

## Characterization of Reactive Sites in Supported Catalysts by $^{51}\text{V}/^{15}\text{N}$ Rotational Echo Double Resonance NMR Spectroscopy: Formation of Phenylimido Groups at Surface-Bound Oxovanadium Sites

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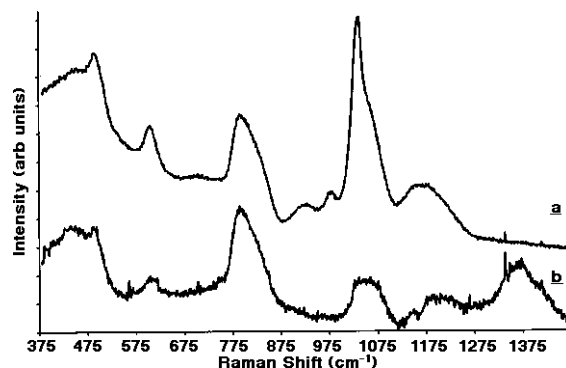
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Surface-supported transition metals containing multiply bonded ligand systems such as akylidene and imido groups have long been proposed as key intermediates in heterogeneous catalytic reactions such as olefin metathesis, polymerization, and ammoxidation.<sup>1–5</sup> Despite the importance of these proposed species, their positive characterization on catalyst surfaces has been difficult due to their low concentration and transient nature. Recently, organometallic species already containing these functional groups have been successfully grafted to silica surfaces.<sup>6–9</sup> While this approach unambiguously demonstrates the efficacy of these sites as catalysts, a question still remains as to whether these or similar functional groups are generated on conventionally supported heterogeneous catalysts under typical catalytic conditions. We report here the generation of metal–imido functional groups at discrete silica-supported vanadium-oxo sites under catalytic conditions. Specifically, vanadium-oxo groups in a silica xerogel matrix react cleanly and quantitatively with aniline in a gas–solid reaction to generate a phenylimido group at the vanadium center with concomitant elimination of water. Characterization of metal–imido bond formation was carried out using  $^{51}\text{V}/^{15}\text{N}$  rotational echo double resonance (REDOR) NMR spectroscopy where the more sensitive quadrupolar  $^{51}\text{V}$  nucleus was monitored while the  $^{15}\text{N}$  nucleus was pulsed.<sup>10</sup> While REDOR has been used to characterize a number of dense and porous inorganic solids and both one- and two-dimensional solid-state NMR have been used to characterize surface-grafted organometallic species, we believe this is the first use of REDOR to elucidate such sites.<sup>11–14</sup>

Vanadium oxide supported on silica was fabricated using an established sol–gel derived procedure (see Supporting Information).<sup>15,16</sup> Exposure of a monolithic 0.25 mol % V–silica xerogel to vapor phase aniline in a dry nitrogen flow as a function of temperature was monitored in situ by UV–vis spectroscopy. As the temperature was increased, systematic changes in the UV–vis spectrum began to occur between 120 and 175 °C with what appears to be clean conversion to a distinct product observed at 175 °C under a constant flow of aniline for 24 h (Figure S1, Supporting Information). The volatile products of the reaction were collected in an LN<sub>2</sub> trap. Analysis of the recovered products by gas chromatography revealed that water was a primary product of the reaction. Quantitative analysis of the amount of water generated when 1.688 g of 5 mol % vanadium–silica is converted to the product found  $0.962 \pm 0.017$  mol of water produced per mole of V.

Structural changes in the vanadium site as a function of the extent of reaction can be seen directly by Raman spectroscopy (Figure 1). The peak at  $1040\text{ cm}^{-1}$ , which is assigned to the terminal V=O stretch, drops in intensity as the reaction proceeds until,



**Figure 1.** Raman spectra (351-nm excitation) of 0.5 mol % V. (a) Unreacted and (b) reacted in aniline/Ar flow at 175 °C for 40 min.

when no more changes in the UV–vis spectrum are observed, it is essentially gone.<sup>17</sup> Concomitant with the loss of the terminal V=O stretch is the formation of a new peak at  $1370\text{ cm}^{-1}$  observed in the spectrum of the reacted material.

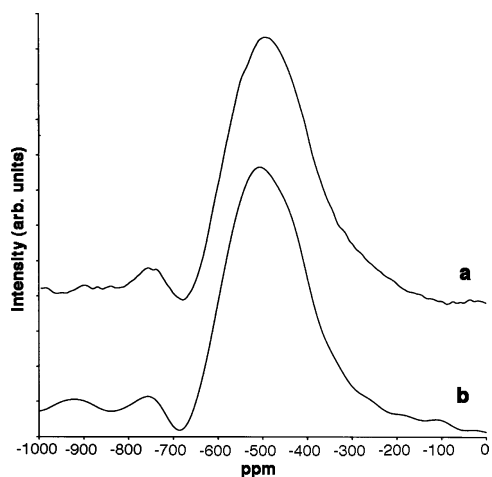
The formation of water as a principal product at a stoichiometry approaching 1:1 is consistent with known reactions of amines with terminal metal oxo groups to form metal–imido complexes.<sup>18</sup> The new Raman peak at  $1370\text{ cm}^{-1}$  is also characteristic of arylimido formation. In particular, metal arylimido groups have characteristic bands, thought to be coupled M=N–CPh modes, usually occurring between  $1250$  and  $1360\text{ cm}^{-1}$ .<sup>19</sup> The observed band is consistent with this, albeit slightly above this range due to, in part, its convolution with the silica mode.

$^{15}\text{N}$ -Labeled samples were prepared by perfusion of  $^{15}\text{N}$ -labeled aniline into a 3.0 mol % vanadium xerogel, which was heated to 175 °C to generate the product. Before collecting the NMR spectrum, we removed excess aniline by flowing Ar over the sample for 30 min at 175 °C followed by evacuation to  $10^{-3}$  Torr. Solid-state MAS NMR spectroscopy resolved a single peak in the  $^{15}\text{N}$  NMR at  $-335$  ppm relative to nitromethane, indicating the formation of a single N-containing product (Figure S2a, Supporting Information)

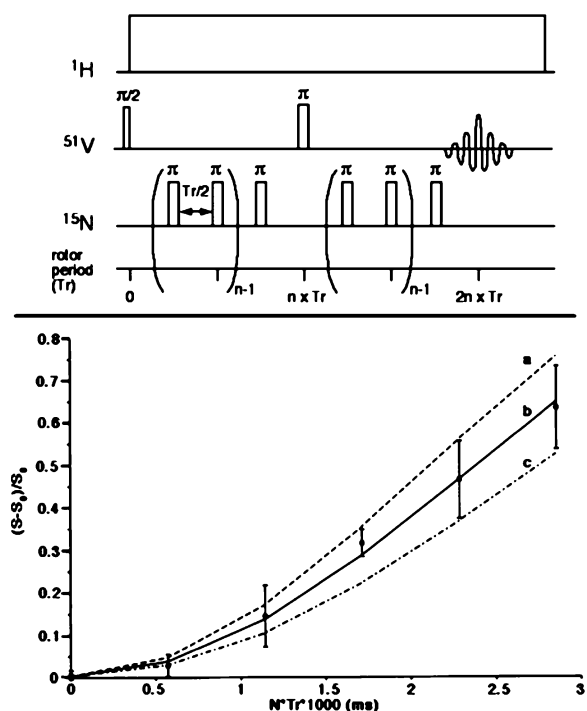
To determine the proton environment around the nitrogen, a dephasing experiment was carried out where the  $^{15}\text{N}$  signal, enhanced by cross polarization from protons, is detected using the Hahn-echo sequence with a total of two rotational periods, during which the  $^1\text{H}$  decoupling is switched off for a given time (called dephasing time) to dephase the  $^{15}\text{N}$  signal.<sup>20</sup> The proximity of the  $^1\text{H}$  to the  $^{15}\text{N}$  can be estimated from the intensity of the  $^{15}\text{N}$  signal as a function of dephasing time.  $^{15}\text{N}$  spectra were collected with 50 and 100  $\mu\text{s}$  of dephasing (Figure S2b,c, Supporting Information). The proton coupling is weak with virtually no attenuation of the  $^{15}\text{N}$  signal observed at 50  $\mu\text{s}$  dephasing time and significant attenuation occurring at 100  $\mu\text{s}$ . Protons directly bonded to the

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**Figure 2.**  $^{51}\text{V}$  solid-state MAS NMR (3.5 kHz spin rate) of (a) control and (b) aniline reacted 3 mol % V-silica referenced to  $\text{VOCl}_3$ .



**Figure 3.** Pulse pattern (top) and plot of data and fits (lower). Dipolar coupling: (a) 460 Hz, dashed line, (b) 419 Hz, solid line, and (c) 376 Hz, long/short dashed line.

nitrogen in amino or amido groups would show significant dephasing at short (50  $\mu\text{s}$ ) times, hence the observed, weak dephasing is the result of protons on the phenyl ring, consistent with phenylimido.

The  $^{51}\text{V}$  spectra of the unreacted and reacted material are quite similar, with both showing a single resonance at  $-494$  and  $-506$  ppm, respectively (Figure 2). REDOR was used to establish the presence of direct covalent bonding between the V and the N. Because of the low concentration of sites present on the surface, the REDOR fraction was measured by monitoring the more intense  $^{51}\text{V}$  NMR signal, while applying two  $\pi$ -pulses per rotor period using the pulse sequence shown in Figure 3, top. The  $^{51}\text{V}$  echo was measured with and without the  $^{15}\text{N}$  pulses, and the REDOR fraction,  $\Delta S/S_0$ , was plotted as a function of rotor evolution (Figure 3, bottom).

Consistent with a short covalent bond length, after 3 ms of dephasing 60% of the signal is lost. The best fit of the data, using the equations given in ref 10, was with a dipolar coupling constant of 419 Hz. In small molecule analogues, vanadium(V)–nitrogen covalent lengths typically range from around 1.60–1.70 Å for arylimido groups and 1.9–2.0 Å for amido groups.<sup>21–25</sup> Consistent with these covalent lengths, the V–N bond length obtained from the fit was 1.96 ( $\pm 0.09$ ) Å. While this is longer than expected for an imide, it has been established that bond length estimates determined from fits to the REDOR experiment tend to be longer than the experimental distances found through X-ray crystallography. This has been attributed to molecular motion and thermal dynamics that may partially average the dipolar couplings between two spins.<sup>26</sup>

Finally, the prepared vanadium–imido groups supported on silica are highly reactive. Exposure to benzaldehyde vapors at room temperature results in the formation of *N*-benzylideneaniline with concomitant recovery of the terminal V=O stretch in the Raman spectrum (Figure S3, Supporting Information).

**Acknowledgment.** Funding was provided by the Air Force Office of Scientific Research through MURI 1606U8.

**Supporting Information Available:** Material synthesis, UV–vis monitoring of the reaction with aniline,  $^{15}\text{N}$  dephasing, and reaction of vanadium–imido group. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA052579C