Catalytic Decomposition of Phenyl Acetate by Halide Clusters of Nb, Mo, Ta, and W Possessing Octahedral Metal Core

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The application of hexanuclear halide clusters as catalysts was made. Molecular halide clusters of Nb, Mo, Ta, and W possessing an octahedral metal core were treated in a helium stream at 250 °C for 1 h before introduction of phenyl acetate. These clusters served as catalysts for decomposition of the ester to phenol and ketene. Raman and X-ray analyses showed that the development of the catalytic activity was attributable to the partial loss of the inner halogen ligands.

Extensive effort has been directed at the syntheses of halide clusters.[1] However, studies on the reactivity of halide clusters have been quite limited. Reactivity with organic or inorganic reagents has been seen mainly in the field of ligand exchange reactions, though a reaction with hydrogen has been reported.[2] In contrast to carbonyl clusters, halide clusters have not been used as catalysts as far as we know,[3] though one of the typical clusters Mo_6Cl_{12} was synthesized more than 140 years ago. Halide clusters are generally synthesized by comproportionation of the metal with the corresponding mononuclear metal halide at elevated temperatures in a sealed tube. Such a treatment may yield the halide clusters too stable to react with organic compounds and thus be utilized as catalysts. Most of the cluster halides have an octahedral metal array structure, which is comprised in the bulk metal, with terminally coordinating, bridging, or triply bridging halogen π-donor ligands. The oxidation numbers of the metals are around +2, which is the intermediate between those of the bulk metal and oxide. If some of the halide ligands are removed while leaving the metal framework intact, the exposed metal of this unusual oxidation state would react with organic substances in a unique fashion, and the metal framework would be expected to be stable at high temperatures. Hence attempts were made to utilize the halide clusters as catalysts. Fries rearrangement of phenyl acetate was chosen as a test reaction, as removal of the halogen ligands was expected to bring Lewis acidity to the cluster and only one component is enough to test the reaction.

Unsupported halide clusters $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (**1**)[4] in a glass reaction tube were preliminarily treated in a stream of helium for 1 h at an elevated temperature before introduction of phenyl acetate to the gas flow reaction system at the same temperature. Phenol and ketene were the only products proving that **1** served as a catalyst for decomposition. Formation of *o*- and *p*-acetylphenol was not detected. No catalytic activities were observed below 100 °C, and a slight activity was evident at 150 °C. Treatment above 200 °C gave **1** substantial catalytic activity and the activity enhanced with increasing temperature. Thermal activation of the cluster is necessary for the catalysis. Table 1 lists the catalytic activities of halide clusters and the related compound tested. This table shows that Nb metal had no catalytic activity under the same reaction conditions. Niobium pentachloride was not applied to the catalysis under the same reaction conditions as its boiling point is as low as 250 °C. These results clearly show that **1** developed into a novel catalyst. Table 1 shows that halide clusters of Mo, Ta, and W with octahedrally arranged M_6 metal cores also had catalytic activity. Hence the characteristic feature of this cluster catalysis is activity at low temperature and simple reaction product, whereas pyrolysis of phenyl acetate requires reaction temperatures higher than *ca.* 700 °C[5] and the reaction over zeolite catalysts always accompanies Fries rearrangement as a side reaction.[6]

Table 1. Activity of halide cluster catalyst[a]

Catalyst	Conversion / %[b]
$[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (**1**)	25.3
$[(Nb_6Br_{12})Cl_2(H_2O)_4]\cdot 4H_2O$	48.9
$(H_3O)[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ (**2**)	5.6
$[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$	3.2
$(H_3O)[(W_6Cl_8)Cl_6]\cdot 6H_2O$	6.2
Nb metal	0.0

[a] Catalysts were treated at 250 °C for 1 h followed by the reaction at the same temperature. Catalyst: 30 mg (150–200 mesh), He: 40 mL/min, phenyl acetate: 0.1 mL/h. [b] Conversion = phennol / (phenyl acetate + phenol) × 100 at 3 h.

Figure 1 shows the catalytic activities of **1** and $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ (**2**)[7] treated at various temperatures in helium stream for 1 h and then allowed to react with phenyl

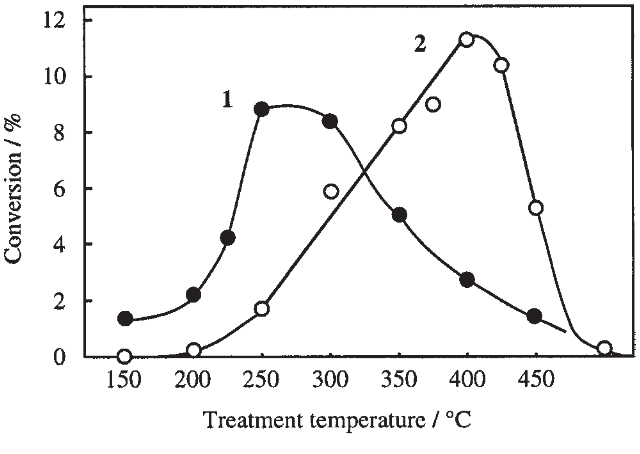

Figure 1. Effect of treatment temperature on catalytic activity. After treatment of $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (**1**: ●) and $(H_3O)_2[Mo_6Cl_{14}]\cdot 6H_2O$ (**2**: ○) in a helium stream (40 mL/min) for 1 h, reactions were made by introduction of phenyl acetate (0.1 mL/h) at 150 °C. Conversion = phenol / (phenyl acetate + phenol) × 100 at 3 h.

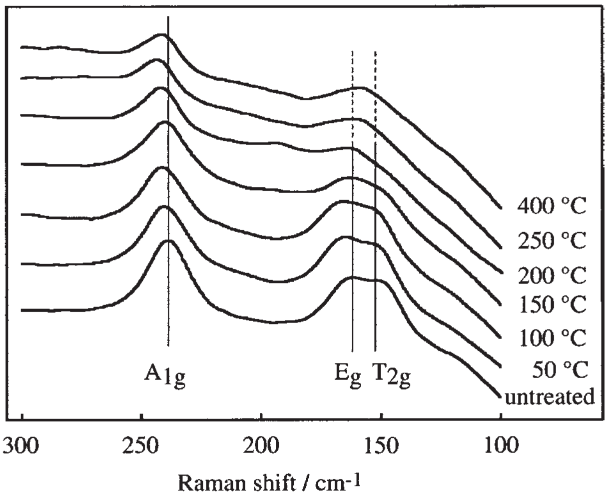

Figure 2. Raman spectra of $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (**1**) treated at various temperatures in a helium stream for 1 h.

acetate at 150 °C. Clusters **1** and **2** revealed the maximum activities by treatment at around 250 °C and 400 °C respectively.

The Raman spectra of **1** treated at various temperatures for 1 h in helium streams are shown in Figure 2. The spectra markedly changed beyond 250 °C with increasing temperature. The Raman shift caused by the vibration of Nb–Cl^a or Nb–O has not been attributed for this complex. However, the band at 239 cm^{-1} is assigned to the breathing motion of the Nb_6 octahedron (A_{1g}), whereas those at 161 and 152 cm^{-1} are attributed to edge bridging Nb–Cl^i breathing vibrations (E_g and T_{2g}, respectively).[8] Crystal structural data revealed that the differences in M–M distances parallel the observed variations in the Raman shift.[9] The variations of the observed shift of the A_{1g} M_6 band are almost entirely accounted for by differences in the M–M force constant that accompany dissimilarities in the M–M bond distances.[9] The band of the Nb_6 A_{1g} vibration mode begins to shift to higher energy by treatment and has the maximum shift at 250 °C. The loss of some internal Cl ligands can increase the Nb–Nb bond order of the Nb_6 octahedron, which may be ascribed to the higher energy shift. However, the Nb_6 metal framework remains the same. Above 250 °C, the two Raman bands originally at 161 and 152 cm^{-1} due to edge bridging Nb–Cl^i breathing vibrations were replaced with a new band, which suggests that the structure of the coordinating Cl ligands changed above this temperature. It is at this temperature that the catalytic activity is the highest. Hence, the catalytic activity of **1** may be attributed to the appearance of the non-coordinated metal atoms of the cluster metal core. The X-ray diffraction patterns of the same samples were recorded. The change of the X-ray diffraction pattern shows that treatment above 100 °C changes **1** to an amorphous compound that is not the extended M–Cl–M bonded solid compound Nb_6Cl_{14} ($[Nb_6Cl^i_{10}Cl^{i(a)}_{2/2}]Cl^a_{4/2}Cl^{a(i)}_{2/2}$) prepared by a different route.[10] Furthermore, the change of the crystal structure, which could be caused by removal of the outer halogen ligand or coordinated water, did not give rise to the catalytic activity.

The Raman spectra of **2** treated at various temperatures for 1 h in helium streams were measured. A marked change of Mo–Cl^i vibrations beyond 200 °C is quite similar to the corresponding change shown in Figure 2, indicating partial loss of some internal Cl ligands. The X-ray diffraction patterns of **2** are shown in Figure 3. The cluster changed from $(H_3O)_2[Mo_6Cl_{14}]\cdot 6H_2O$ *via* $[Mo_6Cl_{12}]\cdot 8H_2O$ and $[Mo_6Cl_{12}]\cdot 2H_2O$ to an extended M–Cl–M bonded solid compound Mo_6Cl_{12} ($[Mo_6Cl^i_8]Cl^a_2Cl^a_{4/2}$)[7] when heat was applied up to 450 °C. Thus in contrast to **1**, formation of the solid state network is likely to keep the activated non-coordinated metal atoms intact, and hence retain the catalytic activity.

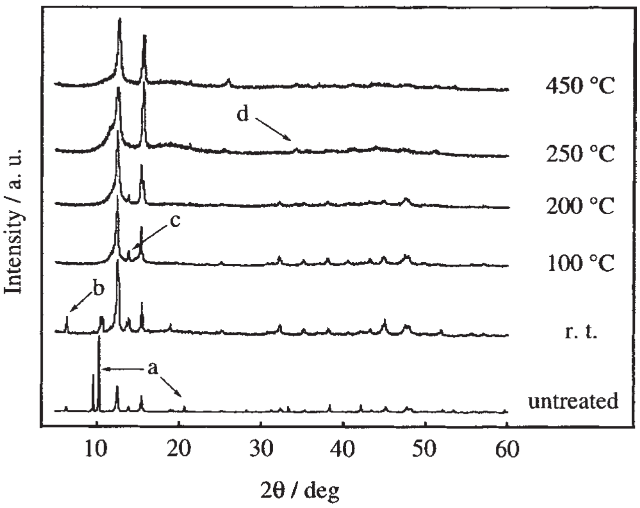

Figure 3. XRD patterns of $(H_3O)_2[Mo_6Cl_{14}]\cdot 6H_2O$ (**2**) treated at various temperatures in a helium stream for 1 h. All the identified compounds have two strong diffraction peaks at 12.4–12.6 and 15.3–15.6 degree.Unique diffraction peaks of each compound are indicated: (a) for **2**, (b) for $[Mo_6Cl_{12}]\cdot 8H_2O$, (c) for $[Mo_6Cl_{12}]\cdot 2H_2O$, and (d) for Mo_6Cl_{12}.

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References and Notes

1 S. C. Lee and R. H. Holm, *Angew. Chem., Int. Ed. Engl.*, **29**, 840 (1990).
2 H. Imoto and J. D. Corbett, *Inorg. Chem.*, **19**, 1241 (1980).
3 N. Prokopuk and D. F. Shriver, *Adv. Inorg. Chem.*, **46**, 1 (1999); G. J. Miller, *J. Alloys Compd.*, **229**, 93 (1995).
4 F. W. Koknat, J. A. Parsons, and A. Vongvusharintra, *Inorg. Chem.*, **13**, 1699 (1974).
5 E. Ghibaudi and A. J. Colussi, *Int. J. Chem. Kinet.*, **16**, 1575 (1984).
6 Y. Pouilloux, J. P. Bodibo, I. Neves, M. Gubelmann, G. Perot, and M. Guisnet, *Stud. Surf. Sci. Catal.*, **59**, 513 (1991).
7 P. Nannelli and B. P. Block, *Inorg. Synth.*, **12**, 170 (1970).
8 K. Harder and W. Preetz, *Z. Anorg. Allg. Chem.*, **591**, 32 (1990).
9 J. R. Schoonover, T. C. Zietlow, D. L. Clark, J. A. Heppert, M. H. Chisholm, H. B. Gray, A. P. Sattelberger, and W. H. Woodruff, *Inorg. Chem.*, **35**, 6606 (1996).
10 A. Simon, H. G. Schnering, H. Wöhrle, and H. Schäfer, *Z. Anorg. Allg. Chem.*, **339**, 155 (1965).