PREPARATION AND CHARACTERIZATION OF VANADO-, FERRI-, AND GALLOSILICATE CATALYSTS IN THE PRESENCE OF FLUORIDE IONS

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Abstract — Vanado-, ferri-, and gallosilicate catalysts were prepared from the mixtures containing colloidal silica, corresponding metal source, tetrapropylammonium bromide, and NH_4F by hydrothermal crystallization at 175°C for 7 days. The pH value of the reaction mixture was low (pH<8) compared to the conventional methods. The metal compounds have higher solubilites in these conditions than conventional conditions (pH>10). The size distribution and the size of final products were found to be more homogeneous and larger than those of metallosilicates prepared in strong alkaline media. The characterization of metallosilicates with IR, X-ray diffraction, SEM, EPR, and ^{29}Si MAS NMR, indicated that corresponding metal atoms were successfully incorporated into the tetrahedral lattice sites of the ZSM-5 structure.

INTRODUCTION

The isomorphous substitution of various metal ions into the aluminium lattice sites in the ZSM-5 structure will greatly modify the nature of the active sites in ZSM-5, especially acid-base property. The differences in the metal-oxygen bond length and in the coordination of oxygen around the metal ion will finely control the pore structure inside the ZSM-5 structure. Therefore, the preparation of metallosilicates containing metal ions in the ZSM-5 structure has aroused considerable interest in the past decade. However, only a limited number of metallosilicates have been prepared. This seems to be due to the lack of the precursor compounds of metal atoms, soluble in the alkaline medium, to be substituted into the aluminium sites. In general, silica-based zeolites such as ZSM-5 were prepared by hydrothermal crystallization of alkaline reaction mixtures above pH 10 [1]. Kessler et al. have recently proposed a new preparation method of ZSM-5 by hydrothermal crystallization in the presence of F⁻ ions [2, 3]. This method has successfully been applied to prepare the borosilicate analogue of ZSM-5 [2, 3]. In the present study, we report the preparation of vanadosilicate, ferrisilicate, and gallosilicate from

the reaction mixtures containing F⁻ ions below pH 8. Although these metallosilicate catalysts have been reported in the recent literature [4-7], they have been prepared from the alkaline reaction mixtures at pH> 10. The characterization of the prepared metallosilicates with IR, EPR, ^{29}Si NMR, and SEM was also described.

EXPERIMENTAL

1. Preparation of Metallosilicates

Vanado-, ferri-, and gallosilicate were prepared by hydrothermal crystallization under autogenic pressure at 175°C for 7 days from the reaction mixtures containing colloidal silica (Ludox HS-40, SiO_2 40 wt%), tetrapropylammonium bromide (TPABr), NH_4F, and corresponding metal source. For the preparation of vanadosilicate, $VOSO_4 \cdot 5H_2O$ or NH_4VO_3 was used as a vanadium source. $Fe(NO_3)_3 \cdot 9H_2O$ and $Ga(NO_3)_3 \cdot 9H_2O$ were used as iron and gallium sources, respectively. The final reaction mixtures were aged at room temperature for 1 day, before they were transferred into teflon-lined autoclaves. After reaction the samples were washed with dilute ammonical solution and distilled water. The samples were calcined at 550°C in air to remove the templating agents. Table 1 showed the detailed informations on the preparation of metallosil-

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Table 1. Detailed informations on the preparation of metallosilicates

Sample	Metal source	Mole ratio of reactant mixture					pH of reactant mixture	Color of reactant mixture
		Si	M	F	TPA	H_2O		
Vanadosilicate	$VOSO_4 \cdot 5H_2O$	40	1	40	6	1600	7.5	blue
	NH_4VO_3	40	1	40	6	1600	7.9	yellow
Ferrisilicate	$Fe(NO_3)_3 \cdot 9H_2O$	40	1	40	6	1600	7.5	yellow
Gallosilicate	$Ga(NO_3)_3 \cdot 9H_2O$	40	1	40	6	1600	7.6	white

icates.

2. Characterization of Metallosilicates

Elemental analyses were done by atomic absorption spectroscopy. X-ray diffraction patterns were taken on a Rigaku D/Max II-A diffractometer using Ni-filtered Cu Kα radiation. The IR spectra were recorded with an Analect 6160 Fourier Transformed spectrometer applying the KBr wafer technique. BET surface areas of the prepared metallosilicates were measured by Micromeritics Digisorb 2600. The morphology of the prepared metallosilicates were studied by ISI model SX-30E scanning electron microscope. The EPR spectra were recorded on a Bruker ER-200D-SRC spectrometer. The g-value was calibrated with strong pitch (g=2.0028) and DPPH (g=2.0036). The ^{29}Si MAS NMR spectra were obtained on a Bruker AM-200 NMR spectrometer with a standard magic angle spinning (MAS) probe at 39.76 MHz (4.7 T magnetic field). The spectra were recorded using 90° (10 μs) pulses, a 4s recycle delay, and 50.0 kHz sweep width. Typically, 2000 free induction decays were accumulated. The Delrin sample holder was spun at 3.8 kHz. Chemical shifts were measured using the external tetramethylsilane (TMS) as a standard.

RESULTS AND DISCUSSION

1. Preparation of Metallosilicates

In preparing vanado- or ferrisilicate gel containing F ions, the gel was not homogeneous when NH_4F was added to colloidal silica before the addition of corresponding metal source to the colloidal silica. However, gallosilicate gel was formed homogeneously regardless of the addition order of NH_4F. It was recommended that vanadium or iron source should be added to silica before the addition of NH_4F in order to obtain homogeneous gel. This seems to be due to the difficulty in the formation of the precursors of vanadium or iron with silica, since the most of silica species were blocked by F ions if F ions were added prior to metal compounds. It was reported that F ions readily reacted with silicate in aqueous media [8, 9] and the complexation ability of silica with F

Table 2. Element analysis of prepared metallosilicates

Sample	Metal source	Atomic ratios of product		
		Si/M	Si/F	M/F
Vanadosilicate	$VOSO_4 \cdot 5H_2O$	325.7	30.5	0.094
Vanadosilicate	NH_4VO_3	152.4	31.1	0.20
Vanadosilicate[a]	$VOSO_4 \cdot 5H_2O$	174.	–	–
Vanadosilicate[a]	NH_4VO_3	infinity	–	–
Ferrisilicate	$Fe(NO_3)_3 \cdot 9H_2O$	44.4	65.4	1.47
Gallosilicate	$Ga(NO_3)_3 \cdot 9H_2O$	43.5	70.1	1.61

[a]quoted from the result of Miyamoto et al.[10].

ions was greater than that of vanadium or ferric ions with F ions. In contrast, it is sufficiently soluble for gallium to form a homogeneous gel with silica at similar pH values.

The surface areas of the prepared vanadosilicate, ferrisilicate and gallosilicate are 407, 324, and 329 m^2 g^{-2}, respectively, indicating that the catalysts prepared in this study are highly porous materials.

2. Elemental Analyses

The final compositions of metallosilicates were summarized in Table 2. Miyamoto et al. [10] prepared vanadosilicate from various vanadium sources by their own rapid crystallization method. Only a half of $VOSO_4 \cdot 5H_2O$ added to the reaction mixture (Si/V = 90) was incorporated into the lattice of vanadosilicate (Si/V = 174). They failed the preparation of vanadosilicate with NH_4VO_3 as a vanadium source. It was proposed that V^{5+} ions from NH_4VO_3 could not form a stable complex with silica. However, in the presence of F ions, the preparation of vanadosilicate from NH_4VO_3 was successful as shown in Table 2. The vanadium content in the final product (Si/V = 152.4) is approximately two times larger than that prepared from $VOSO_4 \cdot 5H_2O$ as a vanadium source (Si/V = 325.7).

About 30% of vanadium present in the reactant mixture was incorporated into the lattice structure of vanadosilicate in the final product, while about 90% of gallium and iron sources in the reactant mixture were incorporated into gallosilicate and ferrisilicate, respectively. The atomic ratios of Si/F in the ferrisilicate and gallosilicate are twice larger than that of Si/F
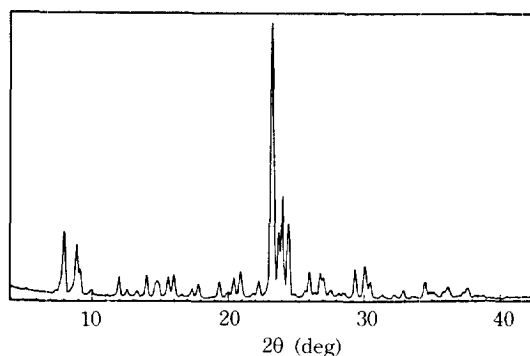
Fig. 1. X-ray diffraction pattern of vanadosilicate using NH₄VO₃ as a vanadium source.

in vanadosilicate. This seems to be due to the lower solubility of vanadium than iron or gallium in the pH range between 7 and 8. This can be explained by the less complexing ability of F ions with vanadium ions in the reactant mixture resulting in the less participation of vanadium ions in the crystal growth process.

3. X-ray Diffraction and Infrared Study

X-ray diffraction pattern of the vanadosilicate (Fig. 1) and infrared spectra of vanado-, ferri-, and gallosilicate (Fig. 2) prepared in the presence of F ions indicated that they have a ZSM-5 structure. Other phases were not observed in the X-ray diffraction patterns.

Szostak and Thomas [11] assigned the band at 798 cm⁻¹ to the Si-O-Si symmetric stretching vibration in their infrared study of ZSM-5. The wavenumber of symmetric Si-O-Al stretching band is almost the same as that of symmetric Si-O-Si stretching band because of the small difference in the mass between Al atom and Si atom. However, Si-O-Fe symmetric stretching band can be differentiated from Si-O-Si band because of the large difference in the mass between Si and Fe atom. Ferrisilicates (SiO₂/Fe₂O₃=15-30) prepared in an alkaline medium have a new weak band at 656 cm⁻², which was assigned to the symmetric Si-O-Fe stretching vibration [6]. The infrared spectrum of ferrisilicate prepared in this work [Fig. 2(b)] shows a weak band at 650 cm⁻², which can be assigned to the symmetric Si-O-Fe stretching band. Similarly, a weak band is observed at 670 cm⁻¹ for vanadosilicate [Fig. 2(c)]. Hence, this band can be assigned to the symmetric Si-O-V stretching band. All the bands of metallosilicates were slightly shifted to lower wavenumbers when Al atom was replaced by heavier Fe, V, and Ga atoms indicating that Fe, V, and Ga were incorporated into the ZSM-5 structure.

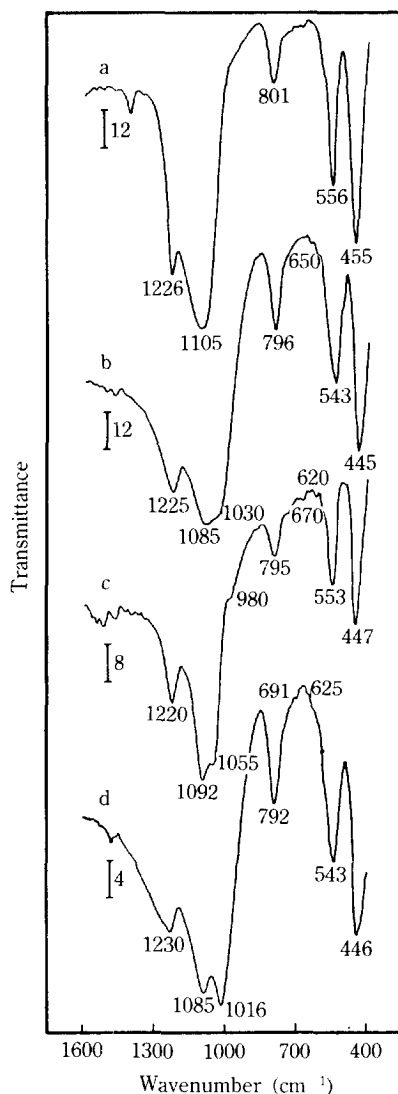The most intense absorption band which occurs around 1100 cm⁻¹ is assigned to the asymmetric vi-

Fig. 2. Infrared spectra of (a) ZSM-5, (b) ferrisilicate, (c) vanadosilicate and (d) gallosilicate.

bration of T-O band, where T is Al or Si atom [12]. This band is shifted to lower wavenumber as compared to ZSM-5 when Al atom is replaced with Fe, V, and Ga atom. Substitution of Al for Si in the framework causes a shift to lower wavenumber owing to the longer Al-O bond length (1.75 A) as compared to the Si-O bond length (1.60 A) [12]. Borade recently reported that the shift in the main asymmetric band towards lower wavenumber on the substitution of iron in the ZSM-5 structure is due to the longer Fe-O bond length (1.84 A) [5]. As shown in Fig. 2(b), (c), and (d), asymmetric T-O stretching bands of metallosili-
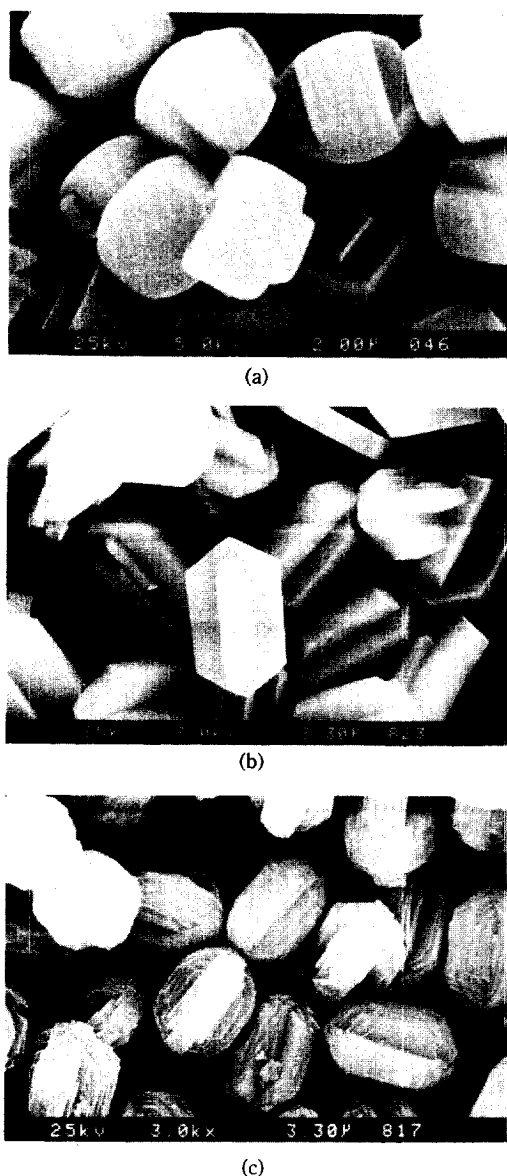
(a)

(b)

(c)

Fig. 3. SEM pictures of (a) vanadosilicate, (b) ferrisilicate, and (c) gallosilicate.

$g_\perp = 1.998$, $A_\perp = 78G$

(a)

$G = 2.5 \times 10^3$

200G

$g_{11} = 1.939$, $A_{11} = 185G$

$g_\perp = 1.995$ $A_\perp = 77G$

(b)

$G = 1.0 \times 10^3$

$g_{11} = 1.935$, $A_{11} = 184G$

(c)

$G = 1.0 \times 10^3$

$g_\perp = 1.997$, $A_\perp = 84G$
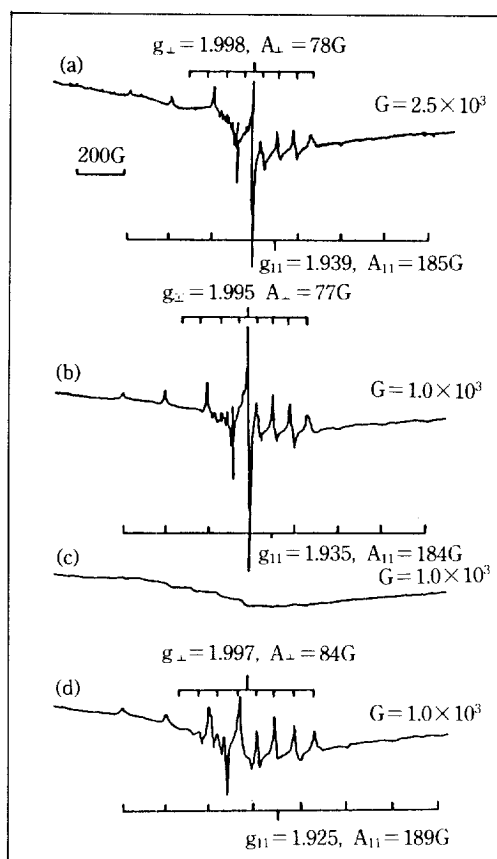
(d)

$G = 1.0 \times 10^3$

$g_{11} = 1.925$, $A_{11} = 189G$

Fig. 4. EPR spectra of vanadosilicates: the as-prepared sample using (a) $VOSO_4 5H_2O$ and (b) NH_4VO_3 as a vanadium source, (c) the calcined sample of sample (b) at 500°C, and (d) the reduced sample of sample (c) at 450°C.

$VF_3 \cdot 3H_2O$ and $GaF_3 \cdot 3H_2O$ [13]. Hence, it can be concluded from the infrared results that V, Fe, and Ga atoms were incorporated into the ZSM-5 structure in the presence of F ions.

4. Crystalline Morphology

SEM pictures of prepared vanado-, ferri-, and gallosilicate were shown in Fig. 3. Regardless of vanadium source compound, vanadosilicate has a shape of twinned crystal interconnected with two hexagonal prisms [Fig. 3(a)]. The size of crystal is about 6 μm and homogeneous, which is quite different from the morphology of vanadosilicate prepared by rapid thermal crystallization method [4, 10]. Ferrisilicate has a shape of twinned crystal interconnected with two elongated hexagonal plates with the dimension of $2 \times 7 \times 12$ μm [Fig. 3(b)]. However, ferrisilicate prepared in an alkaline medium consisted of spherulitic aggregates (3-4
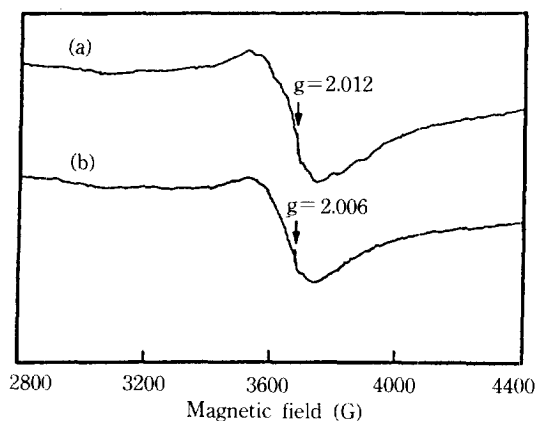
cates prepared were shifted to lower wavenumbers and were splitted into doublet when T is Fe, V, and Ga. This is due to the lowering symmetry from tetrahedral unit to trigonal unit because of longer T-O bond length (where T=V, Fe, and Ga) as compared to the Si-O bond length.

Infrared spectra of vanadosilicate and gallosilicate do not show any bands ascribed to the bands of oxide, hydroxide and fluoride such as V_2O_4, V_6O_{13}, V_2O_5, Ga_2O_3,

Fig. 5. EPR spectra of (a) the mixture of silica, NH₄VO₃, and NH₄F dehydrated at 50°C and (b) the mixture of silica, NH₄VO₃, NH₄F, and TPABr dehydrated at 50°C.

Fig. 6. EPR spectrum of ferrisilicate.

μm) of rod-like crystals, stacked radially [5]. Ferrisilicate prepared by rapid thermal crystallization method has a shape of sphere with its size less than 3 μm [14]. Gallosilicate consisted of aggregates of different size of hexagonal plate interconnected with each other at the center [Fig. 3(c)]. The crystal size is smaller than 10 μm. Guth et al. reported that the large prismatic crystals of 800 μm in length are observed for silicalite prepared in the presence of F ions [3].

It is clear that the morphology and size of metallosilicate crystals depend on the type of metals added to the reaction mixture, suggesting that a small amount of metals added play an important role as nuclei in the growth of crystals. It was reported that 24 distinct tetrahedral Si atom sites are present in the ZSM-5 structure [15]. The metal ion added might replaced a certain Si atom site preferentially in the ZSM-5 structure, which will affect the orientation of crystal growth.

5. EPR Study

Miyamoto et al. reported that the vanadosilicate prepared from VCl₃, VOSO₄·5H₂O, V(C₅H₇O₂)₃ or VOC₂O₄ as a vanadium source showed a hyperfine structure of V⁴⁺ in the EPR spectra, while from NH₄VO₃ as a vanadium source did not show a hyperfine structure [10]. However, vanadosilicate prepared from NH₄VO₃ in our study also showed a hyperfine structure [Fig. 4(b)]. This difference must be related to the presence of F ions which reduced the V⁵⁺ ion in NH₄VO₃ to V⁴⁺ during the reaction. The further additon of TPABr did not change EPR spectrum much [Fig. 5(b)], indicating that NH₄F reduced NH₄VO₃ in the gel phase.

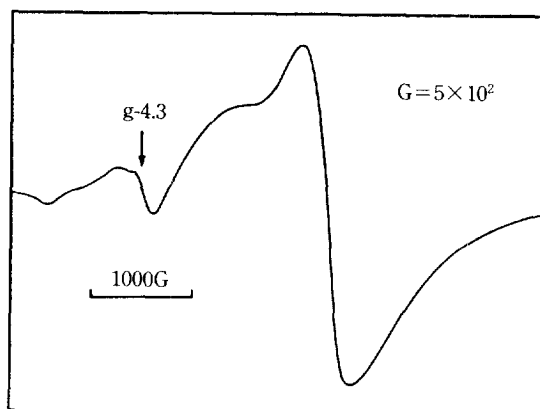The broad feature of EPR bands is attributed to the undispersed V⁴⁺ species. Takahashi et al. reported
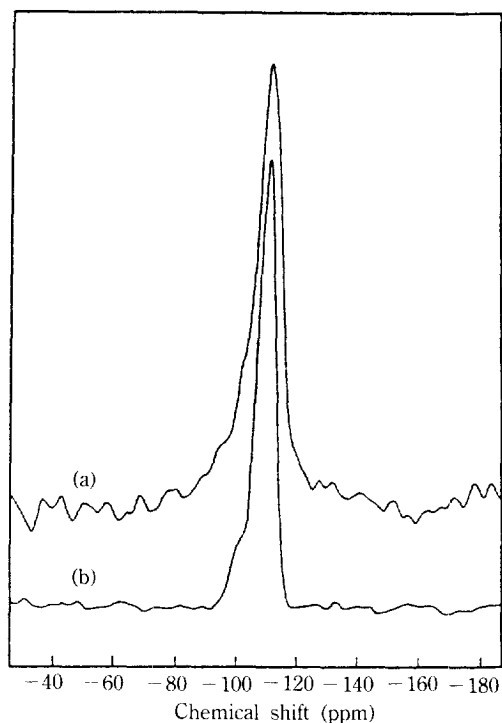

Fig. 7. ²⁹Si MAS NMR spectra of (a) ferrisilicate and (b) gallosilicate.

that dispersed vanadium ion showed a hyperfine structure but no hyperfines could be observed from the agglomerated vanadium species [16]. The EPR spectrum of a simple mixture of NH₄VO₃, silica, and NH₄F, dehydrated at 50°C, showed the EPR band of agglomerated V⁴⁺ overlapped with weak hyperfine splitting bands at the center [Fig. 5(a)]. V⁴⁺ ion of the simple mixture presented in Fig. 5(a) and (b) cannot be dispersed because crystal growth was not proceeded com-
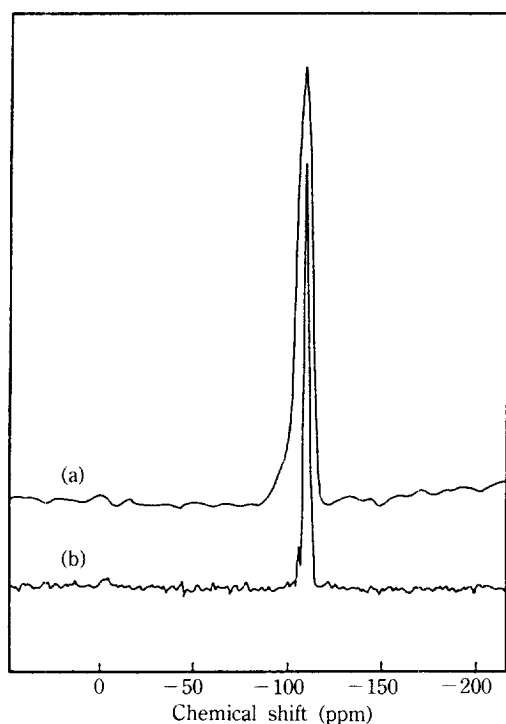
Fig. 8. ^{29}Si MAS NMR spectra of vanadosilicates (a) as-prepared and (b) calcined at 550°C.

Table 3. Assignment of ^{29}Si NMR band of vanado-, ferri-, and gallosilicate

Sample	Chemical shift (ppm from TMS)	Half band width(Hz)	Tentative assignments
Vanadosilicate			
as synthesized	− 109.5 (s)	330	Si (4Si)
	− 105.0 (sh)		Si (1V, 3Si)
calcined at 500°C	− 109.5 (s)	110	Si (4Si)
	− 105.8 (w)		Si (1V, 3Si)
Ferrisilicate	− 109.3 (s)	380	Si (4Si)
	− 102.0 (sh)		Si (1Fe, 3Si)
Gallosilicate	− 108.7 (s)	270	Si (4Si)
	− 102.0 (sh)		Si (1Ga, 3Si)

s, strong; sh, shoulder; w, weak

pletely. However, after crystallization of 7 days, hyperfine structure of V^{4+} was developed clearly indicating that V^{4+} was well dispersed in the crystal structure.

The parameters of EPR bands ($g_\perp = 1.995$, $A_\perp = 77$ G, $g_{11} = 1.935$, $A_{11} = 184$ G) in our sample is pretty close to the values of Miyamoto et al. ($g_\perp = 2.015$, $A_\perp = 91$ G $g_{11} = 1.957$, $A_{11} = 196$ G). Calcination of vanadosilicate at 550°C oxidized most of V^{4+} into V^{5+} resulting in the disappearance of V^{4+} hyperfine structure [Fig. 4 (c)]. The reduction of this sample at 450°C with H_2 restored the V^{4+} hyperfine structure [Fig. 4(d)]. The application of vanadosilicate as a catalyst in the redox reaction might be possible and is currently being studied in our laboratory. The EPR spectrum of ferrisilicate is presented in Fig. 6. The band at g= 4.3 indicated that Fe is present in the tetrahedral lattice site [6, 17].

6. ^{29}Si MAS NMR Study

^{29}Si NMR spectra of ferrisilicate and gallosilicate are shown in Fig. 7(a) and (b), respectively. It was reported that the half-band width of ^{29}Si NMR band increased with the paramagnetic iron content in the ferrisilicate [17, 18]. This NMR linebroadening was caused by the incorporation of paramagnetic iron into the tet-

rahedral sites of ZSM-5. The band at − 109.3 ppm of ferrisilicate was broad because of the presence of paramagnetic iron ion. The shoulder at − 105 ppm can be assigned to Si (1Fe, 3Si) similar to the result of Ball et al. [17]. The shoulder at − 102 ppm of gallosilicate [Fig. 7(b)] seems to be due to Si(1Ga, 3Si) structure, which is consistent with the assignment of Hayashi et al. that Si(1Ga, 3Si) band appeared between − 99.0 and 107.0 ppm in ^{29}Si NMR of gallosilicate [19].

^{29}Si MAS NMR spectra of as prepared and calcined vanadosilicate samples, which were prepared from NH_4-VO_3 as a vanadium source, were shown in Fig. 8. The ^{29}Si NMR band of vanadosilicate as shown in Fig. 8(a) (half-band width=330 Hz) appeared at − 109.5 ppm with a shoulder at − 105 ppm. After calcination at 550°C, however, the half-band-width of the band at − 109.5 ppm decreased one third of that before calcination and a weak band appeared at − 105.8 ppm [Fig. 8(b)]. Our EPR study of vanadosilicates confirmed that the oxidation states of vanadium before and after calcination are + 4 and + 5, respectively. Hence, it can be concluded that this NMR linenarrowing is caused by the vanadium present in the ZSM-5 structure as a diamagnetic species, because calcination at 550°C oxidized paramagnetic V^{4+} to diamagnetic V^{5+}. In addition, the band at − 105.8 ppm in the ^{29}Si NMR spectrum of vanadosilicate calcined can be assigned to Si (1V, 3Si). In ZSM-5, Si (1Al, 3Si) has a band around at − 105 ppm [15]. ^{29}Si MAS NMR result was summarized in Table 3.

CONCLUSION

Vanado-, ferri-, and gallosilicate catalysts were prepared in the presence of F ions below pH 8. The addition of F ions provides the soluble species of the mixture of silica and metal ion precursor at the

pH value of 8 and helps metal source compounds to be incorporate into the tetrahedral sites of Si atoms. In the preparation of vanadosilicate with NH_4VO_3 in the presence of F^- ions, V^{5+} in NH_4VO_3 was reduced to V^{4+}. The crystal morphologies of prepared metallo-silicate are different from those prepared in a strong alkaline medium (pH>10). The sizes of crystals prepared in the presence of F^- ions are more homogeneous and larger than those of conventional methods. Characterization of prepared metallosilicates with IR, X-ray diffraction, EPR, ^{29}Si NMR, and SEM indicated that corresponding metal atoms are incorporated into the tetrahedral sites of the ZSM-5 structure.

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