

Dynamic reaction characteristics affected by water molecules during the methanol to olefin conversion on NiAPSO-34 catalysts

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Abstract

As a method of more stable and quantitative ethylene synthesis at complete methanol conversion, water addition in the reaction was done. The presence of water affected on the coordination of Al or P, and it consequently led to the structural change of NiAPSO-34 crystals. In spite of the partial structural change, the water addition with a proper concentration into the methanol conversion reaction was effective for the increase of selectivity to ethylene, and kept the activity at a constant level. From the results of NH_3 -TPD and IR spectra, it was certified that the amounts of Brønsted acid sites in the catalyst was affected by the steam, and this was adopted to the improvement in the catalytic performance of the methanol conversion. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: NiAPSO-34; Methanol conversion; Ethylene synthesis; Effect of H_2O addition; Brønsted acid sites; Structural change

1. Introduction

After the oil crises, a number of studies on the synthesis of light olefins from alternative resources has been done; however, the route of methanol to olefin conversion (MTO) using zeolites or zeolitic materials as the catalyst has gathered the great attention from the view point of its excellent selectivity, especially the negligible formation of methane and light paraffins [1,2].

Since the vulnerable point of the route is the fast deactivation of the zeolitic catalysts such as chabazite owing to the coke formation on the

too strong acidity distributed on the large cavities, many trials have been made to moderate the acidity by neutralization using basic materials [3–5]; however, in general, such a post-treatment had not solved the problem essentially.

Some silicoaluminophosphates such as SAPO-34 was then adopted to this purpose because of its genuine weaker acidity, although it has the same crystalline structure as chabazite [6–8]. The significant improvement in ethylene selectivity was then achieved by the incorporation of Ni into the framework of SAPO-34-(NiAPSO-34) [9], and it was recognized by other researchers [10,11]. However, the acidity of the catalyst is considerably weak, and it would be sensitively affected by the reaction environment, especially by water. Because wa-

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ter is often adsorbed on the acidic sites and/or active sites more strongly than other reactants and products, and water is frequently used as the desorbing reagent for the enhancement in desorption of products [12,13].

Moreover, as a method regulating acidity of catalyst, water has been introduced into the reaction systems [14–16]. In these papers, it has been proved that the water added on $\text{AlPO}_4\text{-18}$ behaves like methanol [14]. The interaction of methanol and water with acidic sites of zeolites were studied with state of the art models and method [15]. Furthermore, when the water molecule was adsorbed on framework, it was reported that the transition structure had two type with different potential energy, and it was explained that the ion complex form more stable than neutral form in energetic [16]. However, in spite of these many reports, the role of water molecule adsorbed on NiAPSO-34 catalyst in methanol conversion have not been clarified clearly.

On the other hand, when water was combined with the catalyst too strongly, the hydrothermal condition would damage the catalyst structure. In fact, it was reported that SAPO-34 received the structural damage by the contact with water vapor below 100°C ; however, above that temperature even 900°C , it showed the enough stability [17,18]. Therefore, the effect of water on the catalytic performance of NiAPSO-34 during the reaction is significant subject to maintain the catalytic stability.

In this study, the effect of water was then investigated by the contact of water vapor with catalyst and the addition of water vapor in the reaction gas. The change in characteristics of catalyst and its catalytic performance were then comparatively examined.

2. Experimental

2.1. Catalyst

The catalyst was prepared by applying the rapid crystallization method [9,19] to the proce-

cedure for the synthesis of NiAPSO-34. The preparation procedure of the hydrogel for the crystal precursor is described as follows: a 61.275-g portion of aluminum isopropoxide and 0.327 g of nickel nitrate were added to 126.223 g of tetraethylammonium hydroxide placed in a 500-ml beaker, and the mixture was then stirred vigorously by a homogenizer for 5 min. A 9.012-g portion of cataloid, 34.587 g of phosphoric acid, and 30 ml of water were then successively poured into the mixture while stirring. The composition of the final gel mixture was $(\text{TEA})_2\text{O}:0.0075\text{NiO}:0.3\text{SiO}_2:\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:10\text{H}_2\text{O}$. The gel formed was additionally stirred for 10 min. It was transferred into a teflon vessel of 3.0-cm inner diameter and put into an autoclave to provide the hydrothermal crystallization. This was placed in an oven at 200°C for 8 h. The crystal formed was washed repeatedly with distilled water by using a centrifuge, followed by drying at 100°C for 12 h and calcination in air at 600°C for 3 h. It was tableted, crushed and sieved to 20–24 mesh to provide the reaction.

The XRD pattern of the crystal was identified as that of SAPO-34 [6]. The morphology of the crystal was a cubic-like chabazite structure, and the crystal size was 1.0–1.5 μm . The composition of elements analyzed by ICP was Al 1.00, P 0.99, Si 0.11, and Ni 0.001 atomic ratio. The BET surface area of calcined catalyst was $545\text{ m}^2/\text{g}$.

2.2. Method of contact with water vapor

Adsorption of water vapor was carried out as follows: the sample was heated from room temperature to 500°C with a constant heating rate of $3^\circ\text{C}/\text{min}$ in N_2 flow, and kept at that temperature for 30 min. It was then exposed to a stream containing 10–60 mol% steam diluted by N_2 at 100 or 450°C for 2 h with a gaseous hourly space velocity (GHSV) of 500 h^{-1} .

The mixture of water and methanol was used as a feed to the reaction of methanol conversion. The concentration of the mixture was de-

terminated from each mole–vapor enthalpy and the boiling point data of methanol–water mixture [20]. The feed was introduced into a saturator and diluted with N₂ with a GHSV of 500 h⁻¹, and it was then inserted into the catalyst bed for methanol conversion.

2.3. Characterization

Powder X-ray diffraction analysis (XRD) for the catalyst samples was done by using a Shimadzu XD-DI with Nickel filtered Cu K_α radiation (30 kV, 30 mA) at an angle of 2θ range from 5 to 50°.

The change in weight by adsorption and desorption was measured by a microthermo differential and gravimetric analyzer Shimadzu DT-40. A 20-mg portion of α-alumina was used as the reference sample.

The coordination state of Al and P in framework was analyzed by magic angle spinning (MAS)-NMR using a JEOL GSX-270 solid state, high resolution spectrometer. The scan times were over 400 while Al(NO₃)₃ and H₃PO₄ were used as the standard references. High-power decoupling experiments were carried out at 40° with 40.4 MHz for ²⁷Al and at 40° with 193 MHz for ³¹P.

IR spectra were recorded on a Nicolet MAGNA-IR 560 spectrometer with Fourier transform at room temperature by diffuse reflectance method. A 15-mg portion (Sample: KBr = 1:3) of powder sample was packed in a ceramic cell with 5-mm inner diameter which was fixed with a high temperature diffuse reflectance unit. It was treated at 500°C for 15 min in a 30 ml/min N₂ flow before measure-

ment. Fifty scans were accumulated under 4.0 cm⁻¹ resolution.

Acidity of catalyst was estimated by TPD profiles of pre-adsorbed NH₃ using with a Quadruple Mass Spectrometer (M-QA100F) of BEL JAPAN Adsorption of ammonia was done at above 100°C to restrain influence of water.

2.4. Conversion reaction of methanol

Each methanol conversion reaction was carried out by using an ordinary continuous flow reactor. A 0.325-g portion (0.35 ml) of the catalyst was packed into a quartz tubular reactor having 5.0-mm inner diameter, and a reaction gas composed of 15 mol% methanol and 0–10 mol% water vapor diluted with N₂ was allowed to flow with a GHSV of 500 h⁻¹ at a temperature range from 200 to 500°C, for 1–5 h on stream.

The products were analyzed by three FID-type gas chromatographs, Shimadzu GC7A, 12A, and 14A, equipped with integrators. Analyses for methanol and dimethyl ether, C₁–C₄ hydrocarbons, gasoline range hydrocarbons, and CO_x were carried out by using columns porapark T, VZ-10, silicon OV-101, and activated carbon, respectively.

3. Results and discussion

3.1. Stability of NiAPSO-34 under hydrothermal conditions

In Table 1, the amounts of water desorbed from the catalysts treated and non-treated with

Table 1
Desorption amounts of H₂O pre-adsorbed on NiAPSO-34

Catalyst	Condition of treatment	Amount of H ₂ O desorbed (wt.%)	
		30–300°C	300–600°C
NiASPO-34	Stored in dry box ^a	20.86	0.23
NiAPSO-34	H ₂ O adsorption ^b	17.77	1.12

^aAfter the calculation, the sample was exposed over saturated NH₄HO₃ solution at room temperature for 1 day.

^b10 mol% H₂O—90 mol% N₂; GHSV, 500 h⁻¹; treated at 450°C for 2 h.

steam are compared. These consist of two types; one appears at a low temperature range around 30–300°C and another appears at a high temperature range around 300–600°C. The low and high temperature peaks correspond to physical adsorption and chemisorption on NiAPSO-34 crystals, respectively. The amounts of water desorbed at the high temperature range for the catalyst heated at room temperature was considerably smaller; however, for the catalyst treated at the high temperature was much greater than of the former.

The sample was treated with steam under different conditions, and the XRD patterns for these samples are shown in Fig. 1. As shown in this figure, the samples was almost broken-down by the treatment at below 100°C. It has been reported that a high temperature, around 450°C, is a proper reaction temperature for the methanol-to-ethylene conversion on the NiAPSO-34 catalyst [9]. At this temperature, the structural change was scarcely found even with the 30 mol% steam treatment, but with 60 mol% steam treatment at the same temperature, the structure broke down. Recently, it was reported by a few paper that aluminophosphate molecular sieves, in comparison with aluminosilicate zeolites,

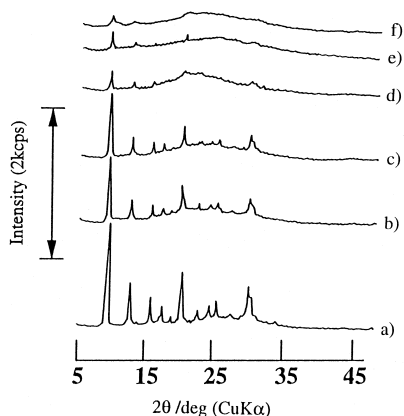


Fig. 1. XRD patterns for catalysts treated with steam under different conditions. (a) Calcined at 600°C for 3 h in the atmosphere; (b) 10 mol% steam diluted by N₂ at 450°C; (c) 30 mol% steam diluted by N₂ at 450°C; (d) 60 mol% steam diluted by N₂ at 450°C; (e) 10 mol% steam diluted by N₂ at 100°C; (f) in liquid water at 80°C for 6 h.

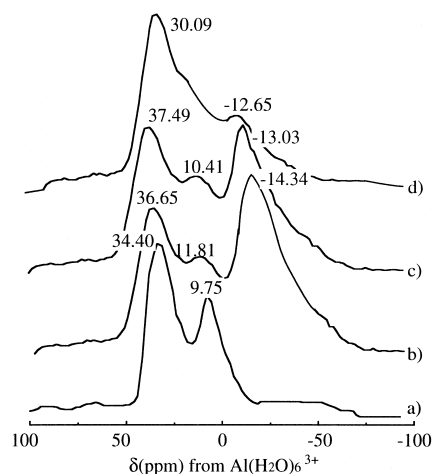


Fig. 2. ²⁷Al MAS-NMR spectra for catalysts treated with steam under different conditions. (a) Uncalcined; (b) after the calcination, the sample was treated with 10 mol% steam diluted with N₂ at 450°C; (c) after the calcination, the sample was exposed over saturated NH₄NO₃ solution at room temperature for 1 day; (d) calcined at 600°C for 3 h in the atmosphere.

show various peculiarities concerning their interaction with water [17]. The problem to be considered is structural damage caused by the water adsorption. In particular, it has been reported that the structural damage occurred at a temperature between 50 and 100°C, when SAPO-34 was exposed to a flow of air saturated with water vapor [18]. The result obtained here shows the fact that aluminophosphate molecular sieves is weaker against water adsorption than aluminosilicate crystals, i.e., zeolites. However, it involves also a fact that these are stable as the catalysts under an appropriate condition at proper temperature with water amount.

MAS-NMR spectra of ²⁷Al and ³¹P for modified samples are shown in Figs. 2 and 3. These NMR studies are suitable to explain coordinated environments for the Al and P atoms of NiAPSO-34 crystal. However, the Si incorporation was insufficient, because it was distributed with asymmetric to framework in small amounts. From these results, it is affirmed that the presence of water molecules involved different aluminum environments [21,22]. In results of the ²⁷Al MAS-NMR spectra of samples, the Al situ-

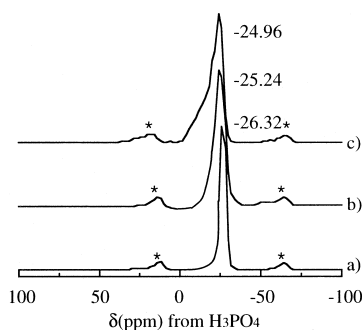


Fig. 3. ^{31}P MAS-NMR spectra for catalysts treated with steam under different conditions. (a) Uncalcined; (b) calcined at 600°C for 3 h in the atmosphere; (c) after the calcination, the sample was treated with 10 mol% steam diluted with N_2 at 450°C .

ations with three broad lines, around -13 ppm as rehydration type, around -10 ppm as five coordination occurred by attachment of one water molecule, and around 40 ppm as dehydration type are shown. Compared with the sample just after calcination, all of the three type bands of Al was clearly shown, in particular, around -13 ppm band assigned to octahedral situation appeared strongly for the sample kept for 1 day exposed over saturated $\text{NH}_4(\text{NO}_3)$ solution. This indicates that the Al atoms given to the line at -13 ppm strongly interacts with water molecules, and this band disappears under a condition of dehydration and also as shown in the samples immediately after calcination and the uncalcined. Furthermore, the more the water molecules was adsorbed to catalyst, the more this band was increased and shifted into downfield. The chemical shift was assumed to come from alternation of the Al nuclear symmetric and distortion of the neighboring framework geometry.

On the other hand, as shown in Fig. 3, since as-synthesized NiAPSO-34 contained template, the ^{31}P MAS-NMR spectra appeared as a single sharp and symmetrical line. However, as shown, for the sample with absorbed water, this was more broaden and asymmetric, and the chemical shifts occurred to upfield corresponding to dehydration change into a symmetric and rather sharp line. Therefore, from these results, this

spectral change clearly indicates that the asymmetrical line resulting from the water molecule attacking P atom, and the coordination of the P atom in NiAPSO-34 was changed, and then, consequently it gave an influence on the catalytic activity.

3.2. Change in acidity of NiAPSO-34 by treatments with steam

In Fig. 4, NH_3 -TPD profiles for samples treated with and without water are compared. These profiles consist of two peaks; one appears at a low temperature range around 150 – 180°C and another appears at a high temperature range around 300 – 350°C . The low and high temperature peaks correspond to the weak and strong acid sites, respectively. As shown, in the profile of the sample non-treated by water (a), the strength of acidity corresponding to the high temperature was significantly larger than that of the low temperature one. However, for the samples with treated with steam, the strong acid sites are remarkably reduced, while the weak acidity is not so much changed. Furthermore, the amounts of adsorbed water molecules are increased as mentioned above, and the strong acid sites are more reduced.

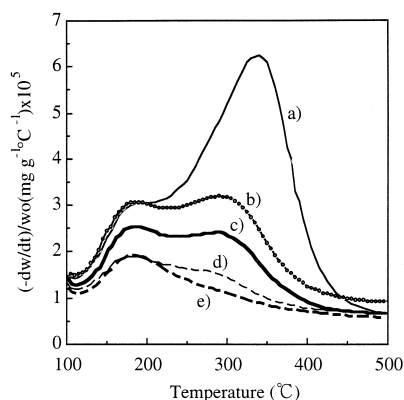


Fig. 4. NH_3 -TPD profiles for catalysts treated with steam under different conditions. (a) Without water adsorption; (b) adsorbed by 10 mol% water at 450°C for 2 h; (c) adsorbed by 30 mol% water at 450°C for 2 h; (d) adsorbed by 30 mol% water at 100°C for 2 h; (e) treated in liquid water at 80°C for 6 h.

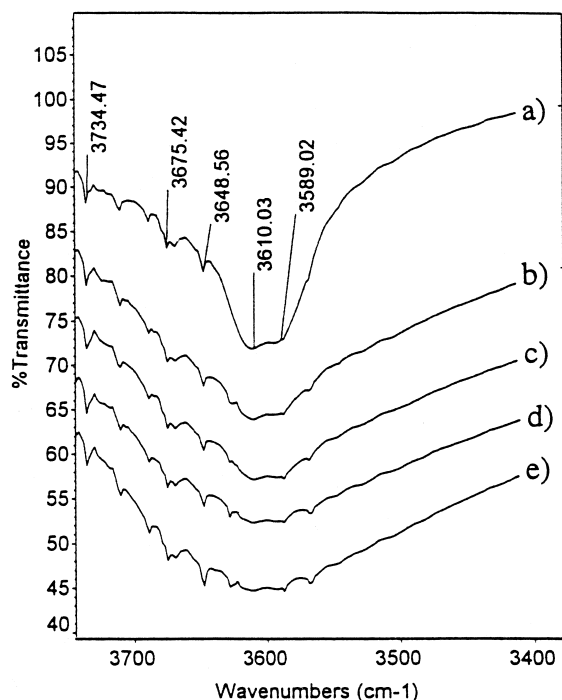


Fig. 5. FT-IR spectra for catalysts treated with steam under different conditions. (a)–(e) are explained in Fig. 4.

In Fig. 5, the diffusive reflectance FT-IR spectra for the samples treated with steam are presented in the region of fundamental OH stretching vibrations. In this paper, these bands are acquired after treatment at 450°C for 15 min. Irrespective of the treated conditions, a hydroxyl band at about 3610 and 3589 cm^{-1}

are observed in all samples. With an increase in the amount of water added, the intensity of the band at 3589 cm^{-1} become strong, compared with that of 3610 cm^{-1} . It indicates that the acidity assigned to Al–OH is changed by adsorption of water. The intensity of bands at around 3675 cm^{-1} for all samples changes in somewhat degree, and it further increased by the addition of water. In particular, it is remarkable that the peak intensity is strong for the band at 3648 cm^{-1} till addition of 30% water. Recently, in accordance with the literatures [23,24], Zibrowius et al. [25] assigned various bands of SAPO-34. The bands at 3690, 3675, and 3648 cm^{-1} are very closed to hydroxyl group contacting with an amorphous aluminophosphate, as ascribed to fundamental stretching vibrations of surface POH or AlOH groups, while the band at 3735 cm^{-1} is assigned to terminal SiOH groups. Therefore, the increase in the bands at 3675 and 3648 cm^{-1} means that amorphous aluminum atoms were increased by dealumination owing to addition of water. Compared with other bands, the bands at 3610 and 3589 cm^{-1} which would be used as acid sites for methanol conversion were decreased. It indicates that the acid sites are properly relaxed by water adsorption, and consequently it might lead to higher ethylene selectivity.

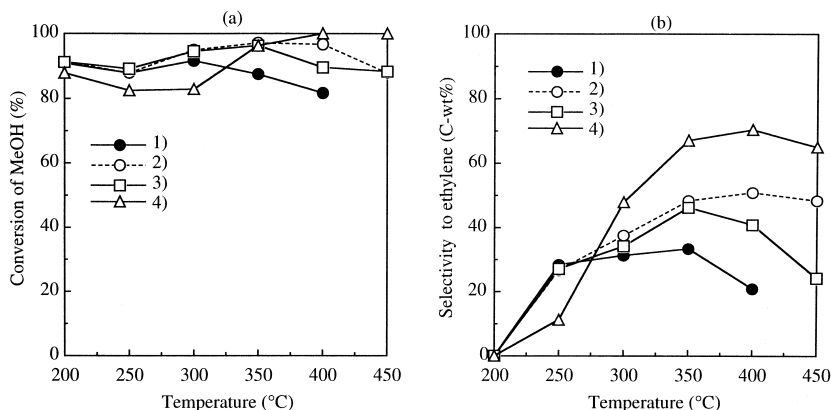


Fig. 6. Effect of concentration of H_2O added on the catalytic performance. (a) Conversion of MeOH; (b) Selectivity to ethylene. 15 mol% MeOH-balance N_2 : (1) without H_2O ; (2) 2 mol% H_2O ; (3) 5 mol% H_2O ; (4) 10 mol% H_2O . Reaction conditions: GHSV, 500 h^{-1} ; Time on stream, every 1 h while elevating temperature.

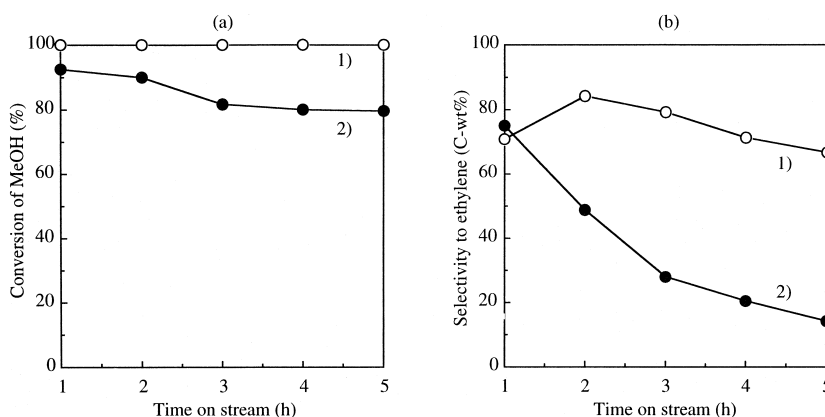


Fig. 7. Effect of H₂O addition on the catalytic performance. (a) Conversion of MeOH; (b) Selectivity to ethylene. 15 mol% MeOH-balance N₂: (1) without H₂O; (2) 10 mol% H₂O. Reaction conditions: GHSV, 500 h⁻¹; Time on stream, 5 h; Reaction temperature, 450°C.

3.3. Methanol conversion

The changes of methanol conversion and selectivity to ethylene caused by water addition to the feed are shown in this Fig. 6(a) and (b), respectively, as a function of temperature. Addition of water remarkably increased the selectivity to ethylene at higher temperature range. Especially, addition of 10 mol% water, enhanced the methanol conversion to 100% and the selectivity to ethylene 70%. These correspond to the results of FT-IR which displayed

the relaxation of acid sites in the sample treated with water as mentioned above.

In Fig. 7(a) and (b), the catalytic performances between the reactions with and without addition of 10 mol% H₂O to the reactant are shown. As shown in case of H₂O addition, the conversion of MeOH was kept as 100% during the test (5 h) and the selectivity to ethylene was kept as high as 80%. The role of water to the catalyst would be ascribed to the supply of protons to the Brønsted acid sites which are responsible for the objective reactions. The cat-

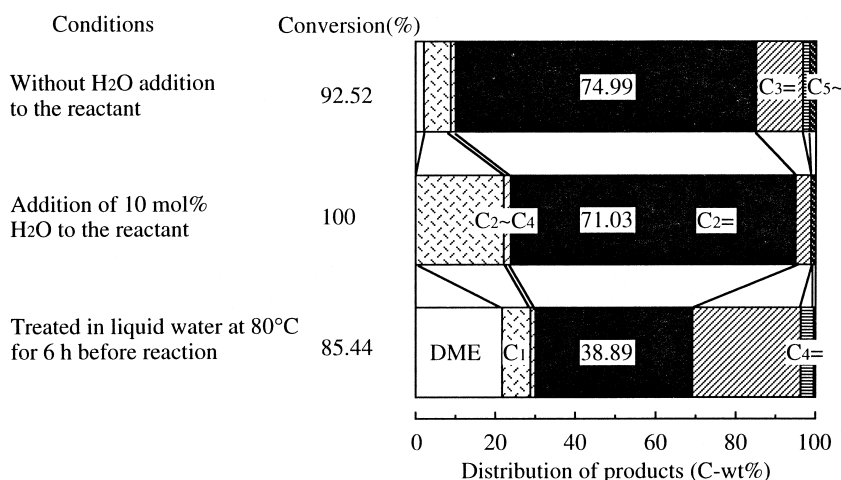


Fig. 8. Product distributions of the reactions with and without H₂O addition. Reaction conditions: 15 mol% MeOH, without or with 10 mol% H₂O balance N₂; GHSV, 500 h⁻¹; time on stream, 1 h; reaction temperature, 450°C.

alytic performance was much better than that of the case without H₂O addition.

The product distributions on 1-h steam for the reactions with and without H₂O addition are shown in Fig. 8. Apparently, at the beginning of time on stream, the ethylene selectivity in the case of without H₂O addition was higher than the case of with H₂O addition. However, as mentioned above in the case of without H₂O addition, the selectivity to ethylene decreased with an increase of time on stream. In order to compare the result of the reaction on the catalyst pre-treated with liquid water at 80°C for 6 h is shown in the same figure. By the treatment with liquid water, the crystalline structure was broken as shown in Fig. 1, and gave a poor performance in the methanol to ethylene conversion reaction. Therefore, proper conditions to add water vapor into the reactant, such as 10 mol% H₂O at the reaction temperature around 450°C, are necessary to obtain the continuous catalytic performance with a high selectivity to ethylene.

Effect of space velocity on the catalytic performance under the condition of 10 mol% H₂O addition is shown in Fig. 9. With an increase in GHSV, the conversion decreased in somewhat extent and the selectivity to ethylene decreases rather markedly. This would be attributed to the

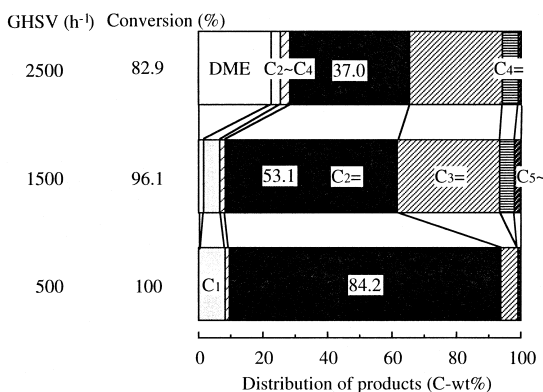


Fig. 9. Effect of space velocity on the product. Reaction conditions: 15 mol% MeOH–10 mol% H₂O–75 mol% N₂; time on stream, 1 h; reaction temperature, 450°C.

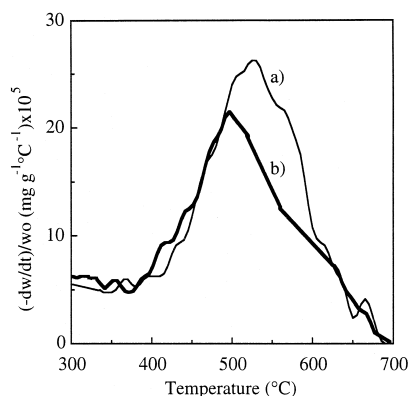


Fig. 10. Profiles of temperature-programmed oxidation for the deposited coke on catalysts during the reactions with and without water. (a) Reaction without H₂O; (b) reaction with 10 mol% H₂O. Reaction conditions: 15 mol% MeOH, without or with 10 mol% H₂O balance N₂; GHSV, 500 h⁻¹; time on stream, 5 h; reaction temperature, 450°C. TPO conditions: used catalysts: 20 mg, 75% O₂–25% N₂; temperature rise: 10°C/min.

contact with excessive water leading to collapse of structure.

The coke deposited on the catalysts was analyzed by temperature-programmed oxidation (TPO) and the profiles are shown in Fig. 10. Compared with the reaction without water, the amount of coke deposited in the reaction with water was significantly small indicating that water retards the coke formation.

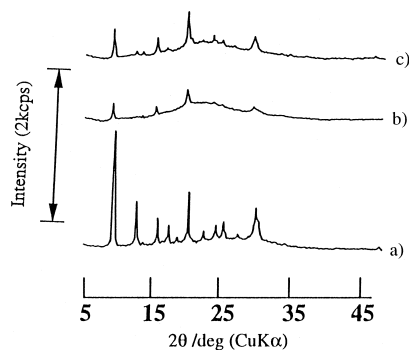


Fig. 11. XRD patterns for catalysts after the methanol conversion reaction shown in (a) and (b) of Fig. 7. (a) Before use for the methanol conversion reaction; (b) after use for the reaction without H₂O addition; (c) after use for the reaction with 10 mol% H₂O addition.

3.4. Structural change after the methanol conversion reaction

In order to examine the structural stability during the reaction, XRD patterns of samples of before and after use were measured. The results are shown in Fig. 11. The peak intensities for XRD patterns of used catalysts were markedly reduced, irrespective of the reaction conditions with or without water addition. However, the structural damage for the catalyst with water addition was still less than that without water addition after methanol conversion, suggesting that the deposited coke would partly reduce the crystals and bring about its some destruction at such a considerably higher temperature condition.

4. Conclusions

The selectivity to ethylene in methanol conversion reaction on a NiAPSO-34 catalyst was remarkably enhanced and the conversion of methanol was kept at a high level by the addition of water to the reactant. The coke deposit was decreased and structural change was retarded by the addition of water with a proper concentration such as 10 mol%. It is considered that water molecules provide protons to the Brønsted acid sites and maintain the catalytic performance.

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