

# Variable catalytic behavior of Nb, Mo, Ta, W, and Re halide clusters: Isomerization of alkynes to conjugated dienes under nitrogen and hydrogenation to alkenes under hydrogen

Satoshi Kamiguchi<sup>a,\*</sup>, Satoko Takaku<sup>b</sup>, Mitsuo Kodomari<sup>b</sup>, Teiji Chihara<sup>a</sup>

<sup>a</sup> *The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-0198, Japan*

<sup>b</sup> *Department of Applied Chemistry, Shibaura Institute of Technology, Toyosu, Koto-ku, Tokyo 135-8548, Japan*

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## Abstract

When a tantalum chloride cluster  $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  (**1**) was treated in a nitrogen stream at temperatures above 300 °C, a catalytic activity developed for the isomerization of pentynes and hexynes to the corresponding conjugated dienes with smaller amounts of allenes. Niobium and tungsten clusters with the same metal framework also catalyzed the reactions. In a hydrogen stream, niobium, molybdenum, and tungsten clusters, and a trinuclear rhenium cluster catalyzed the partial hydrogenation of alkynes to the corresponding alkenes. The isomerization activity was ascribed to the Brønsted acidity of hydroxo species of the activated cluster complexes, and the hydrogenation activity was attributed to the nature of the metal atoms incorporated in the cluster.

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## 1. Introduction

Many halide clusters have been synthesized since the first report was published on the synthesis of the halide cluster  $\text{MoCl}_2$  in 1859 [1]. These clusters have characteristic features, such as multi-center and multi-electron systems, an intermediate oxidation state of the metal atoms, and a high thermal stability. However, they were merely a candidate for catalysts [2,3]. In recent years, we have reported on a series of reactions catalyzed by halide clusters that have revealed two catalytic features: solid acid catalysts [4–10] and catalysts similar to the platinum group metals [11,12]. To understand the scope and limitations of halide cluster catalysis, these complexes have been applied to various reactions. In this paper, we report on the different catalytic reactions of halide cluster catalysts: the isomerization of alkynes to conjugated dienes under nitrogen and their hydrogenation to alkenes under hydrogen.

Isomerization of alkynes to conjugated dienes and allenes has been reported over several base catalysts:  $\text{NaOBU}^t$  [13],  $\text{KOBU}^t$  [13,14],  $\text{KOH}$  [15], alkaline earth metal oxides [16], and basic zeolites [17,18]. Base-modified  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2\text{--Al}_2\text{O}_3$  have also been used [18]. Acid catalysts, such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  [18],  $\text{SiO}_2\text{--Al}_2\text{O}_3$  [19], and  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  [20] have also been applied to the reaction. However, other types of catalyst have not been reported as being used in this reaction.

The hydrogenation of alkynes proceeds over the platinum group metals [21,22]. In particular, metallic palladium, such as  $\text{Pd}/\text{CaCO}_3$  or  $\text{Pd}/\text{BaSO}_4$  partially hydrogenates alkynes to alkenes in a selective manner owing to the strong adsorption of the alkyne on the catalyst.

## 2. Experimental

The cluster complexes,  $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  [23],  $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$  [24],  $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  (**1**) [23],  $[(\text{Ta}_6\text{Br}_{12})\text{Br}_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  [23], and  $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$  [25] were prepared according to published procedures, followed by repeated recrystallization

\* Corresponding author. Tel.: +81 48 467 9401; fax: +81 48 462 4631.  
E-mail address: [kamigu@riken.jp](mailto:kamigu@riken.jp) (S. Kamiguchi).

to yield well-formed crystals. The cluster  $[\text{Re}_3\text{Cl}_3]\text{Cl}_3\text{Cl}_{6/2}$  was commercially available, and was used without further purification. Crystals of the clusters were crushed, screened to 150–200 mesh, and used as unsupported catalysts. The organic substrates used were commercial products (>98%), and were used as received.

Raman spectra of the cluster samples (80 mg) in a glass reaction tube were recorded in situ using a Kaiser Optical Systems HoloLab 5000 Spectrometer and an Nd-YAG laser operating at  $\lambda = 532 \text{ nm}$  with a 7.6 mm focusing lens. The data counts were accumulated 30 times in 1 s intervals. Then, 30 mg of the cluster samples was transferred into an airtight sample holder in a glove box for powder X-ray diffraction (XRD) analysis. The XRD data were recorded using a MacScience MXP21TA-PO X-ray diffractometer employing  $\text{Cu K}\alpha$  radiation and a scan rate of  $2^\circ \text{ min}^{-1}$ .

A conventional vertical glass fixed-bed microreactor with a continuous gas flow system was used in the experiments operating at atmospheric pressure [5]. Typically, a weighed crushed crystal sample of **1** (80 mg) was packed in a glass reaction tube (ID = 3 mm) with the aid of quartz glass wool. This was then placed in the center of an electric furnace. The catalyst sample was initially heated from room temperature to  $400^\circ\text{C}$  for a period of 1 h in flowing nitrogen (1.8 L/h). The sample temperature reached the furnace set point after a period of 15 min. The reaction was initiated by feeding 2-pentyne ( $52 \mu\text{L/h}$ ,  $0.50 \text{ mmol/h}$ ) into the nitrogen stream at  $400^\circ\text{C}$  using a syringe pump. The reaction was monitored every 20 min by sampling the reaction gas (1 mL) through a six-way valve maintained at  $60^\circ\text{C}$ , followed by analysis using an online gas-liquid chromatograph (GLC) (Shimadzu GC14B gas chromatograph fitted with a flame ionization detector with a sebaconitrile on Uniport C packed column). The reactor effluent was frozen in a dry ice trap for subsequent analyses using a second GLC (GL Sciences 353B gas chromatograph fitted with a flame ionization detector with a DB-1 capillary column or a DB-WAX capillary column) and a Hewlett-Packard 5890 Series II gas chromatograph coupled with a Jeol Automass System II with a DB-1 capillary column (GC/MS). Each product was isolated using a preparative GLC (Shimadzu 14B gas chromatograph fitted with a thermal conductivity detector) and identified by using NMR (Jeol JNM AL-400 NMR spectrometer).

### 3. Results and discussion

#### 3.1. Reaction under nitrogen

A typical reaction profile for 2-pentyne over  $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$  (**1**) under nitrogen at  $400^\circ\text{C}$  is plotted in Fig. 1. The catalytic activity decreased with time. Elemental analysis of **1** conducted after a reaction time of 5 h revealed that it contained 1.3 wt.% carbon. The deposition of coke will retard any catalytic activity. Coking is inevitable in a gas–solid catalytic reaction, and a similar effect has been reported for fluorinated  $\text{Al}_2\text{O}_3$  [26]. The selectivity leveled off after a period of 1 h. The main reaction was isomerization, yielding 1,3-pentadiene with a selectivity of 56%. The turnover frequency per cluster during a period of

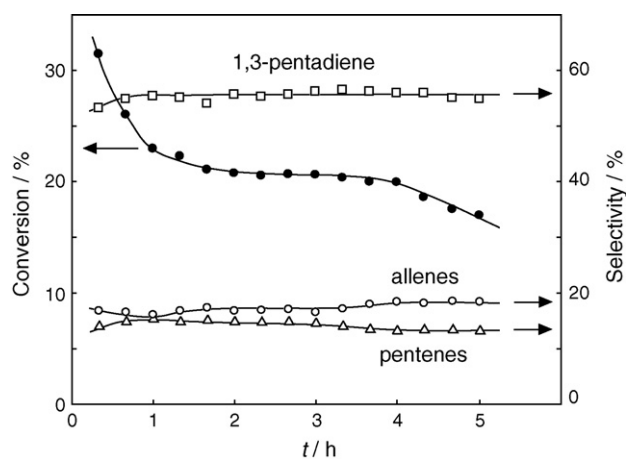


Fig. 1. A typical reaction profile of 2-pentyne catalyzed by  $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$  (**1**) under flowing nitrogen. Following treatment of **1** (80 mg) in a nitrogen stream (1.8 L/h) at  $400^\circ\text{C}$  for a period of 1 h, the reaction was initiated by the introduction of 2-pentyne ( $52 \mu\text{L/h}$ ,  $0.50 \text{ mmol/h}$ ) into the nitrogen stream at  $400^\circ\text{C}$ . Conversion = products/(products + recovered 2-pentyne)  $\times 100$  (%); selectivity = product/(total amount of products)  $\times 100$  (%). Key: conversion (closed circles); selectivity for 1,3-pentadiene (open squares); selectivity for 1,2- and 2,3-pentadienes (open circles); selectivity for 1- and 2-pentenes (open triangles). The selectivity for 2-methyl-2-butene (around 1.5%) and the hydrogenolysis products such as methane, ethane, and ethylene (around 11.0%) have been omitted for clarity.

3–4 h was  $2.2 \text{ (h}^{-1}\text{)}$ , assuming that all the cluster molecules were active and exposed to the atmosphere. The material balance after 3–4 h was 89.0%, with 20% conversion. The conversion was proportional to the amount of **1** and nitrogen carrier gas, and inversely proportional to the amount of 2-pentyne added. These findings indicate that 2-pentyne was in the saturated adsorption state.

The catalytic activity of various halide clusters of Group 5–7 metals and related compounds under nitrogen at  $400^\circ\text{C}$  is listed in Table 1. Cluster **1** catalyzed the isomerization of 2-pentyne to yield 1,3-pentadiene preferentially (entry 3). Both tantalum metal and no catalyst exhibited zero catalytic activity under the same reaction conditions (entries 14 and 15). Tantalum pentachloride cannot be used as a catalyst under these reaction conditions as it boils at  $234^\circ\text{C}$ . From these results, we can conclude that **1** developed catalytic activity by taking advantage of its low vapor pressure, as well as its high melting point. When the reaction was performed under helium or argon gas over **1**, the selectivity was virtually the same as that under nitrogen (entries 3–5), indicating that these inert gases did not participate in the reaction. The niobium and tungsten chloride clusters and the tantalum bromide cluster catalyzed isomerization to yield 1,3-pentadiene preferentially (entries 1, 6, and 7). However, the catalytic activity of the molybdenum chloride cluster was low (entry 2), and no catalytic activity was observed over the rhenium chloride cluster (entry 8).

The reactivity of some alkynes over **1** under nitrogen is summarized in Table 2. In four out of five cases, the main products were conjugated dienes: 1,3-pentadiene from pentyne and 2,4-hexadiene from hexyne. The reactivity order of the pentyne was 2-pentyne > 1-pentyne, and that of the hexynes was 3-

Table 1  
Isomerization and hydrogenation of 2-pentyne over various halide cluster catalysts<sup>a</sup>

Entry	Catalyst	Carrier gas	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>c</sup>					Hydrogenolysis products <sup>d</sup>	Other product <sup>e</sup>
				Isomerization		Hydrogenation				
				1,3-Pentadiene ( <i>cis</i> %)	Allenes	1-Pentene	2-Pentene ( <i>cis</i> %)	Pentane		
1	[(Nb <sub>6</sub> Cl <sub>12</sub> )Cl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].4H <sub>2</sub> O	N <sub>2</sub>	5.2	27.1 (25.3)	22.0	1.1	16.0 (57.1)	0.0	32.5	1.3
2	(H <sub>3</sub> O) <sub>2</sub> [(Mo <sub>6</sub> Cl <sub>8</sub> )Cl <sub>6</sub> ].6H <sub>2</sub> O	N <sub>2</sub>	0.8	14.9 (28.9)	24.7	0.2	2.9 (82.6)	0.0	57.2	0.1
3	[(Ta <sub>6</sub> Cl <sub>12</sub> )Cl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].4H <sub>2</sub> O ( <b>1</b> )	N <sub>2</sub>	20.4	56.1 (39.8)	16.9	1.5	13.1 (47.5)	0.0	10.9	1.5
4	[(Ta <sub>6</sub> Cl <sub>12</sub> )Cl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].4H <sub>2</sub> O ( <b>1</b> )	He	9.2	54.6 (30.6)	15.9	1.4	12.5 (57.7)	0.0	13.2	2.4
5	[(Ta <sub>6</sub> Cl <sub>12</sub> )Cl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].4H <sub>2</sub> O ( <b>1</b> )	Ar	12.6	50.4 (37.0)	21.6	1.2	12.4 (47.7)	0.0	14.0	1.4
6	[(Ta <sub>6</sub> Br <sub>12</sub> )Br <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].4H <sub>2</sub> O	N <sub>2</sub>	1.8	36.2 (37.8)	26.4	1.0	8.9 (45.7)	0.0	25.3	2.2
7	(H <sub>3</sub> O) <sub>2</sub> [(W <sub>6</sub> Cl <sub>8</sub> )Cl <sub>6</sub> ].6H <sub>2</sub> O	N <sub>2</sub>	1.3	39.6 (26.0)	32.3	0.1	1.9 (82.8)	0.0	26.1	0.0
8	[Re <sub>3</sub> Cl <sub>3</sub> ]Cl <sub>3</sub> Cl <sub>6/2</sub>	N <sub>2</sub>	0.0							
9	[(Nb <sub>6</sub> Cl <sub>12</sub> )Cl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].4H <sub>2</sub> O	H <sub>2</sub>	28.0	9.6 (28.8)	6.4	1.9	68.8 (71.2)	0.6	12.1	0.6
10	(H <sub>3</sub> O) <sub>2</sub> [(Mo <sub>6</sub> Cl <sub>8</sub> )Cl <sub>6</sub> ].6H <sub>2</sub> O	H <sub>2</sub>	18.3	10.4 (29.5)	7.5	7.4	61.9 (94.1)	0.4	12.4	0.0
11	[(Ta <sub>6</sub> Cl <sub>12</sub> )Cl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].4H <sub>2</sub> O ( <b>1</b> )	H <sub>2</sub>	19.7	46.7 (41.6)	16.5	1.7	18.8 (47.6)	0.6	13.7	1.9
12	(H <sub>3</sub> O) <sub>2</sub> [(W <sub>6</sub> Cl <sub>8</sub> )Cl <sub>6</sub> ].6H <sub>2</sub> O	H <sub>2</sub>	78.6	28.2 (32.8)	2.4	9.5	41.8 (46.1)	1.3	13.3	3.5
13	[Re <sub>3</sub> Cl <sub>3</sub> ]Cl <sub>3</sub> Cl <sub>6/2</sub>	H <sub>2</sub>	9.1	7.9 (31.8)	6.9	7.9	57.8 (90.1)	0.5	19.0	0.0
14	Ta metal	N <sub>2</sub>	0.0							
15	None	N <sub>2</sub>	0.0							

<sup>a</sup> After treatment of catalyst (80 mg) in a stream of carrier gas (1.8 L/h) at 400 °C for 1 h, the reaction was initiated by introduction of 2-pentyne (52 μL/h, 0.50 mmol/h) at 400 °C.

<sup>b</sup> Conversion = products/(products + recovered 2-pentyne) × 100 (%) at 3 h after the reaction had commenced.

<sup>c</sup> Selectivity = product/(total amount of products) × 100 (%) at 3 h after the reaction had commenced.

<sup>d</sup> Methane, ethane, ethylene, etc.

<sup>e</sup> 2-Methyl-2-butene.

Table 2  
Reaction of alkynes over  $[(Ta_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$  (**1**) under nitrogen<sup>a</sup>

Substrate	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>c</sup>						
		Isomerization				Hydrogenation <sup>d</sup>	Hydrogenolysis products <sup>e</sup>	Other products
		1,3-Diene	2,4-Diene	Allenes	2-Alkyne	Alkenes		
1-Pentyne	6.7	36.1		21.9	16.1	13.3	9.9	2.7 <sup>f</sup>
2-Pentyne	20.4	56.1		16.9	–	14.6	10.9	1.5 <sup>f</sup>
1-Hexyne	5.7	3.9	20.2	8.2	8.4	11.7	21.3	26.3 <sup>g</sup>
2-Hexyne	13.6	10.3	45.2	7.8	–	8.4	10.3	18.0 <sup>g</sup>
3-Hexyne	19.6	14.4	53.5	11.6	3.4	5.7	4.9	6.5 <sup>h</sup>

<sup>a</sup> The reactions were performed in a stream of nitrogen (1.8 L/h) at 400 °C using a 0.50 mmol/h substrate. The other reaction conditions are the same as those listed in Table 1.

<sup>b</sup> Conversion = products/(products + recovered alkyne) × 100 (%) at 3 h after the reaction had commenced.

<sup>c</sup> Selectivity = product/(total amount of products) × 100 (%) at 3 h after the reaction had commenced.

<sup>d</sup> No alkane was detected.

<sup>e</sup> Methane, ethane, ethylene, etc.

<sup>f</sup> 2-Methyl-2-butene.

<sup>g</sup> 1-Methyl-1-cyclopentene, 2-methyl-2-pentene, etc.

<sup>h</sup> 2-Methyl-2-pentene, etc.

hexyne > 2-hexyne > 1-hexyne, indicating that the inner alkynes have a higher reactivity than the corresponding terminal alkynes. This order of reactivity is the reverse of that reported for base catalysts such as NaOBu<sup>t</sup> and KOBu<sup>t</sup> [13], whereas no data on the reactivity order has been reported in the case of acid catalysts. Isomerization of alkynes is initiated by protonation at the triple bond [19]. The electron density of the triple bond is higher for more substituted alkynes. Thus, inner alkynes would be expected to have a higher reactivity for isomerization over Brønsted acid catalysts, which is the case for halide cluster **1**.

The effect of the reaction temperature on the reaction of 2-pentyne over **1** is shown in Fig. 2. No substantial catalytic

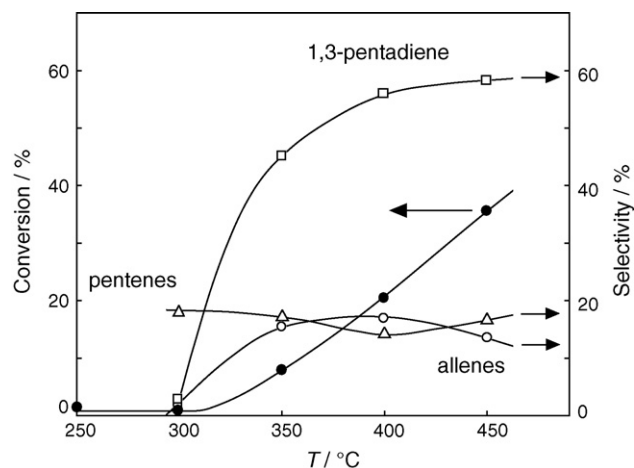


Fig. 2. Effect of temperature on the reaction of 2-pentyne over  $[(Ta_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$  (**1**) under flowing nitrogen at 3 h after the reaction had commenced. The other reaction conditions are the same as described in the caption to Fig. 1. Key: conversion (closed circles); selectivity for 1,3-pentadiene (open squares); selectivity for 1,2- and 2,3-pentadienes (open circles); and selectivity for 1- and 2-pentenes (open triangles). The selectivity for 2-methyl-2-butene and the hydrogenolysis products (e.g., methane, ethane, and ethylene) have been omitted for clarity. The selectivity for 2-methyl-2-butene was 2.9% at 350 °C, 1.5% at 400 °C, and 1.4% at 450 °C. The selectivity for the hydrogenolysis products was 18.8% at 350 °C, 10.9% at 400 °C, and 9.9% at 450 °C.

activity was observed below a temperature of 300 °C, while treatment above 300 °C resulted in catalytic activity being exhibited. Thermal treatment of the cluster gave rise to catalytic activity, since **1** has no metal–metal multiple bonds and is a coordinatively saturated complex. The catalytic activity enhanced with increasing treatment and reaction temperature. At temperatures above 350 °C, the main reaction was isomerization yielding 1,3-pentadiene.

XRD analysis was carried out on cluster **1** treated at various temperatures under nitrogen for a period of 1 h. The cluster changed to an amorphous compound above temperatures of 100 °C [5], which is attributable to the elimination of the crystallization water [27]. The Raman spectra of the heat-treated clusters are shown in Fig. 3. The peak of the untreated cluster

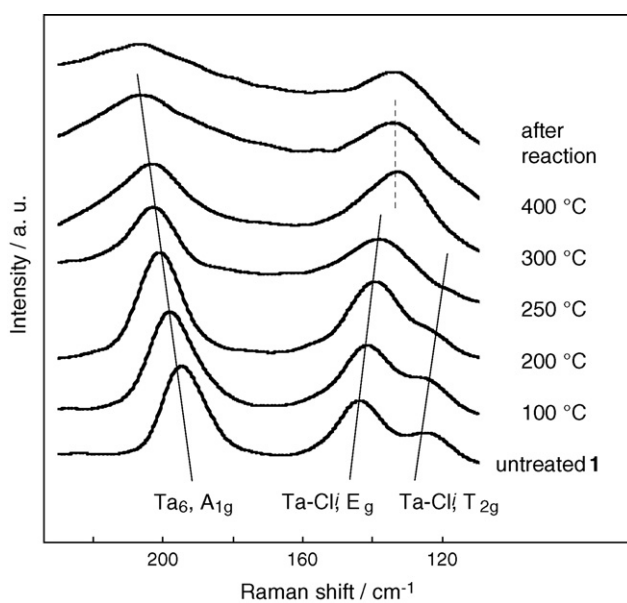
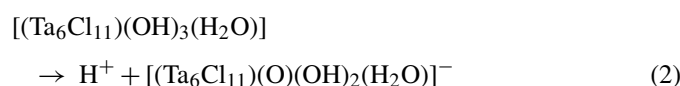
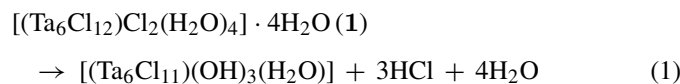


Fig. 3. Raman spectra of  $[(Ta_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$  (**1**) treated at various temperatures in flowing nitrogen for a period of 1 h. The Raman spectrum of **1** after a reaction time of 3 h at 400 °C is also shown.

occurring at  $194\text{ cm}^{-1}$  is assigned to the breathing motion of the  $\text{Ta}_6$  octahedron ( $A_{1g}$ ), whereas peaks occurring at  $144$  and  $125\text{ cm}^{-1}$  are attributed to edge-bridging  $\text{Ta}-\text{Cl}^i$  breathing vibrations ( $E_g$  and  $T_{2g}$ , respectively) [28], where  $i$  refers to the inner ligand [29]. These three peaks were retained up to  $250^\circ\text{C}$ . At temperatures above  $300^\circ\text{C}$ , the peak assigned to the breathing motion of the  $\text{Ta}_6$  octahedron remained intact, whereas the two Raman peaks attributed to the  $\text{Ta}-\text{Cl}^i$  vibrations were replaced with a new peak located centrally between these peaks, suggesting that some of the coordinating  $\text{Cl}^i$  ligands were eliminated above  $300^\circ\text{C}$ . This temperature is the same as that where catalytic activity emerged (Fig. 2). No appreciable changes in the Raman spectrum were observed after a reaction time of 3 h with 2-pentyne at  $400^\circ\text{C}$ .

Elemental analyses of tantalum (67.2%) and chlorine (25.3%) in a sample of **1** treated at  $400^\circ\text{C}$  for 1 h showed that, on average, it changed to  $\text{Ta}_6\text{Cl}_{11.5}$  with a residue (7.5%) that presumably originated from the coordinated water. IR analysis of adsorbed pyridine on the activated  $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}/\text{SiO}_2$  showed the presence of a Brønsted acid site, but not a Lewis acid site [9]. Intense evolution of HCl was observed on treatment of **1** above  $300^\circ\text{C}$ , while the evolution of  $\text{Cl}_2$  was not detected in our experiments. Based on these findings, we concluded that when the cluster was heated, the halogen ligands of **1** reacted with the coordinated water, eliminating HCl to give a hydroxo species, such as  $[(\text{Ta}_6\text{Cl}_{11})(\text{OH})_3(\text{H}_2\text{O})]$  (Eq. (1)). A Brønsted acid site originating from the hydroxo ligand would be the active site for isomerization of alkynes (Eq. (2)) [30]. The rhenium cluster  $[\text{Re}_3\text{Cl}_3]\text{Cl}_3\text{Cl}_{6/2}$  showed no catalytic activity under nitrogen (Table 1, entry 8), which can be ascribed to the absence of coordinated water.



Activation of coordinated water on heteropolyacid is reported to develop Brønsted acidity, which is enhanced by addition of water vapor [31]. However, the catalytic activity of **1** was not increased by addition of water vapor in this reaction.

The niobium, tantalum, and tungsten halide clusters exhibited partial hydrogenation of 2-pentyne to 1- and 2-pentenes, with a total selectivity of 2–17% under nitrogen (Table 1, entries 1, 3, 6, and 7). Cluster **1** subjected after a reaction time of 5 h contained 1.3 wt.% carbon as mentioned above. When the carbon is assumed to be formed from 2-pentyne, the liberated hydrogen ( $14\text{ }\mu\text{mol/h}$ ) is comparable to that required for the partial hydrogenation of 2-pentyne.

### 3.2. Reaction under hydrogen

The catalytic activity of the halide clusters in a hydrogen stream for 2-pentyne is listed in Table 1. The activity and selectivity of **1** under hydrogen was virtually the same as that under

nitrogen (entries 3 and 11). The Raman spectrum of **1** treated under hydrogen at each temperature was identical to that under nitrogen. Thus, atmospheric hydrogen participated in neither the activation of **1** nor the reaction with 2-pentyne.

In the case of the niobium, molybdenum, and tungsten clusters, the catalytic activity increased noticeably under hydrogen, and the main reaction changed to hydrogenation, yielding 2-pentene with a selectivity of 42–69% (entries 9, 10, and 12). When pyridine equimolar to 2-pentyne was added to the hydrogen stream over the niobium cluster, conversion for isomerization was reduced to about one-third, but that for hydrogenation was virtually unchanged, indicating that the active site for hydrogenation was not the Brønsted acid site. Hydrogenation of alkynes is exclusively catalyzed by the platinum group metals [21,22], and therefore, the halide clusters exhibited a similar catalytic behavior to that of the platinum group metals. The active sites of the halide clusters for hydrogenation would be the niobium, molybdenum, or tungsten metal atoms, which can become isoelectronic with the platinum group metals by accepting valence electrons from the halogen ligands [11,12]. The carbides of molybdenum and tungsten have been reported to undergo similar catalyses to those of the platinum group metals. This has been explained by the addition of the carbon atom valence electrons to the molybdenum and tungsten metal atoms, which changes their electron distribution to be similar to that of the platinum group metals [32].

The niobium, molybdenum, and tungsten clusters showed little ability to form the complete hydrogenation product, pentane, from 2-pentyne (entries 9, 10, and 12). When 1-pentene was allowed to react over the niobium cluster under the same conditions, the conversion was 67%, and the selectivity for isomerization to 2-pentene was as high as 87%, resulting in an approximate equilibrium composition of 1- and 2-pentenes [33]. In contrast, the selectivity for hydrogenation was as low as 2%. Consequently, the halide clusters catalyzed partial hydrogenation of alkynes to alkenes selectively. Metallic palladium catalyzes partial hydrogenation of alkynes to alkenes selectively, as long as the alkynes are present, and it catalyzes alkene isomerization at a faster rate than alkene hydrogenation under ambient hydrogen pressure [21,22]. Thus, the halide clusters exhibited a similar catalytic behavior to that of metallic palladium.

The rhenium cluster catalyzed the partial hydrogenation of 2-pentyne to yield 2-pentene with a selectivity of 58% under hydrogen (Table 1, entry 13). This cluster has been reported to change to metallic rhenium on treatment with hydrogen at temperatures above  $250^\circ\text{C}$  [34], and this was confirmed in our reaction system [7]. The catalytic species for hydrogenation is ascribed to metallic rhenium, since  $\text{Re}/\text{MgO}$  has also been reported to catalyze the reaction [35].

## 4. Conclusions

When the tantalum chloride cluster  $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  (**1**) was treated in a nitrogen stream at temperatures above  $300^\circ\text{C}$ , it changed to a hydroxo complex, e.g.,  $[(\text{Ta}_6\text{Cl}_{11})(\text{OH})_3(\text{H}_2\text{O})]$ . The hydroxo group of this com-

plex exhibited Brønsted acidity, and catalyzed the isomerization of alkynes to conjugated dienes. Niobium and tungsten clusters with the same metal framework also catalyzed the reaction. In a hydrogen stream, the niobium, molybdenum, and tungsten clusters catalyzed the partial hydrogenation of alkynes to alkenes. The hydrogenation of alkynes is catalyzed by the platinum group metals exclusively. The hydrogenation activity of these halide clusters is ascribed to the metal atom that accepts electrons from the halogen ligands leading to isoelectronic with the platinum group metals.

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