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# The reaction of $CO_2$ with $CH_4$ to synthesize $H_2$ and CO over nickel-loaded Y-zeolites

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Nickel metal introduced into Y-zeolite exhibited a high catalytic activity in the dehydrogenation of methane and in the hydrogenation of carbon dioxide with methane to obtain hydrogen and CO at about 850 K. The activity strongly depended on the nickel amount in NaY, and the catalytic properties were influenced by the kind of cations in the Y-zeolite. The higher $CO_2$ conversion was obtained over Ni supported on non-acidic zeolites.

**Keywords:** nickel; Y-zeolite; ion exchange; hydrogenation of carbon dioxide; methane; hydrogen; carbon monoxide; acid strength; electrostatic field

## 1. Introduction

Carbon dioxide may replace steam to a large extent and be used as oxidant in the reforming process (Midrex process) [1]. The increasing interest for C1-chemistry has created synthesis gas with low $H_2/CO$ ratio, which can be obtained by adding $CO_2$ to the reformer feedstock [2]. Nakamura et al. [3] have studied the synthesis gas formation by partial oxidation of methane ($CH_4 + \frac{1}{2}O_2 \rightleftharpoons CO + 2H_2$) and have reported that the synthesis gas was produced by combination of the $CH_4$–$CO_2$ reaction and the water–gas shift reaction over Rh, Ru and Ni catalysts.

It is of interest to utilize these less valuable substances for the direct catalytic pro-

duction of more valuable chemicals at relatively low reaction temperature from the standpoint of reducing $CO_2$ emission. In this work, we have demonstrated that nickel metals introduced into Y-zeolites have very high catalytic activity for the direct reaction of $CO_2$ with $CH_4$. This study aims basically at understanding the mode of activation of reactants over Ni/zeolites and the effect of acid–base properties of the support on the activity of nickel metal in zeolite. However, nickel metal introduced into zeolite support has been little explored as a catalyst for $CO_2$ hydrogenation until now.

## 2. Experimental

The sodium form of Y-zeolite (NaY, $SiO_3/Al_2O_3$) was synthesized from the $7Na_2O$–$Al_2O_3$–$10SiO_2$–$280H_2O$ substrate [4]. Sodium aluminate (Junsei, 32.6% $Na_2O$–35.7% $Al_2O_3$), fine amorphous silica powder (KoFran Co., 91.8% $SiO_2$–8.2% $H_2O$) and sodium hydroxide (Junsei, 95%) were used for NaY preparation. The reaction mixture was stirred for 30 min and aged at 303 K for 24 h in a stainless steel tube (100 ml capacity). The hydrothermal synthesis reaction was carried out at 373 K without agitation. The solid products were washed, filtered and dried at 393 K for 12 h. Alkaline cation exchanged Y-zeolites were prepared by ion-exchanging NaY with an desired alkaline chloride solution at 353 K for 48 h, followed by repeatedly washing with distilled water and drying at 393 K overnight. The ammonium form was converted into the proton form by calcination in a vertical furnace under an air stream at 823 K for 4 h. Nickel ion exchanges were also performed with 1 N nickel nitrate solution at 353 K. The crystalline phase of the zeolite was identified using an X-ray diffractometer (Philips PW-1700, Cu Kα, Ni filter) and the morphology was examined with a scanning electron microscope (Hitachi X-650). Supported nickel catalysts were prepared by impregnating the alkaline cation exchanged zeolites, silica or alumina with an aqueous solution of $Ni(NO_3)_2$. The catalysts were dried in air at 393 K for 10 h after the evaporation of water, and calcined at 773 K for 3 h. $Ni^{2+}$ exchanged Y-zeolites or calcined samples were reduced in a hydrogen stream at 673–773 K for 5 h. Pd and Pt supported Y-zeolites were also prepared in a similar way for the comparison of their catalytic properties.

The hydrogenation reaction of $CO_2$ with $CH_4$ was carried out in a continuous-flow quartz reactor of 10 mm i.d. × 30 cm at atmospheric pressure. The purity of all reactants was ultra-high: $CO_2$ (99.99%), $H_2$ (99.99%), $CH_4$ (99.9%) and He (99.99%). The reaction mixture, which consisted of a 2/1/1 mixture of $He/CH_4/CO_2$, was then introduced into the system. The total flow rate at the reactor outlet was kept at 80–100 $cm^3$/min. The effluent gas was withdrawn periodically and analysed by gas chromatography. The temperature-programmed desorption (TPD) spectra of $CO_2$ desorbed from nickel/supports or supports without nickel metal were measured. 0.1 g of catalyst sample was placed in a small

quartz reactor and reduced in a hydrogen stream for 5 h at 773 K, and cooled in helium. Then $CO_2$ was adsorbed at 323 or 373 K. The relative amount of gases desorbed from the catalyst was determined by TCD in the helium stream with a heating rate of 10 K/min up to 800 K. For temperature-programmed reaction, a mass spectrometer was used to analyse the composition of the effluent stream. The kinetic experiment was performed in a differential reactor mode (<10% conversion) in the reaction temperature range of 673–723 K. The reciprocal space velocity ($W/F_{CO_2}$) was 0.1–30 g h $mol^{-1}$ and the partial pressure ranges of the reactants were 0.02–0.43 atm for hydrogen and 0.02–0.11 atm for carbon dioxide respectively. The data could be fitted into a simple power rate raw type expression by multivariable linear regression.

Coke deposited on the catalysts was examined by TG and DTA.

## 3. Result

The time courses for the reaction of $CO_2$ with $CH_4$ over Ni/NaY and $Ni/Al_2O_3$ are shown in fig. 1. Ni/NaY catalysed the reaction to equilibrium. The reaction products of the $CO_2 + CH_4$ reaction were CO, $H_2$ and $H_2O$ over all catalysts. When the freshly prepared Ni/NaY was exposed to the reactants $CO_2$ and $CH_4$, the decline of $CO_2$ conversion was rapid initially but the decline ceased after

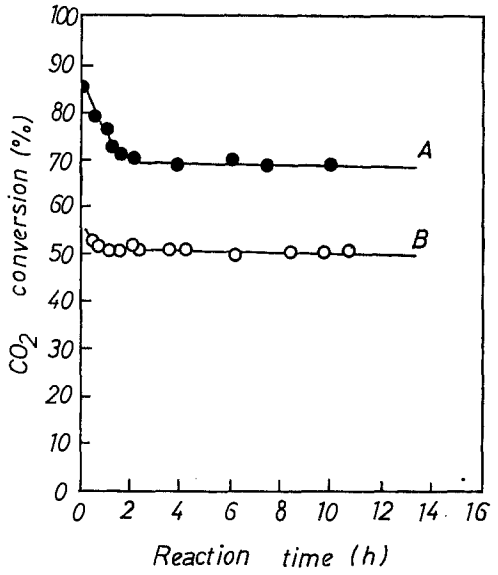


Fig. 1. The effect of reaction time on $CO_2$ conversion in the reaction of $CO_2$ with $CH_4$. Catalyst: 2 wt% Ni/NaY (A), 5 wt% $Ni/Al_2O_3$ (B). Reaction temp.: 873 K; mole ratio: $He/CH_4/CO_2 = 2/1/1$; $W/F_{(CO_2+CH_4)} = 10.1$ (g-zeolite h/mol); 1 g catalyst used. Catalysts were reduced in a $H_2$ stream at 773 K for 3 h. The calculated equilibrium conversion is 80% for the reaction $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$ at 873 K.

2 h of reaction. During the prolonged reaction time no decrease in the crystallinity of the zeolite was observed by X-ray diffraction analysis.

Table 1 shows the conversion of carbon dioxide and that of methane over various catalysts containing Ni, Pd and Pt metals. Ni supported on NaY zeolite showed a high catalytic activity for the dehydrogenation of methane and the hydrogenation of $CO_2$ at about 850 K. The conversion of $CO_2$ over this catalyst reached up to 84%. The higher yield of CO and $H_2$ was obtained over zeolite supports as compared with other oxide supports such as alumina and silica.

Zeolite itself without Ni had no catalytic activity for this reaction. $Ni^{2+}$ ions in the cationic positions of zeolite also did not have any catalytic activity. But by treating $Ni^{2+}$ ion exchanged Y-zeolite with hydrogen at elevated temperature, metallic Ni was formed and protons also appeared ($Ni^{2+} + H_2 \rightarrow Ni^0 + 2H^+$). Dehydrogenation of methane took place over both NiO and reduced Ni metals, when only methane was used as a reactant. Nickel oxide (NiO) introduced into zeolite, silica or alumina support showed similar catalytic properties as those obtained over Ni metals. In the case of nickel oxide catalyst, the hydrogen produced by dehydrogenation of methane has led to the reduction of NiO into Ni metals with release of water.

The dependence of the amount of Ni loaded over NaY on the formation rate of hydrogen and carbon monoxide at 873 K is shown in fig. 2. The activity strongly depended on the nickel amount over NaY, and the maximum conversion of $CO_2$ and $CH_4$ was obtained at 3.3 wt% Ni loading. The formation rate of $H_2$ and CO decreased sharply, when the amount of Ni exceeded more than 2 wt%.

The acid–base properties of zeolites can be modified by exchanging $Na^+$ ions in zeolite with various cations. In order to obtain information about the metal–support interactions which can result in electron transfer between the Ni metal and

Table 1
Catalytic activities of supported metal catalysts for $CH_4$–$CO_2$ reaction [a]

| Catalyst | Conversion (%) | | Formation rate (mol/h mol-metal) | |
|---|---|---|---|---|
| | $CO_2$ | $CH_4$ | CO | $H_2$ |
| $Ni^{2+}$ exchanged Y | trace | trace | – | – |
| $Ni^{2+}$ exchanged Y after $H_2$ reduction at 773 K | 68.4 | 59.7 | 22.4 | 19.9 |
| 2 wt% Ni/NaY | 84.0 | 77.9 | 124.1 | 116.3 |
| 2 wt% Ni/Na-mordenite | 51.1 | 49.7 | 74.2 | 71.8 |
| 2 wt% Ni/$Al_2O_3$ | 36.3 | 33.7 | 53.9 | 49.6 |
| 2 wt% Ni/$SiO_2$ | 14.9 | 12.5 | 22.6 | 18.7 |
| 2 wt% Pd/NaY | 29.2 | 24.8 | 78.3 | 65.8 |
| 2 wt% Pt/NaY | 16.3 | 11.2 | 80.5 | 57.3 |

[a] Reaction temperature: 873 K; $He/CH_4/CO_2$ mole ratio; 2/1/1; $W/F_{(CO_2+CH_4)} = 10.1$ (g-zeolite h/mol). Metal catalyst was reduced in a $H_2$ stream at 773 K for 5 h. $CO_2$ conversion tends to decrease after the start of run. These conversions were obtained initially.

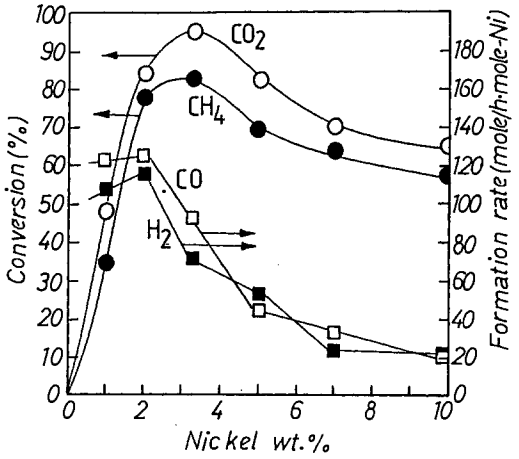


Fig. 2. The effect of the amount of Ni over NaY on the catalytic activity in the reaction of $CO_2$ with $CH_4$. Same reaction conditions as in fig. 1.

support, the reaction of $CO_2$ with $CH_4$ was performed over Ni metals introduced into different cation exchanged Y-zeolites. Fig. 3 shows the formation rate of hydrogen and the conversion of carbon dioxide obtained over various nickel containing catalysts. Ni supported on Y-zeolites with alkali cations has much higher catalytic activity than Ni/HY, Ni/MgY and $Ni^{2+}$ ion-exchanged Y-zeolite, which were used after hydrogen reduction. A higher $CO_2$ conversion was obtained over

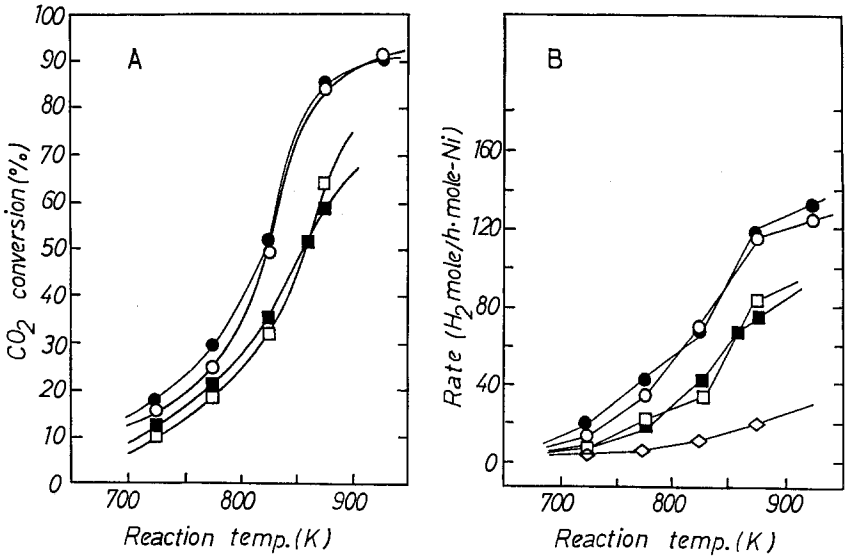


Fig. 3. The effect of cations in Y-zeolite on $CO_2$ conversion (A) and the formation rate of hydrogen (B) in the $CO_2 + CH_4$ reaction. NaY (○), KY (●), HY (□), MgY (■), $Ni^{2+}$ ion exchanged Y after $H_2$ reduction (◇). Same reaction conditions as in fig. 1. *The conversions were obtained initially.*

Ni supported on non-acidic zeolites. The effect of the cation in the Y-zeolite on the catalytic activity in $CO_2$ conversion was examined in more detail. The relationship between the electronegativity of Y-zeolite [12] and the catalytic activity could be drawn as shown in fig. 4. $CO_2$ conversion dereased in the following order:

$$KY > NaY > LiY > BaY > MgY .$$

This figure indicates that nickel metal supported over highly electronegative zeolite has lower hydrogenation activity. As the electrostatic field of the zeolite increased, the $CO_2$ conversion decreased in the $CO_2 + CH_4$ reaction.

The difference in the adsorption strength and capacity of $CO_2$ over Ni/supports were measured by TPD. The profile in TPD runs shows the difference in the adsorption strength and capacity of $CO_2$ over Ni/NaY, Ni/MgY and Ni/HY, as compared in fig. 5. The acid strength of pure zeolite support decreases in the order of HY > MgY > NaY, and the result of fig. 5 indicates that the difference in the $CO_2$ adsorption properties over Ni/zeolites is brought about by the difference in the acid–base properties of supports. The $CO_2$ desorbed in a single peak with a peak temperature of 230°C over Ni/NaY, whereas the $CO_2$ from Ni/MgY and Ni/HY desorbed in two or three distinct peaks continuing to high temperature. Moreover, when the measurement of $CO_2$ desorbed from pure zeolite was carried out by TPD, the peaks of desorbed $CO_2$ were observed around 300–500°C for only MgY and HY zeolite without nickel metal. On the other hand, the small desorption peak of $CO_2$ was measured around 200°C on NaY.

Fig. 6 shows the result of temperature programmed reaction of $CO_2$ adsorbed at 50°C on the Ni/NaY catalyst. This reaction was then started at a heating rate of 10 K/min in a stream containing 20 vol% hydrogen after $CO_2$ adsorption. The

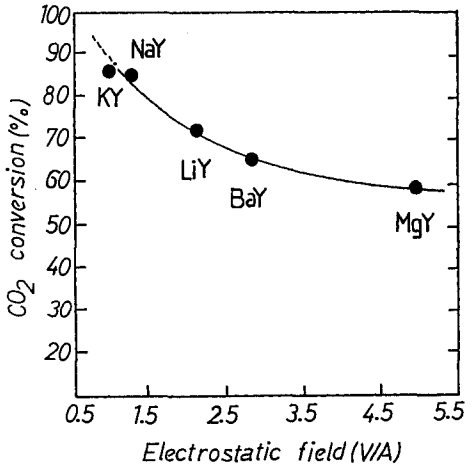


Fig. 4. The effect of electrostatic field of the zeolite on $CO_2$ conversion. Same reaction conditions as in fig. 1.

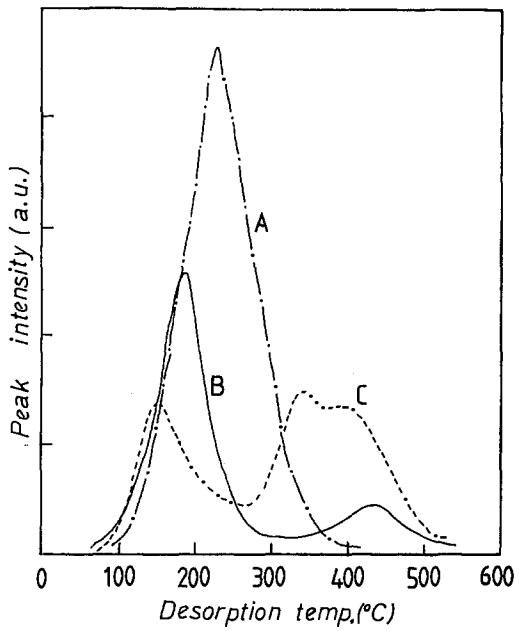


Fig. 5. Temperature programmed desorption spectra of $CO_2$ desorbed from Ni/NaY (A), Ni/MgY (B) and Ni/HY (C). 3.3 wt% Ni/Y-zeolite, $CO_2$ is initially adsorbed at 323 K.

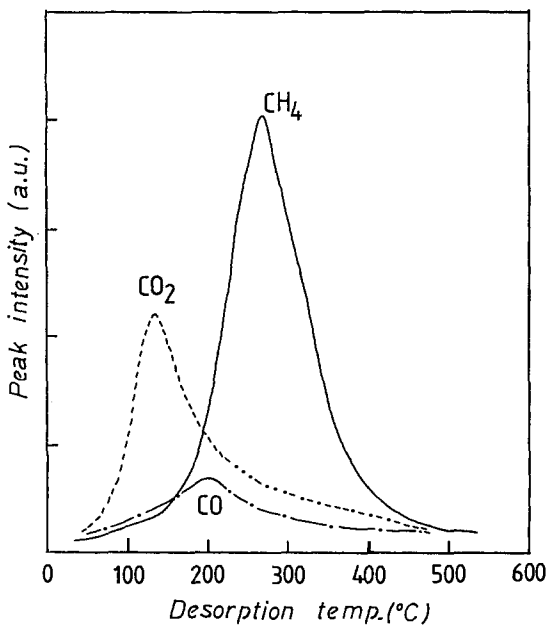


Fig. 6. Methane formation in temperature programmed reaction of $CO_2$ adsorbed on 3.3 wt% Ni/NaY with $H_2$ + He stream. $CO_2$ is initially adsorbed at 323 K.

peak of unreacted $CO_2$ was observed around 140°C. This peak may be corresponding to physically adsorbed or slightly chemisorbed species. One small peak of CO and a strong $CH_4$ peak were observed to occur at 200 and 280°C respectively. In the reaction of $CO_2$ with $H_2$, carbon monoxide was produced as a by-product throughout the reaction temperature, and the methane selectivity increased, instead of the decrease in CO selectivity, as the contact time increased. Judging by these results, methane seems to be produced by the reduction of $CO_2$ via CO as intermediate species at relatively low reaction temperature.

The properties of carbons deposited on Ni/zeolite after the reaction of $CO_2$ with $CH_4$ were examined by TG and DTA, as shown in fig. 7. Coke formation increased as the reaction time elapsed and as the amount of nickel on the support increased. For all the zeolite catalysts, the DTA curve showed one exothermic peak at around 850 K, indicating very similar properties of carbons over the catalysts. When the dehydrogenation of methane was carried out over nickel metal in the absence of $CO_2$, the amount of coke accumulated on the nickel was over 50 wt%, and the same exothermic DTA peak was observed around 850 K.

## 4. Discussion

The formation of hydrogen and CO is known to occur especially at higher temperature with nickel catalyst according to the following reaction:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 . \quad (1)$$

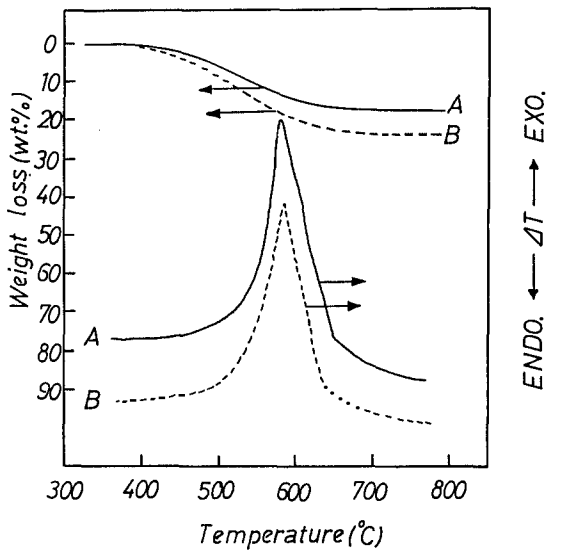


Fig. 7. DTA and TG diagrams of coke-deposited 2 wt% Ni/NaY (A) and 2 wt% Ni/HY (B) after $CO_2 + CH_4$ reaction for 4 h. Heating rate: 5 K/min in air.

In this study, water was observed in the products and the coke was deposited over catalysts. The produced water undergoes plausibly secondary reaction with methane around this reaction temperature:

$$CH_4 + H_2O \rightarrow CO + 3H_2 . \quad (2)$$

The stoichiometry of reaction (1) should give equal conversions for $CH_4$ and $CO_2$, but this is not observed in table 1. This means that some $CO_2$ is hydrogenated to give $CH_4$ and $H_2O$ (methanation), or CO can be formed by recombination of surface carbon and water ($C + H_2O \rightleftharpoons CO + H_2$). Furthermore, the lower yield of hydrogen and the formation of $H_2O$ may be explained by the consideration of the $CO_2 + H_2 \rightleftharpoons CO + H_2O$ reaction.

The result shown in fig. 2 indicates that the dispersion of Ni metal would be important for the difference of catalytic activity, and the active sites for the catalysis could be small metal particles. Vannice [5] and Bhatia et al. [6] have reported that the specific methanation activity increased with increasing nickel crystallite size and the existence of an optimum crystallite size has been suggested. Even though the nickel could be introduced into the intracrystalline structure of zeolite as atomically dispersed species during the preparation, the nickel particles are no longer bounded to the zeolite surfaces and are free to migrate and agglomerate into crystallites of metallic nickel. The hydrogenation activity was dependent on the kind of cation in Y-zeolites and was increased as the acidic strength of zeolite decreased as shown in fig. 3. The strong influence of the kind of cation on the catalytic activity suggests that the catalytically active species may be highly dispersed in the zeolite [7], and these active species remain in zeolite pores near the cations, even though the catalyst was heated at a temperature as high as 873 K. These results also indicate that the support can influence the metal phase in ways other than the change in pertaining to dispersion, and the strength of partial electron transfer from nickel metal to the zeolite cations could result in the different catalytic properties and sorption properties. Tauster et al. [8] have reported that the different sorption capacity is responsible for the chemical interaction between the metal and the support, not due to metal agglomeration. Huang and Richardson [9] have concluded that the higher activity of the less acidic support in the hydrogenation of CO was most probably due to less poisoning by carbonaceous residues due to surface hydroxyl groups migrating to the nickel metal. In addition, acidity may change the character of the nickel through electron transfer across the metal–support interface [10]. As described above, in the case of $Ni^{2+}$ ion-exchanged Y-zeolite, the hydrogen reduction treatment also leads to the formation of acid sites with nickel metals. So this catalyst exhibited the same catalytic activities as nickel metal supported on the acidic HY. Ward [11,12] has reported that the concentration of the Brønsted sites increased with increasing electrostatic field and decreasing cation radius as follows:

$$MgY > CaY > SrY > BaY .$$

It is well known that the divalent cations such as $Mg^{2+}$ and $Ca^{2+}$ localized and their associated electrostatic field may induce the dissociation of coordinated water molecules to produce $MOH^+$ and proton ($H^+$) species. Accordingly Brønsted acidity can be generated in Y-zeolites by exchanging the $Na^+$ ions with alkaline earth ions, and thus the MgY support is more acidic than a comparable NaY support.

It seems that the catalytic activity could be correlated with the change in the nature of Ni agglomerates and in the adsorption properties of metal and supports.

When the reaction of $CO_2$ with $H_2$ was carried out over Ni/NaY, the methane formation rate was found to follow an order of 3.31 to −0.51 with respect to $CO_2$ partial pressure, and a 1.41–3.64 order on the partial pressure of hydrogen. This clearly shows that $CO_2$ and $H_2$ are competing for adsorption sites, and as the reaction temperature increases it becomes increasingly difficult for hydrogen to be adsorbed on the nickel surfaces. The amount of adsorbed $CO_2$ was fairly high on alumina and zeolite, but it was small on $SiO_2$. This result shows that, besides nickel metal, the acidic sites and the cations in the zeolite contribute to the adsorption of $CO_2$. As a result, the peaks around 300–500°C on the TPD curve in fig. 5 could be attributed to the interaction of $CO_2$ not with nickel metal, but with the surface of the zeolite. There exists a direct interaction of $CO_2$ with the cation of the zeolite by an ion–dipolar interaction such as $M^{n+}$- - - O=C=O [11]. Park et al. [13] have found a correlation between the electrostatic field strength of exchanged cations in the zeolite and interacting $CO_2$ molecules, and have shown that the strength of interaction between them has the following order: $Mg^{2+} > Ca^{2+} > Li^+ > Na^+$.

In addition, in fig. 5, the peaks of $CO_2$ desorption were observed around 160, 190 and 220°C over Ni/HY, Ni/MgY and Ni/NaY respectively. This result shows that the $CO_2$ adsorption strength decreases in the order of Ni/NaY > Ni/MgY > Ni/HY. These desorbed peaks under 300°C may be caused presumably by the desorption of $CO_2$ from the nickel metals. Even though $CO_2$ molecules can be adsorbed on the cationic sites in zeolites, they are certainly adsorbed over nickel metals. Furthermore, the formation of methane has to involve the surface reaction between the chemisorbed species on metal catalysts. The adsorption strength between $CO_2$ and Ni metals over zeolite seemed to decrease, as the acidity of zeolite support decreased. It seems likely that the greater the acidity of the support, the greater the electron deficient character of the metal. Sauvion et al. [14] have suggested the indirect influence of the acidity of the support on the reactivity of the nickel particles. The presence of electron acceptor sites on the support can explain that some electron depletion occurs at the metallic surface or small crystallites of the metal, leading to strong metal–support interactions. Then such an electron depletion of the metal can enhance its affinity to chemisorb electron donating molecules such as hydrogen, but hinder the adsorption of the electrophilic reactants. Accordingly, the TPD peaks of $CO_2$ found near 200°C would suggest that the strength of adsorptive carbonate type bond such as Ni–CO and Ni–$CO_2$ could be weaker as the electronic density of nickel metal decreased by the presence of the acid sites and multivalent cations. It is reasonable that the dissociative adsorption

of $H_2$, CO and $CO_2$ occurs only on the nickel metal and not the support. On the basis of the $CO_2$ hydrogenation mechanism as proposed by many authors [15–17], the accrued selectivity to the products would be associated with a more efficient hydrogenation of the active carbon on nickel metals. In the hydrogenation reaction of $CO_2$, it is well known that the dissociative reduction of one or two molecules of $CO_2$ can lead to CO or surface carbon, together with oxide or carbonate entities respectively.

The carbon deposits on metal can be caused by the decomposition of CO and $CH_4$, or of other gaseous reactions [18]:

$$2CO \rightleftharpoons C + CO_2, \qquad CH_4 \rightleftharpoons C + 2H_2,$$
$$CO + H_2 \rightleftharpoons C + H_2O, \qquad CO_2 + 2H_2 \rightleftharpoons C + 2H_2O.$$

These reactions will be favored by metals acting as oxygen acceptors. The carbon species originally produced are believed to be atomic carbon [19,20] and they are known to be very reactive and an important intermediate in reactions such as methanation or methane steam reforming [21,22]. In fact, steam is the most effective gasifying agent [23], and it is possible that carbon and oxygen on surface recombine to form CO [24]. As a result, carbons may also be a major intermediate in $CO_2 + CH_4$ reaction, and the produced water in this system is expected to react with reactive surface carbon to give $H_2$, CO and $CO_2$.

Consequently, for the $CH_4$ reforming by $CO_2$, $CO_2$ hydrogenation proceeds through adsorbed species produced by dehydrogenation of methane and the dissociation of the C–H bond in the $CH_4$ would be a rate-determining step. The dissociative adsorption of $CO_2$ on nickel surfaces would be important in the same manner as the hydrogenation of $CO_2$ with hydrogen. The carbons deposited on nickel catalyst are believed to be important intermediate species in the reaction of $CO_2$ with $CH_4$ as well as in the hydrogenation of $CO_2$. However, the relative surface concentrations and the coverage variation for different exposures of adsorbed reactants could account for the difference in the catalytic properties.

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