Catalytic dehydrohalogenation of alkyl halides by Nb, Mo, Ta, and W halide clusters with an octahedral metal framework and by a Re chloride cluster with a triangular metal framework

Satoshi Kamiguchi [a], Masaki Watanabe [b], Kunihiko Kondo [b],
Mitsuo Kodomari [b], Teiji Chihara [a],*

[a] *The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-0198, Japan*
[b] *Department of Applied Chemistry, Shibaura Institute of Technology, Shibaura, Minato-ku, Tokyo 108-8548, Japan*

Abstract

The catalytic dehydrohalogenation of fluoro-, chloro-, bromo-, and iodopentanes to yield pentene is studied in a gas flow reactor under 1 atm of helium or hydrogen. The catalysts used are crushed crystals of molecular Nb, Mo, Ta, and W halide clusters possessing an octahedral metal framework and of a solid state Re chloride cluster possessing a triangular metal framework. All of the former clusters develop catalytic activity for dehydrohalogenation of 1-halogenated pentenes yielding 1-pentene and *cis*- and *trans*-2-pentenes in a helium or hydrogen stream when the clusters are preliminarily treated at 300 °C. The Re cluster develops catalytic activity for the same reaction in a stream of helium above 175 °C, while in a stream of hydrogen at 300 °C, it is reduced to metallic Re to catalyze both dehydrohalogenation and hydrodehalogenation (hydrogenolysis) concurrently, yielding pentenes and pentane. Even the C–F bond of 1-fluoropentane is hydrogenolyzed by the Re metal.
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1. Introduction

Since the first report on the synthesis of a halide cluster, MoCl$_2$, was published in 1859 [1], several halide clusters have been synthesized with desirable and well-defined properties addressing high-temperature superconductivity, metallic conductivity at elevated temperatures, low-dimensional electronic or magnetic properties, good thermal stability, and catalytic activity [2–4]. However, little work has been reported on their behavior as catalysts [5–7]. We have recently reported that the halide clusters develop catalytic activity for isomerization of olefins [8], dehydration of alcohols [9], and decomposition of phenyl acetate to phenol and ketone [10] after they are pretreated at elevated temperatures. We therefore have started to study reactions catalyzed by halide clusters to investigate the scope and limitation of cluster catalysis. This paper is concerned with one of the reactions that we have found, namely, dehydrohalogenation of halogenated alkanes to yield olefins by halide cluster catalysts.

Various types of compounds have been reported as catalysts for the dehydrohalogenation of halogenated

* Corresponding author. Tel.: +81-48-467-9399;
fax: +81-48-462-4631.
E-mail address: chihara@postman.riken.go.jp (T. Chihara).

hydrocarbons. Arene carbonyl complexes of group 6 metals are reported to be homogeneous catalysts in the liquid-phase [11,12]. Ferric bromide, ferrous bromide, and iron are heterogeneous catalysts used in CCl_4 solution [13]; silica gel is also used as a heterogeneous catalyst in CCl_4 solution [14]. The suspensions of metallic Cu, Raney Cu, and $CuCrO_2$ are employed in squalane [15]. There are only few examples of such liquid-phase reactions. In most cases, a gas-phase reaction system is used for the reaction on solid catalysts. Metal (Ni) [16,17], metal oxide (MgO) [18], metal chloride oxide [19], metal sulfate [20,21], aluminosilicates [22], and solid acid and base [23] have been employed as the catalyst. Metal halides such as $MgCl_2$ [18], KBr [24], NaCl [25], and $ZnCl_2$ [26] are also the catalysts, and the last one is used as a molten salt. The last group, metal halides, are normal salts that comprise ionic metals and ionic halogens. In this paper, we report a new type of catalyst, a halide cluster, in which metal atoms are not ionic but are coordinated with non-ionic halogen ligands.

2. Experimental

2.1. Material and characterization

The cluster complexes $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (**1**) [27], $[(Nb_6Br_{12})Br_2(H_2O)_4]\cdot 4H_2O$ [27], $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ [28], $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ [27], and $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot 6H_2O$ [29] were prepared according to published procedures followed by repeated recrystallization to give well-grown crystals. The complex Re_3Cl_9 ($[Re_3Cl_3^i]Cl_3^aCl_{6/2}^{a-a}$, **2**) was commercially available (Furuya Metal) and used without further purification. Crystals of the complexes were crushed and screened to 150–200 mesh. Halogenated pentanes were commercial products and used as received. Powder X-ray diffraction (XRD) was performed with a Rigaku RAD-3R X-ray diffractometer using Cu Kα radiation at a scan rate of $2°$/min. Raman spectra of the cluster samples in glass reaction tubes were recorded in situ on a Kaiser Optical Systems HoloLab 5000 with an Nd-YAG laser operated at 532 nm and with a 7.6 mm focus lens. Counts were accumulated 30 times at 1 s intervals. The trapped products were analyzed by GC/MS (Hewlett-Packard 5890 Series II gas chromatograph coupled with a Jeol Automass System II, a 15 m × 0.25 mm × 0.25 μm DB-1 capillary column, helium carrier gas) and GLC (GL Sciences 353B gas chromatograph fitted with a flame ionization detector, a 30 m × 0.25 mm × 0.25 μm DB-1 capillary column, helium carrier gas). In the GLC analysis all of the products were identified by comparison with authentic samples obtained commercially. The catalytic activities were evaluated by an on-line GLC (Shimadzu 14B gas chromatograph fitted with a flame ionization detector, a 2 m × 3 mm 3% silicone OV-17 on Chromosorb WAW-DMCS packed column and a 11.5 m × 3 mm 25% sebaconitrile on Uniport B packed column, nitrogen carrier gas).

2.2. Apparatus and procedures

A conventional apparatus for gas flow reaction was used [8]. The gas flow rate (20 ml/min) was controlled by an orifice-type flow regulator at 1 atm and introduced to a temperature-controlled stainless steel tube with glass lining (3 m × 2 mm i.d.) used as a pre-heater for the carrier gas (He or H_2). The general procedure consisted of packing a known mass of cluster complex (30 mg) in an electrically heated vertical tubular Pyrex glass reactor (3 mm i.d.) with the aid of quartz glass wool. Catalyst pre-treatment was performed in situ immediately prior to reaction under a stream of the gas at the operating temperature for 1 h. Liquid reactant was introduced at a controlled rate (1.66 mmol/h) via a motor-driven glass syringe pump through a T-joint attached before the stainless steel tube to pre-heat the gas to the same temperature as the reactor. Gaseous products were introduced to a temperature controlled gas sampler (1 ml) connected to a six-way valve and analyzed by the on-line GLC. The reactor effluent was frozen in a dry-ice trap for subsequent analysis, which was performed using the GLC with the capillary column.

In a typical example, $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (**1**) (30 mg) packed in the reactor was treated in a stream of helium (20 ml/min) at 300 °C for 1 h and then liquid 1-chloropentane (0.20 ml/h, 1.66 mmol/h) was introduced via the syringe pump to the stream of helium at 300 °C. The product in the gas sampler was analyzed at 15 min intervals by the on-line gas chromatography. Analysis of the trapped products showed that the material balance was 81% (0–1 h),

92% (1–2 h), and 93–94% (2–5 h) recovery. In this paper, conversion and selectivity will be discussed based on the data from on-line GLC analyses.

3. Results and discussion

3.1. Activation of halide cluster

Powdered crystals of $[(Nb_6Cl^i_{12})Cl^a_2(H_2O)_4]\cdot4H_2O$ (**1**) (Scheme 1) were packed in a glass reaction tube and heated in a stream of helium for 1 h. The reaction was commenced immediately by introduction of 1-chloropentane into the stream of helium at the same temperature. Typical reaction profiles are illustrated in Fig. 1. No catalytic reactions were observed below 175 °C; however, treatment above 200 °C brought about the catalytic activity for dehydrohalogenation to yield 1-pentene and *cis*- and *trans*-2-pentenes. In each experiment, the catalytic activity decreased with time but leveled off after 4 h. Formation of coke may retard the reactions. The activity increased with increasing temperature as Fig. 1 shows. Blank experiment showed that 1-chloropentane spontaneously decomposed above 325 °C, yielding a variety of products including the pentenes as minor products. The

$[(Nb_6Cl^i_{12})Cl^a_2(H_2O)_4]\cdot4H_2O$ (**1**)
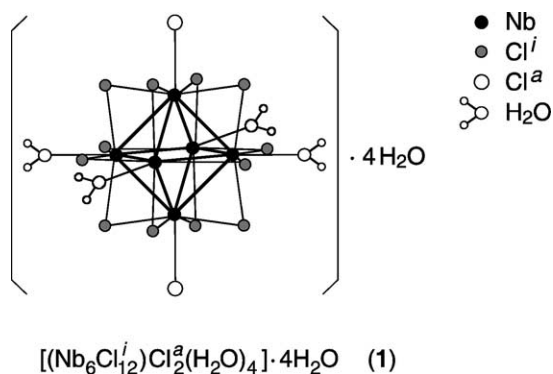
Scheme 1.

reaction rates were proportional to the amount of the catalyst. The reaction was first order with respect to the feed amount of 1-chloropentane as long as the amount was smaller than 0.024 ml/h (0.20 mmol/h), and zero order in the feed amount greater than 0.10 ml/h (0.83 mmol/h), where 1-chloropentane was in saturated adsorption. Subsequent experiments were performed in this saturated region.

The effect of reaction temperature on the reactivity of 1-chloropentane over **1** and the product distribution are shown in Fig. 2. The main reaction
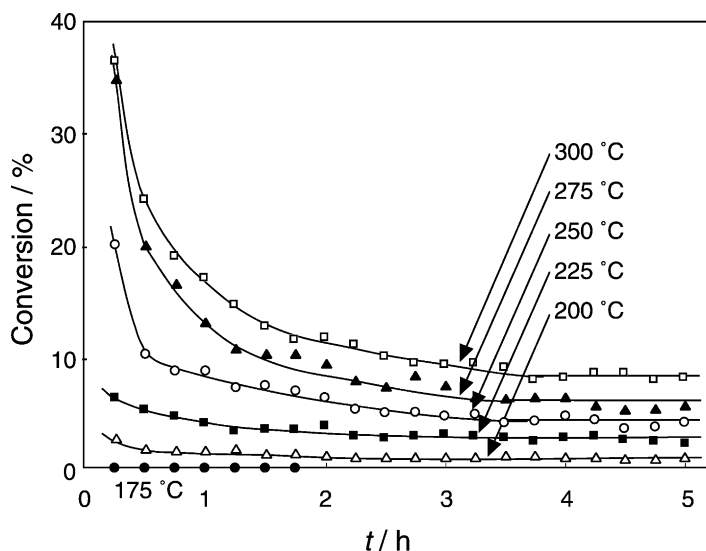

Fig. 1. Reaction profile of 1-chloropentane over $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (**1**). After treatment of **1** (30 mg) with He (20 ml/min) for 1 h, reaction was commenced by introduction of 1-chloropentane (0.20 ml/h) at the same temperature. Conversion = products/(products + recovered material) × 100 (%).
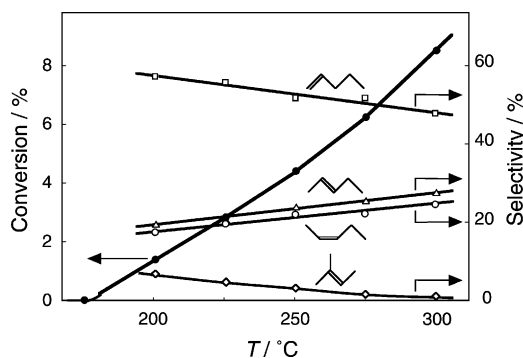
Fig. 2. Effect of temperature on reactivity and selectivity of dehydrohalogenation of 1-chloropentane over $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (1) at 5 h after reaction had started. Other conditions are the same as in Fig. 1. Conversion = products/(products + recovered material) × 100 (%); selectivity = product/(total amount of products) × 100 (%).

was dehydrohalogenation to provide 1-, *cis*-2-, and *trans*-2-pentenes, and hydrodehalogenation (dehalogenation or hydrogenolysis) to yield pentane was not observed at all. A small amount of 2-methyl-2-butene was formed, showing that skeletal rearrangement occurred slightly. Other isomeric 2-methylbutenes were not detected, as 2-methyl-2-butene is the sole trisubstituted ethylene and hence the most stable isomer among the three methylbutenes [30].

As mentioned above, the halide clusters catalyzed isomerization of olefins [8]. Then isomerization in the presence of halogenated hydrocarbon was examined.

When 1-hexene (1.66 mmol/h) in the presence of an equimolar amount of 1-chloropentane was subjected to the reaction over **1** at 300 °C, no isomerization of 1-hexene to *cis*- and *trans*-2-hexenes was observed and only dehydrohalogenation yielding pentenes occurred. In competitive reaction over heterogeneous catalysts, the amount of adsorption is proportional to each adsorption coefficient [31]. Accordingly, only a substrate with considerably larger adsorption coefficient is exclusively adsorbed on the catalyst and reacts leaving the other intact. The result indicates that the adsorption coefficient of the halogenated hydrocarbon on the cluster is significantly larger than that of the olefin. Consequently, successive isomerization of the olefin produced by dehydrohalogenation can be ruled out under these reaction conditions.

The effect of the carrier gas was examined. The catalytic activities and selectivities of **1** in streams of helium and hydrogen are plotted in Fig. 3a and b, respectively. Despite the decreasing catalytic activities with time in both gas streams, the selectivities remained constant from the initial stage of the reactions, which suggests that the reaction mechanism did not change with time. The activities and the selectivities shown in these figures are practically identical, implying that hydrogen did not chemically participate in this reaction. The *cis/trans* selectivities of 2-pentene remained in a relative narrow range and the ratios (0.89) are approximately comparable with that of thermal equilibrium (0.61 at 300 °C). On the other hand,
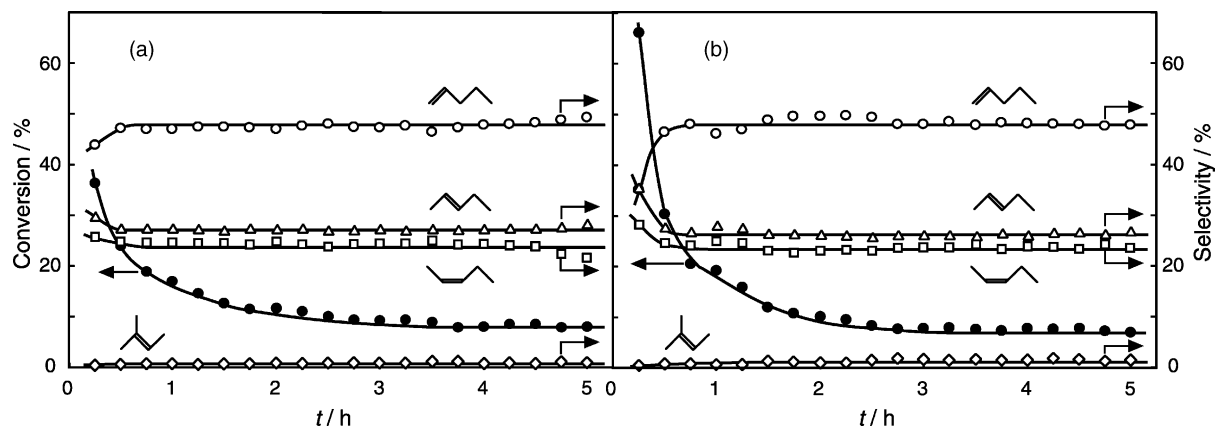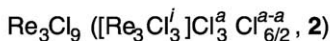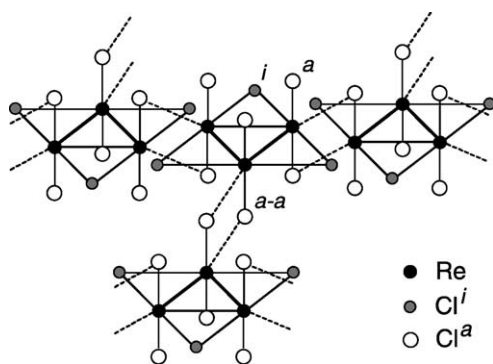

Fig. 3. Catalytic activity and selectivity of $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (**1**) in dehydrohalogenation of 1-chloropentane in a stream of (a) He and (b) H_2 at 300 °C. Other conditions are the same as in Fig. 1.

Scheme 2.

Fig. 4. Effect of temperature on reactivity and selectivity of dehydrohalogenation of 1-chloropentane over Re_3Cl_9 (**2**) in He at 5 h after reaction had started. Other conditions are the same as in Fig. 1.

the 1-pentene/2-pentene ratios (0.94) are far from that of thermal equilibrium (0.13 at 300 °C) [30].

The same reaction was examined using the Re cluster, Re_3Cl_9 (**2**) (Scheme 2), as a catalyst in a stream of helium at different temperatures; the results are shown in Fig. 4. The activity of **2** appeared by treatment at 175 °C, which is a little lower than the corresponding temperature for **1**. The selectivities remained almost unchanged. The *cis/trans* (0.62) and 1-pentene/2-pentene rations (0.28) are roughly in accord with those of thermal equilibrium (0.61 and 0.13 at 300 °C, respectively), which suggests that the precursors of the products are in equilibrium. The effects of the carrier gases, helium and hydrogen, at 300 °C are shown in Fig. 5a and b. Again, the activi-
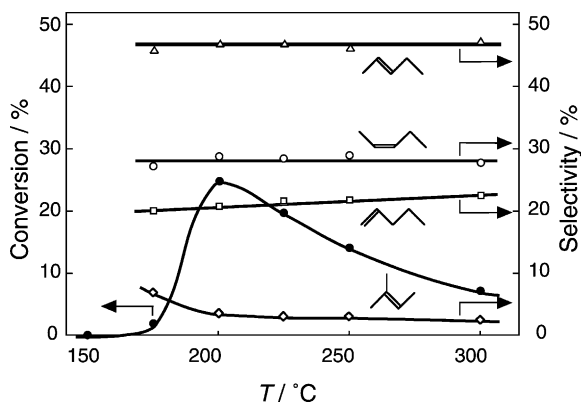
ties decreased with time but the selectivities remained substantially constant from the initial stage of the reactions. The reaction mechanisms over **2** did not change in the course of the reactions either. A remarkable feature of **2** is that hydrogenolysis also occurred in the hydrogen stream to yield pentane in 38% selectivity, in contrast to the reaction in the stream of helium in which only dehydrohalogenation occurred. Complex **2** is reported to change to metallic rhenium by treatment with hydrogen at 250–300 °C [32], which has been confirmed by an XRD analysis (see Fig. 6). In this case, hydrogen participated chemically both as a reagent for the reduction of rhenium(III)
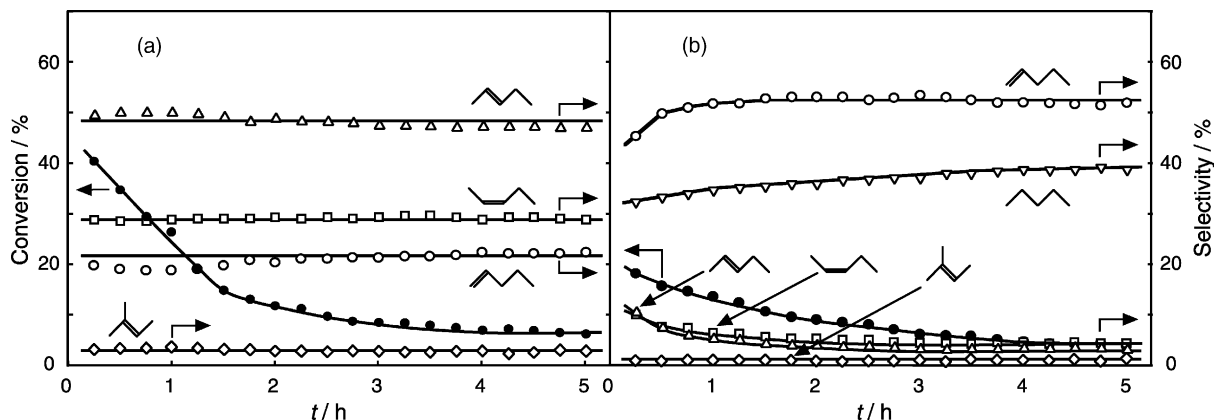

Fig. 5. Catalytic activity and selectivity of Re_3Cl_9 (**2**) in dehydrohalogenation and hydrogenolysis of 1-chloropentane in a stream of (a) He and (b) H_2 at 300 °C. Other conditions are the same as in Fig. 1.
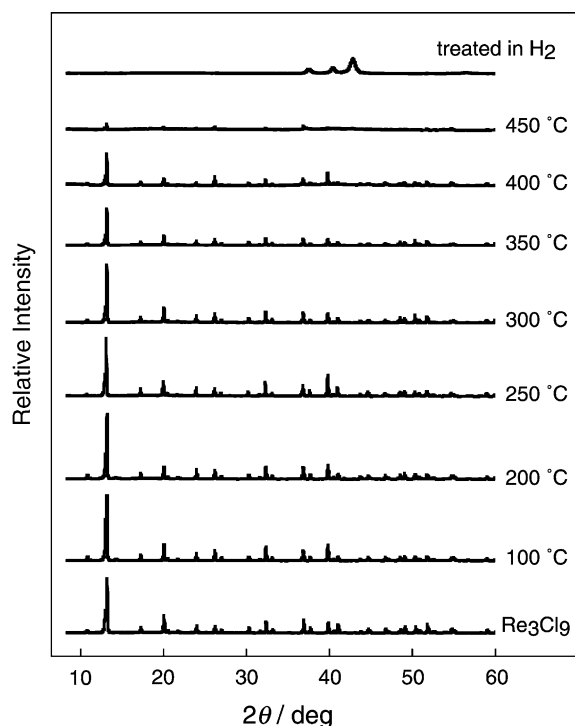
Fig. 6. XRD patterns of Re_3Cl_9 (**2**) treated at various temperatures with He (20 ml/min) for 1 h. Top pattern is that of **2** treated in a H_2 stream (20 ml/min) for 1 h at 300 °C showing reduction of **2** to metallic Re.

chloride **2** and as a reagent for hydrogenolysis of 1-chloropentane to pentane. Rhenium is located in a neighboring position to the platinum group metals in the periodic table, and is similar to them in some properties. Rhenium metal, as well as its oxide, sulfide, and selenide, is a catalyst for hydrogenation of organic compounds [33,34]; however, it has not been reported to catalyze hydrogenolysis [35]. Thus, this is the first example of hydrogenolysis by rhenium metal.

Catalytic activities of several halide clusters tested for dehydrohalogenation of 1-chloropentane are listed in Table 1, which shows that all clusters tested developed catalytic activity in helium or hydrogen stream. Niobium metal powder had no catalytic activity. Niobium pentachloride was not applied to this reaction system because of its low boiling point (250 °C), although it could be used as a catalyst under other conditions, e.g. in a closed reaction system. One advantage of halide clusters is their low vapor

pressure, enabling application at high temperatures in an open reaction system. Skeletal rearrangement to yield 2-methyl-2-butene was observed to a small extent on every catalyst. As Table 1 shows, one of the striking features of these catalysts, except **2**, is that each cluster exhibited practically the same catalytic activity and selectivity under helium and hydrogen streams. Moreover, the selectivities of Nb and Ta of group 5 metal clusters are similar, and those of Mo and W of group 6 metal clusters are similar. On the other hand, the selectivity of the Re cluster depends on the gas used, as mentioned above.

3.2. Reactivity of halogenated pentanes

The catalytic activity and selectivity of Nb cluster **1** for various halogenated pentanes are listed in Table 2. Cluster **1** dehydrohalogenated all halogen compounds tested. As Table 2 shows, the reactivity and selectivity in helium were quite similar to those in hydrogen for every halogenated pentane. Again, the similarity of both the reactivity and selectivity under helium and hydrogen gases indicates that hydrogen did not operate chemically, although the heat of adsorption of hydrogen on group 5 and 6 metals is quite high [36,37]. The reactivity order of the halogen substituents was $F \gg Cl > Br > I$, which is the reverse of that observed in catalytic hydrogenolysis over platinum group metals [38,39]. There have been no systematic data on the reactivity order of the halogen substituents in dehydrohalogenation. Only partial data can be seen: $Br-C_2H_5 > I-C_2H_5$ over rare-earth-exchanged 13X zeolite to yield ethylene [22] and generally $Cl \approx Br$ over solid acids and $Cl < Br$ over solid bases [21]. The higher reactivity of 2-chloropentane compared with 1-chloropentane matches the well-known increasing activity order of primary, secondary, and tertiary carbon atoms in dehydrohalogenation [40].

Reactivities of halogenated pentanes catalyzed by Re_3Cl_9 (**2**) in helium or hydrogen stream are summarized in Table 3. All halogenated pentanes tested were catalytically dehydrohalogenated by **2**. The reactivity order in a helium stream is $F > Cl > Br > I$, as in the case of **1**. This order might be due to the larger equilibrium constant of the lighter halogens, as expressed in Eq. (1) [22], or due to steric crowding of these rather

Table 1
Dehydrohalogenation of 1-chloropentane over halide cluster[a]

Halide cluster	Carrier gas	Conversion (%)[b]	Selectivity (%)[c]				
			Pentane	1-Pentene	cis-2-Pentene	trans-2-Pentene	2-Methyl-2-butene
$[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (1)	He	8.5	0.0	47.3	24.3	27.3	1.1
$[(Nb_6Br_{12})Br_2(H_2O)_4]\cdot 4H_2O$	He	4.8	0.0	48.9	21.7	27.0	2.4
$(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$	He	35.9	0.0	23.8	28.4	45.9	1.9
$[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$	He	5.2	0.0	54.3	22.7	21.0	2.0
$(H_3O)_2[(W_6Cl_8)Cl_6]\cdot 6H_2O$	He	1.9	0.0	30.3	26.1	38.8	4.8
Re_3Cl_9 (2)	He	7.1	0.0	21.6	29.0	46.8	2.6
$[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (1)	H$_2$	7.7	0.0	48.0	26.5	23.9	1.6
$(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$	H$_2$	62.6	0.0	22.4	29.4	45.7	2.5
$[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$	H$_2$	8.1	0.0	54.4	23.5	22.1	0.0
$(H_3O)_2[(W_6Cl_8)Cl_6]\cdot 6H_2O$	H$_2$	0.0	–	–	–	–	–
$(H_3O)_2[(W_6Cl_8)Cl_6]\cdot 6H_2O$[d]	H$_2$	12.3	0.0	40.8	28.0	31.2	0.0
Re_3Cl_9 (2)	H$_2$	5.1	38.4	52.3	4.7	3.4	1.2
Nb metal[e]	He	0.0	–	–	–	–	–
–	He	0.0	–	–	–	–	–

[a] After treatment of halide cluster (30 mg) in the stream of carrier gas (20 ml/min) at 300 °C for 1 h, reaction was started by introduction of 1-chloropentane (0.2 ml/h, 1.66 mmol/h) at the same temperature.
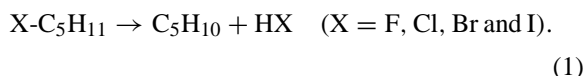
[b] Conversion = products/(products + recovered material) × 100 (%) at 5 h after reaction started.

[c] Selectivity = product/(total amount of products) × 100 (%) at 5 h after reaction started.

[d] 1-Fluoropentane was used as substrate.

[e] 150–200 mesh of Nb metal was used.

bulky halide cluster catalysts:

$$X\text{-}C_5H_{11} \rightarrow C_5H_{10} + HX \quad (X = F, Cl, Br\ and\ I).$$
(1)

Rhenium metal, formed from **2** in a stream of hydrogen, catalyzed both dehydrohalogenation and hydrogenolysis of all halogenated pentanes tested. Re metal and its related compounds are known to be hydrogenation catalysts as mentioned above. Hence, the appearance of hydrogenolysis activity of Re metal may not be surprising. However, Re metal obtained from reduction of cluster **2** has caused the hydrogenolysis of the C–F bond, which is quite difficult to

Table 2
Dehydrohalogenation of halogenated pentanes over $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (1)[a]

X-C$_5$H$_{11}$	Carrier gas	Conversion (%)[b]	Selectivity (%)[c]				
			Pentane	1-Pentene	cis-2-Pentene	trans-2-Pentene	2-Methyl-2-butene
X = 1-F	He	83.1	0.0	38.5	29.1	32.4	0.0
X = 1-Cl	He	8.5	0.0	47.3	24.3	27.3	1.1
X = 2-Cl	He	89.8	0.0	17.5	39.3	43.2	0.0
X = 1-Br	He	6.8	0.0	51.9	18.4	27.6	2.1
X = 1-I	He	1.6	0.0	56.7	20.1	23.2	0.0
X = 1-F	H$_2$	71.3	0.0	38.7	28.9	32.4	0.0
X = 1-Cl	H$_2$	7.7	0.0	48.0	23.9	26.5	1.6
X = 2-Cl	H$_2$	97.0	0.0	17.4	39.1	43.5	0.0
X = 1-Br	H$_2$	2.6	0.0	51.7	20.6	26.3	1.4
X = 1-I	H$_2$	2.5	0.0	55.4	18.8	24.1	1.7

[a] After treatment of cluster **1** (30 mg) in the stream of carrier gas (20 ml/min) at 300 °C for 1 h, reaction was started by introduction of halogenated pentane (1.66 mmol/h) at the same temperature.

[b] Conversion = products/(products + recovered material) × 100 (%) at 5 h after reaction started.

[c] Selectivity = product/(total amount products) × 100 (%) at 5 h after reaction started.

Table 3
Dehydrohalogenation and hydrodehalogenation of halogenated pentanes over Re_3Cl_9 (**2**)[a]

X-C_5H_{11}	Carrier gas	Conversion (%)[b]	Selectivity (%)[c]				
			Pentane	1-Pentene	cis-2-Pentene	trans-2-Pentene	2-Methyl-2-butene
X = F	He	14.3	0.0	30.1	30.1	39.8	0.0
X = 1-Cl	He	7.1	0.0	21.6	29.0	46.8	2.6
X = 2-Cl	He	29.7	0.0	17.6	35.1	47.3	0.0
X = 1-Br	He	5.7	0.0	22.9	28.2	45.0	3.9
X = 1-I	He	0.0	–	–	–	–	–
X = 1-F	H_2	5.6	14.0	14.1	24.0	47.9	0.0
X = 1-Cl	H_2	5.1	38.4	52.3	4.7	3.4	1.2
X = 2-Cl	H_2	91.6	2.2	20.2	34.3	43.3	0.0
X = 1-Br	H_2	4.7	40.9	37.2	7.6	12.7	1.6
X = 1-I	H_2	4.9	37.9	43.5	9.9	8.7	0.0

[a] After treatment of cluster **2** (30 mg) in the stream of carrier gas (20 ml/min) at 300 °C for 1 h, reaction was started by introduction of halogenated pentane (1.66 mmol/h) at the same temperature.

[b] Conversion = products/(products + recovered material) × 100 (%) at 5 h after reaction started.

[c] Selectivity = product/(total amount of products) × 100 (%) at 5 h after reaction started.

hydrogenolyze by catalytic means. It has been reported in the hydrogenolysis of halogen substituents, RX to RH, that the reactivity order is RI > RBr > RCl and that RF cannot be converted to RH by catalytic means [38,39].

3.3. Activation of Re_3Cl_9 (**2**)

The XRD patterns of **2** treated at various temperatures in helium streams for 1 h are shown in Fig. 6, and the Raman spectra of these samples are illustrated in Fig. 7. The crystal structure and unit cell dimensions of **2** were retained up to 400 °C, while the crystallinity decreased above 350 °C, as Fig. 6 shows. The Raman spectrum noticeably changed on treatment at 300 °C. At this temperature, the peaks attributable to the Re–Cl and Re–Re vibration modes [41] almost disappeared. The samples treated at 350 and 400 °C have a special feature: they mostly maintained the original crystal structure but the constituent is no longer the same as that of **2**. This apparent disagreement can be interpreted by partial decomposition of the component cluster [Re_3Cl_9] unit, which remains in the same position of the crystal lattice. The generation of Cl_2 gas was not detected throughout the treatment. However, slight evolution of HCl gas was observed at the vent when **1** was treated in a stream of helium at 150 °C, and strong evolution began when treated above 200 °C. Partial
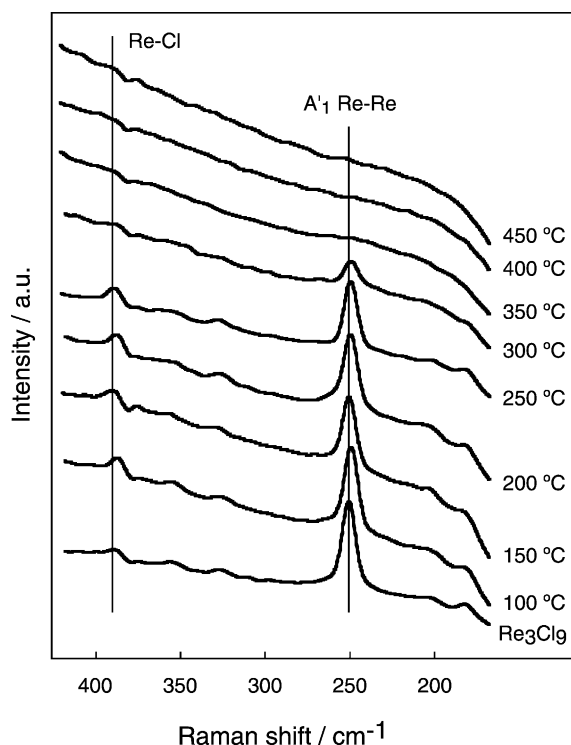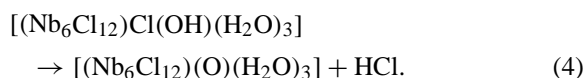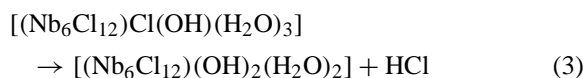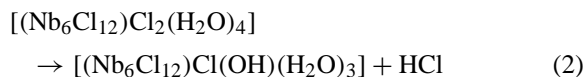

Fig. 7. Raman spectra of Re_3Cl_9 (**2**) treated at various temperatures with He (20 ml/min) for 1 h.
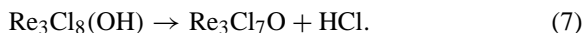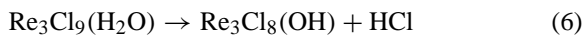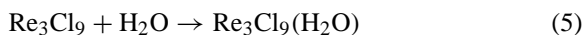
decomposition of the cluster presumably started as low as 175 °C to develop catalytically active sites, although the catalytic activity above 325 °C cannot be examined owing to the spontaneous decomposition of the alkyl halide. No appreciable changes of these XRD patterns and Raman spectra were observed after 5 h reactions with 1-chloropentane at each treatment temperature.

It is difficult to dissolve freshly prepared Re_3Cl_9 ($[Re_3Cl_3^i]Cl_3^aCl_{6/2}^{a-a}$, **2**) which consists of $[Re_3Cl_3^i]Cl_3^a$ moiety linked by weak halide bridges $Cl_{6/2}^{a-a}$ (Scheme 2). However, after exposure to a solvent followed by removal of the solvent, it becomes much more soluble in many solvents. This is due to initial disruption of the tight Re_3Cl_9 structure, which remains disrupted after removal of the first solvent [42]. Cluster **2** itself is a thermally stable complex at least up to 450 °C, at which temperature it can be purified by vacuum sublimation [32], presumably by breaking the cluster bridges, $Cl_{6/2}^{a-a}$, in the solid state. Although **2** is decomposed in aqueous solution, it reacts with a number of Lewis bases with retention of the triangular metal framework to form complexes of the type $L_3Re_3Cl_9$, where L = triphenylphosphine, pyridine, etc. [43]. Trace amounts of water contained in the reaction system would be incorporated in this solid cluster as coordinated water.

Groups 5 and 6 metals are electropositive and oxophilic elements, and its low oxidation state in the oxides and halides is possible only when the metal–metal bonds stabilize the metal atom. The metal–halogen bond is so strong that hydrogen gas will not reduce the cluster under normal conditions. When the cluster is heated under a helium or hydrogen gas, most probable reaction that will occur is disproportionation with participation of the coordinated water or crystallization water evolving HCl, as exemplified in Eqs. (2)–(4) [8]:

$$[(Nb_6Cl_{12})Cl_2(H_2O)_4]$$
$$\rightarrow [(Nb_6Cl_{12})Cl(OH)(H_2O)_3] + HCl \quad (2)$$

$$[(Nb_6Cl_{12})Cl(OH)(H_2O)_3]$$
$$\rightarrow [(Nb_6Cl_{12})(OH)_2(H_2O)_2] + HCl \quad (3)$$

$$[(Nb_6Cl_{12})Cl(OH)(H_2O)_3]$$
$$\rightarrow [(Nb_6Cl_{12})(O)(H_2O)_3] + HCl. \quad (4)$$

Similarly, **2** should be activated by treatment under a stream of helium to form Re–OH or Re–O species, as expressed in Eqs. (5)–(7):

$$Re_3Cl_9 + H_2O \rightarrow Re_3Cl_9(H_2O) \quad (5)$$

$$Re_3Cl_9(H_2O) \rightarrow Re_3Cl_8(OH) + HCl \quad (6)$$

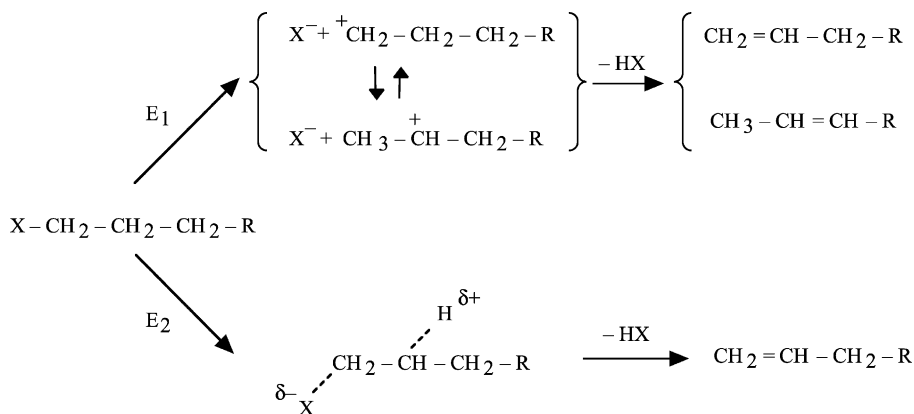$$Re_3Cl_8(OH) \rightarrow Re_3Cl_7O + HCl. \quad (7)$$

Thus, the catalytic activity of the cluster would be attributed to the acid site of the metal–OH moiety (hydroxo cluster) or metal–O moiety (oxo cluster) with retention of the cluster metal framework.

3.4. Reaction mechanism of dehydrohalogenation

The conceivable reaction mechanisms of the dehydrohalogenation reactions are either the monomolecular elimination (E_1) or bimolecular elimination (E_2). These reaction pathways are illustrated in Scheme 3. In the E_1 mechanism, the reaction begins with the abstraction of the halogen X, since it is more electronegative than H. The first step gives a carbonium ion, which loses a proton in the second step. In the E_2 mechanism, H and X are abstracted in one step [40,44]. The E_1 mechanism has been observed mainly in gas-phase dehydrohalogenation reactions with acidic catalysts: Ni/SiO_2 [16], $MgCl_2$ [18], and various solid acids [21]. The reactions over rare-earth-exchanged X zeolites also proceed by the E_1 mechanism, and the reactivity order Br > I is reported [22], which is the same as our observations (Table 3 under helium and Table 2). On the other hand, basic catalysts, MgO [18], sulfates of groups 5–7 metals [20], and various solid bases [21], have been proposed to facilitate the reaction by the E_2 mechanism. In this case, the reactivity order of the halogens is Cl < Br, which is in reverse order.

Table 1 shows that all of the clusters of groups 5–7 metals converted 1-chloropentane into 2-pentene in approximately 50% selectivity, and Table 2 shows that **1** catalyzed all of the 1-halogenated pentanes to 2-pentene in approximately 50% selectivity. If the dehydrohalogenation proceeded by the single-step E_2 mechanism, 1-pentene would be the main product. The formation of a considerable amount of 2-pentenes indicates the existence of the cationic intermediate whose lifetime is long enough to cause the migration of the neighboring hydrogen. The production

$$X-CH_2-CH_2-CH_2-R \xrightarrow{E_1} \begin{Bmatrix} X^- + {}^+CH_2-CH_2-CH_2-R \\ \updownarrow \\ X^- + CH_3-\overset{+}{CH}-CH_2-R \end{Bmatrix} \xrightarrow{-HX} \begin{Bmatrix} CH_2=CH-CH_2-R \\ CH_3-CH=CH-R \end{Bmatrix}$$

$$X-CH_2-CH_2-CH_2-R \xrightarrow{E_2} \underset{\delta-}{\overset{H^{\delta+}}{\underset{X}{CH_2-CH-CH_2-R}}} \xrightarrow{-HX} CH_2=CH-CH_2-R$$

Scheme 3.

of a small amount of 2-methyl-2-butene also agrees with this consideration, since it indicates the skeletal rearrangement during the reaction. Fig. 2 shows that the higher reaction temperature resulted in the higher selectivity for the thermodynamically stable 2-pentenes. This may be due to the fast equilibration at higher temperatures between the primary and the secondary carbocation intermediate starting from the former. Approach to the equilibrium composition of the product at higher temperature has been reported in the dehydrohalogenation of 1- and 2-chlorobutanes by the E_1 mechanism over $MgCl_2$ as a Lewis acid catalyst [18]. The high selectivity for 2-pentenes from 2-chloropentane (Table 3 under helium and Table 2) agrees with this finding, because the secondary carbocation intermediate is more stable, reacting without any migration. In the E_2 mechanism, the sterically easily accessible 1-hydrogen atom of 2-chloropentane should be preferentially removed to yield 1-pentene. Thus, the selectivity for the products also indicates that the dehydrohalogenation over the clusters follows the E_1 mechanism.

Cluster **2** treated in helium or hydrogen stream has been confirmed to have no catalytic activity for isomerization of olefins [8]. In a stream of helium, the characteristics of catalysis over **2** are similar to those over other clusters examined. In contrast, when **2** was converted to metallic Re by hydrogen reduction, the selectivities for *cis*- and *trans*-2-pentenes drastically decreased to 5 and 3%, respectively, the selectivity for 1-pentene increased to 52%, and hydrogenolysis to yield pentane developed into 38%

selectivity in the reaction of 1-chloropentane (Table 3 and Fig. 5). Similar results were observed for the reaction products of other halogenated pentanes, except for 1-fluoropentane (Table 3). Furthermore, 1-iodopentane reacted on this catalyst. The active site and the reaction mechanism for the metallic Re catalyst must be entirely different from those discussed for the cluster catalysts. It has been confirmed that metallic Re did not catalyze hydrogenation of olefinic double bonds under these reaction conditions [8]; therefore, the pentane was produced directly from halogenated pentanes. Apparently, hydrogen was consumed to facilitate the hydrogenolysis. In the case of hydrogenolysis by hydrogenation catalysts such as copper chromite, copper-on-silica, and Raney copper, chemisorbed hydrogen takes part in the reaction mechanisms, although the specific role of hydrogen is not clear [15]. The high selectivity for 1-pentene along with low selectivity for 2-hexenes clearly shows that the dehydrohalogenation predominantly follows the E2 mechanism on the Re metal catalyst.

4. Conclusions

Molecular halide clusters of groups 5 and 6 metals developed catalytic activity for dehydrohalogenation of 1-fluoro-, 1-chloro-, 1-bromo-, and 1-iodopentanes yielding a mixture of 1-, *cis*-2-, and *trans*-2-pentenes, when the clusters were initially treated in helium or hydrogen stream at 200–300 °C. The solid state Re cluster Re_3Cl_9 (**2**) also developed the catalytic activity

for dehydrohalogenation when treated under helium above 175 °C. The reactions proceeded by a unimolecular elimination (E_1) mechanism involving rearrangement of the carbonium ion intermediate.

On the other hand, when **2** was treated in a stream of hydrogen at 300 °C it was reduced to metallic Re, which catalyzed both hydrodehalogenation (hydrogenolysis) yielding pentane and dehydrohalogenation yielding pentenes concurrently. Even the C–F bond was hydrogenolyzed by this catalyst. The main product of the dehydrohalogenation from 1-chloro-, 1-bromo-, and 1-iodopentane is 1-pentene, which indicates that the reaction proceeded by the single step E_2 mechanism.

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