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Table 1.

Molecules	Phase transition (°C)^a	Enthalpy change (kJ/mol)
350-22	46 °C	13.3
550-22	64 °C	16.7
750-22	68 °C	76.8
1000-22	68 °C	112.9

^{a}Temperatures are determined by DSC heating scan and attributed to the conformational change in the PEO unit as compared to the temperature dependent Raman spectroscopy.

ment in a coil unit. If the coil is bent, the bond angle along either the carbon-carbon or the carbon-oxygen axis near the junction is subject to change, leading to a new conformer, with the rest segments remained unchanged.

A temperature dependent Raman experiment was performed to further check whether or not the intramolecular interactions are the origin of the 846 cm^1 band. As the temperature increases the 846 cm^{-1} band in 1000-22 gradually diminishes and finally all the bands in 1000-22 become similar to those of the other derivatives at 100 °C, reflecting the unfolding of the coil unit at high temperature (Figure 2). This observation is supported by the DSC study. The coil length dependent variation of the enthalpy change (ΔH) during the phase transition is considered to be associated with the motion of the PEO unit; the value of ΔH for 1000-22 is by far the greatest among the derivatives as shown in Table 1. It is noteworthy that the ΔH increases slightly from 350-22 to 550-22, but suddenly rises at 750-22 indicating that a significant physical change starts with the coil length of $n=17$. This behavior can be also interpreted in terms of the intramolecular interaction resulted from the folding within a long coil unit. For 1000-22, the folding of the coil unit, which is accompanied by the bending of the segment, is more easily formed than for 750-22, thereby generates the modified conformer of which overall molecular shape is significantly different from those of the other derivatives. As a result, the recovery from the folding to the unfolding configuration, which occurs via the breaking of

the dipole interaction within the folded chains, will need more energy than that only from the intermolecular interactions, as clearly supported by the DSC result.

In summary, the intramolecular interactions within the coil unit in the liquid crystalline rod-coil molecule was observed for the first time by Raman spectroscopy. As the PEO coil length increases the 846 cm^{-1} band becomes distinct at low temperature and gradually disappears with increasing temperature. Judging from the experimental results of both Raman spectroscopy and DSC, we conclude that the chain folding of the PEO coil unit is induced as its length is increased.

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Thermogravimetric Study on Reactivity of Carbon Dioxide and Methane over Supported Nickel Reforming Catalysts

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Formation of coke over catalysts during reforming process of methane has been considered seriously as a main reason for catalyst deactivation.[1] In particular, in the CO_2 reforming of methane (so-called "*dry reforming*") coke formation was known to be more serious than any other reforming reactions. This has prevented the easy comm-

ercialization of the dry reforming process. However, this process provides one of the useful methods as the chemical utilization of CO_2 and CH_4 since these gases are considered as notorious greenhouse gases.[2] In addition, from the industrial viewpoint the reaction is also potentially beneficial since it produces CO-rich synthesis gas (H_2/CO) with high

purity rather than steam reforming or partial oxidation of methane does.[3] Supported Ni catalyst is well known as the most typical catalyst for the reforming reactions.[4] To avoid the rapid coke deposition on reforming catalyst, it is essential to elucidate the reactivity of CO_2 and CH_4 on catalyst surfaces in the dry reforming reaction. Previously, we have suggested that zeolite-supported KNiCa catalyst exhibited high activity as well as strong coke resistance for the dry reforming into synthesis gas.[5] The aim of this study is to investigate the activity behavior of CO_2 and CH_4 on the designed catalyst and the role of alkaline metal promoters in the reaction with thermogravimetry.

Zeolite-supported Ni and KNiCa catalysts were prepared by molten-salt method,[5] which were designated as Ni/ZSI and KNiCa/ZSI, respectively, hereinafter. The support was a highly siliceous ZSM-5 zeolite (UOP S-115) mixed with alumina. The loading of metallic nickel on both catalysts was equally 5.3 wt.%. The molar ratio of KNiCa oxide in KNiCa/ZSI was K : Ni : Ca=0.08 : 1.0 : 2.2. The catalytic reaction was carried out in a fixed-bed quartz reactor (i.d., 4 mm) at atmospheric pressure. The catalysts were reduced in the reactor with 5% H_2 in N_2 at 700 °C for 1 h prior to each activity test. Surface dispersion of Ni on the reduced catalysts was determined by static equilibrium H_2 adsorption at 23 °C using Micromeritics' chemisorption analyzer (model ASAP 2000C). Gravimetric changes of the reduced catalysts according to the treatment with methane at 600 °C were measured by IGA (Intelligent gravimetric analyzer, Hiden IGA-002). 51 mg of fresh catalyst was loaded on sample pan which was placed in a gravimetric chamber for thermogravimetric analysis. Temperature-programmed treatment with CO_2 (CO_2-TPO) on the catalysts carburized with methane at 600 °C and temperature-programmed desorption of CO_2 (CO_2-TPD) of reduced Ni catalysts were also investigated by IGA, coupled with mass spectrometer (Hiden DSMS). *In-situ* FT-IR spectroscopic studies were performed in a quartz cell installed self-supported wafers which were treated under vacuum or underwent the same treatment with catalyst testing. Pulse reactions of CO_2 and CH_4 on the reduced KNiCa/ZSI catalyst were conducted in a pulse microreactor (i.d., 4 mm), which was connected to a column of gas chromatograph and a gas sampling valve. In order to clarify whether dehydrogenation of methane is the rate-determining step, CH_4/CD_4 isotope effects were investigated by performing the CH_4+CO_2 and CD_4+CO_2 reactions alternatively over the catalysts in a microreactor at 700 °C.

KNiCa/ZSI catalyst exhibits high activity and high resistance against coke formation in the CO_2 reforming of methane.[5] As shown in Figure 1, its high activity attained to near equilibrium conversions of CO_2 and CH_4 to produce CO and H_2 without catalyst deactivation over 140 h at 800 °C. On the other hand, Ni/ZSI catalyst is also highly active at initial period of reaction, but it is subjected to severe catalyst deactivation due to large coke deposition after 10 h.

Ni dispersions of catalysts reduced at 700 °C are 6.6% for Ni/ZSI and 2.0% for KNiCa/ZSI, respectively. This indicates that the addition of alkaline promoters causes to decrease Ni dispersion of ZSI-supported Ni catalyst.

Weight changes of supported Ni and KNiCa catalysts occurred during methane and subsequent CO_2 treatments are displayed in Figure 2. It is observed from these gravimetric
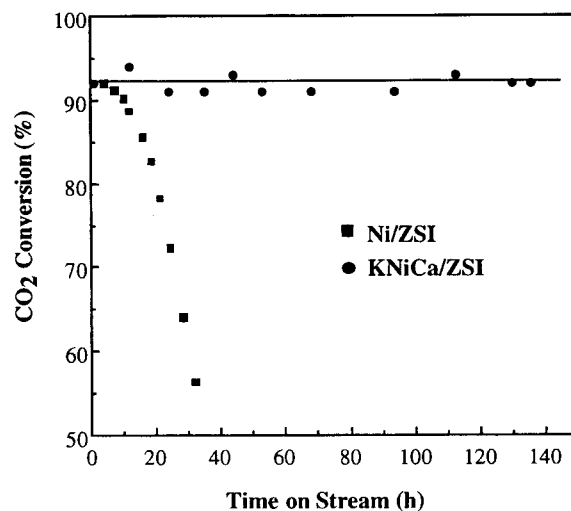

Figure 1. Activity of Ni/ZSI and KNiCa/ZSI catalysts for CO_2 reforming of methane at 800 °C. Reaction conditions: CH_4/CO_2= 1, P_{CO2}=24 kPa, P_{tot}=101 kPa, GHSV=60,000/h, N_2 as the balance gas.

analysis data that methane is more easily decomposed on the reduced surface of Ni/ZSI catalyst than on KNiCa/ZSI one. From weight gain on the catalysts during methane treatment, we can confirm that decomposition activity of methane over Ni/ZSI (0.21 g-coke/g-cat.) is almost 8 times higher than that of KNiCa/ZSI (0.026 g-coke/g-cat.). As we have observed whisker-like carbon filament over Ni/ZSI catalyst after the reaction,[6] it is generally known that whisker-type carbon tends to be formed on supported Ni catalyst under methane flowing through methane decomposition.[1,7] Considering surface Ni dispersion and the increased weight after methane decomposition, the ratios of formed carbon to
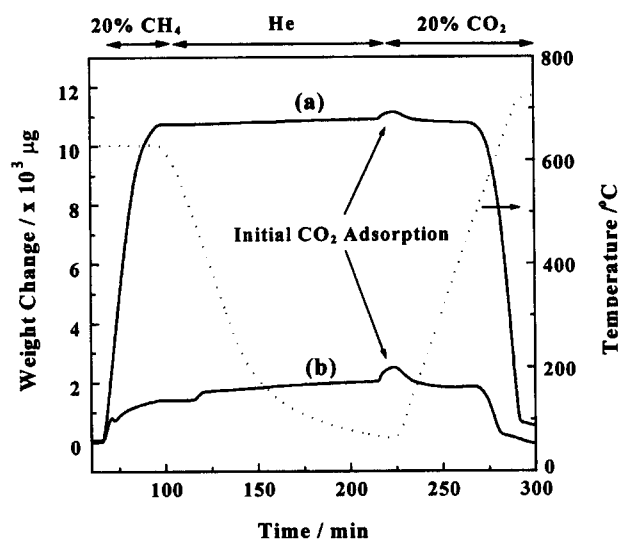

Figure 2. Gravimetric analyses of zeolite-supported Ni catalysts depending on reactions with methane and carbon dioxide: (a) Ni/ZSI and (b) KNiCa/ZSI. Catalysts were carburized with 20 vol.% CH_4 (50 mL/min) diluted in He at 600 °C for 30 min followed by oxidation with 20 vol.% CO_2 (50 mL/min) diluted in He as increasing temperature in a rate of 10 °C/min.
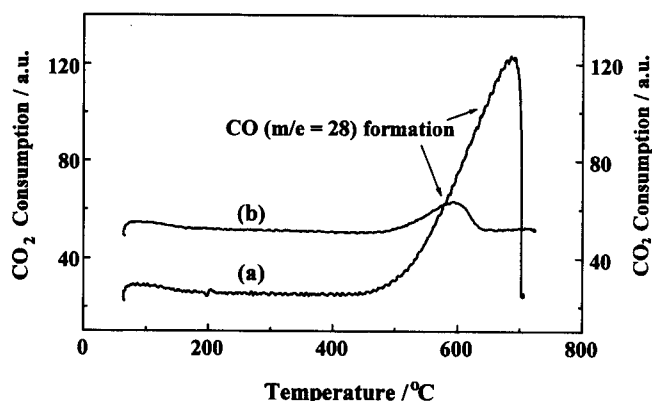
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Figure 3. CO_2-TPO profiles of supported Ni catalysts after carburization with 20 vol.% CH_4 (50 mL/min) diluted in He at 600 °C for 1 h: (a) Ni/ZSI and (b) KNiCa/ZSI. In CO_2-TPO runs, carburized catalysts were oxidized with 20 vol.% CO_2 (50 mL/min) diluted in He as increasing temperature in a rate of 10 °C/min.

surface Ni, C/Ni_s, on the catalysts are much higher than 1, indicating the formation of bulk-like carbon filament together with surface carbon. After methane flowing these carburized catalysts were flushed with He gas and then treated with CO_2 up to 700 °C. After this treatment the initial weight of KNiCa/ZSI catalyst was recovered. However, the resulting Ni/ZSI catalyst was not fully recovered. Profile of its weight change by CO_2 treatment indicates that carbon species are still remained on catalyst surface. Even after treating the carburized Ni/ZSI catalyst with CO_2 up to 700 °C, weight of the used catalyst increases by 1.3 wt.% compared to that of fresh catalyst. This residual coke on Ni/ZSI catalyst can be completely removed with CO_2 treatment at 800-850 °C. On the other hand, the reactivity of KNiCa/ZSI catalyst for the CO_2 dissociation at 600 °C is larger than that of Ni/ZSI.[8]

Figure 3 shows differential profiles on weight loss of catalysts as a function of temperature during CO_2-TPO experiments, which were done after carburization of catalysts with methane at 600 °C for 30 min. The weight loss and mass number of a product generated from carburized catalyst surface by CO_2 treatment with the increase of temperature is identified as CO molecules. This indicates that carbon dioxide plays a role as an oxidant to remove surface carbon species through reverse Boudouard reaction ($C+CO_2 \rightarrow 2CO$). It is noted that there is no formation of water on the carburized Ni surface during CO_2-TPO experiment. Hence, it is assumed that surface carbon species formed on the catalyst are presented mainly as a type of Ni-C(s). This assumption can also be supported by the *in-situ* FT-IR analysis of supported Ni catalyst.[9] It is proposed by the fact that no distinct C-H bands on the catalyst surface are detected in the region of 2700-3100 cm^{-1} corresponding to CH_x adsorbed species after the reforming reaction or CH_4 treatment into *in-situ* cell at 700 °C. This postulation is in good agreement with Zhang and Verykios' suggestion that the surface carbon species on the working Ni catalysts contain no C-H bond, indicating that the the surface carbon species are H-deficient, *i.e.*, CH_x, x is equal to or close to zero.[10]

FT-IR observation of the reduced catalysts reveals that

the behavior of adsorbed CO_2 on KNiCa/ZSI is greatly different from that on Ni/ZSI. FT-IR spectrum of the reduced KNiCa/ZSI catalyst upon the CO_2 adsorption or the reforming reaction shows two distinct bands at 1480 and 1410 cm^{-1}. These are assigned to asymmetric $(v_{as}(OCO))$ and symmetric stretching vibration $(v_s(OCO))$ modes of monodentate carbonate species, respectively, which are supposed to be coordinated to calcium or potassium oxide of the catalyst. However, these bands are not appeared in the case of Ni/ZSI catalyst.[9] The formation of carbonate species upon the CO_2 adsorption sites of the basic catalyst surface would result in high stability of KNiCa/ZSI catalyst due to the prevention of coke deposition on its surface. CO_2-TPD profiles of Ni/ZSI and KNiCa/ZSI catalysts suggest that the integrated amount of CO_2 desorption on KNiCa/ZSI catalyst is larger than that on Ni/ZSI catalyst. Another difference is that CO_2-TPD profile of KNiCa/ZSI exhibits a large desorption peak above 600 °C, which is not observed on Ni/ZSI. This desorption peak indicates the formation of surface carbonate, mainly on Ca promoter due to its greater amount of composition, coincided with the FT-IR result upon the CO_2 adsorption and subsequent desorption.

The dissociative adsorption of CO_2 to produce CO and oxygen on metallic Ni surface of KNiCa/ZSI catalyst are also confirmed from pulse reactions of these gases at 600 °C.[8] Observed results of CO_2 and CH_4 pulse reactions show different behaviors for the dissociation of CO_2 and CH_4 according to the surroundings of catalyst surface. The exposure of CH_4 pulses on the reduced Ni surface of the catalyst produces only H_2 in the gas phase stream, while CO and H_2O are generated together with H_2 when the catalyst is exposed to several CH_4 pulses at 600 °C after the treatment of several CO_2 pulses on the reduced catalyst surface. This explains that surface oxygen species are formed and probably remains on catalyst surface during CO_2 pulses. These oxygen species partially play a role as an oxidant for methane oxidation. The formation of H_2 from CH_4 pulses after the reaction with several CO_2 pulses is lower than that on the freshly reduced catalyst. This is attributed to the loss of hydrogen by its oxidation into water through the surface reaction with the oxygen species formed from adsorbed CO_2. When the catalyst is exposed again to the CO_2 pulses after sequential pulses of CO_2 followed with CH_4, the formation of CO increases with 4 times higher than that of the freshly reduced catalyst at initial stage. Similarly, when the catalyst after exposing several CH_4 pulses at 600 °C is contacted with CO_2 pulses, the amounts of CO formed are much higher than those on the freshly reduced catalyst. These results suggest that catalyst surface is mainly covered with the adsorbed carbon and atomic oxygen intermediates during the reforming reaction.

By performing the CH_4+CO_2 and CD_4+CO_2 reactions alternatively over zeolite-supported Ni catalysts in a microreactor at 700 °C, there are no deuterium isotope effects on CO formation in the process of the CO_2 reforming.[8] When $R_{CO}(CH_4)/R_{CO}(CD_4)$ is defined as the ratio of the rate of CO formation obtained when using CH_4/CO_2 mixture to that when using CD_4+CO_2 mixture, the values of $R_{CO}(CH_4)/R_{CO}$ (CD_4) for KNiCa/ZSI and Ni/ZSI catalysts at 700 °C are 1.00 and 1.04, respectively. This suggests that the rates of CO formation, R_{CO}, over KNiCa/ZSI and Ni/ZSI catalysts is

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not significantly reduced upon replacing CH_4 with CD_4 in the feed mixture, indicating that breaking of the C-H bond of CH_4 molecule is a fast step over these catalysts. This means that the reaction between surface carbon species and the oxidant species (surface oxygen or surface carbonates) would be a rate-determining step over these catalysts.

Consequently, this study demonstrates that metallic Ni sites have strong reactivity on methane, while alkaline metal promoters on carbon dioxide. The retardation of coke deposition on KNiCa/ZSI catalyst is attributed to the abundantly adsorbed CO_2 species. Over the Ni/ZSI catalyst, the surface without potassium and calcium oxides is more reactive with methane. On the other hand, the surface having such promoters is more eligible toward the adsorption and the dissociation of carbon dioxide. Since coke deposition is mainly caused by methane decomposition, the catalyst surface covered with the adsorbed CO_2 or the reactive oxygen species from the dissociation of CO_2 can prevent from coke deposition. The addition of alkaline metal promoters also seems to greatly suppress the activity of supported Ni catalyst for the direct decomposition of methane. In the dry reforming, each dissociation of CO_2 and CH_4 is the initial step to produce CO and H_2, respectively. However, the surface reactions between the adsorbed carbon (Ni-C (s)) and the oxygen (Ni-O(s)) species into carbon monoxide is plausibly proposed as a rate-determining step in this reaction. This step leads to producing the stoichiometric ratio of H_2/CO as an unity in dry reforming and consequently metallic nickel species can be regenerated through the elimination of surface carbon species. Especially, the oxidation step of surface carbon with surface oxygen or sur-

face carbonates over KNiCa/ZSI catalyst is proved to be helpful to eliminate surface carbon species effectively.

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Chloroformyloxylation of Cinnamic Acid and Cinnamonitrile Derivatives by Using the HCl/DMF/Potassium Peroxymonosulfate (Oxone) System

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Halofunctionalization of olefins toward synthetically useful substrates such as halohydrins, β-haloethers, and β-haloesters has received much attention.[1] These compounds were generally prepared from the combination of positive halogen source and appropriate nucleophile sources such as water, alcohols, or carboxylic acids.[2] The chloroformyloxylation achieved by the attack of N,N-dimethylformamide and 1,2-acetoxychlorination by N,N-dimethylacetamide as a nucleophile has been studied.[3]

In the course of our recent studies on the reaction of various kinds of organic substrates with HCl/DMF/Oxone (or m-CPBA) system,[3a-d,4] we presumed to examine the reaction of α,β-unsaturated carboxylic acids or nitriles. In the reactions our interest was focused on whether chloroformyloxylated

derivatives were formed as in the case of α,β-unsaturated esters[4] or β-chlorostyrene derivatives could be generated *via* the Hunsdiecker type reaction mechanism[5] as exemplified in Scheme 1. Thus, we examined the reaction with some cinnamic acid and cinnamonitrile derivatives, and describe the preliminary results in this report.

The reaction of cinnamic acid (**1a**) with this reagent system afforded a mixture of chloroformyloxylated derivative (**2a**, 40%) and chlorohydrin derivative (**3a**, 25%). In the reaction mixtures, we could not observe β-chlorostyrene, the Hunsdiecker reaction product. In the cases of 4-chlorocinnamic acid (**1b**) and 4-methylcinnamic acid (**1c**) the corresponding chloroformyloxylated derivatives were obtained as the major product, and we could observe trace amounts