Catalytic dehydration of alcohol to olefin and ether by halide clusters of Nb, Mo, Ta and W possessing an octahedral metal core

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Molecular halide clusters, $[(M_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (M = Nb, Ta) and $(H_3O)_2[(M_6Cl_8)Cl_6]\cdot 6H_2O$ (M = Mo, W), develop catalytic activity for the dehydration of alcohols to yield olefins and ethers when they are treated at 300 °C. The activity of the W cluster appears at 250 °C at which temperature it changes to the poorly crystallized three-dimensional linked cluster $[W_6Cl^i_8]Cl^a_4Cl^{a-a}_{4/2}$, and decreases at 400 °C at which temperature the crystallinity improves.

KEY WORDS: halide cluster; catalytic dehydration of alcohol; thermal treatment; formation of olefin; retention of cluster framework.

1. Introduction

Many halide clusters have been reported since the first synthesis of the halide cluster $MoCl_2$ in 1859 [1]. Seventeen metals of groups III to VII, co-ordinated with four kinds of halogen ligands, constitute the halide clusters [2]. Because high temperatures (600–1000 °C) are generally required for the synthesis of the halide clusters and they are thermally quite stable, attempts to utilize them as catalysts have been prevented [3]. With the substantiation of halide cluster catalysis through the decomposition reaction of phenyl acetate to phenol and ketene [4], we have commenced an investigation addressing the scope and nature of halide cluster catalysis. A simple reaction, the dehydration of alcohols, is well-known, and hence various types of catalysts for it have been reported. Solid acid catalysts such as alumina [5] and zeolite [6], and solid base catalysts such as thorium oxide [7] have been reported as catalysts. This reaction has been found to be catalyzed by halide clusters. The present report describes this catalysis, and presents evidence that this dehydration involves novel cluster catalysis with retention of the cluster framework.

2. Experimental

Single crystals of the cluster complexes were crushed and screened to 150–200 mesh. The reaction was performed in a conventional continuous-flow microreactor operated at atmospheric pressure. In a typical experiment, a weighed cluster sample (30 mg) was put in a Pyrex tube (3 mm i.d.) placed in the center of an electric furnace. The sample was initially treated at an elevated temperature for 1 h in a stream of helium (20 mL/m). Then the reaction was initiated by feeding ethanol (0.24 mL/h) into the stream of helium using a micro-feeder at the same temperature. The reaction was monitored by sampling the reaction gas (1 mL) using a six-way valve followed by analysis using on-line GLC.

3. Results and discussion

Typical reaction profiles catalyzed by $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot 6H_2O$ (**1**) are plotted in figure 1. No catalytic activity was observed below 225 °C. Treatment above this temperature produced substantial catalytic activity. In all of the experiments the catalytic activity decreased with time, but converged to constant activity after 5 h. Table 1 lists the catalytic activity of various halide clusters at 5 h after the reactions had started at 300 °C. Table 1 shows that all the clusters tested developed catalytic activity. 1-Propanol, 1-buranol and 1-pentanol yielded the corresponding olefins exclusively. The effect of the treatment temperature of **1** was examined and the results are presented in figure 2. The catalytic activity appeared in a narrow temperature range, 225–350 °C, with the activity increasing with increasing temperature, the maximum activity occurring at around 300–330 °C. Dehydration of ethanol proceeded to yield ethylene as a major product with ether and acetaldehyde diethyl acetal, and no other reactions were observed.

The X-ray diffraction patterns of **1** treated at various temperatures in helium streams for 1 h are shown in figure 3, along with that of an authentic sample of $[W_6Cl_{12}]$ ($[W_6Cl^i_8]Cl^a_2Cl^{a-a}_{4/2}$) (**2**) prepared according to the reported method (scheme 1) [8]. The samples treated

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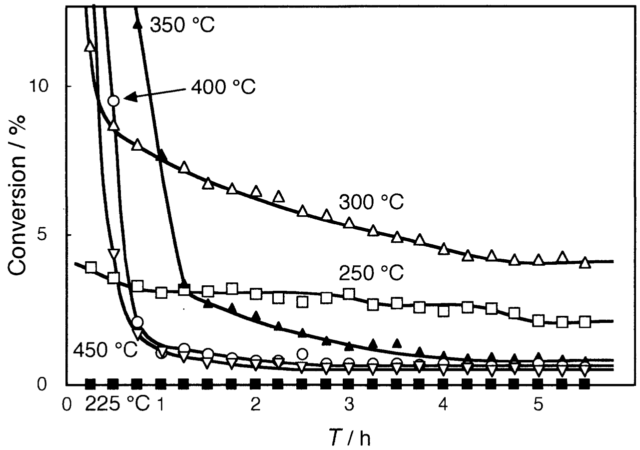


Figure 1. Reaction profile of dehydration of ethanol over $(H_3O)_2$-$[(W_6Cl_6]\cdot6H_2O$ (**1**). Conversion = (ethylene + ether × 2 + acetal × 3)/(ethanol + ethylene + ether × 2 + acetal × 3) × 100 (%).

at 150–200 °C are assigned to $[(W_6Cl_8)Cl_4(H_2O)_2]$ (**3**) [9] and that at 450 °C to **2** [10]. The temperature (250 °C) at which the catalytic activity developed is the appearance temperature of **2**. As figure 3 shows, when the treatment temperature increased, the most intense peak at $\theta = 11.74°$ of the 250 °C-treated sample progressively shifted to higher angle, $\theta = 12.44°$ for the 450 °C-treated sample, and the broad peak changed to a sharp peak, indicating a decrease in the unit cell dimensions and an improvement in the crystallinity. When **3** changes to **2**, coordinated water is lost in the solid state. The catalytic activity, however, almost disappeared when the crystallization was completed by treatment above 400 °C.

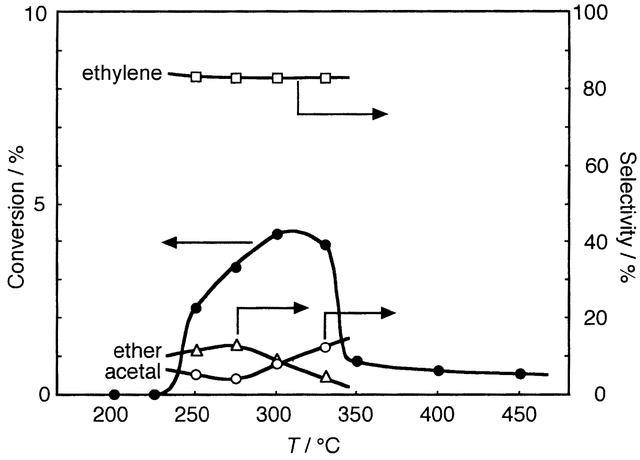


Figure 2. Temperature dependence of dehydration of ethanol over $(H_3O)_2$-$[(W_6Cl_6]\cdot6H_2O$ (**1**). Conversion = (ethylene + ether × 2 + acetal × 3)/(ethanol + ethylene + ether × 2 + acetal × 3) × 100 (%) at 5 h after reaction started. Selectivity = (ethylene, ether × 2 or acetal × 3)/(ethylene + ether × 2 + acetal × 3) × 100 (%).

The Raman spectra of the same samples are illustrated in figure 4. Although characterization of the peaks of **2** and **3** is not available, that of **1** has been reported [11]. The band due to the A_{1g} breathing motion of the W_6 octahedron coincidentally overlaps that of the W_6Cl_8 A_{1g} cage breathing mode at 300 cm^{-1}. This peak, and the assigned peaks of the W–W vibration of W_6 at 153 cm^{-1} and the W–Cl vibration of W_6Cl_8 at 215 cm^{-1} of **1**, disappeared above 150 °C. However, the Raman spectrum of the sample treated at 450 °C and the authentic sample of **2** were in accord. The most intense peak of the 250 °C-treated sample at 267.3 cm^{-1} shifted

Table 1
Dehydration of alcohol over halide cluster[a]

Alcohol	Catalyst	Conversion (%)[b]	Selectivity (%)[c]			
			1-Olefin	2-Olefin	Ether	Acetal
Ethanol	$[(Nb_6Cl^i_{12})Cl^a_2(H_2O)_4]\cdot4H_2O$ (**1**)	9.6	60.9		34.2	4.9
	$(H_3O)_2[(Mo_6Cl^i_8)Cl^a_6]\cdot6H_2O$	0.0	–		–	–
	$[(Ta_6Cl^i_{12})Cl^a_2(H_2O)_4]\cdot4H_2O$	7.3	79.4		17.0	3.6
	$(H_3O)_2[(W_6Cl^i_8)Cl^a_6]\cdot6H_2O$ (**2**)	4.2	82.6		9.4	8.0
	W metal	0.0	–		–	–
	None	0.0	–		–	–
1-Propanol	$[(Nb_6Cl^i_{12})Cl^a_2(H_2O)_4]\cdot4H_2O$ (**1**)	61.3	100.0		–	–
	$(H_3O)_2[(Mo_6Cl^i_8)Cl^a_6]\cdot6H_2O$	2.3	100.0		–	–
	$[(Ta_6Cl^i_{12})Cl^a_2(H_2O)_4]\cdot4H_2O$	9.0	100.0		–	–
	$(H_3O)_2[(W_6Cl^i_8)Cl^a_6]\cdot6H_2O$ (**2**)	9.7	100.0		–	–
1-Butanol	$[(Nb_6Cl^i_{12})Cl^a_2(H_2O)_4]\cdot4H_2O$ (**1**)	27.6	56.2	26.1	–	–
	$(H_3O)_2[(Mo_6Cl^i_8)Cl^a_6]\cdot6H_2O$ (**2**)	2.7	42.0	58.0	–	–
1-Pentanol	$[(Nb_6Cl^i_{12})Cl^a_2(H_2O)_4]\cdot4H_2O$ (**1**)	4.8	54.9	45.1	–	–
	$(H_3O)_2[(W_6Cl^i_8)Cl^a_6]\cdot6H_2O$ (**2**)	2.3	41.1	58.9	–	–

[a] Catalyst was treated at 300 °C for 1 h followed by reaction at the same temperature. Catalyst: 30 mg (150–200 mesh), He: 20 mL/min, ethanol: 4.2 mmol/h.
[b] Conversion = (olefin + ether × 2 + acetal × 3)/(alcohol + olefin + ether × 2 + acetal × 3) × 100 (%) at 5 h after reaction started.
[c] Selectivity = (olefin, ether × 2 or acetal × 3)/(olefin + ether × 2 + acetal × 3) × 100 (%).

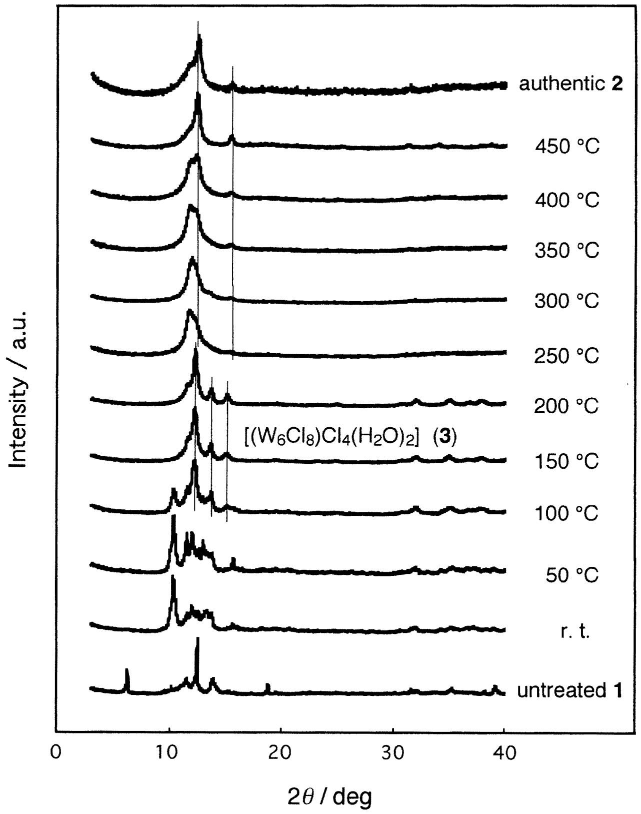


Figure 3. XRD patterns of $(H_3O)_2[(W_6Cl_8)Cl_6]{\cdot}6H_2O$ (**1**) treated at various temperatures with He (20 mL/min) for 1 h. The XRD pattern of $[W_6Cl_{12}]$ (**2**) is also shown.

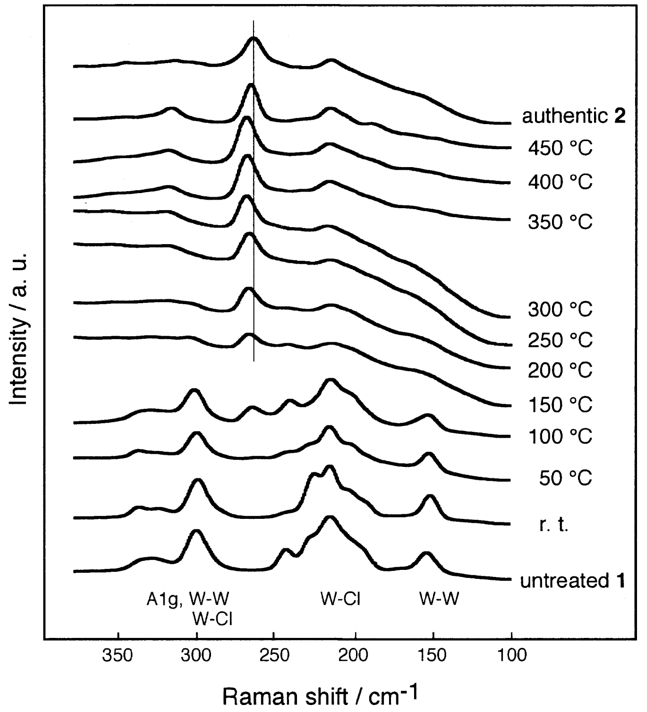
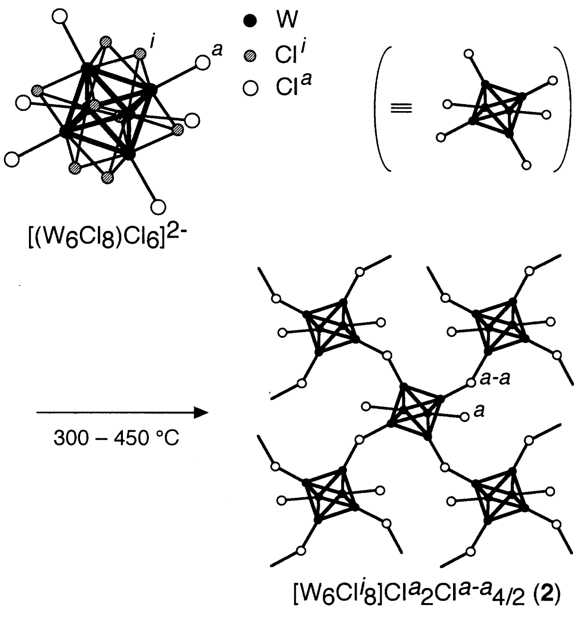


Figure 4. Raman spectra of $(H_3O)_2[(W_6Cl_8)Cl_6]{\cdot}6H_2O$ (**1**) treated at various temperatures with He (20 mL/min) for 1 h. The Raman spectrum of $[W_6Cl_{12}]$ (**2**) is also shown.

to a lower wavenumber when heated and converged to 264.3 cm^{-1} of the authentic sample of **2**. These results also indicate that the catalytic activity appeared when poorly crystallized **2** was formed, and then decreased when the catalytically active species retained the octahedral metal framework, since subsequent application of heat to the active catalyst yielded solid-state **2**. No appreciable changes of the XRD patterns and Raman spectra were observed after subsequent 5 h reactions with alcohols at the same temperatures. The formation of coke possibly suppressed this reaction.



Scheme 1.

Analytical data of Cl and W in the treated samples showed that the relative amount of Cl to W decreased with an increase in the treatment temperature, and that experimentally the species $W_6Cl_{11.8}$ and $W_6Cl_{11.3}$ on average were formed by treatment at 300 and 400 °C. X-ray analyses, as well as Raman analyses, however, clearly showed that each sample is a solid-state crystal of **2**. Hence, the catalytic activity of the cluster can be attributed to defective $[W_6Cl_{12}$ species missing a Cl ligand contained in the poorly crystallized **2**. The subsequent disappearance of the catalytic activity by heat treatment could be ascribed to the inclusion of the species as a component in the completely packed and well-grown crystal system of **2**, which could prevent diffusion of ethanol through gaps in the crystals.

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