EXAFS/FTIR Characterization and Selective Hydration of Acetonitrile on Silica-Supported $[(RhCp^*)_4V_6O_{19}]$

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Silica-supported $[(RhCp^*)_4V_6O_{19}]$ exhibited high catalytic activities in the gas-phase hydration of acetonitrile towards acetamide at 350-473 K with selectivity of over 97% and dehydrogenation of 2-propanol to acetone. EXAFS, XPS and FTIR studies suggested that thermal evacuation of silica-supported $[(RhCp^*)_4V_6O_{19}]$ at 473 K led to the removal of the bridged oxygen atoms in the V_6O_{19} framework. The resulting deoxygenated samples enhanced the acetonitrile hydration, while catalyzed the dehydration of 2-propanol to propene besides the dehydrogenation reaction, probably owing to the newly generated Lewis acid site.

Recently, novel cluster complexes called "cubane-type metal oxide clusters" such as $[(MCp^*)_4Mo_4O_{16}]$ and $[(MCp^*)_4V_6O_{19}]$ (M=Rh, Ir; Cp* = pentamethylcyclopentadienyl) have been synthesized,[1] and gained an interesting attention as molecular modelling of the infinite stepped layer structure of the MoO_3 and V_2O_5 crystals which are used as heterogeneous catalysts for the selective oxidation of organic compounds.[2] The $[(MCp^*)_4V_6O_{19}]$(M=Rh, Ir) are quadruple cubane-type clusters having cubic units fused together by sharing faces (Figure 1). It is of interest to find that the bridging oxygens in $[(MCp^*)_4V_6O_{19}]$ (M=Rh, Ir) interact with H_2O and that even aprotic molecules like acetonitrile are activated by existence of an unusually short distance of C-H···O bond.[6] In aqueous solution, copper, nickel, and titanium catalysts have been used for the hydration of nitriles to the corresponding amides.[3-5] We would like to report here the structural characterization of thermally activated $[(RhCp^*)_4V_6O_{19}]$ on silica by EXAFS, FTIR and XPS, and their catalytic behavior in the gas phase hydration of acetonitrile and dehydration / dehydrogenation of 2-propanol.

$[(RhCp^*)_4V_6O_{19}]$ was synthesized according to the method reported elsewhere.[6] Dichloromethane solution of $[(RhCp^*)_4V_6O_{19}]$ was impregnated on silica followed by evacuation at 300 K to remove solvent. The catalyst was used without any activation process or evacuation at 473 K prior to the reaction. The weight loading of the cluster in each sample was 15-20 wt% per supporting silica. The reaction was carried out using a closed circulation system equipped with a TCD gas chromatograph using Gaskuropack 54 column. IR spectra were measured by using a SHIMADZU FTIR 8100M with resolution of 2 cm-1. Rh and V K-edge EXAFS spectra were measured by transmission mode at BL-10B and BL-7C, respectively, of Photon Factory in the National Laboratory for High Energy Physics. XPS of Rh_{3d} and V_{2p} spectra of the silica-supported $[(RhCp^*)_4V_6O_{19}]$ were recorded by the VG ESCALAB 3MarkII (Mg Kα hν=1253.6 eV, 10 KV, 10 mA). The binding energies were normalized using Au wire($Au_{4f7/2}$=83.8 eV) and SiO_2 support (Si_{2p}=103.4 eV) as internal standards.

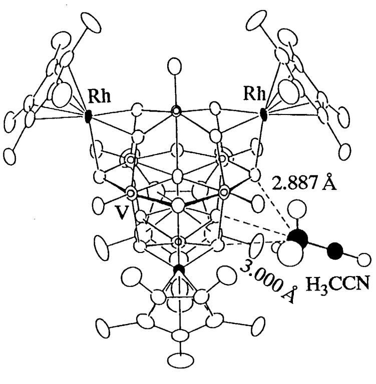

Figure 1. Molecular structure of $[(RhCp^*)_4V_6O_{19}]\cdot3CH_3CN\cdot H_2O$ (ORTEP diagram) ; Acetonitrile molecule is located on the center of triangular cluster face comprised of the bridging oxygen atoms. The methyl group of acetonitrile is directed toward the triangular face.[1]

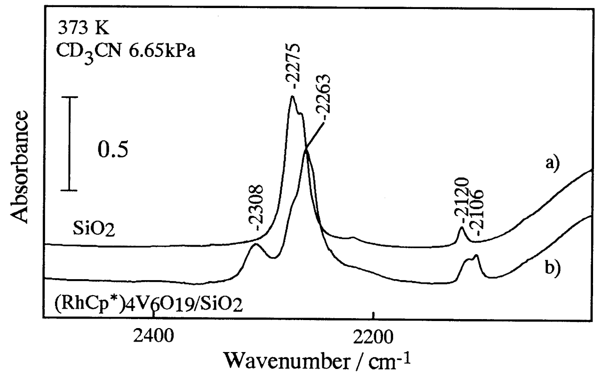

Figure 2. FTIR spectra of : (a) SiO_2 after adsorption of CD_3CN, (b) $(RhCp^*)_4V_6O_{19}/SiO_2$ after adsorption of CD_3CN.

Figure 2 shows IR spectra of adsorbed CD_3CN. ν(CD) of the adsorbed CD_3CN on SiO_2 and $[(RhCp^*)_4V_6O_{19}]$ on silica were observed at 2120 and 2106 cm-1, respectively. The latter was redshifted by 14 cm-1 comparing with the former, which suggested that the methyl group of CD_3CN was chemically activated with the three bridging oxygen atoms in the $[(RhCp^*)_4V_6O_{19}]$, as shown in Figure 1.

Figure 3 shows Fourier transform of V K-edge EXAFS functions of supported $[(RhCp^*)_4V_6O_{19}]$ evacuated at various temperatures. Contribution of V-O and V-M (V-O-M) (M = Rh, V) were observed at 1.50 and 2.74 Å, respectively. Curve fitting analysis of the V-O peak revealed that coordination number (CN) of $V{=}O_{terminal}$ (CN=0.8, R=1.62 Å) remained similar value below 473 K, to these of the fresh sample (CN=1.0, R=1.62 Å) and precursor $[(RhCp^*)_4V_6O_{19}]$ cluster in crystal. While, the CN of $V\text{-}O_{bridge}$ (CN=2.7, R=1.93 Å) decreased to be 70 % of that of initial value (CN=4.0, R=1.89 Å). The distances of $V{=}O_{terminal}$ and $V\text{-}O_{bridge}$ remain unchanged by the evacuation. Distances of Rh-C (2.20 Å) and Rh-O (2.08 Å) did not changed by the evacuation at 473 K. The CN of Rh-C and Rh-O were decreased by the evacuation at 473 K, CN of Rh-O decreasing from 3.0 to 2.3 and that of Rh-C decreasing from 5.0 to 4.0. The contribution of V-Rh (V-O-Rh) and V-V (V-O-V) were drastically suppressed after the evacuation at 473 K. This suppression may not be caused by the separation of V_6O_{19} cluster and RhCp* ligands but by the deviation of V-Rh (V-O-Rh) and V-V (V-O-V)

Table 1. Performance of catalysts for hydration of acetonitrile[a]

Catalyst	Hydration of acetonitrile	
	Rate of formation[b] acetamide $\times 10^{-4}$	Selectivity / %
(I) $(RhCp^*)_4V_6O_{19}$ 300K evac.	1.9	97
(II) $(RhCp^*)_4V_6O_{19}$ 473K evac.	3.1	100
(III) $[\{(n\text{-}C_4H_9)_4N\}_3\ (V_{10}O_{28}H_3)]$ 300K evac.	0.00	N.M.[c]
(IV) V_2O_5 300K evac.	0.02	N.M.[c]

[a] $P_{(CH_3CN)}=P_{(H_2O)}=1.3$kPa; 373 K.
[b] Rate of formation of acetamide / mol • mol-cat^{-1} • s^{-1} : [c]Non measurable.

Table 2. Performance of catalysts for hydration and hydrogenation of 2-propanol[a]

Catalyst	Rate of formation[b] acetone $\times 10^{-4}$	Rate of formation[b] propene $\times 10^{-4}$
(I) $(RhCp^*)_4V_6O_{19}$ 300K evac.	39	0
(II) $(RhCp^*)_4V_6O_{19}$ 473K evac.	45	1.6

[a] $P_{(2\text{-Propanol})}=2.6$ kPa ; 373 K
[b] Rate of formation / mol • mol-cat-1 • s-1

distances. As V and Rh (or V) were not bound directly but via the bridged oxygen, the deviation of these distances should be increased by the removal of bridged oxygen. Accordingly, the EXAFS analysis implied that a part of bridged oxygens of V-O-Rh and one forth of Cp* coordinating on Rh atoms were removed by the evacuation at 400-473 K, being accompanied by loss of long range order with remaining short range order of the $[(RhCp^*)_4V_6O_{19}]$ cluster framework.

XPS peak positions showed that the disc sample of the silica supported $[(RhCp^*)_4V_6O_{19}]$ at 373 K consists of Rh^{3+} ($Rh_{3d5/2,\ 3/2}$=311.2 and 315.8 eV) and V^{5+}($V_{2p3/2}$=518.7 eV) which were basically same as those in $[(RhCp^*)_4V_6O_{19}]$ in crystal. It was interesting to find that the valence state of a half of Rh in the sample was changed from Rh^{3+} to Rh^{2+}($Rh_{3d5/2,\ 3/2}$=308.9, 313.7 eV) as a result of the thermal evacuation at 473 K in 10^{-7} Torr. On the other hand, all V atoms in the resulting sample remained unchanged in the state of V^{5+}. It is suggested that the coordinatively unsaturated V^{5+} were generated by the thermal evacuation at 473 K, owing to the removal of oxygen and the partial reduction of Rh capping vanadate cluster.

Table 1 shows the rates of formation and products selectivities in the gas-phase hydration of acetonitrile at 373 K on the silica-supported $[(RhCp^*)_4V_6O_{19}]$, varying evacuation temperatures at 300 K (I) and 473 K (II). The silica-supported $[\{(n\text{-}C_4H_9)_4N\}_3(V_{10}O_{28}H_3)]$ (III) and V_2O_5(IV) were also employed in the hydration reaction. The supported $[(RhCp^*)_4V_6O_{19}]$(I) performed the catalytic hydration of acetonitrile to acetamide with the selectivity of more than 97%. By contrast, the conventional V_2O_5 (IV) and non-capped vanadate cluster (III) were inactive or negligibly active for the reaction. Furthermore, the reaction rate and selectivity on the supported $[(RhCp^*)_4V_6O_{19}]$ were enhanced considerably by the thermal evacuation at 473 K for 1h. To make insight into the nature of active site, 2-propanol was admitted on the samples (I) and (II). It is of interest to find that the sample(I) provided the selective formation of acetone due to the dehydrogenation of 2-propanol, as represented in Table 2. In contrast to this, the samples(II) gave a mixture of acetone and propene in the reaction of 2-propanol. These results suggested that catalyst(I) had basic sites alone, whereas catalyst (II) consists of the inherent basic sites and the newly generated acidic sites. The activity enhancement in the hydration of acetonitrile might be associated with the additional acidic sites generated by the thermal evacuation. This agreed with the IR study in pyridine chemisorption. When the self-supported disc sample of (I) after the heat treatment in vacuo at 473 K for 1h was exposed to pyridine vapor (2 torr) at 300 K, an intense IR band at 1451, 1605 cm^{-1} characteristic of pyridine coordinated with a Lewis acid was observed. By contrast, no appreciable peak at 1451, 1605 cm^{-1} could be observed on the sample (I). Accordingly, the Lewis acid site may be resulted from the coordinative unsaturated V^{5+} probably due to the removal oxygen atoms as suggested by EXAFS and XPS data.

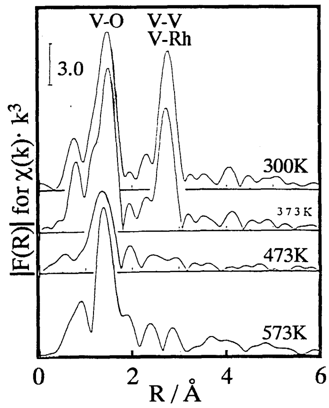

Figure 3. Magnitudes of Fourier transform of normalized k^3 weighted EXAFS of $(RhCp^*)_4V_6O_{19}/SiO_2$ evacuated at various temperatures.

In summary, the supported $[(RhCp^*)_4V_6O_{19}]$ was active and selective catalyst for the hydration of acetonitrile to acetamide and dehydrogenation of 2-propanol to acetone under the mild conditions. EXAFS, FTIR and XPS measurements implied that a part of bridging oxygen (V-O-Rh) in the V_6O_{19} framework was removed by the evacuation at 400-473 K. Formation of such a Lewis acid site promotes the hydration of acetonitrile, whereas catalyzes the dehydration of 2-propanol to propene.

The EXAFS experiments were carried out under the approval of the EXAFS program committee (Proposal No. 93G167) .

References and Notes

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