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Determination of the Coordination Geometry of Supported Vanadium Catalysts by Electron Spin Echo Modulation Analysis

Electron spin echo modulation analysis was used to characterize the coordination geometry of the paramagnetic vanadium species formed in the 0.25% V_2O_5 in SiO_2 with D_2O adsorbate. The deuterium modulation indicates one deuteron at 0.23 nm and four deuterons at 0.26 nm. The four farther deuterons are interpreted as due to two-coordinated water molecules.

INTRODUCTION

Supported vanadium catalysts have been extensively used in various reactions such as the oxidation of hydrocarbons, the reaction of NO with NH_3, oxidation of CO, etc. (*1–4*). A number of papers have since been published emphasizing the role of V═O in these reactions but none of them were able to clearly characterize the coordination of vanadium on the supported catalysts. Van Reijen and Cossee (*5*) postulated, on the basis of a comparison with their results on chromyl ions, that in the case of vanadium supported on silica $(VO_4)^{4-}$ units are initially present after calcination of the support and after adsorption of NH_3 or H_2O they change to $(VO)^{2+}$ in square pyramidal coordination, presumably coordinating to only one adsorbate molecule. Kazansky and co-workers (*6–9*) also suggested that adsorbate molecules somehow change the coordination sphere of the V^{4+} to form the vanadyl species on supported vanadium catalysts.

In recent years we have shown (*10–13*) that the technique of electron spin echo modulation analysis can be exploited to obtain valuable information on short-range order in disordered systems. Using this method Cu^{2+} in Cu/SiO_2 systems (*13*) was shown to be coordinated to two water or two ammonia molecules. In this communication we show that the vanadyl species formed in the V_2O_5/SiO_2 system is also coordinated to two water molecules.

EXPERIMENTAL

Silica (Alfa Chemicals) with a surface area of 400 m^2/g was thoroughly washed with 1 *M* HCl to remove the impurity Fe^{3+} which otherwise adversely affects the phase memory time of the electron spin echo signals. The supported catalysts were made by impregnation with aqueous solutions of NH_4VO_3 followed by calcination in air at 450–500°C. The vanadium content in the supports was 0.25 and 0.5% by weight. Higher content of vanadium was found to be unsuitable for electron spin echo measurements. The calcined sample was dehydrated in vacuum (10^{-5} Torr) at 500°C and then reduced with H_2 (50 Torr) at the same temperature. Then the sample was cooled to ambient temperature before exposing to D_2O (Aldrich gold label), ND_3, or CD_3OH (Stohler isotopes).

The ESR spectra were recorded on a Varian E-4 spectrometer and the electron spin echo spectra were recorded with a home-built (*14*) spectrometer at 4.2K.

RESULTS AND DISCUSSION

The ESR spectra are similar to those reported (*1–9*) for the activated catalyst as well as for the catalyst exposed to D_2O. In fact, the vanadyl species was found to form even during the calcination stage itself, presumably through reduction by the NH_3 generated by the decomposition of NH_4VO_3.

The theory and applications of electron spin echo modulation have been described

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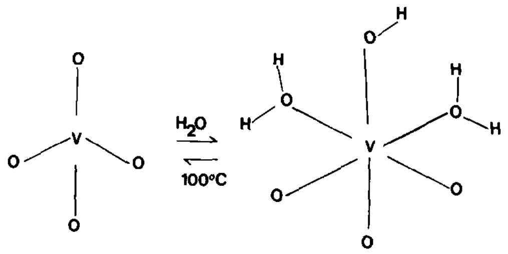
in detail (*10–15*). When a paramagnetic system is subjected to suitable sequences of microwave pulses, microwave echoes are generated due to reformation of magnetization. Since the nearby nuclei are also simultaneously excited, these echoes are modulated by the characteristic Larmor frequencies of the interacting nuclei. These modulations can be analyzed to yield information about the distance between the paramagnetic ion and the interacting nuclei, the number of such nuclei, and the isotropic hyperfine coupling (*16*).

The experimental and simulated two-pulse electron spin echo spectra for the 0.25% $V_2O_5 : SiO_2 : D_2O$ system are shown in Fig. 1. The best fit is achieved for a two-shell picture of one nearby deuteron at 0.23 nm and four slightly more distant deuterons at 0.26 nm. The agreement between the simulated and experimental spectra is excellent. Assuming nearly tetrahedral orbitals on the oxygen, the vanadium-to-oxygen distances are calculated to be 0.17 and 0.20 nm, respectively. The four deuterons could either mean four-coordinated hydroxyl groups or two-coordinated water molecules in the vanadyl species.



However, heating at 100°C is sufficient to destroy the vanadyl species. This supports an assignment with two-coordinated waters shown above, since dehydration generally occurs at much lower temperatures than dehydroxylation. The latter typically occurs at 400–500°C. The ESR results on vanadyl species have not unambiguously distinguished between distorted octahedral or square pyramidal geometries (*1–9*). It should be noted that the close proton observed need not be coordinated to the vanadyl oxygen but can be due to a nearby silanol group.

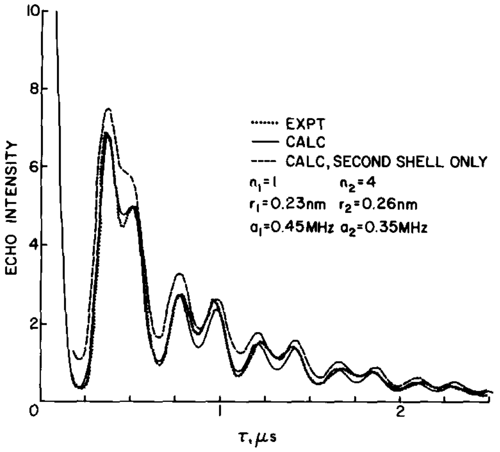


FIG. 1. Experimental and simulated two-pulse electron spin echo spectra for the (0.25%) $V_2O_5 : SiO_2 : D_2O$ system. The decay function used in the simulation is $g(\tau) = \exp(2.65 - 1.5\tau + 0.1\tau^2 - 0.005\tau^3)$. The improvement in the fit, especially in the first period, on including a closer deuteron is clearly seen.

The first model also requires that some of the water molecules be split on adsorption since it is unlikely that vanadium would coordinate to four silanol groups. It is interesting to note that the $V–O_w$ distance of 0.20 nm compares well with the vanadium–oxygen distances in vanadyl acetylacetonate rather than with those in the $VO(H_2O)_5^{2+}$ complex observed in $VOSO_4 \cdot 5H_2O$, where $V–O_w$ is 0.23 nm. However, the vanadium–oxygen distances are known (*17*) to be determined by the host lattice constraints.

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