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Nanocomposite Gels between $[V_{10}O_{28}]^{6-}$ and $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ Polyoxometalate Clusters

Hyuk Choi,[†] Young-Uk Kwon,*[,†] and Oc Hee Han[‡]

Department of Chemistry, Sungkyunkwan University, Suwon, 440-746, Korea, and Korea Basic Science Institute, Taejon, 305-333, Korea

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Polyoxometalates have been the subject in many areas of materials science.[1] Recently, many new hybrid materials utilizing polyoxometalates as building blocks have been synthesized mainly in the forms of organic/inorganic and organometallic/inorganic salts.[2] However, the organic molecules and/or moieties limit the thermal stability of these composites. There have been some papers on pure inorganic hybrid materials with better thermal stability but mainly based on sol−gel approaches.[3]

Currently, we are exploring the possibility of pure inorganic hybrids by combining cationic and anionic polyoxometalate cluster ions. In this paper, we report our first results from the $[V_{10}O_{28}]^{6-}[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ($V_{10}-Al_{13}$) system that resulted in a pure inorganic monolithic gel. Inside the monolith, the cluster identities are found to be almost intact, suggesting that this constitutes a new class of materials, namely, intercluster nanocomposites.

Aqueous solutions of Al_{13}[4] and V_{10}[5] were prepared according to the literature procedures starting with $AlCl_3{\cdot}6H_2O$ and $NaVO_3$, respectively. Direct combination of the V_{10} ($[V^{5+}] = 0.15$M, 250 mL) and Al_{13} ($[Al^{3+}] = 0.25$M, 200 mL) solutions immediately formed a yellowish orange colored suspension solution. The pH of the mixed solution initially dropped from 3.9 to 3.4 over first 5 min, rose to 3.8 afterward, and stabilized at this value. After the solution was allowed to stand overnight, the suspended hydrogel precipitated out of the solution. Once formed, the hydrogel is stable in acidic conditions down to pH = 1, indicating that the hydrogel has a network structure; otherwise, the Al_{13} ion will decompose into $[Al(H_2O)_6]^{3+}$ and the hydrogel disintegrate in this pH range. The precipitate was isolated by filtration and washed with distilled water. Upon drying in a desiccator over several days, the filtrate turned into a reddish brown monolithic gel (Figure 1).

ICP elemental analysis performed on a Perkins-Elmer/Plasma 40 Instrument of the monolithic gel resulted in a metal ratio of Al:V:Na = 1.29:1:0.03. If the precipitate was formed by the ionic interaction between Al_{13} and V_{10} only, the expected Al:V ratio would be 1.1:1 (Al_{13}:V_{10} = 6:7). Instead, the Al:V ratio indicates that the Al_{13}:V_{10} ratio is close to 1:1 implying one-to-one association of the cluster ions. This is understandable because the microscopic packing of the clusters must be governed by the electrostatic interactions; the charge and size imbalance from 1:1 association being resolved by incorporating other small ions such as Na^+, OH^-,

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[†] Sungkyunkwan University.

[‡] Korea Basic Science Institute.

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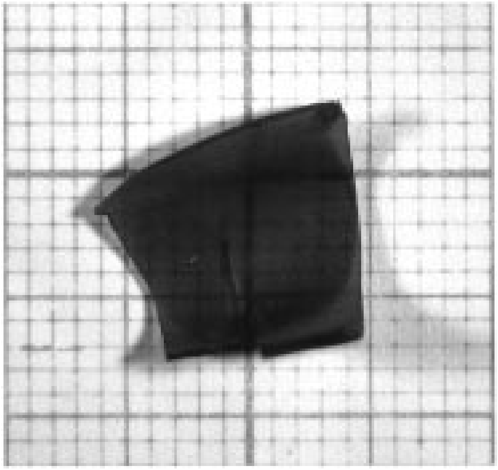

Figure 1. Optical micrograph of the composite monolithic gel composed of $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ and $[V_{10}O_{28}]^{6-}$ cluster ions.

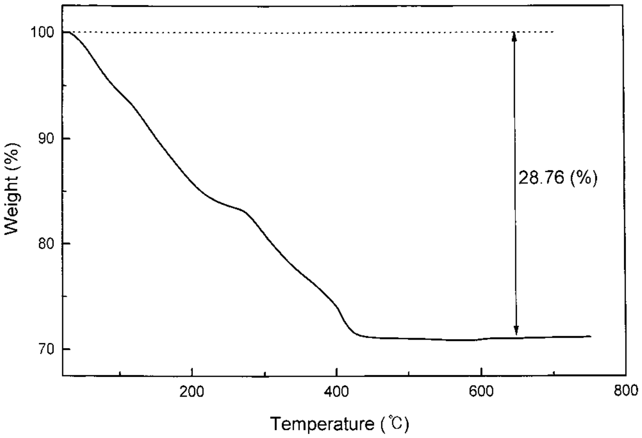

Figure 2. Thermogravimetric data of composite monolithic gel.

and Cl^- in the solution. The presence of Na^+ in the gel can be explained by the large Na^+-V_{10} association constant in the solution.[6] Although not tested in the elemental analysis, there also should be OH^- and/or Cl^- in the gel to balance the ionic charges. The initial drop of pH during the mixing implies that there is OH^- formed within the gel body.

Thermogravimetric (TG) analysis of the monolith performed with a TA4000/SDT 2960 thermogravimetric analyzer at a heating rate 10 °C/min in air showed approximately four steps of weight losses total of 29% in the temperature range 30−420 °C due to H_2O of various nature in the gel (Figure 2). After 420 °C, there is no further weight loss up to 800 °C. The product after heating at above 550 °C was identified as a mixture of $AlVO_4$[7] and a small amount of impurity of unknown nature by powder X-ray diffraction. With the elemental and TG analyses results, the composition of the monolith was deduced to be $Na_{0.3}[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}][V_{10}O_{28}]X_{1.3}(H_2O)_{35.5}$ (X = Cl, OH). However, because the solid-state NMR data suggest that the Al_{13} units are partially condensed in the monolith (below), the formula is better expressed as $Na_{0.3}[AlO_4Al_{12}(OH)_{24}(H_2O)_{12-x}][V_{10}O_{28}]X_{1.3}(H_2O)_{35.5+x}$.

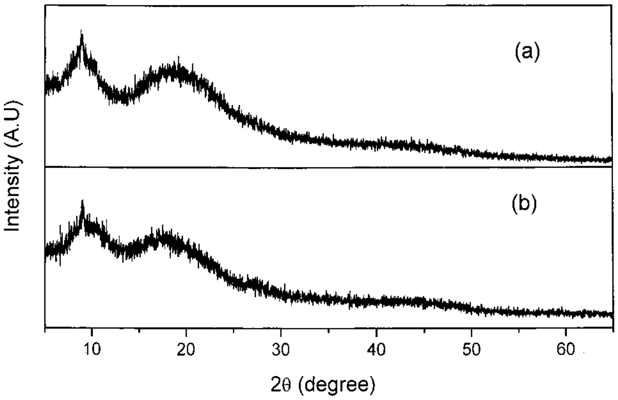

Figure 3. Powder X-ray diffraction patterns of (a) hydrogel and (b) monolithic gel.

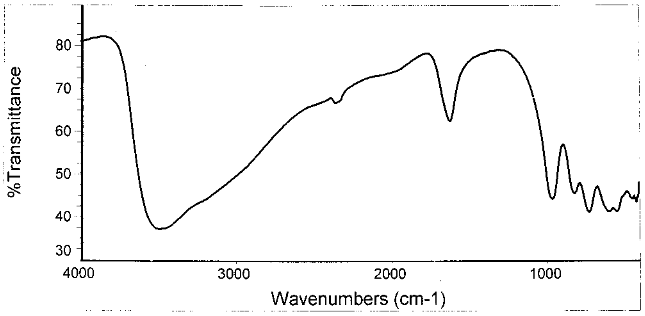

Figure 4. Infrared spectrum of the monolithic gel. The spectrum of the hydrogel is essentially the same and is not shown.

Powder X-ray diffraction patterns of the hydrogel and monolithic gel are identical and show that they are amorphous. (Figure 3) However, the powder patterns of the gels show two very broad peaks centered at $2\theta = 8.9°$ ($d = {\sim}10$ Å) and 17.7° (~5 Å) with peak widths about 3° indicating a short-range ordering with coherence length of about 30 Å according to the Scherrer equation which appears to be due to the ordering of the cationic and anionic clusters.

The infrared spectra taken on KBr pellets, recorded on a Nicolet 205 FT-IR spectrometer, of the monolith is shown in Figure 4. The spectrum of the hydrogel (not shown) is essentially the same. They show the characteristic peaks for the V_{10} (at 975, 820, 750, 604 cm^{-1}) and Al_{13} (at 727, 636 cm^{-1}) clusters as well as the strong peak of H_2O at 3500 cm^{-1}, suggesting that the cluster identities are preserved.

Solid-state NMR spectroscopic data of the hydrogel and the monolith recorded on a Bruker DSX 400 spectrometer are compared with those of Al_{13} and V_{10} in Figure 5. The sharp 61 ppm peak of Al_{13} is assigned to the tetrahedral (*Td*) Al in the core of the cluster.[8] The other 12 octahedral (*Oh*) Al's give a broad peak centered near −30 ppm ($\delta_i \approx 13$ ppm). The NMR spectrum for V_{10} shows two sets of peaks with a intensity ratio of 4:1. The center peak at −501 ppm and its spinning sidebands are assigned to the eight peripheral V atoms whose VO_6 octahedra have terminal V−O bonds while the center peak at −432 ppm and its spinning sidebands are assigned to the two inner V

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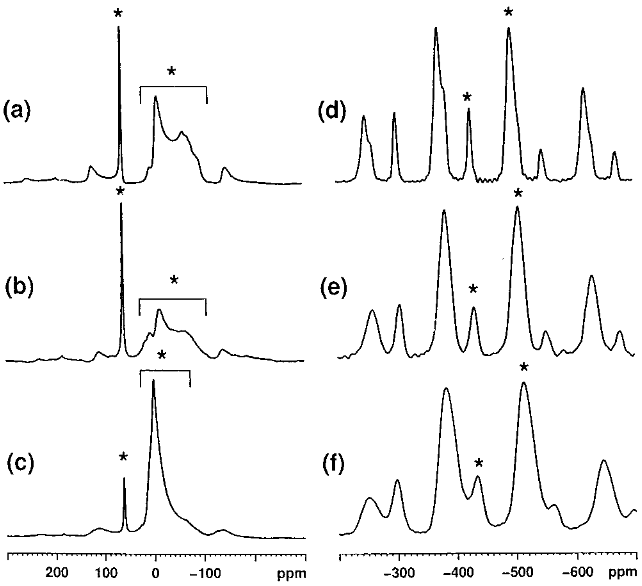

Figure 5. ^{27}Al solid-state MAS NMR spectra of (a) $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SO}_4)_{3.5}$, (b) hydrogel, and (c) monolithic gel, and ^{51}V solid-state MAS NMR spectra of (d) $\text{Na}_6[\text{V}_{10}\text{O}_{28}]\cdot(\text{H}_2\text{O})_x$, (e) hydrogel, and (f) monolithic gel. Center peaks are marked by asterisks (∗) in the spectra.

atoms whose octahedra share all of the oxygen atoms with neighbors.[9,10]

In the hydrogel, the two center peaks in the ^{51}V spectra are shifted upfield (to −511 and −436 ppm, respectively) and broadened slightly from those of V_{10} cluster. The *Oh* Al peak is a little distorted from that in Al_{13} spectra while the *Td* Al peak and the relative peak areas of the two peaks are unchanged. These minor changes of Al and V spectra are consistent with our model that the hydrogel is formed by the aggregation of the ionic clusters resulting in slight surface modifications but preserving the cluster identities. Notice that V and Al in outer sites in the ion clusters show more change in the spectra than in core sites.

The V spectrum of the monolith shows further broadened and upfield shifted peaks (to −518 ppm and −439 ppm) but still similar to the reference. Contrarily, the *Oh* Al peak shape is changed while the 61 ppm *Td* Al peak is maintained but with reduced intensity. The *Oh* Al peak can be explained as an overlap of a broad peak similar to the hydrogel and a sharp peak at 0 ppm similar to that of AlP_2, a dimer of Al_{13} clusters, which has only *Oh* Al sites whose signature is an asymmetric peak near 0 ppm ($\delta_i \approx 16$ ppm).[11] Therefore, the changes of the Al spectrum imply that the Al_{13} clusters are fused into larger units similar to AlP_2, sacrificing some of the *Td* Al. This is understandable because Al_{13}, larger than V_{10} in size, can have contacts with one another in the hydrogel and can undergo dimerization and/or condensation reactions. It seems also possible that the Al_{13} clusters undergo condensation reactions with V_{10} through the following reaction:

$$-\text{Al}(\text{H}_2\text{O}) + \text{O}{=}\text{V}- \rightarrow -\text{Al}-\text{O}-\text{V}- + \text{H}_2\text{O}$$

where $-\text{Al}(\text{H}_2\text{O})$ and $-\text{V}{=}\text{O}$ are the environments of the peripheral metal atoms of the clusters. The upfield shift of the V NMR peaks, especially the greater peak shift of the peripheral V atoms, supports this view although we do not have any direct evidence for the Al−O−V bond formation. On the basis of the NMR data, the structure of the monolith can be described as a network of fused Al_{13} units with encaged V_{10} units maybe with partial linkages between Al_{13} and V_{10} clusters.

The immediate formation of the hydrogel from mixing of Al_{13} and V_{10} solutions can be understood by an analogy to the alkali halide cases.[12] In the latter, the tendency to form salt precipitate out of solution increases as the size difference between the oppositely charged ions decreases because of the increase of the lattice energy gain with respect to the hydration energies of the ions. Without the counter cluster ions present, the individual clusters will remain in the solution because the counterions, Cl^- and Na^+, are much smaller than the clusters favoring the hydration energies over the lattice energies. As soon as the two solutions are mixed, because of the close size and charge matches of the cluster ions, the intercluster ionic interactions will overwhelm the hydration energies favoring precipitate formation. The short-range ordering found in the X-ray patterns can be taken as an evidence that the clusters form a pseudo-lattice inside the gels. As the NMR data suggest, the formation of the monolith upon drying the hydrogel appears to be driven by the covalent bond formation among Al_{13} clusters and may be between Al_{13} and V_{10} clusters.

In summary, we have prepared pure inorganic hybrid hydrogel and monolithic gel of Al_{13} and V_{10} polyoxometalate clusters with a novel and simple approach of mixing the solutions of the clusters. The gels have a short-range ordering due to the 1:1 ordering of the clusters. The infrared spectra and the solid-state NMR spectroscopic data for both Al and V indicate that the cluster identities are preserved inside the hydrogel and partly inside the monolithic gel.

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