

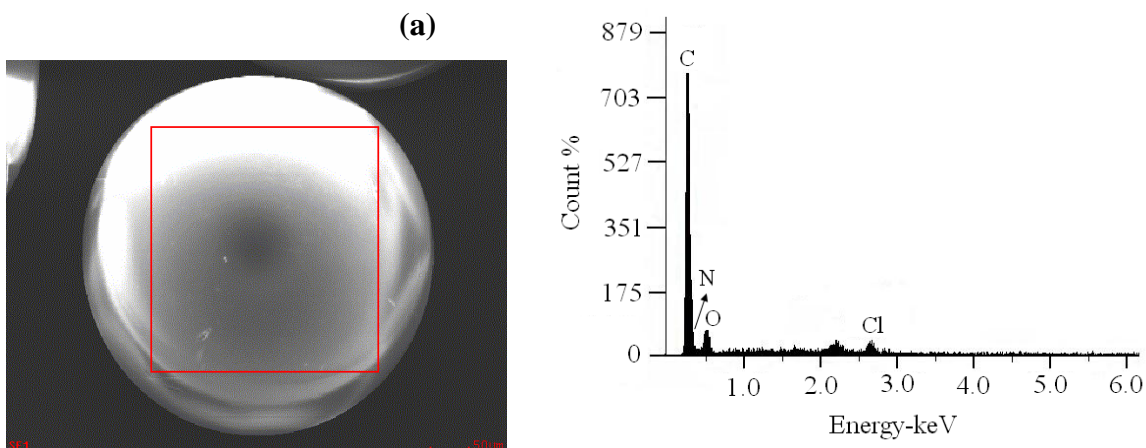
Supplementary Information

Polymer-Bound Oxidovanadium(IV) and Dioxidovanadium(V) Complexes: Synthesis, Characterization and Catalytic Application for the Hydroamination of Styrene and Vinyl Pyridine

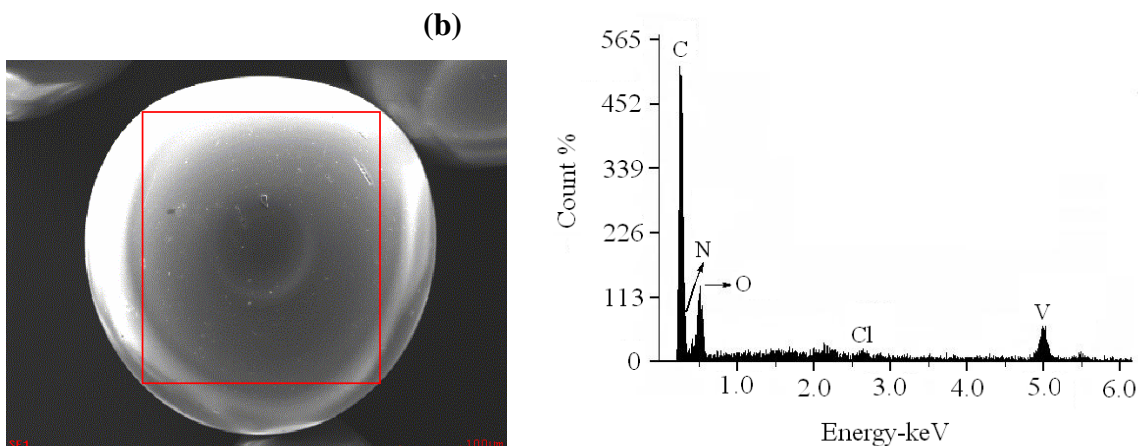
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Field emission-scanning electron microscope (FE-SEM) and energy dispersive X-ray analysis (EDX) studies

Field emission scanning electron micrographs (FE-SEM) of pure chloromethylated polystyrene, polymer-bound ligand, PS-Hfsal-aepy and complexes were recorded taking a single bead of each to understand the morphological changes occurring at various levels of syntheses. A light roughening of the top layer of bead having polymer-anchored ligand as compared to the relatively smooth and flat surface of the neat polystyrene bead suggests the change of nature of bead upon covalent bonding. Images of beads with metal complex show further roughening of the top layer which is possibly due to interaction of metal ions with ligand to adapt to the fixed geometry of the complex. Some of these images are reproduced in Fig. SI-1. The Energy dispersive X-ray analysis (EDX) profiles of two representative samples are also presented in the Fig. SI-1.



PS-[Hfsal-aepy] (**I**)



PS-[V^{IV}O(fsal-aepy)(acac)] (**1**)

Fig. SI-1 FE-SEM (left) and EDX (right) profiles of (a) PS-Hfsal-aepy (**I**) and (b) PS-[V^{IV}O(fsal-aepy)(acac)] **1**. Red square in left figures shows the spotted area for EDX.

IR spectral study

The chloromethylated polystyrene shows strong peaks at 1264 and 673 cm^{-1} in the IR spectrum²⁴ and absence of these peaks in PS-Hfsal-aepy suggests the covalent bonding of chloromethylated polystyrene with Hfsal-aepy. The polymer-anchored ligand exhibits a sharp band at 1670 cm^{-1} due to the $\nu(\text{C}=\text{O})$. Existence of this band suggests covalent bond formation between the ligand and the polymer through an ester group. A band corresponding to $\nu(\text{C}=\text{N})$ at 1630 cm^{-1} in PS-Hfsal-aepy shifts to lower wave numbers, thereby indicating the coordination of azomethine nitrogen to the metal ions. The presence of multiple bands of medium intensity covering the 2900-2800 cm^{-1} regions is consistent with the presence of $-\text{CH}_2$ groups. In addition, PS-[V^{IV}O(fsal-aepy)(acac)] exhibits a medium intensity band at 982 cm^{-1} due to $\nu(\text{V}=\text{O})$, indicating the existence of V=O bonds. Similarly the dioxido complex PS-[V^VO₂(fsal-aepy)] exhibits two such bands at 958 and 931 cm^{-1} corresponding to $\nu_{\text{antisym}}(\text{O}=\text{V}=\text{O})$ and $\nu_{\text{sym}}(\text{O}=\text{V}=\text{O})$ modes, respectively.²⁵ Non-polymer bound vanadium complexes (see Table SI-1) also exhibit spectral patterns very close to polymer-anchored analogues, also similar to those reported in the literature.²⁶

Table SI-1 IR spectral data of ligand and complexes.

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{V}=\text{O})$
PS-Hfsal-aepy II	1670	1630	-
PS-[V ^{IV} O(fsal-aepy)(acac)] 1	1668	1600	981
PS-[V ^V O ₂ (fsal-aepy)] 2	1674	1603	958, 931
Hsal-aepy I	-	1632	-
[V ^{IV} O(sal-aepy)(acac)] 3	-	1596	934
[V ^V O ₂ (sal-aepy)] 4	-	1601	964, 919

EPR spectra of a methanolic solution of the neat complex [V^{IV}O(sal-aepy)(acac)] **3 upon adding styrene**

EPR spectra have been recorded in order to find evidence for the intermediate species formed during the catalytic cycle. The neat complex [V^{IV}O(sal-aepy)(acac)] **3** was dissolved in MeOH (4 mM), different amounts of styrene were added, samples were taken and frozen and the spectra recorded (see Fig. 10). After addition of ca. 10 equiv. of styrene, the spin Hamiltonian parameters obtained are: $g_{\parallel} = 1.949$, $g_{\perp} = 1.979$, $A_{\parallel} = 162.8 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp} = 58.1 \times 10^{-4} \text{ cm}^{-1}$. This spectrum very slightly differs from the complex in the absence of styrene (see Fig. SI-2 and Table 4). These results may be considered to give some indication of the interaction of styrene with the metal complex detected by EPR. This interaction is weak and from the EPR spectra recorded it appears that there is no coordination of styrene to the V^{IV}-center.

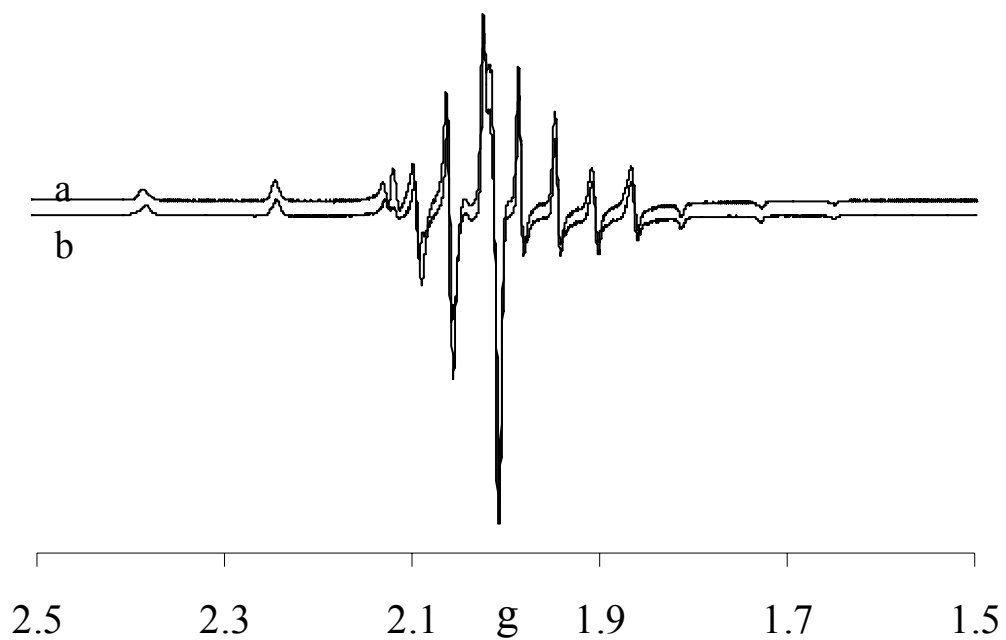
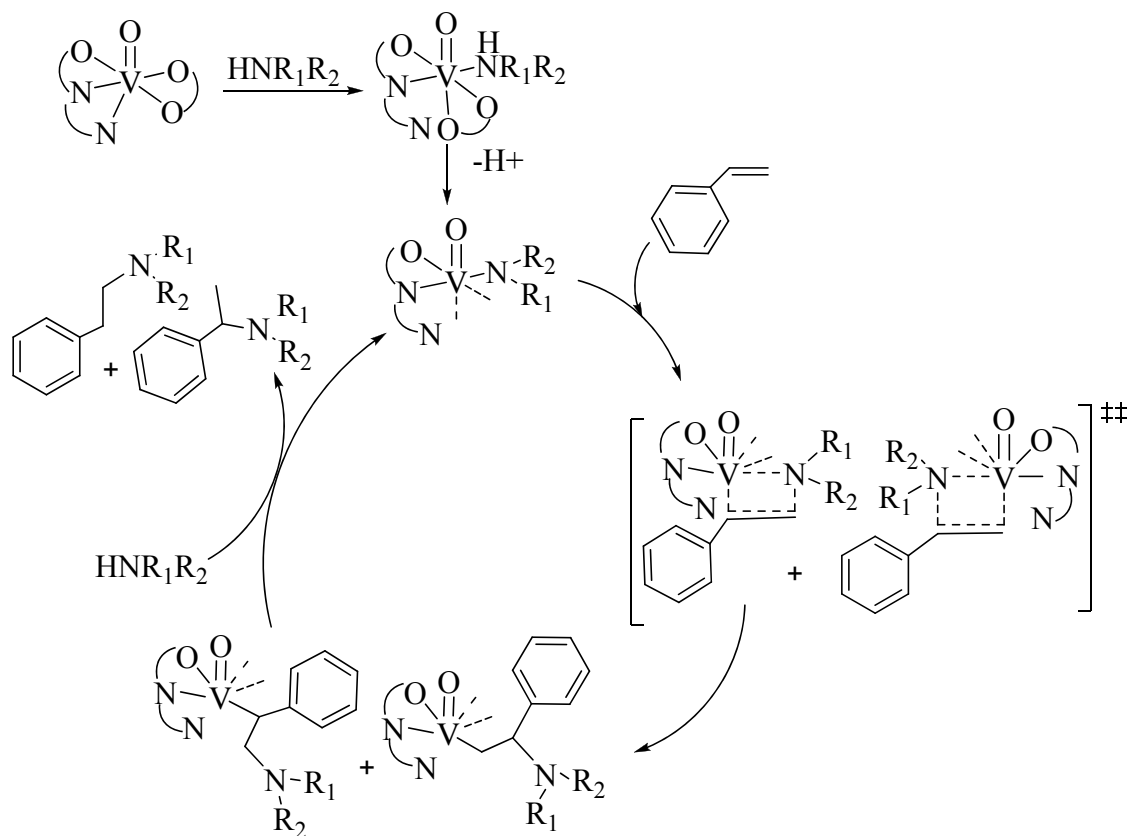


Fig. SI-2 EPR spectra of frozen methanolic solutions, ca. 4 mM of $[V^{IV}O(\text{fsal-aepy})(\text{acac})]$ (**3**) (a) before and (b) after addition of 10 equiv. styrene dissolved in MeOH. Styrene : complex molar ratio = 10

Outline of the catalytic hydroamination processes of $[V^{IV}O(\text{fsal-aepe})(\text{acac})] \mathbf{3}$



Scheme SI-1 Outline of the catalytic hydroamination processes of $[V^{IV}O(\text{fsal-aepe})(\text{acac})] \mathbf{3}$ (4 mM) in MeOH, showing the proposed intermediates formed. $\text{O} _ \text{O} \equiv \text{acac}^-$; $\text{O} _ \text{N} _ \text{N} \equiv \text{sal-aepe}$ ligand.

In order to the amine to coordinate to the V^{IV} -centre in complex $[V^{IV}O(\text{fsal-aepe})(\text{acac})] \mathbf{3}$, at least one of the coordinated atoms in $\mathbf{3}$ must break its bond to V^{IV} . In Scheme SI-1 only a tentative schematic outline of the binding mode is given assuming a bidentate binding of the sal-aepe upon binding of the amine ligand. Another possibility is the hydrolysis one or two of the O-atoms of the acac^- ligand upon binding of the amine.

For the formation of the amide a proton acceptor must exist. In the outline of Scheme SI-1, the non-coordinating N-atom may be bound to the H-atom from the amine, therefore

acting as a base. In the alternative case where the two O-atoms hydrolyse, the acac^- would then possibly act as a base towards the HNR_1R_2 ligand yielding Hacac upon hydrolysis, thereby favoring the formation of the $[\text{V}^{\text{IV}}\text{O}(\text{fsal-aepy})(\text{amide})]$ complex, necessary for the catalytic cycle proposed. The termination of the catalytic cycle would then be the acac^- ligand coordinating again instead of the amine. The outline of the catalytic cycle would then correspond to what is shown in Scheme 7 (here considering a V^{V} -sal-aepy complex).