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Reforming of Methane with Carbon Dioxide over Nickel-loaded Zeolite Catalysts

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Catalytic performance of nickel-loaded zeolite-based supports for CO₂ reforming of methane was investigated. Among the three zeolites (H-Y, H-mordenite, and Na-mordenite), H-mordenite was the best support for the reaction, probably due to its thermal stability. The initial activity of Ni/H-mordenite (Ni/HM) was higher than that of conventional Ni/alumina catalyst (Ni/Al₂O₃), whereas deactivation of the former was slightly faster. A physical mixture of alumina and zeolite was a more effective support than zeolite. The resulting Ni/H-mordenite-alumina catalyst (Ni/HM-Al₂O₃) showed the highest performance among the catalysts tested. Under the conditions of atmospheric pressure of CO₂/CH₄/He stream (20/20/40 ml/min) at 750°C, the initial CO₂ conversion was 95% and this value was maintained for more than 20 h. The catalytic performance of Ni/HM-Al₂O₃ was higher than that of Ni/Al₂O₃.

Keywords

Methane reforming, Carbon dioxide, Nickel, Mordenite, Alumina

1. Introduction

Reforming of natural gas with carbon dioxide, *i.e.* dry reforming of methane, is a very important reaction both theoretically and industrially^{1)~3)} because of its implications in the following: (1) reduction of the greenhouse gases, carbon dioxide and methane, (2) conversion of natural gas, which is less valuable and less reactive gas as chemicals, to valuable synthesis gas, a mixture of hydrogen and carbon monoxide, (3) effective utilization of low grade natural gas resources containing methane and carbon dioxide, and (4) production of synthesis gas with high CO/H₂ ratio. Hydrogen in the products can be applied as a fuel for fuel cells and synthesis gas can be converted to ultra clean fuels containing no sulfur and fewer aromatics such as gasoline, gasoil, methanol, and dimethyl ether (DME) *via* the Fischer-Tropsch and related reactions. In general, dry reforming is catalyzed by group VIII transition metals, so nickel and noble metals such as rhodium, ruthenium, etc. are candidates for industrial catalysts of the reaction. Nickel is available at a low price and is highly active for this reaction, at least in the initial stage, but loses activity rapidly by carbon deposition. Noble metals have higher activity and

activities are more stable during the reaction period, but are expensive. Therefore, much research has been aimed at preventing the deactivation of nickel-based catalysts by doping of alkali or alkaline earth metals^{4)~6)}, use of basic supports^{7)~10)}, modification of catalysts with secondary transition metals^{11)~13)}, and use of solid solutions of nickel and other metals^{14)~16)}.

Zeolites are one of the most representative supports and are used widely in academic research and the chemical industry. Higher dispersion of active metal species can be expected using zeolite supports. However, dry reforming of methane catalyzed by transition metal-loaded zeolite is not well studied, probably due to their instability under hydrothermal conditions. Ni-ZSM-5 catalyst was prepared by the solid-state reaction of zeolite and nickel nitrate and the applicability of this catalyst to dry reforming of methane and the doping effects of alkali or alkaline earth metals were examined, the results indicating that doping of Ca and K to the catalyst leads to decreased coke deposition during the reforming reaction¹⁷⁾. The applicability of Ni-loaded Y-type zeolite or mordenite for the dry reforming and tri-reforming reactions was also studied¹⁸⁾.

The present study investigated the activity for dry reforming of methane and coke deposition during the reaction using several Ni-loaded zeolite catalysts and found that mixing of zeolite and alumina enhances the

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Table 1 Characterization of the Ni Catalysts Employed

Catalyst	Ni [wt%]	Si/Al	Specific surface area [m ² /g] ^{a)}
Ni/HY	3.2	2.6	634
Ni/HM	2.6	10.0	356
Ni/NaM	2.5	10.0	281
Ni/Al ₂ O ₃	4.1	0.0	302
Ni/HY-Al ₂ O ₃	3.1	— ^{b)}	434
Ni/HM-Al ₂ O ₃	3.1	— ^{b)}	341
Ni/NaM-Al ₂ O ₃	2.9	— ^{b)}	317

a) BET method. After Ni loading.

b) Zeolite : Al₂O₃ = 1 : 1 (wt/wt).

coke resistivity of the catalysts.

2. Experimental

2.1. Preparation and Characterization of Ni-loaded Catalysts

H-mordenite [JRC-Z-HM-20(4), HM] and Na-mordenite [JRC-Z-M-20(1), NaM] were provided by the Catalysis Society of Japan as reference catalysts. H-Y zeolite (HY) and γ -Al₂O₃ were provided by Catalysts & Chemicals Ind. Co., Ltd. and Sumitomo Metal Mining Co., Ltd., respectively.

Mixed supports consisted of zeolite and alumina were prepared according to the following method: Zeolite and alumina (1 : 1, wt/wt, 10 g in total) were mixed in water (100 ml), and the resulting mixture was stirred for 1 h at room temperature, then filtered, and dried at 120°C under atmospheric pressure overnight before nickel loading.

Nickel loading of each support was conducted according to the following procedure: A mixture of aqueous solution of nickel nitrate (25 mM, 100 ml) and support (5 g) was stirred at 50°C for 1 h, then the water was removed under reduced pressure by a rotary evaporator. The resulting solid was dried at 120°C overnight. The contents of nickel in each catalyst were determined using a Rigaku Denki System Type 3270 fluorescence X-ray analyzer. Ni content, surface area, and the ratio of SiO₂/Al₂O₃ of the original zeolite are shown in Table 1.

X-Ray photoelectron spectroscopic and X-ray diffraction analyses of the catalysts were conducted using an ULVAC PHI ESCA5500MT spectrometer and a MacScience MXP18XHF-SRA spectrometer, respectively.

2.2. Catalytic Test

Reforming reactions were carried out at atmospheric pressure in a continuous flow fixed bed reactor using 200 mg of catalyst (pulverized to particle size between 0.6 mm and 1.0 mm) diluted with 1.0 g of sea sand (20–35 mesh, Wako Pure Chemicals Ind. Ltd.). The catalyst was calcined at 450°C for 1 h under a flow of He/O₂ (4/1, total flow 50 ml/min) and reduced at 450°C

for 1 h under a flow of H₂ (50 ml/min), then heated to 750°C (in a typical case). After the temperature of the electric furnace reached the determined temperature, the feed gas (CO₂/CH₄/He = 20/20/40, in ml/min) was introduced into the reactor to start the reaction. The products were analyzed by an on-line gas chromatograph (a Shimadzu GC-17 with a PoraPLOT Q column and a thermal conductivity detector).

2.3. Temperature-programmed Oxidation (TPO) Experiments

The used catalyst (after the reaction of methane with CO₂ at 750°C for 5 h or 24 h, *ca.* 20 mg) was placed on a platinum pan centered in the electric furnace of a Shimadzu TG-50H thermobalance, then the apparatus was heated from room temperature to 800°C at 10°C/min under a flow of air (50 ml/min). Data acquisition and processing were conducted on an IBM compatible PC connected with the thermobalance.

3. Results and Discussion

Dry reforming of methane was conducted using several Ni-loaded catalysts at 750°C under a flow of CO₂/CH₄/He (20/20/40, in ml/min). Before the reaction, the catalysts were calcined under a flow of He/O₂ at 450°C, then reduced with H₂ at the same temperature. The time profile of conversion of CO₂ is summarized in Fig. 1. Using Ni/HY catalyst, the initial conversion of CO₂ was modest, but the catalyst activity decreased to only 15% conversion of CO₂ within 400 min. X-Ray diffraction (XRD) analyses of fresh and used Ni/HY catalysts showed that the crystalline structure of H-Y zeolite was destroyed to produce amorphous Al₂O₃ and SiO₂ during the reaction, which apparently caused the rapid decrease of the Ni/HY catalytic activity. Ni/HM catalyst showed a considerably higher initial activity than Ni/HY and retained the activity for about 24 h: Conversions of CO₂ at 5 h and 24 h were 95% and 92%, respectively. XRD analysis of fresh and used Ni/HM showed the diffractograms were similar, suggesting that the mordenite structure was retained during the reaction. These results may suggest that destroying the zeolite structure correlates with the deactivation of a catalyst. CO₂ conversion of Ni/NaM was similar to that of Ni/HM at an early stage of the reaction, but decreased to 86% after 24 h-reaction. Ni/Al₂O₃ catalyst showed a rather different time profile: Conversion of CO₂ at start point was around 40%, but increased to 83% within 24 h. Nickel aluminate (NiAl₂O₄) generated from calcination of Ni(NO₃)₂/Al₂O₃ is little reduced to Ni⁰ by H₂ at temperatures as low as 400°C^{19,20}. Therefore, reduction of calcined Ni/Al₂O₃ was carried out at 800°C (abbreviated as Ni/Al₂O₃-800). The reaction result is also shown in Fig. 1, indicating that the resulting Ni/Al₂O₃-800 had rather high activity and stability.

Temperature 750°C, Total pressure 0.1 MPa, Flow rate [CO₂] : [CH₄] : [He] = 20 : 20 : 40 ml/min.
 "Ni/Al₂O₃-800" indicates Ni/Al₂O₃ reduced at 800°C.

Fig. 1 Time Profile for CO₂ Conversion in the Reforming Reaction of CH₄ with CO₂ over Various Ni Catalysts

Temperature 750°C, Total pressure 0.1 MPa, Flow rate [CO₂] : [CH₄] : [He] = 20 : 20 : 40 ml/min.

Fig. 2 Time Profile for CH₄ Conversion in the Reforming Reaction of CH₄ with CO₂ over Various Ni Catalysts

The catalytic activity of Ni-loaded mixed support consisted of zeolite and alumina was also examined. These catalysts were calcined and reduced at 450°C before the reaction. At an early stage of the reaction, Ni/HY-Al₂O₃ showed relatively higher activity than Ni/HY or Ni/Al₂O₃, but the CO₂ conversion decreased from 93 to 79% by 24 h. Ni/HM-Al₂O₃ showed the highest activity among the catalysts employed and maintained the activity for 24 h. Ni/NaM-Al₂O₃ showed slightly lower activity than Ni/HM-Al₂O₃. These catalysts showed higher activity although the reduction was carried out at 450°C.

Figure 2 shows conversion of CH₄ in the same reaction as shown in Fig. 1, with similar trends in CO₂ conversion. The ratio of CH₄ conversion over CO₂

conversion decreased according to the following order (at 5 h reaction): Ni/Al₂O₃-800 (0.95) > Ni/NaM-Al₂O₃, Ni/HM (0.94) > Ni/NaM (0.93) > Ni/HY-Al₂O₃, Ni/HM-Al₂O₃ (0.91) > Ni/Al₂O₃ (0.88) > Ni/HY (0.70). With the exception of two catalysts with the lowest activities, Ni/Al₂O₃ and Ni/HY, all values were high and ranged from 0.91 to 0.95.

To investigate the nature of the nickel species on each support, X-ray photoelectron spectra (XPS) of Ni/HM, Ni/Al₂O₃, Ni/Al₂O₃-800, and Ni/HM-Al₂O₃ were measured. Before analysis, the catalysts were calcined at 450°C under He/O₂ and reduced at 450°C (Ni/HM, Ni/Al₂O₃, and Ni/HM-Al₂O₃) or 800°C (Ni/Al₂O₃-800) under hydrogen. The analytical method employed in this study cannot accurately evaluate the

Fig. 3 Ni $2p_{3/2}$ XPS Spectra for Ni-loaded Catalyst (a) and an Example of Curve Resolution of the Spectrum of Ni/HM- Al_2O_3 (b)

Table 2 Concentration of Ni Species Determined by XPS Analysis

	Concentration of Ni species [mol%]		
	NiAl ₂ O ₄	NiO	Ni ⁰
Ni/HM		79 (855.0) ^{a)}	21 (852.0)
Ni/Al ₂ O ₃	54 (856.0)	46 (854.8)	
Ni/Al ₂ O ₃ -800	29 (857.2)	71 (854.8)	
Ni/HM- Al_2O_3	32 (856.6)	53 (855.0)	15 (852.0)

a) Numbers in parenthesis indicate binding energies of each peak (in eV).

ratio of zero-valent nickel (Ni^0) to nickel oxide (NiO), because the catalysts were exposed to air before XPS analyses after reduction. The Ni $2p_{3/2}$ XPS spectra obtained are shown in Fig. 3a). Each spectrum could be separated into six peaks by curve resolution (for example, see Fig. 3b)), three of which were main peaks and the others were satellite peaks. The three main peaks were located at 852.0 eV, 854.8-855.0 eV, and 856.0-857.2 eV (Table 2). The binding energies of Ni $2p_{3/2}$ in Ni^0 , NiO , and NiAl_2O_4 are 852.2 eV²¹⁾, 854-855 eV²¹⁾, and 856-857 eV²¹⁾⁻²³⁾, respectively. Therefore, the three main peaks appeared in the spectra could be assigned to Ni^0 (852.0 eV), NiO (854.8-855.0 eV), and NiAl_2O_4 (856.4-857.2 eV), respectively. Concentrations of nickel species on the catalysts determined by XPS analysis followed by curve resolution are shown in Table 2. The concentration of NiAl_2O_4 was the highest in Ni/Al₂O₃ calcined and reduced at 450°C, whereas NiAl_2O_4 species decreased and NiO increased in Ni/Al₂O₃-800. Major Ni species in Ni/HM were

Temperature 750°C, Total pressure 0.1 MPa, Flow rate [CO_2] : [CH_4] : [He]=20 : 20 : 40 ml/min.

Fig. 4 Activity of Ni-loaded Mixed Support Consisting of HM and Al_2O_3

Ni^0 and NiO . Distribution of Ni-species in Ni/HM- Al_2O_3 was intermediate between those in Ni/HM and Ni/Al₂O₃. Consequently, the concentration of NiAl_2O_4 was in the following order: Ni/HM (0%) < Ni/Al₂O₃-800 (29%) ≤ Ni/HM- Al_2O_3 (32%) < Ni/Al₂O₃ (54%). Therefore, the catalytic activity of Ni/Al₂O₃ reduced at 450°C is expected to be low at an early stage of the reaction. During the reaction, NiAl_2O_4 and/or NiO can be reduced by H_2 and/or CO so that the activity of Ni/Al₂O₃ catalyst for CO_2 and CH_4 conversion increases with reaction duration.

Figure 4 shows the effects of the composition of the support on the activity of the catalysts. Conversion of

Conditions (a): Flow rate of [CO₂] : [CH₄] : [He] = 20/20/40 ml/min, pressure 0.1 MPa.

Conditions (b): [CH₄]/[CO₂] = 1.0 (v/v), [He] = 40 ml/min, pressure 0.1 MPa, temp. 750°C.

Fig. 5 Effects of Reaction Temperature (a) and Flow Rate of CO₂ (b) on Conversion of CO₂ in the Reforming Reaction

CO₂ was highest over Ni/HM-Al₂O₃ catalyst with a support containing 50% H-mordenite. In addition, catalyst deactivation during the 24 h-reaction was minimum with this catalyst. Therefore, the optimum composition of H-mordenite and alumina was 1 : 1. The effects of reaction conditions were also investigated on the activity of the three catalysts, Ni/HM, Ni/Al₂O₃-800, and Ni/HM-Al₂O₃, which had the highest activities among the tested catalysts. **Figure 5** shows the effects of reaction temperature and a flow rate of CO₂ on conversion of CO₂. Change of the reaction temperature from 650 to 800°C caused the CO₂ conversion to vary in the range of 65 to 95%. The order of activity for the catalysts was Ni/HM < Ni/Al₂O₃-800 < Ni/HM-Al₂O₃ regardless of the reaction temperature. Increased space velocity of CO₂ caused the CO₂ conversion to decrease gradually using Ni/HM as the catalyst, whereas CO₂ conversion was almost unchanged using Ni/HM-Al₂O₃ or Ni/Al₂O₃-800. These results indicate that both Ni/HM-Al₂O₃ and Ni/Al₂O₃-800 are good catalysts for dry reforming of methane, and Ni/HM-Al₂O₃ is slightly superior to Ni/Al₂O₃-800.

To investigate the amount and reactivity of carbonaceous materials deposited on the catalysts, temperature programmed oxidation (TPO) experiments of the catalysts were conducted. Differential curves of the TPO data are shown in **Fig. 6a**. Differential curves of all samples had two peaks, one in the lower temperature region assigned as the desorption of adsorbed small molecules, the other corresponding to the oxidation of carbon materials on the catalysts. By integrating these curves, the amounts of small molecules adsorbed and

TPO conditions: room temperature to 800°C, heating rate 10°C/min, under 50 ml/min air stream.

Fig. 6 Differential TPO Profiles of the Catalysts Treated with CO₂/CH₄/He (20/20/40 ml/min) at 750°C for 24 h (a) and Treated with CH₄/He (40/60 ml/min) at 750°C for 5 h (b)

Table 3 Amounts of Carbon Deposited on the Used Catalysts

	Amount of carbon deposited on the catalyst [mg-C/g-cat.]			
	5 h reaction		24 h reaction	
	< 400°C	> 400°C	< 400°C	> 400°C
Ni/HM	39	10	54	21
Ni/HM-Al ₂ O ₃	50	4	35	36
Ni/Al ₂ O ₃ -800	38	17	93	38

carbon deposits on the catalyst could be estimated as shown in **Table 3**. About 2-4 wt% of carbonaceous materials were deposited on the catalyst after the 24 h-reaction, in the following order: Ni/HM (21 mg-C/g-cat.) < Ni/HM-Al₂O₃ (36 mg-C/g-cat.) < Ni/Al₂O₃-800 (38 mg-C/g-cat.). The activation energy for oxidation of carbons can be calculated based on the results of TG analysis²⁴. The energies were 96 kcal/mol for Ni/Al₂O₃-800, 180 kcal/mol for Ni/HM-Al₂O₃, and 213 kcal/mol for Ni/HM. Higher activation energy was associated with lower carbon reactivity, so that Ni/HM had less deposited carbon but lower reactivity than on Ni/Al₂O₃-800, and the carbon characteristics on Ni/HM-Al₂O₃ were intermediate between those of Ni/HM and Ni/Al₂O₃. The unreactive nature of carbon on Ni/HM might be the cause of the deactivation of Ni/HM during the reaction. TPO experiments of the catalysts treated with CH₄/He (40/60, ml/min) at 750°C for 5 h were also conducted, with the results shown in **Fig. 6b**). The temperatures at top of the peak in the higher temperature region and the amount of carbon at the peak were 525°C and 65 mg-C/g-cat. for Ni/Al₂O₃-800, and 646°C and 46 mg-C/g-cat for Ni/HM, respectively. The results also indicate that unreactive carbons were formed on Ni/HM catalyst. The TPO curve of Ni/HM-Al₂O₃ was bimodal, with peaks at 505°C and 646°C and the amounts of carbon was 80 mg-C/g-cat. This indicates that Ni/HM-Al₂O₃ consisted of a physical mixture of Ni/HM and Ni/Al₂O₃.

Both reactive and unreactive carbon species are deposited on the catalysts during the reforming reaction. Reactive carbon consists of graphitic carbons and unreactive carbon consists of amorphous carbons based on TPO, XPS, and XRD analyses of the used catalysts²⁴. Reactive carbon is filamentous and unreactive carbon is moss-like based on scanning electron microscope (SEM) and transmission electron microscope (TEM) observations²⁵. In the present study, TPO experiments of the catalyst treated with CH₄ at 750°C showed two peaks around 505-525°C and around 650°C. Based on the reported results^{24,25}, the TPO peak located in the lower temperature region (505-525°C) might be assigned as graphitic carbon (filamentous carbon) and that in the higher temperature region (ca. 650°C) as amorphous carbon (moss-like

carbon). On the other hand, TPO experiments of the catalysts treated with both CH₄ and CO₂ at 750°C showed only one peak at 630-680°C. Based on the TPO data for the catalysts treated with CH₄, this peak might be assigned as amorphous carbon. Disappearance of graphitic carbon (or filamentous carbon) in the catalysts used in the reforming reaction might indicate gasification of the carbon by carbon dioxide.

The present study investigated the dry reforming reaction of methane using nickel-loaded zeolite-based supports and found that mixed supports of H-mordenite and alumina showed the best catalytic performance. The reason why this catalyst showed the highest activity and highest stability of catalytic performance is unclear. Further study including SEM observation, temperature programmed reduction (TPR) experiments, etc., is now in progress.

4. Conclusion

In the present study, investigation of the activity of Ni-loaded zeolites and zeolite-based supports for dry reforming of methane obtained the following results.

- (1) Activity of the Ni-loaded zeolite catalysts showed the following order: Ni/HM > Ni/NaM > Ni/HY. Ni/HM had the highest activity for dry reforming of methane and retained the activity for 24 h: CO₂ conversion over Ni/HM was 94% and 92% for 5 h- and 24 h-reactions, respectively.
- (2) Mixing of alumina with zeolite could prevent the deactivation of catalyst. Ni/HM-Al₂O₃ tested showed the highest performance among the catalysts in this study and retained the activity for more than 20 h, although the details of the mechanism were unclear.

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要 旨

ニッケル担持ゼオライト触媒を用いたメタンのドライリフォーミング

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ゼオライトをベースとするいくつかの担体に Ni を担持した触媒を用いてメタンのドライ（炭酸ガス）リフォーミング反応を行った。用いた 3 種のゼオライト, H-Y ゼオライト, H-モルデナイト, Na-モルデナイトの中で, H-モルデナイトが最も高活性を示した。参照触媒である Ni/Al₂O₃ と比較すると, ニッケル担持 H-モルデナイト触媒は高い初期活性をもつが, 反応に伴う活性劣化は Ni/Al₂O₃ よりもわずかに速く進行することがわかった。また, ゼオライトとアルミナの混合担体につい

ても活性試験を行ったところ, アルミナと混合することにより, 触媒の活性劣化が抑えられることが明らかとなった。H-モルデナイトとアルミナを混合した担体に Ni を担持した触媒は検討した中で最も高い性能を示し, 常圧の CO₂/CH₄/He 気流下 (20/20/40 ml/min), 750℃ の条件で, CO₂ 初期転化率は 95% を示し, 少なくとも 20 時間以上活性を保つことがわかった。この混合担体に担持した Ni 触媒は, 参照触媒として用いた Ni/Al₂O₃ と比較して高いことがわかった。