Pyrolysis Behavior of Organic–Inorganic Hybrids with Si–O–Nb/Si–O–Ta Oxygen Bridged Heterometallic Bonds

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Si–O–Nb/Si–O–Ta 結合を持つ有機無機ハイブリッドの熱分解挙動に関する研究

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The pyrolysis behavior of organic–inorganic hybrids with Si–O–Nb/Si–O–Ta oxygen bridged heterometallic bonds was investigated. The easy cleavage of Si–O–Nb bonds was confirmed by infrared (IR) spectra, and Si–O–Ta bonds were broken at higher temperatures, suggesting the difference in energy between Si–O and O–M (M=Nb and Ta). The decomposition from *T* unit to *D* and *Q* units was analyzed by ²⁹Si-nuclear magnetic resonance (NMR). The redistribution due to the exchange reactions between Si–O and Si–C bonds was confirmed, which was also supported by thermogravimetric analysis-mass spectroscopy (TG-MS) results. Disiloxane and silane from the hybrid with Si–O–Nb bonds were detected at lower temperatures than those from the hybrids with Si–O–Ta or without Si–O–Nb bonds. The evolution temperature of these gases was close to the cleavage temperature of Si–O–Nb/Si–O–Ta bonds, which indicates that the cleavage of Si–O–Nb/Si–O–Ta bonds affects the redistribution. [Received May 15, 2003; Accepted July 24, 2003]

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1. Introduction

Recently, organic–inorganic hybrid materials containing transition metals have received a considerable attention. The mixing ratio between a siloxane polymer and a transition metal alkoxide affects the mechanical and thermal properties of these materials.¹⁾ The introduction of a transition metal alkoxide gives these materials their desired properties. However, sufficient studies on materials derived from trifunctional silane and transition metal alkoxide have not yet been reported. We might have firstly reported the preparation of organic–inorganic hybrid materials derived from methyltriethoxysilane (MTES) and pentaethoxyniobium/tantalum and the coating on some plastic substrates.^{2)–4)} In particular, MTES is a typical precursor that produces hybrid materials through hydrolysis and condensation reactions. Si–C–O ceramics are obtained by the pyrolysis of hybrid gels. Additionally, the authors reported the synthesis of crack-free ceramics from hybrids with Si–O–M (M: transition metal) bonds.^{2),3)}

However, the pyrolysis behavior of hybrids with Si–O–M bonds has not been investigated to date. To widen the applications, achieve high yield and improve the purity of such hybrids, precise investigation of their pyrolysis behavior should be carried out. The objective of this study is to examine the pyrolysis behavior of organic–inorganic hybrids with Si–O–Nb/Si–O–Ta oxygen bridged heterometallic bonds by IR, NMR and TG-MS.

2. Experimental

MTES, tantalum and niobium pentaethoxides were used as precursors. Acetylacetone was used for the chemical modification of transition metal alkoxides. The molar ratio was maintained at MTES : M(OEt)₅ : HCl : H₂O : EtOH = 1 : 0.05 : 0.005 : 2 : 3 (M=Nb and Ta). The solution was mixed for 0.5 h, cast on teflon dishes and dried at 40, 80 and 200°C. The transparent hybrid gels obtained after drying were heated to 400, 600, 800 and 1000°C in an inert

atmosphere.

TG-MS was carried out from room temperature to 1000°C with RIGAKU THERMO PLUS and SHIMADZU GCMS-QP5050 under flowing He at a heating rate of 10°C/min.

FT-IR analyses were carried out at a resolution of 4 cm⁻¹, with 40 multi scans by a KBr method using SHIMADZU FTIR-8600PC.

²⁹Si-NMR spectra were obtained using JEOL JNM-EXCALIBUR-270 MHz with a ²⁹Si frequency of 53.54 MHz. All the spectra were recorded with the applying proton decoupling. Cross polarization (CP) from proton to ²⁹Si was used. Polydimethylsilane was used as external standard. The samples were packed into a zirconia rotor and the sample spinning speed was approximately 6 kHz. All the spectra were recorded with a repetition time of 7.0 s and a contact time of 5.0 ms.

3. Results and discussion

Figure 1 shows the TG analysis of the hybrids performed from room temperature to 1000°C under flowing He. A gradual weight loss from 400 to 800°C was observed. Ceramic yields up to 1000°C were approximately equal for all pyrolyzed hybrids.

The FT-IR spectra obtained are shown in Fig. 2(A) MTES, Fig. 2(B) MTES+Nb- and Fig. 2(C) MTES+Ta-based hybrid (80°C) and the pyrolyzed products at various temperatures. The bands at around 910–930 cm⁻¹ in Figs. 2(A), (B) and (C) are ascribed to Si–OH, Si–O–Nb and Si–O–Ta, respectively.^{5)–6)} The peak due to Si–O–Nb bonds disappeared at lower temperatures compared with that of Si–O–Ta linkage. Most Si–O–Nb bonds were found to break at around 400°C. In the case of Si–O–Ta bonds, they were cleaved at around 600°C. This difference suggests the lower energy in cleaving Si–O–Nb bonds, corresponding to the difference in energy between oxygen and the metal (Ta or Nb). As seen from the peak at 1275 cm⁻¹

due to Si-CH₃ vibration on each spectrum, a significant decrease in peak intensity was observed at approximately 600–1000°C.

Figure 3 shows the ²⁹Si-CP/MAS NMR spectra of (A) the hybrids (200°C) and (B) the pyrolyzed products. The position (σ) and full width at half maximum (FWHM) are summarized in Table 1. The NMR peak assignment was reported by Babonneau and coworkers^{7,8)} and Radovanovic et al.⁹⁾ The peaks at approximately -20, -65 and -109 ppm are assigned to SiC₂O₂; *D* unit, SiCO₃; *T* unit and SiO₄; *Q* unit, respectively. As seen from Fig. 3(B), the intensities of *D* and *Q* units increased, more than those of the spectra of the hybrids. The existence of *D* and *Q* units indicates the occurrence of the exchange reaction between Si-C and Si-O bonds because original hybrids contain only *T* unit. The peaks of the pyrolyzed MTES+Nb hybrid were broader than those of other products, which might suggest the early decomposition.⁸⁾

Figure 4 shows the MS results of the evolved gases; MTES-, MTES+Nb- and MTES+Ta-based hybrids were pyrolyzed to 1000°C. From the IR result, it was observed that Si-O-Nb bonds were more easily broken than Si-O-Ta bonds. MS analysis also detected the gases, which supports this result. Despite the existence of only one methyl group linked to each Si atom in the original hybrid structure, the fragment of $m/z = 147$ (owing to three methyl groups) was detected, corresponding to (CH₃)₃-Si-O-Si-(CH₃)₂ in (CH₃)₃-Si-O-Si-(CH₃)₃.¹⁰⁾ This fragment was detected at approximately 300–500°C and 500–700°C in MTES+Nb

Fig. 1. TG curves for hybrid heated to 1000°C in He atmosphere.

Fig. 3. ²⁹Si-CP/MAS NMR spectra of (A) hybrids and (B) pyrolyzed hybrids at 600°C under inert atmosphere.

Fig. 2. FT-IR spectra of (A) MTES-, (B) MTES+Nb- and (C) MTES+Ta-based hybrids pyrolyzed at various temperatures.

Table 1. ^{29}Si Chemical Shifts (σ ; ppm) and Full Width at Half Maximum (FWHM; ppm)

Hybrid	Pyrolysis temperatures ($^{\circ}\text{C}$)	σ (ppm)	FWHM (ppm)
MTES	600	-108.7	6.7
		-65.9	6.3
		-57.8	8.5
		-19.5	6.7
MTES+Nb	600	-108.7	14.3
		-65.0	7.5
		-56.5	9.1
		-18.0	8.0
MTES+Ta	600	-109.7	10.8
		-68.5	6.6
		-60.9	9.6
		-22.3	8.2

Fig. 4. MS profiles of hybrids heated to 1000°C in He atmosphere.

and MTES+Ta, respectively. Additionally, the slight formation of volatile silanes such as tetramethylsilane (main fragment; $m/z=73$) was also observed. The evolution of gases such as siloxane and silane indicates the occurrence of the exchange reaction between Si-O and Si-C and the formation of D unit during calcination.^{(8), (10)} Moreover, the gas evolution temperature was very close to the cleavage temperature of Si-O-M bonds. These results suggest that the cleavage of Si-O-M bonds affects the exchange reaction. The pyrolysis reaction is summarized as^{(8)–(10)}

where $T = \text{SiCO}_3$ (-65 ppm), $D = \text{SiC}_2\text{O}_2$ (-20 ppm) and $Q = \text{SiO}_4$ (-109 ppm).

The formation of D and Q units from the starting precursor containing only T units is recognized to be a result of the occurrence of the exchange reaction. The cleavage of Si-O-M bonds may result in the formation of D and Q units through the exchange reaction. Then, CH_4 gas was also observed at high temperatures (approximately 800°C). This result indicates the decomposition of Si- CH_3 bonds, as shown in Fig. 2. The following reactions at high temperatures have been considered as the evolution mechanism of methane^{(8)–(10)}

4. Conclusion

IR, NMR and TG-MS studies on the pyrolysis behavior of organic-inorganic hybrids with Si-O-Nb/Si-O-Ta bonds were carried out. The important results obtained in this study are summarized as follows:

- (1) The cleavage of Si-O-Nb bonds at lowest temperature was confirmed by IR spectra, suggesting a low energy between Si-O and O-Nb in Si-O-Nb bonds.
- (2) The conversion from T unit to D and Q units in the pyrolyzed hybrid was observed. This indicates the occurrence of the exchange reaction between Si-C and Si-O bonds.
- (3) Disiloxane and silane gases were detected by MS analysis, which indicates the occurrence of the exchange reaction between Si-C and Si-O bonds. The evolution temperature of these gases was close to the cleavage temperature of Si-O-Nb/Si-O-Ta bonds.

The cleavage of Si-O-Nb/Si-O-Ta bonds was found to be closely correlated with the exchange reaction between Si-C and Si-O bonds.

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