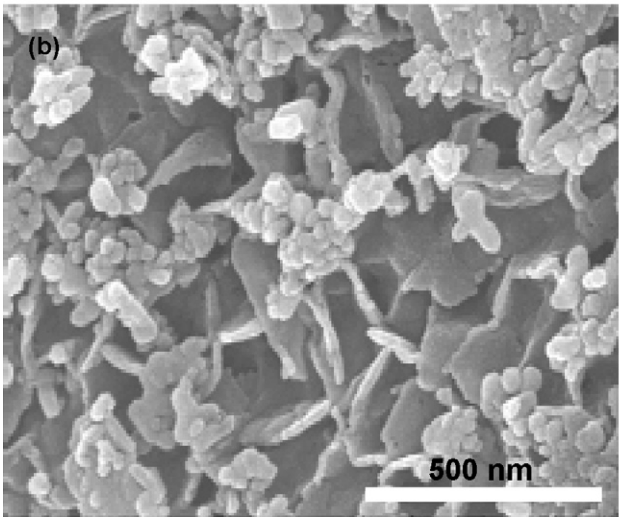


Fig. 3. SEM images of the fresh Ni/MgAl and Pt-Ni/MgAl catalyst. (a) Fresh Ni/MgAl catalyst and (b) fresh Pt-Ni/MgAl catalyst.

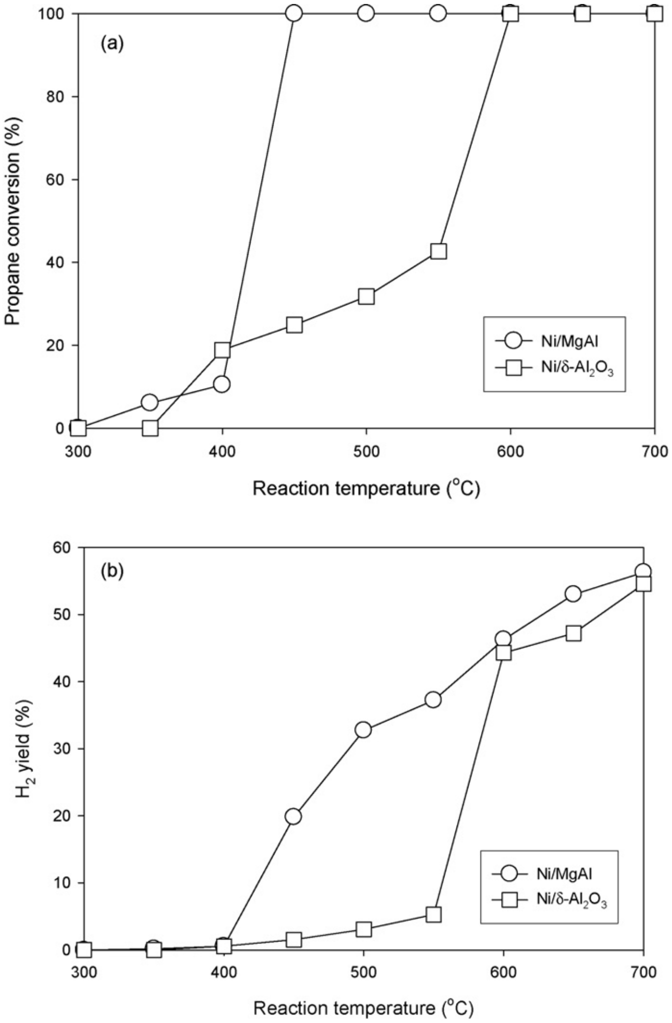


Fig. 4. Comparison of the propane reforming performances for the Ni/MgAl and Ni/δ-Al_2O_3 catalysts. (a) Propane conversion in the products and (b) H_2 yield in the products.

hand, the Ni/MgAl in Fig. 3(a) shows an agglomerated morphology of small-sized particles.

3.2. Effect of noble metal doping on the catalyst activity

Fig. 4 shows the catalyst activity of Ni/MgAl and a Ni catalyst prepared on alumina (Ni/δ-Al_2O_3). Propane conversion on the Ni/δ-Al_2O_3 catalyst began at >400 °C with the propane degrading completely at 600 °C in Fig. 4(a). On the other hand, the propane with the hydrotalcite-type catalyst began to convert at lower temperatures than with Ni/δ-Al_2O_3 and complete conversion occurred at approximately 450 °C. Fig. 4(b) shows the H_2 yield for the Ni/MgAl and Ni/δ-Al_2O_3 catalysts. The Ni/δ-Al_2O_3 catalyst showed below 10% H_2 yield at lower temperatures than 550 °C, while the Ni/MgAl catalyst showed above 20% conversion, even at 450 °C. The higher performances of the Ni/MgAl catalyst is related to more thermal stability and less carbon adsorption than the alumina catalyst, Ni/δ-Al_2O_3. It was observed in the TGA sequence after reaction during 20 h that the Ni/MgAl hydrotalcite-like catalyst had lower weight loss than the alumina catalyst due to lower carbon deposition, giving low deactivation effect of catalyst activity [21].

The activity of the noble metal-doped catalysts was tested in a continuous flow fixed-bed catalytic reactor. Fig. 5(a) shows the propane conversion of the 5% noble metal (Pt, Pd, and Ru)-doped Ni (15%)/MgAl. The propane conversion on the Pd-Ni/MgAl catalyst was similar to that of Ni/MgAl, which shows that propane began to convert from 350 to 400 °C and reached 100% at approximately 400 °C. In contrast, propane conversion on the Pt-Ni/MgAl catalyst began at a lower temperature of 300 °C, showing the highest activity among the catalysts examined. All the catalysts examined showed 100% propane conversion at higher temperatures than 450 °C. The order of the propane conversion from highest to lowest was Pt-Ni/MgAl > Ru-Ni/MgAl > Pd-Ni/MgAl.

The noble metal-doped catalysts showed a H_2 yield of 10–20% at lower temperature than 400 °C in Fig. 5(b). The H_2 yield reached approximately 50–60%, irrespective of the catalysts used. The order of the H_2 yield from highest to lowest was Pt-Ni/MgAl > Ru-Ni/MgAl ≅ Pd-Ni/MgAl. Considering the propane conversion and the H_2 yield, Pt-Ni/MgAl has higher than the other two catalysts. The propane ATR results on the metal-doped catalysts suggest that the higher activity of the noble metal-doped catalysts is related to the higher surface area, more abundantly distributed Ni and higher H_2 adsorption. The BET surface area and the total pore volume of the

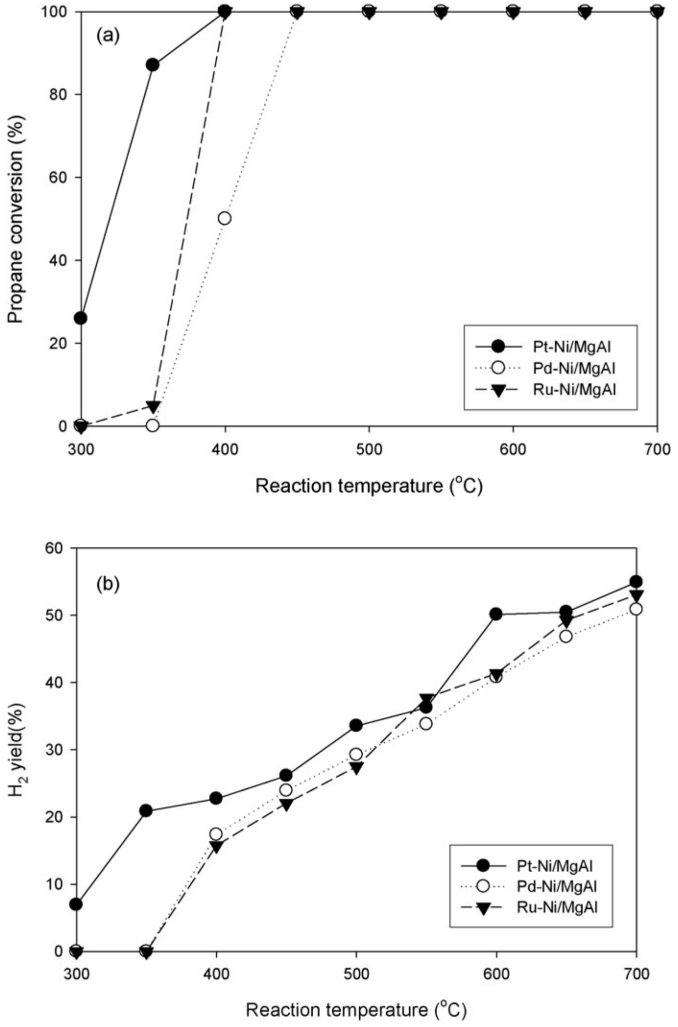


Fig. 5. Propane conversion over M(0.5)-Ni/MgAl hydrotalcite-type catalysts (M = Pt, Ru, and Pd). (a) Propane conversion in the products and (b) H_2 yield in the products.

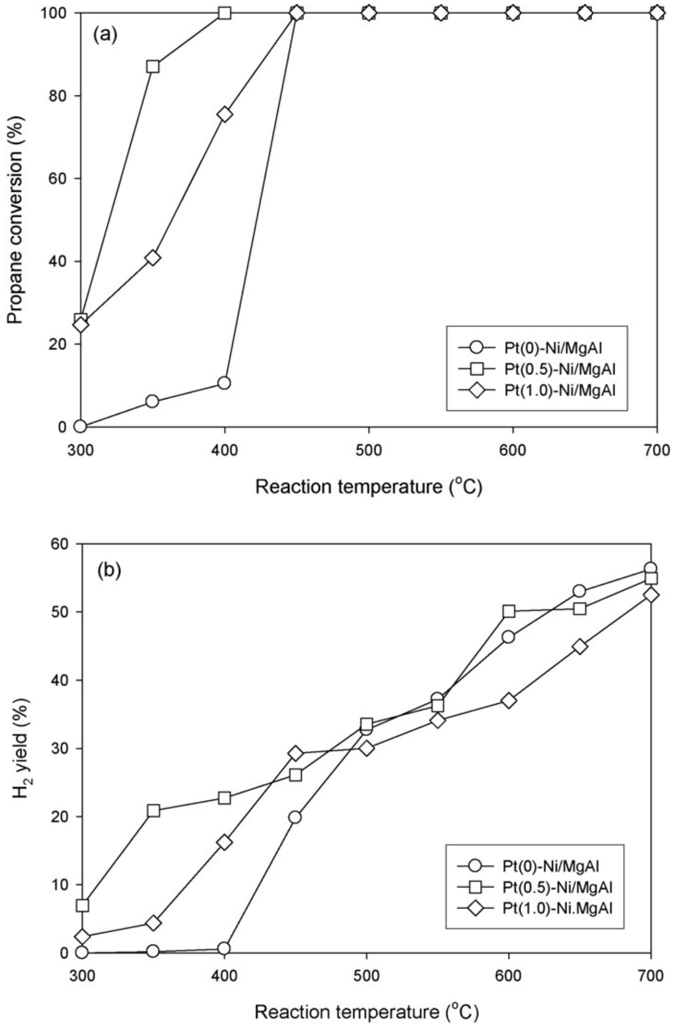


Fig. 6. Influence of the doping level on the propane reforming performance. (a) Propane conversion in the products and (b) H_2 yield in the products.

Pt-Ni/MgAl catalyst were measured to 168.5 m^2/g and 0.083 cm^3/g, much larger than those of Ni/MgAl (134.0 m^2/g and 0.065 cm^3/g) [22]. It is known that novel metal ions are preferentially solved in the layer-type phase to improve stability and resistance to the coke deposition [23,24]. The higher activity in the Pt-doped hydrotalcite-type catalyst is related to the preferential solution in the ternary Ni/MgAl which increases H_2 adsorption on the catalyst surface.

In order to determine the influence of the doped level on the catalyst activity, the Pt-doped Ni/MgAl catalysts were prepared with different Pt concentrations. Fig. 6 shows the propane conversion and H_2 yield for the Pt-Ni/MgAl catalyst. In the figure, the 0.5% Pt-doped catalysts showed the highest catalytic activity. The Pt(1.0)-Ni/MgAl result suggests that an increase in the amount of deposited Pt on the Ni catalyst surface would decrease reaction rate due to decrease in the Ni amount in the ternary Ni/MgAl system [24].

In this study, a hydrotalcite-type Pd-Ni/MgAl catalyst was prepared using a mixed solvent of water and ethanol (50%:50%), which is denoted as Pd-s-Ni/MgAl, in order to increase the dispersion of the catalyst. Table 1 shows the propane conversion and H_2 yield for the Ni/MgAl, Pd-Ni/MgAl, and Pd-s-Ni/MgAl catalysts. At a lower temperature, *i.e.*, 450 °C, the Pd-s-Ni/MgAl catalyst showed lower propane conversion than Pd-Ni/MgAl. The propane conversion for the Pd-s-Ni/MgAl catalyst reached 100% at higher temperatures. Interestingly, the H_2 yield of the Pd-s-Ni/MgAl was

Table 1
Propane conversion and hydrogen yield over the hydrotalcite catalysts.

Catalyst	Propane conversion (%)			H_2 yield (%)		
	400 °C	500 °C	700 °C	400 °C	500 °C	700 °C
Ni/MgAl (aqueous phase)	10.47	100	100	0.57	32.7	56.3
Pd-Ni/MgAl (aqueous phase)	50.0	100	100	17.4	29.2	50.9
Pd-s-Ni/MgAl (water:ethanol = 50%:50%)	42.5	100	100	22.5	41.9	56.8

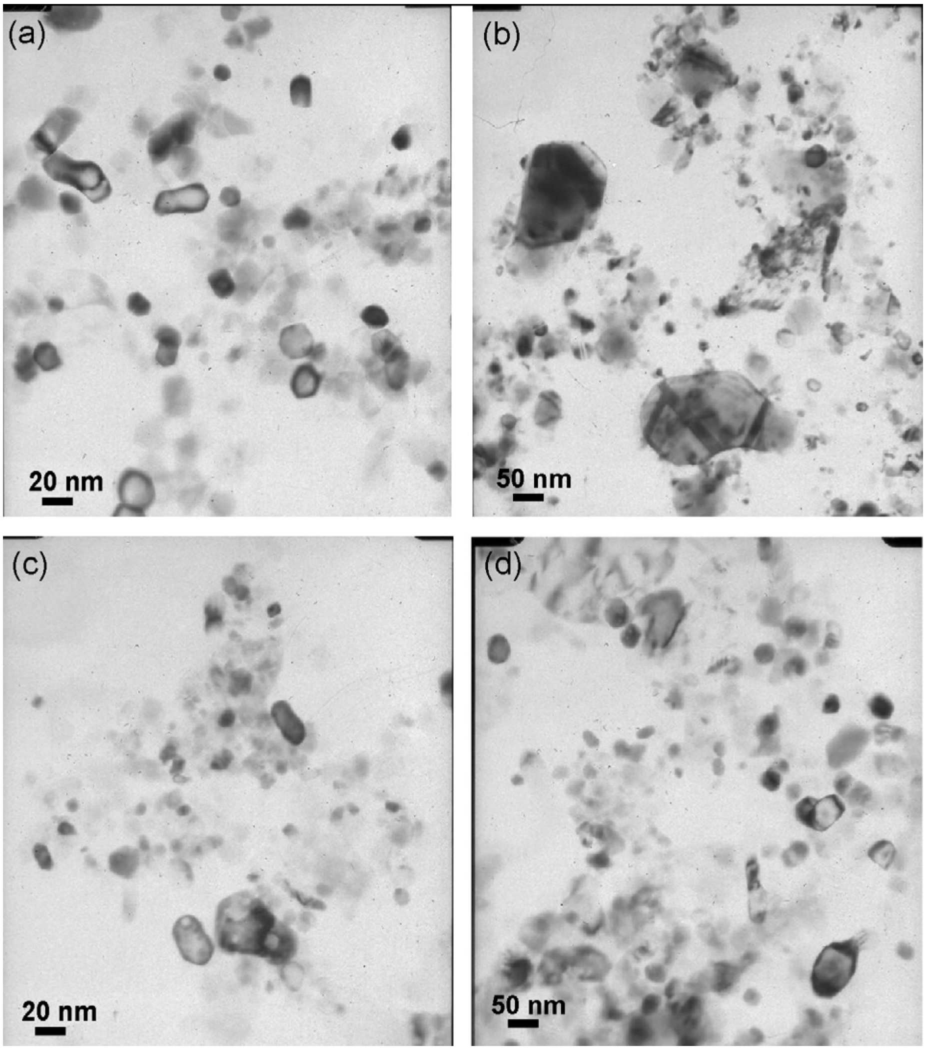


Fig. 7. TEM images of the hydrotalcite-type catalysts (fresh Ni/MgAl (a), reacted Ni/MgAl (b), fresh Pt-Ni/MgAl (c), and reacted Pt-Ni/MgAl (d)).

higher than that of Pd-Ni/MgAl. It is suggested that the Ni in the Pd, Pt compound may be more reducible than the Ni on the hydrotalcite-type catalysts in the presence of the mixed solvent, leading to the formation of small particle on the surface [24]. In addition, less amount of carbon deposition on the surface of the hydrotalcite-type catalysts with the more distributed Ni catalysts increased the reforming performances. It was reported in the previous results that the aggregated Ni particles facilitate the formation of coke residues, which encapsulate or cover metallic Ni particles, and hence the catalyst became deactivated [25].

3.3. *Sustainability of the noble metal-doped catalysts*

The catalyst activity is related to the amount of carbon deposition as well as the dispersion and the particle size. Carbon deposition often has deleterious effects on the stable operation and high conversion of hydrocarbons [25–27]. TEM images of the fresh and reacted catalysts were taken to determine the resistivity of the noble metal-doped catalysts to carbon deposition. Fig. 7 shows TEM images of the fresh and reacted Ni/MgAl and Pt-Ni/MgAl catalysts. The Pt-Ni/MgAl catalyst showed remarkably low levels of carbon deposition compared with Ni/MgAl, which has strong resistivity to carbon deposition.

Carbon deposition on the catalyst surface was analyzed quantitatively by TGA. Fig. 8 shows the TGA results of the Ni/MgAl and Pt(0.5%)-Ni/MgAl after reaction at 700 °C in the continuous fixed-bed reactor. Fig. 8(a) shows 70% of the remaining weight fraction for the fresh Ni/MgAl, meanwhile the reacted catalyst only decreased to 53%. However, the noble metal-doped catalysts showed a slightly lower value (7% difference) at 1000 °C even after reacted, as shown in Fig. 8(b). The TGA analysis results showed that carbon deposition in the Pd-s-Ni/MgAl catalyst rarely occurred during propane reforming, which increased the catalyst activity shown in Table 1.

The performances of the propane ATR over the various catalysts were compared with the reported results in Table 2. The Pt-doped Ni/MgAl catalyst showed better performance than the Ni/MgAl catalyst [27–29]. The higher propane autothermal reforming performance in the hydrotalcite-type catalysts is related to the layered double structures which have large surface area, pore volume and exchangeable anions. In addition, it is thought that the noble metal doping increased the degree of Ni dispersion, thus decreasing level of carbon on the catalyst surface.

Table 2
Propane authothermal reforming performance.

Catalysts/reactor	Catalyst preparation	Reforming conditions	Propane reforming performance (at 400 °C)	Ref
Pt-Ni/δ-Al_2O_3/microreactor (stainless steel, 4 mm i.d.)	Impregnation	350–470 °C $H_2O/C = 7$, $C/O_2 = 2.7$ W/F = 0.51 mg_{cat}s/ml Propane:butane = 50:50	H_2 production 200 μmol/g_{cat}s	[7]
Pt-Ni/δ-Al_2O_3/microreactor (stainless steel, 4 mm i.d.)	Impregnation	350–470 °C $H_2O/C = 3$, $C/O_2 = 1.5$ W/F = 0.51 mg_{cat}s/ml	H_2 production 230 μmol/g_{cat}s	[29]
Pt-Ni/δ-Al_2O_3/microreactor (stainless steel, 4 mm i.d.)	Impregnation	350–470 °C $H_2O/C = 5$, $C/O_2 = 2.12$ W/F = 0.51 mg_{cat}s/ml Propane:butane = 75:25	H_2 production 250 μmol/g_{cat}s	[30]
Ni/α-Al_2O_3/fixed-bed flow reactor (quartz, 16 mm i.d.)	Incipient-wet impregnation	300–700 °C $H/C/O_2 = 3/1/0.37$ GHSV: 9600 ml/g_{cat}h	Conversion: 24% H_2 yield: 0.6%	[31]
Ni/MgAl (hydrotalcite)/fixed-bed flow reactor (quartz, 16 mm i.d.)	Co-precipitation	300–700 °C $H/C/O_2 = 3/1/0.37$ GHSV: 9600 ml/g_{cat}h	Conversion: 10% H_2 yield: 0.6%	[22]
Pt-Ni/MgAl (hydrotalcite)/fixed-bed flow reactor (quartz, 16 mm i.d.)	Co-precipitation	300–700 °C $H/C/O_2 = 3/1/0.37$ GHSV: 9600 ml/g_{cat}h	Conversion: 100% H_2 yield: 18%	This study

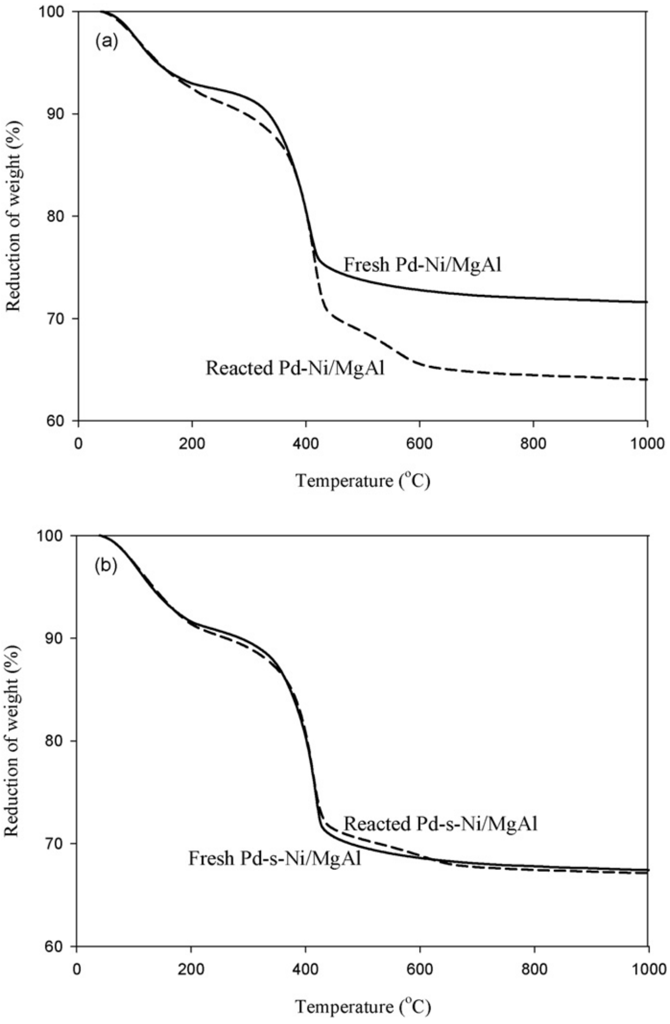


Fig. 8. TGA results of the fresh and reacted hydrotalcite-type catalysts. (a) Pd-Ni/MgAl and (b) Pd-s-Ni/MgAl.

4. Conclusion

The performances of noble metal-doped hydrotalcite-type catalysts in hydrocarbon autothermal reforming for hydrogen production were examined in terms of the conversion and H_2 yield. The catalytic activities were tested in the continuous fixed-bed flow reactor at temperatures ranging from 300 to 700 °C. In the catalytic reaction results, the noble metal-doped hydrotalcite-type catalysts showed higher propane reforming performance due to the more abundantly distributed Ni catalyst particles. The propane performances were affected by the doping level and the type of noble metal used. Thermal gravimetric analysis showed that noble metal doping reduced the level of carbon deposition on the catalyst surface, which enhanced the activity of the hydrotalcite-type catalyst. A mixed solvent of water and alcohol increased the propane reforming performances due to an increase in the degree of dispersion and lower levels of carbon deposition on the catalyst surface. The study showed that the noble metal-doped hydrotalcite-type catalysts increased propane autothermal reforming performances due to higher level of Ni particle dispersion and less carbon deposition on the catalyst surface.

Acknowledgements

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