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# Selective methanation of CO in H<sub>2</sub>-rich gas stream by synthetic nickel-containing smectite based catalysts

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## ABSTRACT

The selective methanation of CO in a H<sub>2</sub>-rich gas stream has been investigated with nickel catalysts including synthetic nickel-containing smectite (SM(Ni)) catalysts undoped and doped with platinum in small quantities and conventional nickel catalysts on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and MgO. The nickel content in SM(Ni) and the nickel loading in the other catalysts were the same, being 35 wt.-%. The CO conversion with SM(Ni) was smaller than those with the conventional supported nickel catalysts at temperatures of 150 °C – 300 °C. However, the former showed the higher selectivity to the methanation of CO of > 95% at 250 °C or below compared to the latter catalysts. The low activity of SM(Ni) was ascribed to a small area of exposed nickel species. The area of exposed nickel species was improved by doping a reduction promoter of platinum to SM(Ni), resulting in an increase in the activity while keeping the high selectivity to the CO methanation. The influence of reduction temperature and platinum loading on the activity and selectivity was investigated.

*Keywords:* CO Removal, Selective methanation, Smectite, Nickel, Platinum doping

## 1. Introduction

The catalytic methanation of CO is a potentially effective method to reduce the content of CO in a H<sub>2</sub>-rich reformat gas mixture, which is produced by steam and dry reforming of several organic compounds and used in fuel cell applications [1]. In this method, H<sub>2</sub> can be used as a reducing agent and no other additional agents are required. However, the methanation of coexisting CO<sub>2</sub> may also occur and wastefully consume a large quantity of H<sub>2</sub>. It is therefore required for catalysts to be highly selective to the methanation of CO. For practical fuel cell applications, the content of CO should be reduced to a trace-level. The acceptable concentrations of CO at Pt anode and at CO-tolerant alloy anodes are < 10 ppm and < 100 ppm, respectively [1]. After the review of Park et al. [1] in 2009, several authors further investigated the selective methanation of CO in H<sub>2</sub>-rich gases using Ru [2-5] and Ni [3] catalysts. Kimura et al. prepared Ru/NiAl<sub>x</sub>O<sub>y</sub> catalysts by spray plasma and reported their good performance [3]. The content CO was reduced to 13 ppm from 1% CO (H<sub>2</sub> 79%, CO<sub>2</sub> 20% (dry basis), H<sub>2</sub>O/CO = 15) over 3% Ru/NiAl<sub>x</sub>O<sub>y</sub> at 230 °C. Tada et al. studied the performance of 0.5 wt.-% Ru-loaded Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> catalysts and showed their effective temperature ranges for the selective methanation of CO, in which CO concentration was < 0.05% and CO<sub>2</sub> conversion was < 1% for a mixture including CO and CO<sub>2</sub> in 0.145% and 15.5%, respectively [4]. For Ni catalysts, Takenaka et al. reported that ZrO<sub>2</sub>-supported 10 wt.-% Ni catalyst was superior to those on TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and MgO [6]. Liu et al. prepared Ni/ZrO<sub>2</sub> catalysts by impregnation and showed that 1.6 wt.-% Ni loaded one was the most active, over which the outlet CO concentration was reduced to < 20 ppm at temperatures of 260 °C – 280 °C and at a GHSV of 10000 h<sup>-1</sup> [7]. Krämer et al. made a comprehensive work in which the performance of a number of various catalysts was tested and compared for the selective CO methanation [8]. They pointed out that Ni-containing mixed oxides were promising catalysts. At present, the selective methanation of CO is still a challenging topic and the present authors have paid their attention to Ni based catalysts. In the present work, nickel-containing mesoporous smectite materials have been synthesized and tested, which contain Ni species in its layered crystal structure and may serve as a precursor for dispersed Ni catalyst. For comparison, several conventional supported Ni catalysts have also been prepared and tested for the title reaction.

Smectite is one of layered clay minerals, in which one layer consists of one octahedral sheet sandwiched by two tetrahedral sheets. The former contains divalent or trivalent cations such as Mg<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> surrounded by six oxygen atoms and the latter Si<sup>4+</sup> cations surrounded by four oxygen atoms. The smectite can be synthesized

by a simple hydrothermal method [9], through which high-surface-area and mesoporous materials are produced. In addition, several divalent and trivalent metal species can be introduced in the octahedral sheet by using different precursors. The smectite may have solid acid and/or base character depending on its composition. The synthetic smectite materials can therefore serve as catalysts and supports due to their flexible structural and chemical features, as demonstrated for several chemical transformations including hydrogenation [10, 11], hydrogenolysis [11], synthesis of dimethyl carbonate [12], transesterification and Knoevenagel reactions [13], steam reforming of acetic acid [14], dry reforming of methane with carbon dioxide [15], and others [16, 17]. The synthetic metal-containing smectite can be used as a catalyst precursor for dispersed metal catalysts. The metal species exist originally in the octahedral sheet but, through heat treatment with H<sub>2</sub>, these species are reduced and form metal clusters/crystallites on the wall of pores. This is promoted in the presence of noble metals like Pt [10]. These metal clusters/crystallites can be exposed to foreign species and thus act as dispersed metal catalysts. Nickel is active to the methanation of CO [6, 7] and so nickel-containing smectite materials have been applied for selective CO removal in a H<sub>2</sub>-rich gas stream in the present work. The activities of nickel-containing smectite catalysts doped and undoped with Pt have been compared with those of several conventional supported Ni catalysts on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, and ZrO<sub>2</sub>. For the former smectite catalysts, the influence of preparation and methanation conditions on the CO removal has been examined and optimized.

## **2. Experimental**

### *2.1. Catalyst preparation*

Nickel-containing smectite materials were prepared in the same manners as described elsewhere [10, 11]. In brief aqueous solutions of water glass (Nippon Chemical, SiO<sub>2</sub> 29.0 wt.-%, Na<sub>2</sub>O 9.4 wt.-%.) and NaOH (Wako Pure Chemical) were mixed and an aqueous solution of NiCl<sub>2</sub> (Wako) was dropped into the mixed solution until the molar ratio of Si/Ni became to 8/6 while stirring. The mixture was stirred for 12 h under ambient conditions and the resultant solid material was separated by filtration and washed with distilled water. The solid material was put into a certain volume of water (20 cm<sup>3</sup>), of which the pH was 7.34, and the slurry obtained was put into a stainless steel autoclave (100 cm<sup>3</sup>). After a heat treatment at 150 °C for 2 h, the solid material produced was separated by filtration and washed with distilled water, dried at 80 °C overnight, and

calcined at 300 °C for 1 h. Platinum was loaded to the nickel-containing smectite material prepared: an aqueous solution of  $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$  (Wako) was impregnated at 70 °C under reduced pressure and the material obtained was dried at 110 °C overnight and calcined at 300 °C for 3 h. The nickel-containing smectite sample will be abbreviated as SM(Ni) in the following. The SM(Ni) samples were reduced in a stream of 4%  $\text{H}_2$  in  $\text{N}_2$  at a rate of  $100 \text{ cm}^3 \text{ min}^{-1}$  and at increasing temperatures at a rate of  $5 \text{ K min}^{-1}$  up to 600 °C, at which these were further reduced for 1 h. In some cases, the samples were reduced at lower and higher temperatures of 500 °C and 700 °C to examine the influence of reduction temperature.

Conventional supported nickel catalysts were also prepared by impregnation using four different support materials:  $\text{SiO}_2$  (GL Science),  $\text{Al}_2\text{O}_3$  (Catalysis Society of Japan, JRC-ALO4),  $\text{MgO}$  (Kishida Chemical), and  $\text{ZrO}_2$  prepared via calcination of  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (Kishida) at 600 °C for 3 h. These support materials were impregnated with an aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Wako) at 70 °C under reduced pressure, dried at 110 °C overnight, and calcined at 500 °C for 3 h. The loading of Ni was 35 wt.-% for these supported catalysts, corresponding to the amount of Ni included in the smectite sample synthesized.

## 2.2. Catalyst characterization

When SM(Ni) was heated in a reducing atmosphere, Ni species moved from the lattice to the surface and formed nanoparticles as described later. The average size of Ni crystallites was determined by X-ray diffraction (XRD) line broadening using JEOL JDX-8020 with Ni-filtered  $\text{CuK}\alpha$  radiation. The average diameter of Ni crystallites,  $D$ , was determined by the Scherrer's equation,  $D = K\lambda/((B - b)\cos\theta)$ , where  $K$  is shape factor (assuming 0.90 in this work),  $\lambda$  the X-ray wavelength (0.15418 nm),  $\theta$  the Bragg angle,  $B$  the line broadening at half the maximum intensity (FWHM) of the Ni(111) diffraction for a sample, and  $b$  the line broadening at FWHM of the Si(220) diffraction for a reference Si crystal. The area of exposed metal species (Ni, Pt) was measured by CO pulse chemisorption (BEL Japan BEL-CAT) at 50 °C using a pulse of 5% CO in He. Prior to the chemisorption, the samples were treated in a stream of 5%  $\text{H}_2$  in He at 600 °C for 1 h. Temperature programmed reduction was conducted for Pt-loaded and unloaded smectite samples, which were heated in a stream of 4 %  $\text{H}_2$  in  $\text{N}_2$  at  $100 \text{ cm}^3 \text{ min}^{-1}$  and at a ramping rate of  $5 \text{ K min}^{-1}$  to 900 °C.

## 2.3. Selective CO methanation

The performance of SM(Ni) and conventional supported Ni catalysts prepared were examined with a continuous fixed bed reactor. A certain amount of catalyst sample was put into the reactor, a stream of 4% H<sub>2</sub> in N<sub>2</sub> was passed at 100 cm<sup>3</sup> min<sup>-1</sup>, and the sample was heated at 5 °C min<sup>-1</sup> up to 600 °C and further treated at this temperature for 1 h. The reactor was cooled to room temperature in a stream of pure N<sub>2</sub> and heated again to a reaction temperature of 150 °C, at which a reaction gaseous mixture of H<sub>2</sub> (23%), CO<sub>2</sub> (7.0%), CO (0.5%) and/or H<sub>2</sub>O (10%) in N<sub>2</sub> was started to pass at 117 cm<sup>3</sup> min<sup>-1</sup>. When water was also included, the gaseous mixture was passed through a water saturator in a water bath maintained at a certain temperature in the same manner as described previously [14]. After 5 min of the introduction of the reaction mixture, the outlet gas mixture was sampled and analyzed by gas chromatographs (Hitachi G3000, 263-30) several times for 2 h. Then, the reactions were conducted at higher temperatures of up to 300 °C in the same manners. The conversion of either CO or CO<sub>2</sub> was determined from its inlet and outlet concentrations. The selectivity to the methanation of CO to CH<sub>4</sub> was calculated by [(inlet CO concentration) – (outlet CO concentration)] / (outlet CH<sub>4</sub> concentration). The reaction experiment was started at a reaction temperature of 150 °C and continued for 2 h. At this temperature the CO conversion was found to decrease during the initial transition period of time and then level off in a few ten minutes, after which a stable CO conversion value was reproduced. The reaction was further continued at a higher temperature, e.g. 200 °C, and a stable CO conversion was obtained from the initial stage of reaction through 2 h. This was also the case for the reactions at higher temperatures. The stable reaction data so collected will be presented in the following.

### **3. Results and discussion**

Nickel species that originally exist in the lattice of octahedral sheets of smectite structure will move to the surface and form metal nanoparticles when SM(Ni) is heated in a reducing atmosphere of H<sub>2</sub> [10]. These Ni nanoparticles could interact with foreign gaseous reacting species and then act as dispersed metal catalysts.

#### *3.1. Nickel-containing smectite based catalysts*

The results of selective CO methanation with SM(Ni) and conventional supported Ni catalysts are compared in Table 1. In some cases at low reaction temperatures, the selectivity values were >> 100%. Carbon monoxide may be consumed via both

methanation and water-gas shift (WGS) reaction. The former produces one H<sub>2</sub>O molecule,  $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ ; when H<sub>2</sub>O molecules formed through the methanation further react with other CO molecules via the latter,  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ , the overall reaction is  $2\text{CO} + 2\text{H}_2 \rightarrow \text{CO}_2 + \text{CH}_4$ . In this case, the selectivity will be 200 %. In reverse, the selectivity will be lowered by the reverse water-gas shift reaction,  $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ , and the methanation of CO<sub>2</sub>. Table 1 shows that SM(Ni) was less active to the methanation of CO compared to the conventional supported Ni catalysts at temperatures examined. It is interesting to note, however, that it showed a high selectivity > 95% even at 250 °C, at which the selectivity was 80% for Ni/SiO<sub>2</sub> and < 35% for Ni/MgO, Ni/ZrO<sub>2</sub>, and Ni/Al<sub>2</sub>O<sub>3</sub>. The area of exposed Ni species determined by CO chemisorption is plotted against the CO conversion obtained at 200 °C in Fig. 1. A good correlation indicates that the lower activity of SM(Ni) is explained by its smaller area of exposed Ni species. Then, an attempt was made to improve the activity of SM(Ni) by doping a small quantity of Pt, which was expected to promote the reduction and increase the number of exposed Ni species.

Table 1, Figure 1

Takenaka et al. previously studied the performance of several supported Ni catalysts, in which the metal loading was 10 wt.-%, and reported that the activity (CO conversion) was Ni/ZrO<sub>2</sub> > Ni/TiO<sub>2</sub> > Ni/SiO<sub>2</sub> > Ni/Al<sub>2</sub>O<sub>3</sub> > Ni/MgO at temperatures of 250 °C and 300 °C [6]. Table 1 also indicates that Ni/ZrO<sub>2</sub> is highly active, similar to their results, but the other catalysts are not different so much in the activity. The difference between the results of Takenaka et al. and those of the present work could be ascribable to differences in the Ni loading and/or the sources of support materials used. Liu et al. examined the influence of Ni loading on ZrO<sub>2</sub> in a range of 0.6 – 15 wt.-% and showed that the optimal loading was 1.6 wt.-%, which resulted in an optimum dispersion of Ni species on ZrO<sub>2</sub> [7].

### 3.2. Nickel-containing smectite based catalysts doped with platinum

The activity of the Pt dopant itself was first examined with a 1 wt.-% Pt/SiO<sub>2</sub> sample prepared by impregnation and it was confirmed to be inactive for the methanation of CO at temperatures of 150 °C – 300 °C. The SM(Ni) sample was doped with Pt in different quantities. The results of Pt-loaded SM(Ni) catalysts are given in Fig. 2. It was observed that the catalytic performance of SM(Ni) was improved by the Pt doping and the effectiveness depended on the Pt loading. The 1 wt.-% Pt/SM(Ni) catalyst was more

active than those doped with Pt in 0.5 wt.-% and 3.0 wt.-%. The maximum performance of 1 wt.-% Pt/SM(Ni) appeared at 210 °C at which the CO conversion was 99.6% and the outlet CO concentration was significantly reduced to a practically desired level of 21 ppm from the inlet concentration of 5000 ppm. The selectivity decreased with reaction temperature in similar manners irrespective of the Pt loading.

Figure 2

TPR was conducted for Pt-doped and undoped SM(Ni) samples to examine the role of Pt dopant (Fig. 3). For Pt-undoped sample, H<sub>2</sub> consumption was found to start at > 400 °C. In contrast, the H<sub>2</sub> consumption began to occur at lower temperature with an increase in the Pt loading. The temperature for the maximum H<sub>2</sub> consumption was around 650 °C for the SM(Ni) sample but it was decreased to around 450 °C for the 3 wt.-% Pt/SM(Ni) sample. That is, the Pt dopant is likely to facilitate the reduction of Ni species that exists originally in the lattice of the SM(Ni) structure (octahedral sheet). The area of exposed Ni species in the Pt-loaded SM(Ni) samples was examined by CO chemisorption, in which a sample was measured twice after the reduction at 300 °C for 1 h and that at 600 °C for 1 h. It was assumed that CO was able to be adsorbed on Pt alone for the 300 °C-reduced sample while on Pt and Ni for the 600 °C-reduced one. The area of exposed Ni species was estimated by the difference between the amounts of CO chemisorbed after the reduction at 300 °C and 600 °C. The results of CO chemisorption obtained are given in Table 2, indicating that the maximum area of exposed Ni species was obtained for the 1 wt.-% Pt/SM(Ni) catalyst. Fig. 4 shows a good correlation between the amount of CO chemisorbed on Ni and the activity (outlet CO concentration at selected reaction temperatures). Therefore, the area of exposed Ni species can be enhanced by the Pt loading and this is a reason for the improved activity of Pt/SM(Ni) catalysts. As mentioned above, the Pt dopant may promote the reduction of Ni species in the lattice of SM(Ni) and the formation of Ni crystallites; as a result, a certain amount of Ni species can be exposed to gaseous reactants and act as active sites for the methanation of CO. The doping of Pt in an excess amount (say 3 wt.-%) is less effective; the reduction of Ni species is further improved but the formation of larger Ni crystallite is promoted, decreasing the area of exposed Ni species. This explanation may be supported by XRD results as shown in Table 2.

Figure 3, Table 2, Figure 4

### *3.3. Optimization of reduction temperature and space velocity for 1 wt.-% Pt/SM(Ni)*



The influence of reduction temperature was examined for the 1 wt.-% Pt doped SM(Ni) catalyst. Table 3 gives the results of the samples reduced at 500, 600, and 700 °C, indicating that the CO conversion was larger with an increase in the reduction temperature. The selectivity to the methanation of CO to CH<sub>4</sub> was > 80% at 200 °C or lower; however, it was < 50% at higher temperatures for the 700 °C-reduced sample. At 250 °C, the samples reduced at 600 °C and 500 °C still had a selectivity level of > 80%. Therefore, the optimum reduction temperature is 600 °C.

Table 3

Finally, the performance of 1 wt.-% Pt/SM(Ni) catalyst reduced at 600 °C was examined at different space velocities. Fig. 5 gives the results obtained with 72000, 43200, and 14400 h<sup>-1</sup>. The selective removal of CO was decreased in the presence of water vapor (10%). However, similar CO conversion levels were obtained at 14400 and 43200 h<sup>-1</sup> at temperatures examined, which were larger than that at 72000 h<sup>-1</sup>. The outlet CO concentration was lowered to the desired level < 100 ppm at 225 and 250 °C when the space velocity was 14400 h<sup>-1</sup>. At a larger velocity of 43200 h<sup>-1</sup>, a minimum outlet CO concentration of 350 ppm was obtained at 250 °C. No good results (outlet CO concentration) were obtained at temperatures examined when the space velocity was 72000 h<sup>-1</sup>.

Figure 5

#### 4. Conclusions

Synthetic nickel-containing smectite material, SM(Ni), reduced at 600 °C is an active catalyst for the selective methanation of CO in a H<sub>2</sub>-rich gas stream at temperatures of 150 °C – 300 °C. The CO conversion over the SM(Ni) is smaller compared to conventional supported Ni catalysts on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and MgO that contain the same amount of Ni (35 wt.-%) as in the SM(Ni). A smaller area of exposed Ni species of the SM(Ni) catalyst is responsible for its lower activity. However, the selectivity of the SM(Ni) catalyst to the selective methanation of CO is higher than those of the supported catalysts. A high selectivity of > 95% can be achieved at 250 °C or below. The activity of SM(Ni) can be improved by doping a small quantity of Pt, which is inactive to the CO methanation, while keeping its high selectivity. The Pt doping facilitates the reduction of Ni species originally contained in the lattice and the subsequent formation of Ni

clusters/crystallites. This results in an increased area of exposed Ni species and thus an enhanced activity. Over 1 wt.-% Pt/SM(Ni) catalyst reduced at 600 °C, the outlet CO concentration is reduced to 25 ppm at 200 °C and 350 ppm at 250 °C in the absence and presence of water vapor (10%), respectively, at a space velocity of 14400 h<sup>-1</sup> for an inlet gas mixtures of CO/H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> = 0.5/23/7/69.5.

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Table 1 Results of selective methanation of CO with SM(Ni) and supported Ni catalysts on different supports at temperatures of 150 °C - 300 °C <sup>a</sup>

Catalyst	150 °C		200 °C		250 °C		300 °C	
	X <sub>CO</sub>	S <sub>CH<sub>4</sub></sub>	X <sub>CO</sub>	S <sub>CH<sub>4</sub></sub>	X <sub>CO</sub>	S <sub>CH<sub>4</sub></sub>	X <sub>CO</sub>	S <sub>CH<sub>4</sub></sub>
SM(Ni)	2.6	– <sup>b</sup>	12	101	58	97	66	39
Ni/SiO <sub>2</sub>	2.8	– <sup>b</sup>	16	109	75	80	67	23
Ni/Al <sub>2</sub> O <sub>3</sub>	17	– <sup>b</sup>	99	65	91	9.5	94	8.2
Ni/ZrO <sub>2</sub>	5.0	– <sup>b</sup>	40	– <sup>b</sup>	95	22	86	8.4
Ni/MgO	0	– <sup>b</sup>	12	– <sup>b</sup>	85	33	77	8.6

<sup>a</sup> X<sub>CO</sub>: CO conversion (%), S<sub>CH<sub>4</sub></sub>: Selectivity (%). <sup>b</sup> S<sub>CH<sub>4</sub></sub> >> 100%.

Reaction conditions: Catalyst 500 mg, Gas flow rate 117 cm<sup>3</sup> min<sup>-1</sup>, Gas composition CO/H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> = 0.5/23/7/69.5.

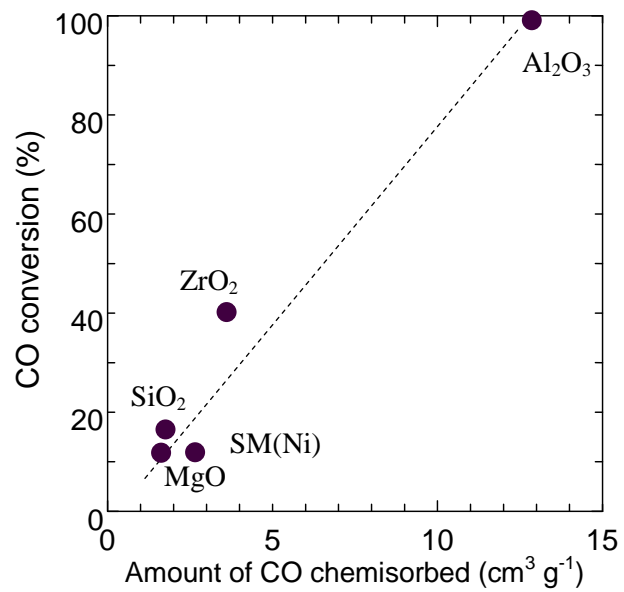


Fig. 1. Relationship between the catalytic activity (CO conversion at 200 °C) and the amount of CO chemisorbed on SM(Ni) and Ni loaded catalysts on different supports given. For reaction conditions, see Table 1.

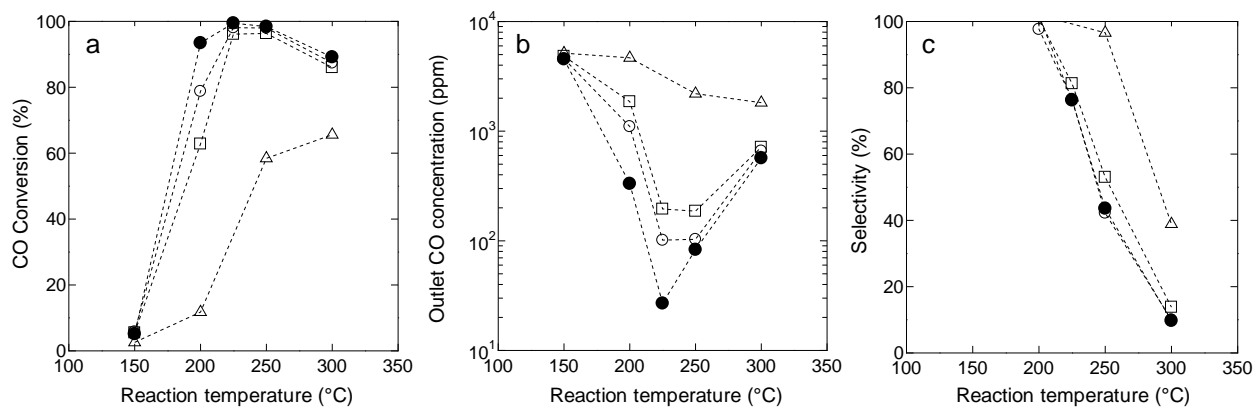


Fig. 2. Influence of Pt loading on the catalytic performance of SM(Ni). Pt loading in wt.-%: (Δ) 0, (○) 0.5, (●) 1.0, (□) 3.0. Reaction conditions: Catalyst 500 mg, Gas flow rate 117 cm<sup>3</sup> min<sup>-1</sup>, Gas composition CO/H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> = 0.5/23/7/69.5.

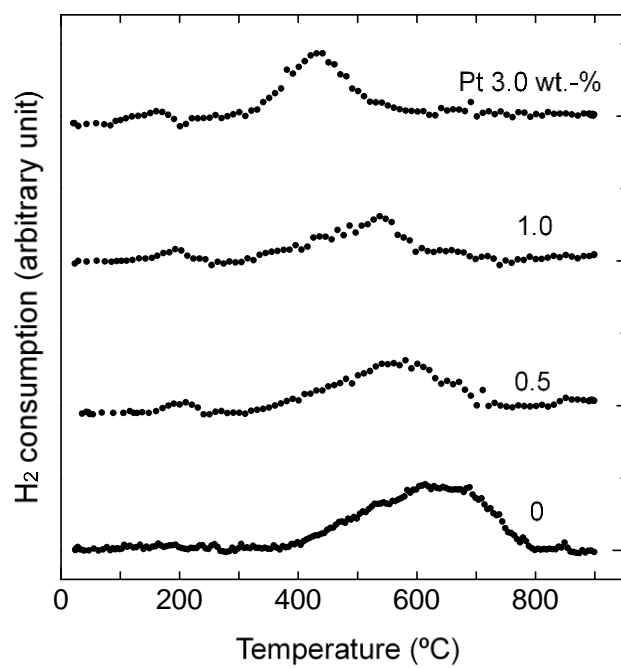


Fig. 3. Temperature programmed reduction results of SM(Ni) samples undoped and doped with Pt in different quantities given.

Table 2 Results of CO chemisorption and XRD for SM(Ni) catalysts undoped and doped with Pt in different amounts

Catalyst	Amount of CO chemisorbed ( $\text{cm}^3 \text{g}^{-1}$ )			$D_{\text{XRD}}$ (nm)
	$\alpha$	$\beta$	$\beta - \alpha$	
SM(Ni)	0	2.67	2.67	14
0.5%Pt/SM(Ni)	0.11	6.77	6.66	6
1.0%Pt/SM(Ni)	1.48	9.40	7.92	7
3.0%Pt/SM(Ni)	1.63	8.71	7.08	15

$\alpha$ ,  $\beta$ : amounts of CO chemisorbed on the catalysts reduced at 300 °C and 600 °C for 1 h, respectively, corresponding to the CO adsorption on Pt alone and on both Pt and Ni.

$D_{\text{XRD}}$ : Nickel crystallite diameter determined by XRD line broadening for the catalysts reduced at 600 °C for 1 h.

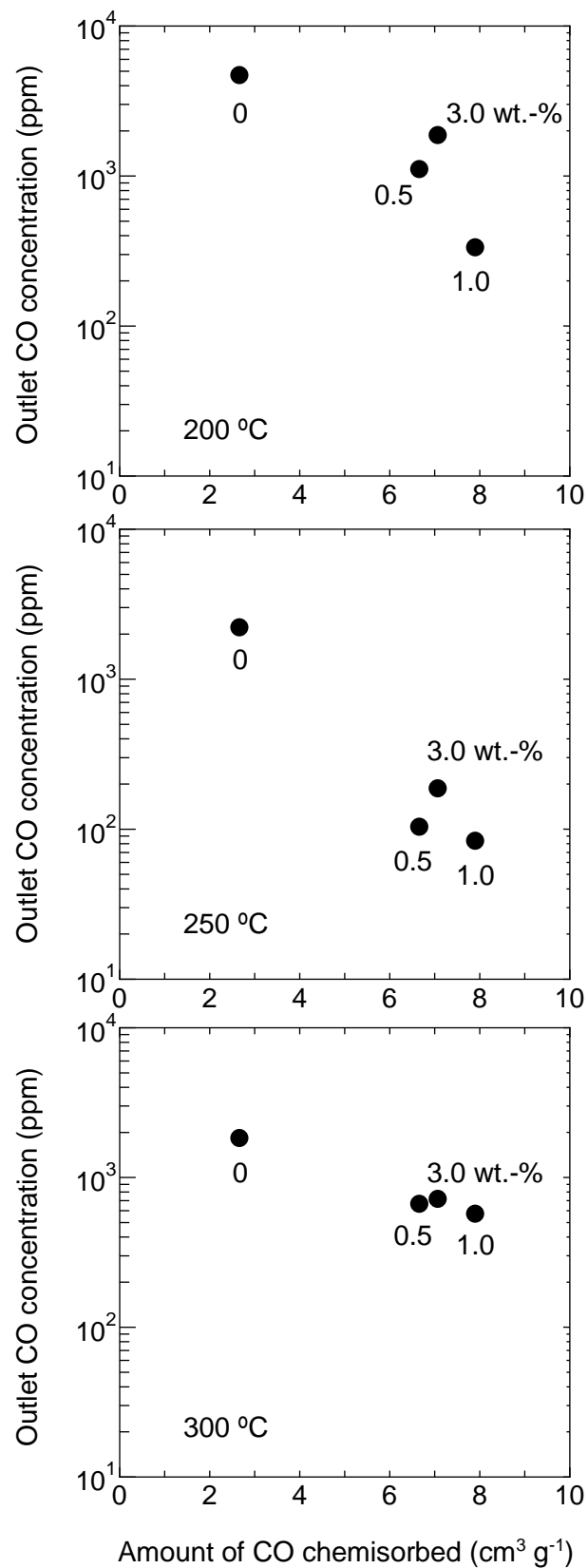


Fig. 4. Relationship between the catalytic activity (outlet CO concentration at 200 °C, 250 °C, and 300 °C) and the amount of CO chemisorbed on exposed Ni species for SM(Ni) catalysts undoped and doped with Pt in different quantities given. For reaction conditions, see Table 1.



Table 3 Influence of reduction temperature on the catalytic performance of 1 wt.-% Pt loaded SM(Ni) at temperatures of 150 °C - 300 °C<sup>a</sup>

Reduction temperature	150 °C		200 °C		250 °C		300 °C	
	X <sub>CO</sub>	S <sub>CH4</sub>	X <sub>CO</sub>	S <sub>CH4</sub>	X <sub>CO</sub>	S <sub>CH4</sub>	X <sub>CO</sub>	S <sub>CH4</sub>
500 °C	2.2	– <sup>b</sup>	12	105	73	91	80	51
600 °C	1.5	– <sup>b</sup>	23	97	76	80	73	24
700 °C	2.7	– <sup>b</sup>	31	100	89	50	73	13

<sup>a</sup> X<sub>CO</sub>: CO conversion (%), S<sub>CH4</sub>: Selectivity (%).<sup>b</sup> S<sub>CH4</sub> >> 100%.

Reaction conditions: Catalyst 100 mg, Space velocity 72000 h<sup>-1</sup>, Gas composition CO/H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O= 0.5/24.5/6.4/59.6/9.

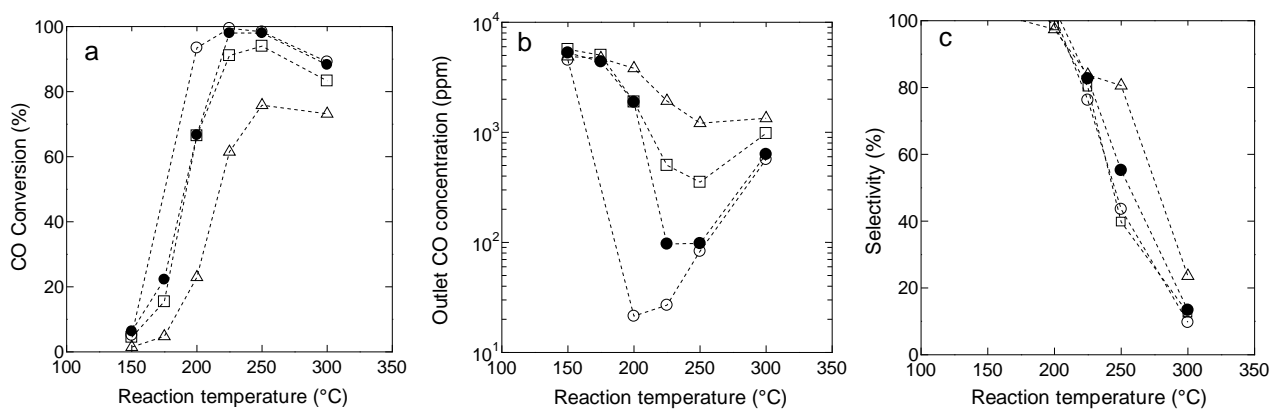
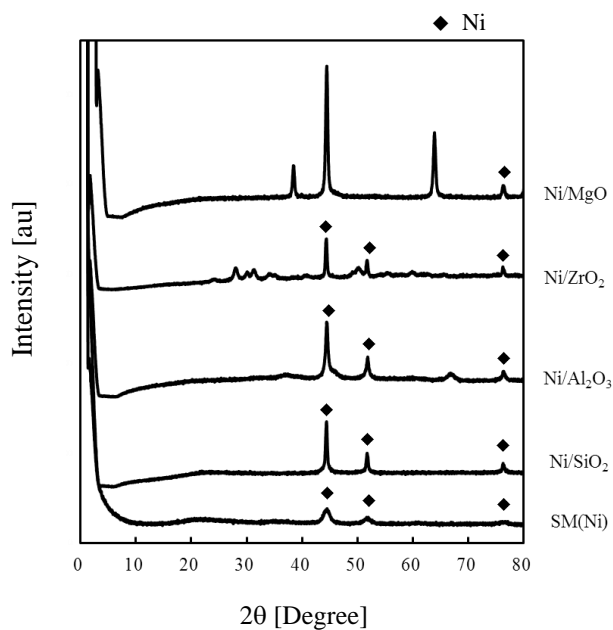


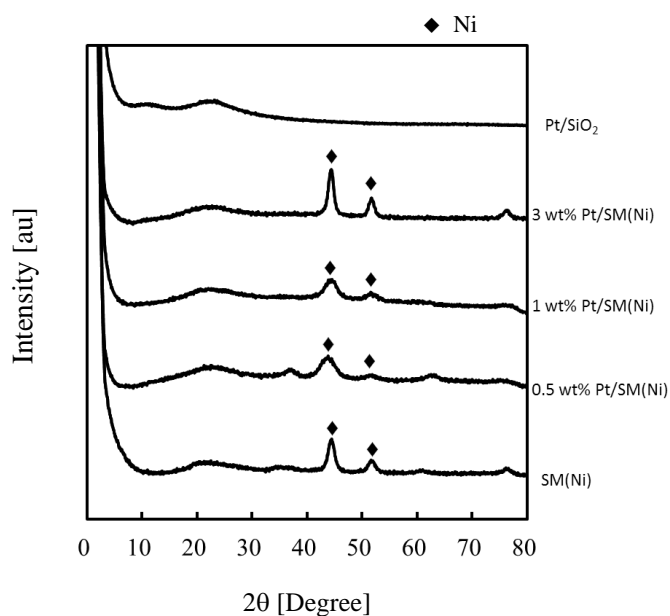
Fig. 5. Influence of water and space velocity on catalytic performance of 1 wt.% Pt - doped SM(Ni) catalyst. Water content: (○) 0%, (Δ, ●, □) 10%. Space velocity: (○, ●) 14400 h<sup>-1</sup>, (□) 43200 h<sup>-1</sup>, (Δ) 72000 h<sup>-1</sup>. Reaction conditions: Gas composition CO/H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> = 0.5/23/7/69.5. Gas flow rate 117 cm<sup>3</sup> min<sup>-1</sup>.

**Supporting Information** for:

“Selective methanation of CO in H<sub>2</sub>-rich gas stream by synthetic nickel-containing smectite based catalysts” by H. Yoshida, K. Watanabe, N. Iwasa, S. Fujita, M. Arai



**Figure S1** XRD patterns of various 35 wt.-% Ni loaded catalysts and SM(Ni) after the reduction at 600 °C (corresponding to Table 1)



**Figure S2** XRD patterns of Pt-loaded and unloaded SM(Ni) samples after the reduction at 600 °C (corresponding to Table 2)