

# Effects of Acidic Properties of FSM-16 on the Catalytic Conversion of 1,2-Propandiol in the Presence and Absence of Hydrogen

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We have earlier showed how the catalytic conversion of 1,2-propandiol to propanal using FSM-16 (#16 folded sheets of mesoporous materials) when molded by wet treatment proceeded more favorably than when using FSM-16 molded by pressurization, while no comparison using other typical acidic catalysts and no examination of the acidic properties of FSM-16 was carried out. In the present study, the conversion using FSM-16 molded by wet treatment and pressurization was compared with that obtained by using typical acidic catalysts such as SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> and MCM-41 (#41 of Mobil Composition of Matter) together with amorphous SiO<sub>2</sub>. Among these catalysts, FSM-16 molded by wet treatment showed the most suitable catalytic activity. In order to examine the effect of the molding procedure for FSM-16 on its structural and acidic properties, FSM-16 molded by both methods was examined using NH<sub>3</sub>-TPD, *in situ* FT-IR using NH<sub>3</sub> as a probe molecule, and Hammett indicators together with XRD and TEM. According to Zaitsev's rule, the present conversion should afford acetone rather than propanal, which indicates that it would proceed via hydro cracking. Therefore, the conversion of 1,2-propandiol using FSM-16 was also examined in the presence and absence of hydrogen. Furthermore, hydration reactions of 1- and 2-propanol when using FSM-16 were examined. Based on the results obtained from this investigation, it was concluded that the conversion using a more acidic FSM-16 molded by wet treatment proceeded through dehydration rather than through hydro cracking.

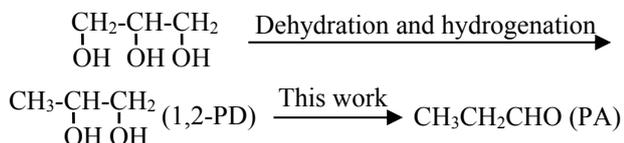
## Introduction

Since an extreme surplus of glycerol is produced as a by-product of biodiesel fuel production, its effective use has recently attracted attention for propanal production (Mori *et al.*, 2009). Glycerol can be favorably converted to 1,2-propandiol (1,2-PD) via dehydration to hydroxyacetone, followed by hydrogenation to the diol (**Figure 1**) (Chiu *et al.*, 2008; Huang *et al.*, 2008; Sato *et al.*, 2009). In a previous paper, we reported that the conversion of 1,2-PD to propanal (PA) effectively proceeded with FSM-16 (#16 folded sheets of mesoporous materials) (Figure 1) (Sugiyama *et al.*, 2013b). FSM-16 was first prepared in 1993 (Inagaki *et al.*, 1993). It is hexagonal and has strong acidic properties comparable to another typical mesoporous silica MCM-41 (#41 of Mobil Composition of Matter) (Iwamoto *et al.*, 2003). Yamamoto *et al.* (1998) concluded that the acidic sites were weakly perturbed silanol groups and that a trace amount of Al in FSM-16, which may be included in sodium silicate powder as the raw material for the preparation of MCM-41, did not affect acidic properties of FSM-16. PA can

convert to methyl methacrylate (Sugiyama *et al.*, 2011, 2013a), which is widely used as the precursor of acrylic resin (Albanesi and Moggi, 1983; Jackson, 2002; So, 2010). Therefore, the catalytic conversion of 1,2-PD to PA is one of the most likely uses of glycerol. In our previous paper (Sugiyama *et al.*, 2013b), the conversion of 1,2-PD to PA effectively proceeded with FSM-16, particularly when molded by wet treatment rather than by typical pressurization. Although the present conversion may occur on the acidic site with FSM-16, as with the typical dehydration of alcohol, comparisons with other typical acidic catalysts and an examination using the acidic properties of FSM-16 were not carried out. Furthermore it is rather strange that the present conversion did not proceed via the usual dehydration route based on Zaitsev's rule, according to which the dehydration of 1,2-PD should form acetone rather than PA. This may indicate that the present conversion proceeds via hydro cracking, rather than dehydration.

Therefore, in the present study, the conversion of 1,2-PD to PA with FSM-16 molded either by wet treatment or by pressurization was compared with that using the silica-supported heteropoly acid,

SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub>, and MCM-41, together with amorphous SiO<sub>2</sub>. Then, the acidic properties of FSM-16 molded by both methods were examined using various techniques such as NH<sub>3</sub>-TPD, *in situ* FT-IR using NH<sub>3</sub> as a probe molecule, and Hammett indicators. Finally, the conversion using FSM-16 was also examined in both the presence and absence of hydrogen in the feed. The dehydrations of 1- and 2-propanol on FSM-16 were also examined in order to elucidate the dehydration behaviors of primary and secondary alcohols.



**Fig. 1** Reaction scheme for the present study

## 1. Experimental

The preparation and molding procedures for FSM-16 were the same as those shown in our previous paper (Sugiyama *et al.*, 2013b). In the present study, FSM-16 molded via wet treatment or pressurization was denoted as W-FSM-16 or P-FSM-16, respectively. Typical impregnation was employed for the preparation of SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> using silicotungstic acid (0.451 g; Nippon Inorganic Colour Chemical Co. Ltd.) and SiO<sub>2</sub> (1.508 g; Q-6-60, Wako Pure Chemical Industries, Ltd.). MCM-41 was prepared using colloidal silica (Snowtex 20, Nissan Chemical Industries, Ltd.) and dodecyltrimethylammonium bromide (Wako Pure Chemical Industries, Ltd.), according to a procedure reported by Iwamoto *et al.* (2003). An amorphous silica, SiO<sub>2</sub> (CAB-O-SIL, Cabot Co.), was used in the present study. MCM-41 was molded via wet treatment, while pressurization was used for the molding of SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> and SiO<sub>2</sub>. The catalysts were characterized using X-ray diffraction (XRD; RINT 2500X (Rigaku Co.) with monochromatized Cu K $\alpha$  radiation). N<sub>2</sub> adsorption-desorption isotherms were obtained using BELSORP-18SP (Bel Japan Inc.). Transmission electron microscopy (TEM) images of the catalysts were recorded using JEM-2100F (JEOL Ltd.). The adsorption behaviors of ammonia on the catalysts were characterized by temperature-programmed desorption (NH<sub>3</sub>-TPD; BELCAT-A-SP, Bel Japan Inc.) and *in situ* infrared spectroscopy (*in situ* NH<sub>3</sub>-FT-IR; FTX3000MX, resolution of 4 cm<sup>-1</sup>, Bio Rad Inc.). In NH<sub>3</sub>-TPD, a catalyst (50 mg) was heated to 773 K at a rate of 10 K/min under a He flow (50.0 sccm (standard cubic centimeter per min)), and was then held at this temperature for 1 h under the He flow. Then, the catalyst was cooled to 373 K under the He flow, and held at this temperature for 10 min. The catalyst was then treated with 5% NH<sub>3</sub>/He (50.0 sccm) for 30 min. After the treatment, He was replenished (50.0 sccm) and

the catalyst was kept in the He flow for 15 min. Then, the catalyst was heated from 373 to 773 K at a rate of 10 K/min under the He flow (30.0 sccm). The desorbed NH<sub>3</sub> from the catalyst during the final process was analyzed using a quadrupole mass spectrometer (OmniStar-s, Pfeiffer Vacuum GmbH). The fragment peak at m/e = 16 was used to monitor the NH<sub>3</sub>. The catalyst was also analyzed using *in situ* NH<sub>3</sub>-FT-IR. A catalyst disc, 13 mm in diameter and approximately 8.5 mg in weight, was degassed in the *in situ* FT-IR cell (Katoh *et al.*, 2012) at 723 K and 6.0×10<sup>-3</sup> Pa for 1 h. Then, the temperature was reduced to 323 K and the IR was monitored at this temperature to obtain a standard spectra. NH<sub>3</sub> gas (13.3 kPa) was introduced into the cell at 323 K for 10 min. The excess NH<sub>3</sub> gas was then degassed from the cell at 323 K in order to monitor the IR. The temperature was increased to 423 K and maintained for 10 min. The IR was again monitored. This process was repeated at 523, 623, and 723 K. Furthermore, acidic properties of the catalysts were also analyzed using Hammett indicators (Hawke and Steigman, 1954). Thermo gravimetric (TG) analysis was carried out with a TG/DTA 6300 apparatus (Seiko Instruments Nanotechnology Inc.) with a heating rate of 5 K/min under flowing air (100 mL/min).

The catalytic conversions of 1,2-PD, 1-propanol, or 2-propanol were performed using a fixed-bed down-flow reactor. Unless otherwise stated, the catalyst (0.15 g, 0.85—1.70 mm) was heated to 673 K, under a continuous flow of He (30 mL/min). It was then pretreated with O<sub>2</sub> or 5% H<sub>2</sub>/He (both at 25 mL/min) for 1 h. After these pretreatments, the temperature was adjusted at 673 K for the conversions of 1,2-PD, 1-propanol, or 2-propanol. Then, a reactant solution of 1,2-PD, 1-propanol, or 2-propanol was supplied from the top of the reactor at a liquid feed rate of 1.7 mL/h, together with He or 5% H<sub>2</sub>/He at 30 mL/min as a diluent gas. In order to examine the contribution of hydro cracking to the conversion of 1,2-PD, 5% H<sub>2</sub>/He was used as the He source. No homogeneous reaction of 1,2-PD, 1-propanol, or 2-propanol was detected under the present reaction conditions. The effluent was collected in methanol under ice cooling conditions and was analyzed using a gas chromatograph (GC-8AP, Shimadzu Corp.) equipped with a 3.2 mm × 2 m glass column (Gaskuropack 55) with a thermal conductivity detector and a capillary gas chromatograph (GC-2010 Plus, Shimadzu Corp.) with a 0.25 μm × 60 m glass column (Stabilwax) and a flame ionization detector.

## 2. Results and Discussion

### 2.1 Comparison of the catalytic activity for the conversion of 1,2-PD on acidic catalysts

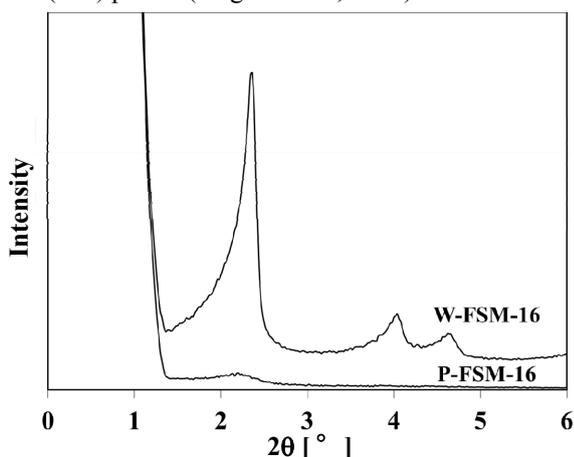
The catalytic activities for the conversion of 1,2-PD using W-FSM-16, P-FSM-16, MCM-41, and SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> are described in **Table 1**. As expected

Catalyst	Time-on-stream [h]	Conv. [%]	Selectivity [%]					Yield [%]
		1,2-PD	Propanal	Acetone	Allyl alcohol	1-Propanol	Others	Propanal
W-FSM-16	0.25	98.8	48.3	13.7	6.3	14.0	17.7	47.7
	1.75	96.1	55.2	15.8	9.7	17.5	1.8	53.0
	4.50	91.0	52.5	15.5	10.3	20.6	1.1	47.8
P-FSM-16	0.25	39.7	67.6	5.0	0.0	0.0	27.4	26.8
	1.75	12.2	68.0	6.5	0.0	0.0	25.5	8.3
	4.50	4.7	84.6	2.6	0.0	0.0	12.8	4.0
MCM-41	0.25	99.2	39.9	2.1	3.1	4.7	50.2	40.0
	1.75	97.7	43.6	2.3	3.3	5.9	44.9	42.6
	4.50	94.5	32.1	1.8	2.8	10.2	53.1	30.3
SiW <sub>12</sub> O <sub>40</sub> /SiO <sub>2</sub>	0.25	99.4	83.9	0.8	2.4	1.7	11.2	83.4
	1.75	14.4	56.0	1.7	4.3	9.5	28.5	8.1
	4.50	5.0	37.9	3.6	2.4	13.8	42.3	1.9

from the previous study ( Sugiyama *et al.*, 2013b), the activities using W-FSM-16 were greater and more stable than those using P-FSM-16. MCM-41 also showed stable activity for the conversion of 1,2-PD, while both the selectivity to and the yield of PA were lower than the values obtained using W-FSM-16. Although the initial activity using SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> was excellent, it also showed the lowest stability for the conversion. The conversion of 1,2-PD using amorphous SiO<sub>2</sub> was less than 0.4% (not shown). Therefore, conversion carried out using W-FSM-16 showed the highest stability and activity. W-FSM-16 and P-FSM-16 catalysts were analyzed using various techniques to examine the effects of molding on their structural and acidic properties.

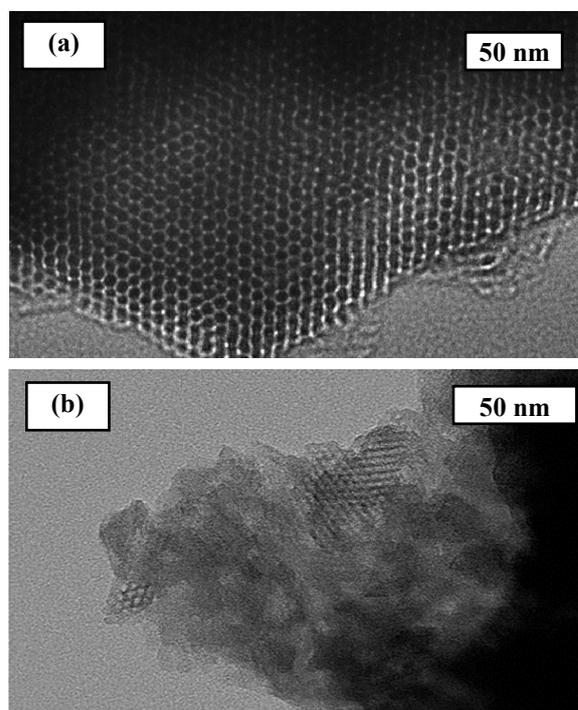
## 2.2 Structural properties of W-FSM-16 and P-FSM-16

As shown in **Figure 2**, the XRD patterns of W-FSM-16 matched with the three diffraction peaks due to the hexagonal structure of FSM-16; these peaks were assigned as diffraction peaks due to the (100), (110), and (200) planes (Inagaki *et al.*, 1993).



**Fig. 2** XRD patterns of W-FSM-16 and P-FSM-16 at diffraction angles lower than 6.0°

However, the XRD patterns of P-FSM-16 did not show the characteristic three peaks, indicating that the hexagonal structure characteristic to FSM-16 was not present in P-FSM-16. A disappearance of the hexagonal structure after the molding by pressurization was also detected by using TEM and N<sub>2</sub> adsorption-desorption isotherms. As shown in **Figure 3 (a)** (Sugiyama *et al.*, 2014 submitted), W-FSM-16 showed a hexagonal structure in its overall TEM image, while only a small part of the TEM image of P-FSM-16 showed a hexagonal structure (**Figure 3 (b)**). This indicates that pressurization deteriorates the hexagonal structure of FSM-16.



**Fig. 3** TEM images of (A) W-FSM-16 and (B) P-FSM-16

The N<sub>2</sub> adsorption-desorption isotherms for W-FSM-16 and P-FSM-16 reported in our previous paper (Sugiyama *et al.*, 2013b) show that W-FSM-16 has a typical type IV curve with a hysteresis loop, indicating the presence of mesopores. In contrast, the isotherm for P-FSM-16 shows a type I curve, indicating the absence of mesopores. Therefore, the surface area, pore volume, and pore size of W-FSM-16, as estimated from the isotherms, are evidently greater than those of P-FSM-16 (Table 2). Since the catalytic activity with W-FSM-16 is more suitable and stable than that with P-FSM-16 (Table 1), it can be concluded that the presence of the hexagonal structure directly contributed to the catalytic activity.

**Table 2** Surface area, pore volume, and pore size of W-FSM-16 and P-FSM-16 obtained from N<sub>2</sub> adsorption-desorption isotherms

	W-FSM-16	P-FSM-16
Surface area [m <sup>2</sup> g <sup>-1</sup> ]	595	476
Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]	0.61	0.34
Pore size [nm]	4.07	2.89

### 2.3 Acidic properties of W-FSM-16 and P-FSM-16

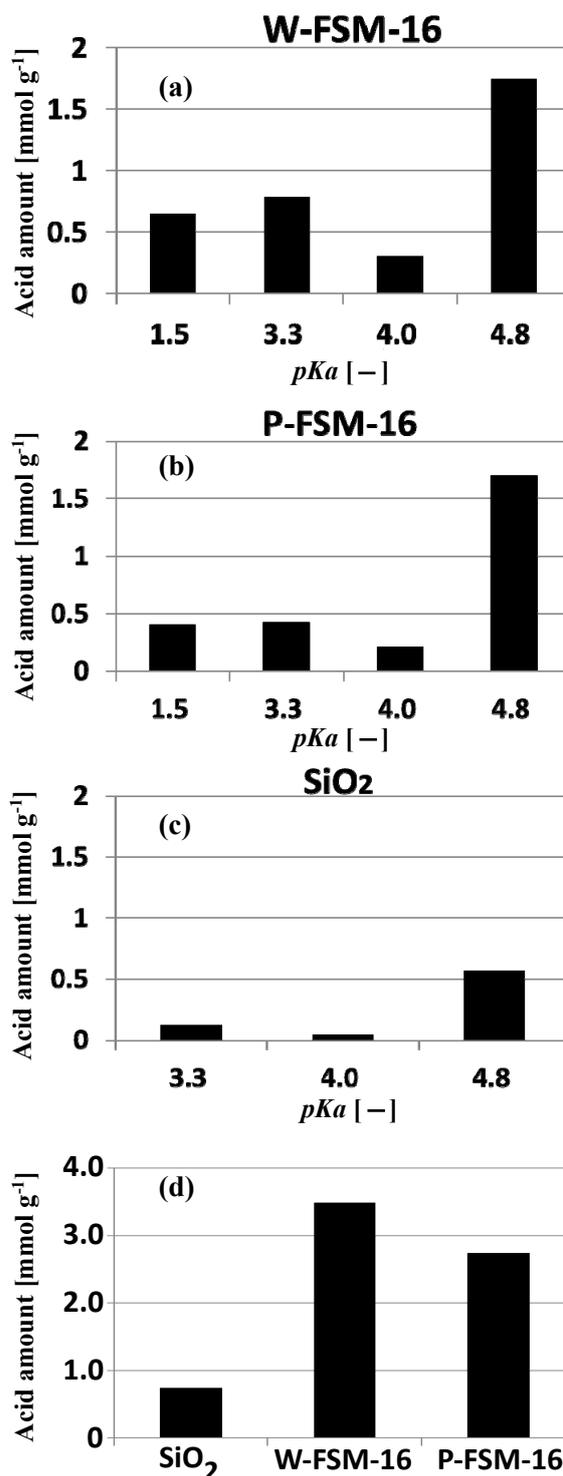
After carefully examining the acidic properties of FSM-16, Yamamoto *et al.* (1998) suggested that the active sites of FSM-16 were weakly perturbed silanol groups while a trace amount of Al derived from the raw material sodium silicate powder did not affect the acidic properties. They have also reported that the greatest acid strength of FSM-16 reached a pKa; -3.0. As shown in Table 3, in which the acid strength of amorphous SiO<sub>2</sub> is also described as a reference, the acid strengths of W-FSM-16 and P-FSM-16 were similar (1.5 < pKa < 4.8) and both had weaker acidity than that found by Yamamoto *et al.* (1998).

**Table 3** Acid strength estimated using Hammett indicator

Hammett indicator	pKa	W-FSM-16	P-FSM-16	SiO <sub>2</sub>
Neutral red	6.8	—	—	—
Methyl red	4.8	+	+	+
4-Phenylazo-1-naphthylamine hydrochloride	4.0	+	+	+
Methyl yellow	3.3	+	+	+
4-Phenylazodiphenylamine	1.5	+	+	—
Dicinnamalacetone	-3.0	—	—	—
Chalcone	-5.8	—	—	—

Although the difference in the catalytic activity of W-FSM-16 and P-FSM-16 could not be explained by acid strength, it is of interest to note the difference in the acid amounts of the two catalysts. As shown in Figure 4, the acid amounts of W-FSM-16 at pKa = 4.8, 4.0, 3.3, and 1.5 (Figure 4 (a)) were evidently greater than those of either P-FSM-16 (Figure 4 (b)) or amorphous SiO<sub>2</sub> (Figure 4 (c)). The total acid amount of W-FSM-16

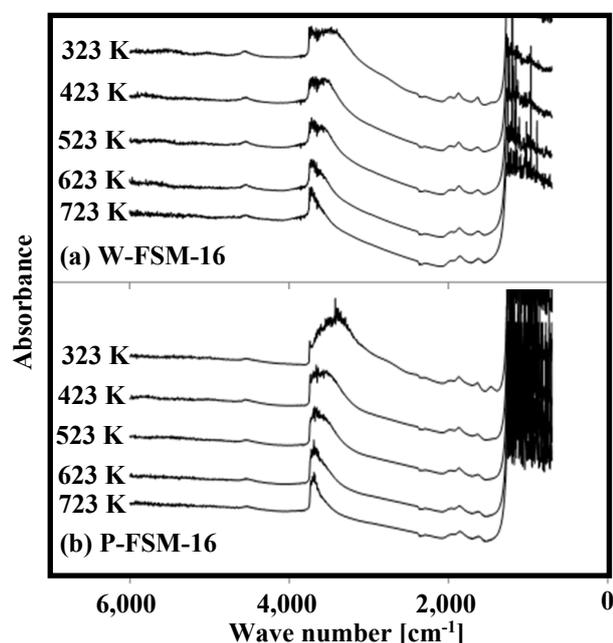
was approximately 1.3- and 4.7-times that of both P-FSM-16 and amorphous SiO<sub>2</sub>, respectively (Figure 4 (d)). Therefore, the greater acid amount of W-FSM-16 also contributed to its catalytic activity.



**Fig. 4** Acid amount of (a) W-FSM-16, (b) P-FSM-16, and (c) SiO<sub>2</sub>, together with the total acid amount of the catalysts (d)

In order to further examine the acidic properties of W-FSM-16 and P-FSM-16, the adsorption-desorption

behavior of  $\text{NH}_3$  was examined using an *in situ* FT-IR cell (Katoh *et al.*, 2012). An IR peak at approximately  $3700\text{ cm}^{-1}$  due to silanol (Yamamoto *et al.*, 1998) was detected from FSM-16 before the adsorption of  $\text{NH}_3$ . After the adsorption of  $\text{NH}_3$  at 323 K, the broader peaks due to the adsorbed  $\text{NH}_3$  at wave numbers lower than  $3700\text{ cm}^{-1}$  were detected for W-FSM-16 and P-FSM-16, while the intensity of the signal observed for P-FSM-16 was greater than that observed for W-FSM-16 (Figure 5). After desorption at 423 K, the decreased ratio of the signal intensity of P-FSM-16 was greater than that of W-FSM-16. These indicate that below 423 K, W-FSM-16 had a stronger acid site than P-FSM-16. After desorption at 523–723 K, no evident difference between either forms of FSM-16 was observed, as shown in Figure 5, indicating that no information on acidic properties at temperatures higher than 423 K was obtained from *in-situ* FT-IR.



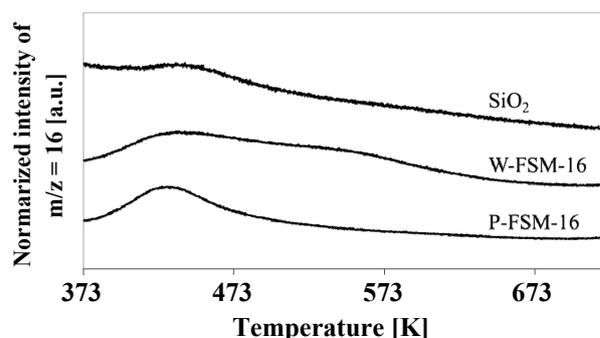
**Fig. 5** *In situ*  $\text{NH}_3$ -FT-IR of (A) W-FSM-16 and (B) P-FSM-16 after  $\text{NH}_3$  adsorption at 323 K, followed by  $\text{NH}_3$  desorption at 423, 523, 623, and 723 K

However, greater acid properties for W-FSM-16 at temperatures higher than 423 K were certainly detected from  $\text{NH}_3$ -TPD (Figure 6). From P-FSM-16 adsorbed with  $\text{NH}_3$ , a desorption peak was mainly detected at 373–473 K, while a broader desorption peak was detected at 373–673 K from W-FSM-16. Therefore, W-FSM-16 possesses greater acidic properties at the reaction temperature for the dehydration of 1,2-PD.

It should be noted that the intensity of the desorption signal from FSM-16 in  $\text{NH}_3$ -TPD was much weaker and essentially similar to that from  $\text{SiO}_2$  (Figure 6). As shown in our previous study (Sugiyama *et al.*, 2010), the catalytic activity for the dehydration of ethanol to ethylene favorably proceeded with FSM-16

as with that of 1,2-PD, indicating that  $\text{NH}_3$ -TPD may not be suitable for estimating the acidic properties of FSM-16.

In the present study, the distinction of Lewis and Brønsted acidic sites was impossible due to the employment of  $\text{NH}_3$  adsorption. Using pyridine adsorption, Yamamoto *et al.* (1998) reported that both Lewis and Brønsted acidic sites are present on FSM-16.

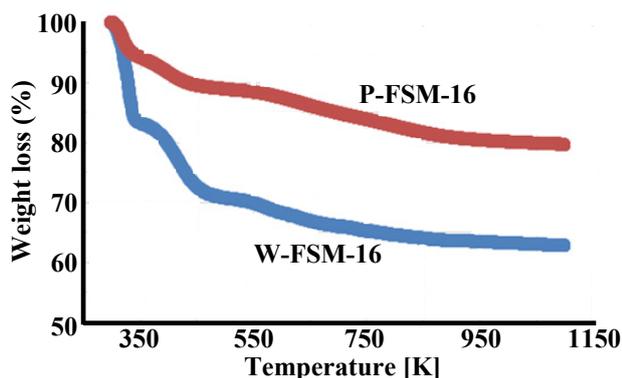


**Fig. 6**  $\text{NH}_3$ -TPD of W-FSM-16, P-FSM-16 and  $\text{SiO}_2$

#### 2.4 Effect of coking on catalyst degradation using W-FSM-16 and P-FSM-16

The differences between W-FSM-16 and P-FSM-16 are explained above by using their structural and acidic properties. However, those properties cannot explain the catalyst degradation using both forms of FSM-16. As described in Table 1, the conversion of 1,2-PD decreased from 98.8% to 91.0% using W-FSM-16 and from 39.7% to 4.7% using P-FSM-16. Therefore, catalyst degradation using P-FSM-16 was more evident than that using W-FSM-16. After the reaction, the color of W-FSM-16 and P-FSM-16 turned from white to gray and black, respectively. Because of these results, we used TG analysis to observe the effect of coking on the catalyst degradation of both forms of FSM-16 recovered after running the conversion of 1,2-PD using these catalysts (Table 1). As shown in Figure 7, the total weight loss of W-FSM-16 was evidently greater than that of P-FSM-16, while the weight loss behavior was dependent on the properties of each catalyst. For example, using W-FSM-16, the weight loss between 373 and 473 K was 10.7%, while it was 8.5% between 473 and 1073 K. With P-FSM-16, 3.7% weight loss was observed between 373 and 473 K and 9.3% weight loss between 473 and 1073 K. Since the catalytic activity of W-FSM-16 was greater than that of P-FSM-16, the greater weight loss for W-FSM-16 may be reasonable. Based on the catalyst degradation behavior and the color change after the reaction, it was concluded that when using W-FSM-16, the formation of coke proceeded in a high dispersion over the surface and on the insides of the mesopores, resulting in a color change to gray and in the avoidance of a complete blockade of the mesopores. Therefore, W-FSM-16 showed a rather stable catalytic activity. In contrast, with P-FSM-16, the formation of coke proceeded

intensively on the surface, resulting in a color change to black and in a complete blockade of the pores, resulting in an evident catalyst degradation.



**Fig. 7** TG curves for W-FSM-16 and P-FSM-16 recovered after obtaining the results shown in Table 1

## 2.5 Dehydration or hydro-cracking?

According to Zaitsev's rule, the dehydration of 1,2-PD should result into acetone. However, the present system formed PA from the dehydration of 1,2-PD. This indicated that the conversion of 1,2-PD to PA may proceed through hydro cracking (Sugiyama *et al.*, 2013b). In order to examine the contribution of hydrogen, the conversion of 1,2-PD was carried out in the presence and absence of H<sub>2</sub> in the feed gas using W-FSM-16 pretreated and unpretreated with H<sub>2</sub>. For this purpose, the weight of the catalyst, flow rate of 1,2-PD and that of the diluent gas (He or 5% H<sub>2</sub>/He), and reaction temperature were adjusted to 0.025 g, 0.6 mL/h, and 10 mL/min, and 673 K, respectively. In an earlier study by Mori *et al.* (2009), it was pointed out that 1-propene-1-ol obtained by the dehydration of 1,2-PD is converted to 1-propanol, followed by the dehydration to propylene in the presence of hydrogen. Therefore, the formation behavior of propylene is also examined in this section.

**Table 4** Effect of hydrogen on the conversion of 1,2-propanediol

Pretreatment		Diluent		TOS <sup>a</sup> [h]	Conv. [%]	Selectivity [%]		
O <sub>2</sub>	5%H <sub>2</sub>	He	5%H <sub>2</sub>			Propanal	C <sub>3</sub> H <sub>6</sub>	Others
○		○		0.25	100.0	68.1	29.7	2.2
○		○		1.75	91.3	69.5	26.0	4.5
○			○	0.25	100.0	64.1	34.2	1.7
○			○	1.75	63.3	46.9	52.0	1.1
	○	○		0.25	100.0	66.2	30.8	3.0
	○	○		1.75	74.9	66.1	36.2	1.7
	○		○	0.25	100.0	66.2	30.7	3.1
	○		○	1.75	52.4	42.2	57.7	0.1

a: Time-on-stream.

As shown in Table 4, in both the presence and absence of H<sub>2</sub> for both the pretreatment and diluent gases, the conversion of 1,2-PD was similar at 0.25 h on-stream. Although the stability of the catalytic

activity was dependent on the presence and absence of H<sub>2</sub> in these gases, acetone was not detected from the conversion of 1,2-PD. This indicates that the conversion of 1,2-PD proceeded through dehydration rather than through hydro cracking.

When the dehydration of 1,2-PD proceeds with FSM-16, it may be possible that the regioselectivity of the dehydration of the corresponding primary or secondary alcohols contributes to the catalytic activity. In order to examine the regioselectivity of the dehydration of 1,2-PD, 1-propanol and 2-propanol were used with a W-FSM-16 catalyst. The results shown in Table 5 were obtained under the reaction conditions such as 0.15 g of W-FSM-16 and 30 mL/min of the He diluent at 573 K, while the catalyst was pretreated with O<sub>2</sub> (25 mL/min) for 1 h at 673 K. As shown in Table 5, the conversion of 2-propanol was evidently greater than that of 1-propanol, indicating that the dehydration of secondary alcohol proceeds more favorably than that of primary alcohol when using FSM-16. Based on these results, it is reasonable that the dehydration of 1,2-PD produces PA rather than acetone when using FSM-16, which contradicts Zaitsev's rule. Interestingly, P-FSM-16 showed lower and more unstable activity than W-FSM-16, as expected from the results on the conversion of 1,2-PD using both FSM-16 catalysts.

**Table 5** Dehydration of 1-propanol and 2-propanol using W-FSM-16 and P-FSM-16

Reactant	TOS <sup>a</sup>	Conv. [%]	Selectivity [%]		
			C <sub>3</sub> H <sub>6</sub>	PE <sup>b</sup>	Others
Catalyst: W-FSM-16					
1-Propanol	0.25	35.6	94.8	2.7	2.5
1-Propanol	4.5	24.2	95.3	2.3	2.4
2-Propanol	0.25	100	100	0	0
2-Propanol	4.5	100	100	0	0
Catalyst: P-FSM-16					
1-Propanol	0.25	22.1	99.9	0	0.1
1-Propanol	4.5	10.8	98.5	0	1.5
2-Propanol	0.25	91.1	100	0	0
2-Propanol	4.5	41.3	100	0	0

a: Time-on-stream [h]. b: n-Propyl ether

## Conclusions

Zaitsev's rule was contradicted when the conversion of 1,2-PD using FSM-16 proceeded through dehydration rather than hydro-cracking due to the regioselective nature of the catalyst, a favorable dehydration of secondary alcohol rather than primary alcohol. Therefore, it was concluded that the conversion of 1,2-PD using FSM-16 proceeds through the dehydration of 1,2-PD to 1-propene-1-ol, followed by the keto-enol tautomerism to PA, as suggested by Mori *et al.* (2009). FSM-16 that maintained its hexagonal structure and possessed greater acidic properties, particularly acid amount, was the most favorable catalyst for the dehydration of 1,2-PD. It

should be noted that pressurization was not suitable for the molding of FSM-16 since it resulted in a collapse of the hexagonal structure, followed by a decrease in the acid amount.

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