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MAS NMR and XRD Study on the Vanadium Site of Vanadium Silicate Mesoporous Molecular Sieve MCM-41

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Received October 2, 1996

A wide range (10<Si/V) of mesoporous vanadium silicate molecular sieves with the MCM-41 structure have been synthesized using vanadyl sulfate as the source of vanadium and characterized by XRD, ^{51}V MAS NMR and ^{29}Si MAS NMR. The increase of the unit cell parameter and the decrease of Q_3/Q_4 ratio of ^{29}Si spectra with the vanadium content suggest the incorporation of vanadium in the framework of MCM-41 structure. ^{51}V MAS NMR demonstrates that vanadiums in as-synthesized V-MCM-41 are present in the chemical environment of octahedra and octahedral vanadium is decreased and tetrahedral vanadium is increased inversely with raising the calcination temperature. Though the thermal treatment in rotor of hydrated sample resulted in the change from tetrahedral environment to octahedral one and the steaming and the acid treatment affect to the chemical environment of vanadium, the spectrum similar to originally calcined sample is regenerated after recalcination. This indicates that the vanadium is belong to the framework in a relatively exposed site. The best quality XRD pattern of the product of Si/V=27 may be attributable to heterogeneous nucleation mechanism. V-MCM-41,s having the Si/V ratio lower than 20 are completely collapsed after calcination.

Introduction

Microporous (pore diameter ≤ 20 Å) and mesoporous (20-100 Å) inorganic materials admit molecules below a certain critical size into their extensive internal space, which makes them of considerable interest as heterogeneous catalysts and sorbents.

In recent years increasing attention has been directed toward the study of new mesoporous material MCM-41,[1] since Kresge *et al.* discovered a new family of molecular sieves designated as M41S. Especially metal-substituted MCM-41 such as Ti,[2] V,[3] Ga,[4] Mn,[5] B[6] and Fe[7] are interesting due to their catalytic properties in addition to the potential of catalytic reaction of large molecule within the mesopore varying from 15 Å to 100 Å. The established importance of vanadium compounds as catalysts for oxidation reactions has made vanadium containing MCM-41 attractive.

V-MCM-41 as well as other vanadium containing molecular sieves which are reported to have superior catalytic activity in the ammoxidation of propane and xylenes,[8,9] oxidation of butadiene to furan,[10] and oxidative dehydrogenation of propane to propylene[11] seem to have different and/or in some case improved catalytic performances compared to supported vanadium oxide catalysts for the selective oxidation of large organic molecules using hydrogen peroxide.[3] Some recent data showed that vanadium in V-MCM-41 belongs to the molecular sieve framework and resides on the surface of the channels in a relatively exposed position. Vanadium in MCM-41 may be either in the framework of molecular sieve or present as some foreign species, possibly bound chemically at the surface.[3]

We have prepared a series of vanadium silicate MCM-41 having a wide range of Si/V ratio more than 10 and especially vanadium highly containing MCM-41 of good quality. The chemical environment of vanadium using ^{51}V MAS NMR was characterized. We want to acquire better understanding of properties of vanadium in order to modify and improve the catalytic activity of V-MCM-41.

Experimental Section

The synthesis of V-MCM-41 was carried out by the following procedure. 6 g of fused silica (Cab-O-Sil, M5, BDH) was added to the NaOH solution made of 1.36 g NaOH (Fision) and 58 g H_2O and stirred for 2 h. To this solution, vanadyl sulfate (VOSO$_4$·3H$_2$O 99%: Aldrich) solution at various concentration depending on the Si/V ratio with 25 g H_2O was added and stirred for 3 h. Surfactant CTABr

(cetyltrimethylammonium bromide 99%: Aldrich) 18.2 g dissolved in 25 g H_2O was added to this solution and stirred for 2 h.[3(a)]

The resulting reaction mixture which has the molar composition of $SiO_2 \cdot xVO_2 \cdot 0.17Na_2O \cdot 0.5CTABr \cdot 60H_2O$ ($x \leq$ 0.06) was overnight for aging and poured into the teflon lined stainless steel autoclave to crystallize under the static condition at 100 °C. The product was filtered and washed with deionized water and ethanol and dried at 70 °C and calcined in air at 120 °C for 3 h, 400 °C for 5 h and 550 °C for 5 h, step by step.

X-ray diffraction pattern were recorded using Philips 1710 powder diffractometer with CuKα radiation (40 kV, 40 mA) 0.02° step size and 1 s step time.

Solid-state magic-angle-spinning (MAS) NMR spectra were recorded at 9.4 T using a Chemagnetics CMX-400 spectrometer and rotors 7 mm in diameter spun at 3 kHz for [29]Si and 4 mm spun at 10 kHz for [51]V. [29]Si spectra were acquired at 79.4 MHz with 30° pulses and 600 sec recycle time and [51]V spectra at 105.2 MHz with <7° pulses and 25 msec recycle time. The chemical shifts are given in ppm from tetramethylsilane (TMS) for [29]Si and $VOCl_3$ as external reference for [51]V.

Result and Discussion

Figure 1 shows the X-ray powder diffraction patterns typical of MCM-41 (Si/V=27) sample before and after calcination. The as-synthesized sample exhibits a very strong peak and four weak peaks. All five XRD reflections can be indexed on a hexagonal lattice.[1(b)] No peak of XRD pattern on the range of more than 20° indicates that as-synthesized V-MCM-41 is free from crystalline V_2O_5. The sample after the calcination exhibits peaks at lower d spacing, indicating a lattice contraction from 39.8 Å to 35.7 Å of (100) peak position upon calcination as shown in Figure 1 inset. This contraction is accompanied by a loss in silanol density via condensation of Si-OH groups[12] and the reduction of crystallite's size is occurred indicating the peak broadening of XRD as shown in Figure 1 inset. Upon calcination of as-synthesized product, the intensity of XRD peak increases significantly. This is caused by the removal of the intercalated organic molecules.[4]

The d value of V-MCM-41 calculated on the basis of (100) peak is significantly higher than those of purely silicious MCM-41 both as-synthesized and calcined and unit

cell parameters increased uniformly with the vanadium content in as-synthesized samples, suggesting the incorporation of vanadium in the framework of the MCM-41 structure.[13] The d values of (100) peak for uncalcined samples varied from 36.9 Å for VM1 to 41.3 Å for VM5 and calcined one from 28.8 Å for VM1 to 37.1 Å for VM5, respectively, as shown in Table 1.

Figure 2 shows that the XRD patterns of as-synthesized V-MCM-41 which have Si/V ratio from 23 to infinity. Though the exact structure of vanadium containing silicate framework in the pore walls is uncertain, the presence of distinct hk0 reflections in the X-ray diffraction data suggests a framework with long range regularity. Especially XRD pattern of Si/V=27 sample shows four weak peaks with the relative intensity more than 1% of strong (100) reflections resulted from good crystallinity of this sample. Because plenty of silanol group in MCM-41 structure make the vanadium of surface stable, it is possible to synthesize the MCM-41 having vanadium ratio higher than other vanadium containing molecular sieves such as V-silicalite, and V-NCL-1.[13] The vanadiums were probably coordinated at the site wherein the concentration of SiOH groups is likely to be high, as suggested in the chemical environment of vanadium silicalite framework.[13] While in the case of silicalite, only some silanol groups are present on the external surface due to defects or crystal faults,[13] most of the surface MCM-41 consist of $Si-O^-N^+$-surfactant or Si-OH.[12]

V-MCM-41 having the ratio lower than Si/V=20 was completely collapsed after calcination even though XRD of
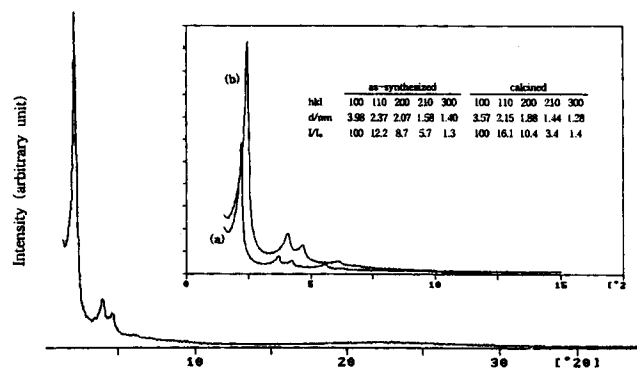

Figure 1. XRD pattern of calcined vanadium silicate MCM-41 (VM-4). Inset: XRD patterns of (a) as-synthesized and (b) calcined one.

Table 1. Properties of vanadium silicate MCM-41

sample[a]	Si/V in gel	FWHM[b] (2θ)	d-spacing (d_{100}/Å)		unit cell parameter[c] (a_o/Å)	
			as-synthesized	calcined	as-synthesized	calcined
VM1	∞	0.28	36.9	28.8	42.6	33.3
VM2	160	0.40	37.3	30.0	43.1	34.6
VM3	67	0.32	38.6	32.1	44.6	37.1
VM4	27	0.24	39.9	35.7	46.1	41.2
VM5	23	0.33	41.3	37.1	47.7	42.8
VM6	20	0.81	41.6	C[d]	48.0	C[d]

[a]All of the samples have a hexagonal phase. [b]Full width (degree) at half maximum of (100) peak of as-synthesized V-MCM-41. [c]$a_o = \frac{2}{\sqrt{3}} d_{100}$. [d]The structure was completely collapsed.
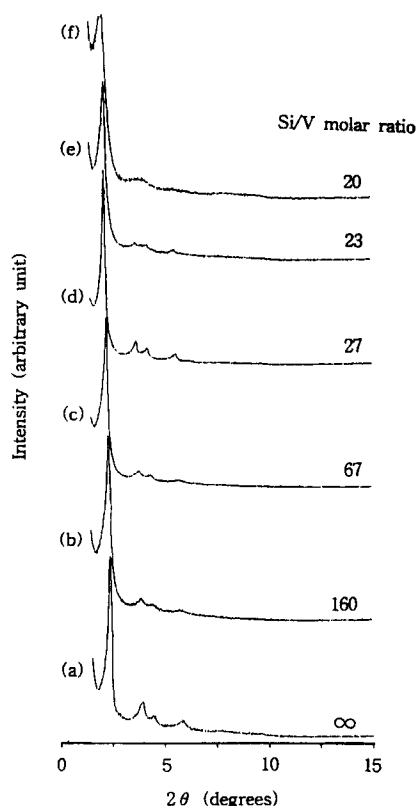
Figure 2. XRD patterns of as-synthesized vanadium silicate MCM-41 with bulk Si/V ratio of (a) infinity, (b) 160, (c) 67, (d) 27, (e) 23 and (f) 20.

Figure 3. ^{29}Si MAS NMR spectra of as-synthesized vanadium silicate MCM-41. The bulk Si/V ratio is (a) 23, (b) 27 (c) 67 and (d) infinity.

as-synthesized sample show the (100) peak at least even the sample of Si/V=10. Even though pure silica polymorph of MCM-41 synthesized using the same procedure except of no vanadium shows good quality XRD pattern, the addition of a very small amount of vanadium source affect to the process of nucleation and/or crystallization during synthesis of vanadium containing MCM-41. Even VM2 of Si/V=160, therefore, shows a significant deterioration of intensity and resolution of XRD pattern. While resolution of XRD pattern of aluminosilicate MCM-41 rapidly deteriorated as the aluminum content of solid increases,[14] the higher the vanadium ratio the better XRD pattern showed until Si/V=27 sample which has the best quality XRD pattern of V-MCM-41. FWHM (full width at half maximum) in Table 1 reflects the best quality of VM4. FWHM is broadened with the deterioration of crystallinity of V-MCM-41. This may be attributable to heterogeneous nucleation mechanism[15] in parallel with typical formation mechanism of mesoporous materials using surfactant as a templating agent. In reaction step of addition of vanadium source to the silica gel, the reaction mixture became more viscous. It may be indicating that vanadium source promote the formation of colloidal particles that contribute to the formation of the ordered hexagonal phase.

Figure 3 illustrates the ^{31}Si MAS NMR spectra of as-synthesized vanadium silicate MCM-41 whose Si/V ratio is (a) 23, (b) 27, (c) 67, and (d) infinity, respectively. On the basis of the chemical shift, the peak at -109 ppm has to be assigned to the Si(OSi)$_4$(Q$_4$) sites. The Si(OSi)$_2$(O$^-$M$^+$)$_2$
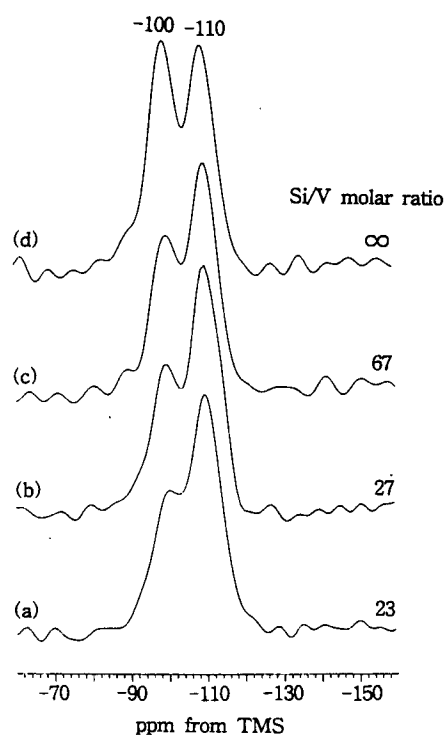
and Si(OSi)$_3$(O$^-$M$^+$) sites, where M$^+$ is the template cation, give peaks at approximately the same position as the Si (OSi)$_2$(OH)$_2$(Q$_2$) and Si(OSi)$_3$OH(Q$_3$) sites, that is at *ca.* -91 and -100 ppm, respectively.[16]

Since ^{29}Si-NMR spectra of V-MCM-41 were very broad and overlapping a broad range of T-O-T bond angle, quantitative analysis was impossible. However obviously the silanol concentration which is represented by Q$_3$/Q$_4$ ratio decreased with increasing the vanadium content. There is a progressive reduction in the intensity of -100 ppm peak with increasing the vanadium content. Q$_3$ sites such as Si (OSi)$_3$(OH) or Si(OSi)$_3$(OM) are partly converted to Q$_4$ sites surrounded by three silicon and one vanadium, indicating that vanadium incorporates in the surface layer of the wall at the expense of the silanol site on the surface.

The increase of the unit cell parameter from XRD patterns and the decrease of Q$_3$/Q$_4$ ratio of ^{29}Si spectra with the vanadium content suggest the incorporation of vanadium in the framework of the MCM-41 structure.

^{51}V NMR spectra are very sensitive to the type of V environment provided by oxygen atoms.[17] In particular, they are sensitive to the change of the V coordination number and to the distortion of local environment of V atoms. Figure 4 shows ^{51}V MAS-NMR spectra of (a) as-synthesized VM-4 and of calcined VM-4 at (b) 400 °C, (c) 450 °C, and (d) 550 °C for 12 h. As illustrated in Figure 4(a), the isotropic chemical shift symbolized by triangle for as-synthesized VM4 was -627 ppm having broad side bands which are bands except of central band at -627 ppm. This is conformed by NMR spinning rate variation method. V atom in as-synthesized V-MCM-41 is possibly present in
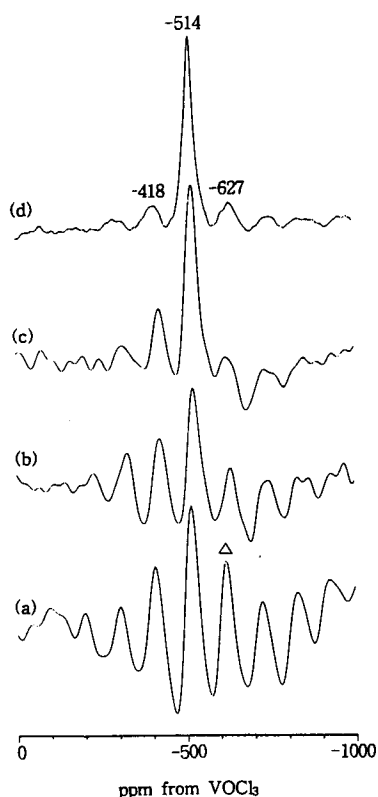
Figure 4. [51]V MAS NMR spectra of (a) as-synthesized VM-4 and of calcined VM-4 at (b) 400 °C, (c) 450 °C and (d) 550 °C.

the chemical environment of octahedra with water molecule (s) and/or silanol OH(s) in the first coordination sphere.[18] However, when as-synthesized sample was calcined, the spectrum was changed dramatically. The peak at – 627 ppm having a broad sideband pattern is decreased and the peak at – – 514 ppm typical of tetrahedral vanadium(V) is increased inversely with raising calcination temperature. This fact is similar to the well known fact of vanadium on silica that the calcination at high temperature results in encapsulation of a large part of the supported species inside SiO$_2$ pores.[19] However, while vanadium species encapsulated inside SiO$_2$ are not influenced by H$_2$O adsorption, the tetrahedral vanadium in MCM-41 converted to the octahedral one after hydration (vide infra). The absence of peak of chemical shift of about – 300 ppm indicates that vanadium highly containing V-MCM-41 is free from V$_2$O$_5$.[20]

Figure 5 shows [51]V MAS-NMR spectra of (a) hydrated VM-4 after calcination and thermally treated hydrated VM-4 in rotor at (b) 80 °C, (c) 100 °C and (d) 150 °C for 10 min and (e) spectrum of recalcined VM-4 at 550 °C after thermal treatment. The peak of – 514 ppm is sharpened and separated to two peaks upon saturating the sample with water vapor, as shown in Figure 5(a). This indicates that water molecules relax the lattice strain, increases the symmetry at the vanadium sites, and reduce the quadrupole line broadening. The occurrence of three sharp peak may be indicative of three slightly different sites of tetrahedral environment because the much narrow band width at half height with anisotropy less than 15 ppm resulted from the monomeric orthovanadates with isolated tetrahedrally coordinated vanadium ions. Two sharp peaks around – 514 ppm and one
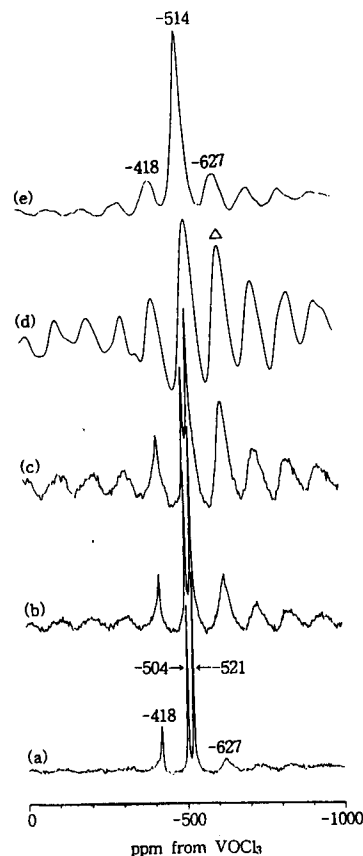

Figure 5. [51]V MAS NMR spectra of (a) hydrated VM-4 after calcination and thermally treated hydrated VM-4 in rotor at (b) 80 °C (c) 100 °C and (d) 150 °C for 10 min, and (e) spectrum of re-calcined VM-4 at 550 °C after thermal treatment.

peak at – 418 ppm may be ascribed to the hexagonal pore shape of MCM-41 or different types of silanol groups on the surface.[21] That is, V in the flat part of the hexagonal pore may be distinguishable from that in the bent part. And trace of – 627 ppm peak is still remained. In thermal treatment of hydrated V-MCM-41 in rotor, – 627 ppm peak with broad side bands is increased and sharp three peaks are decreased with increasing the temperature of sample in rotor (Figure 5(b)-(d)). The spectrum shown in Figure 5(d) is nearly same as that of as-synthesized V-MCM-41. The dramatic change from tetrahedral environment to octahedral one resulted from the coordination of silanol group generated by water at higher temperature. After recalcination at 550 °C of hydrated V-MCM-41, the peaks corresponding tetrahedral environment of V were appeared reversibly (Figure 5(e)).

[51]V-MAS spectrum of calcined V-MCM-41 is different from that of vanadium impregnated on the surface of Si-MCM-41. Vanadium-impregnated and calcined Si-MCM-41 shows [51]V-MAS spectrum nearly same as that of vanadia supported on silica under ambient condition, as shown in Figure 6. In the presence of surface water, vanadia supported on silica is predominantly five-coordinated and present in the form of a hydrated surface phase.[20(c)]

Figure 7 shows the effect of treatment of 1 M ammonium acetate solution for 24 h. After calcination, the spectrum was nearly same as originally calcined sample except that
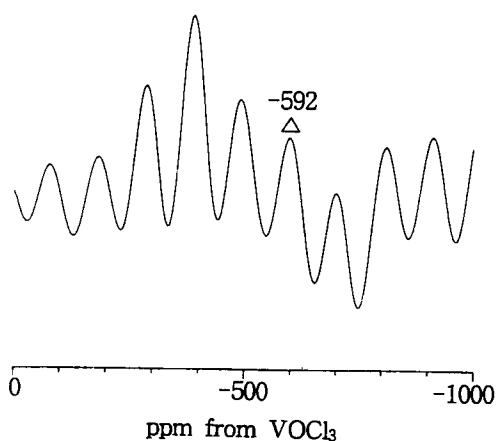
Figure 6. ^{51}V MAS NMR spectrum of vanadium-impregnated and calcined Si-MCM-41.
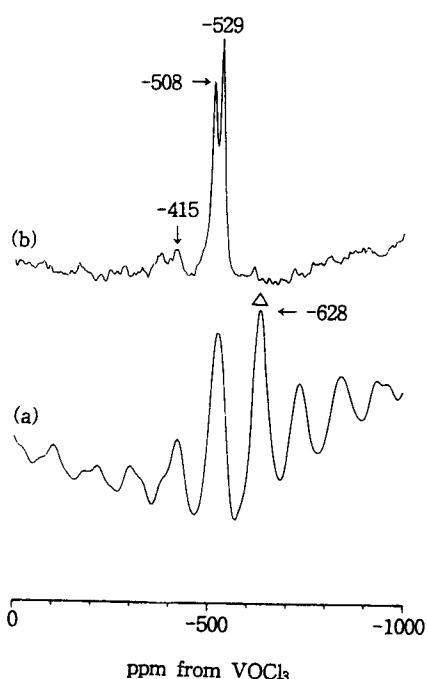

Figure 7. ^{51}V MAS NMR spectra of (a) VM-4 sample treated with 1 M-ammonium acetate solution and (b) recalcined VM-4 at 550 °C after acid treatment.

Figure 8. ^{51}V MAS NMR spectra of (a) VM-4 after steaming at 400 °C for 12 h and (b) recalcined VM-4 at 550 °C after steaming.

the peak at -627 ppm was disappeared. This probably resulted from removing of part of octahedral vanadiums by acid solution.

Figure 8 shows the effect of steaming at 400 °C for 12 h. Another peak at -584 ppm was appeared. After calcination, the spectrum similar to originally calcined sample was regenerated.

Though the thermal treatment in rotor of hydrated sample resulted in the change from tetrahedral environment to octahedral one and the steaming and the acid treatment affect to the chemical environment of vanadium, after recalcination, the spectrum similar to originally calcined sample is regenerated. This indicates that the vanadium is belonging to the framework in a relatively exposed site.
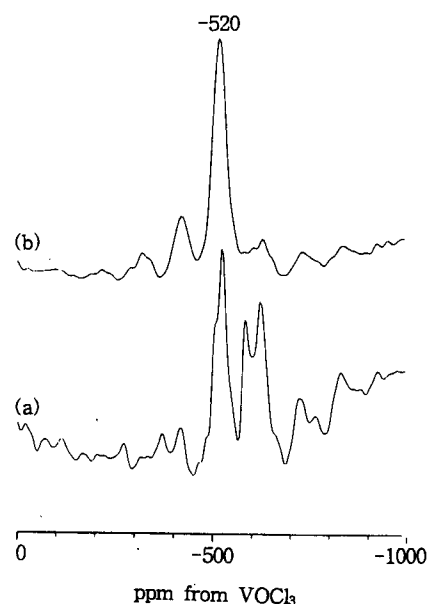
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Synthesis and Characterization of Volatile and Thermally Stable Europium β-Diketonate Complexes

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Preparation and properties of $Eu(hfa)_3 \cdot L$ (Hhfa=hexafluoroacetylacetone, L=bis(2-methoxyethyl)ether, diglyme, and 2,2':6',2"-terpyridine, tpy), which are potential CVD precursors for europium, were investigated. The reaction of the Eu_2O_3 with Hhfa in the presence of tridentate neutral ligand yielded the nine-coordinated $Eu(hfa)_3 \cdot L$. $Eu(hfa)_3 \cdot$ diglyme is air- and moisture-stable and most importantly has good volatility and thermal stability. $Eu(hfa)_3 \cdot$ tpy shows no sublime intact. The complex $Eu(hfa)_3 \cdot$ diglyme has been characterized by an X-ray structure determination; monoclinic $P2_1/n$, a=10.252(1), b=16.051(6), c=19.392(8) Å, β=96.10(2)°, V= 3173(2) Å^3. The europium atom in $Eu(hfa)_3 \cdot$ diglyme adopts a square-antiprismatic geometry with the ninth coordinating oxygen atom capping one of the square faces. All the adducts have been characterized by IR, TGA/DTA.

Introduction

There has been considerable interest in recent years in the development of new precursors for the chemical vapor deposition (CVD) of inorganic materials.[1] In general, such precursors must be volatile, stable to transport to the deposition site, and decompose cleanly to give the desired material. MOCVD allows for the exact control of the film microstructure and stoichiometry which is essential for the manufacture of superconducting devices with optimal and reproducible properties. The chemistry of rare-earth metal β-diketonates and alkoxides is in the progress of rapid development in the last 5 years. The major foreseeable application of such precursors is in the synthesis of electroceramics, *e.g.* superconductors such as $Pb_2Sr_2LnCu_3O_{8-x}$,[2]

$LnBa_2Cu_3O_{7-x}$,[3] and $La_{2-x}Sr_xCuO_4$,[4] piezoelectrics such as $LaCuO_2$,[5] as phosphors,[6] and NMR shift reagents,[7] *e.g.* [{Eu(tmhd)$_3$}$_2$], and [{Pr(tmhd)$_3$}$_2$],(Htmhd=2,2,6,6-tetramethylheptane-3,5-dione). The coordination and the properties of the rare-earth metal compounds[8] can be conveniently modulated by a proper choice of the coordinated ligands (and of the oxidation number of the central metal) in order to obtain suitable volatility and stability to oxygen and moisture and a convenient pyrolytic decomposition mode to give the desired product. In this paper, preparation and properties of $Eu(hfa)_3 \cdot L$ (L=diglyme or tpy) are described. Volatility and stability of two compounds have been compared and the results are expected to envisage for the better CVD precursors of inorganic materials.