

Tin Passivation of Vanadium in Metal-Contaminated Fluid-Cracking Catalysts: Electron Paramagnetic Resonance Studies

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Vanadium interactions with model fluid cracking catalysts and vanadium passivation with tin have been monitored by electron paramagnetic resonance (EPR). Model systems such as EuY, amorphous aluminosilicate gels, and EuY-gel mixtures have been investigated. Vanadium, introduced in the form of vanadyl naphthenate, is stabilized on the zeolite primarily as octahedrally coordinated VO^{2+} cations. In contrast, the gel preferentially sorbs vanadium where it is stabilized mainly in the form of V_2O_5 . The presence of tin on the zeolite favors oxidation of VO^{2+} to V^{5+} and the generation of $\text{Sn}^{-4+}\text{O}-\text{V}^{5+}$ species during steaming. Formation of europium orthovanadate (EuVO_4) is promoted by the presence of excess tin. Removal of Eu^{3+} ions from the zeolite lattice in the form of vanadates contributes to zeolite destabilization; thus excess tin is to be avoided. © 1990 Academic Press, Inc.

INTRODUCTION

In order to better understand metal-surface interactions useful in preparing metal-resistant cracking catalysts, the behavior of Ni and V on the basic components (such as the clay, the amorphous aluminosilicate matrix, and the zeolite) of a fluidized cracking catalyst (FCC) has been recently investigated (1, 2). X-ray photoelectron spectroscopy (XPS) has been used to show that Ni interacts with the clay and the gel to form NiAl_2O_4 surface species and that in steam-aged catalysts Si migrates to the surface where in the presence of Ni it can form inert NiSiO_3 -like compounds. Thus, the ability of a matrix to minimize Ni dispersion and of a clay to form inert Ni species will control the Ni tolerance of the catalyst (1). The zeolite (that is, the cracking component of the catalyst) is not affected by the presence of Ni.

In contrast, laser Raman spectroscopy, XPS, and X-ray diffraction (XRD) data have indicated that steam aging in the pres-

ence of even small amounts (<1.0%) of V can cause the collapse of the zeolite structure with total loss of catalytic activity (2). Cracking components such as CREY (calcined rare-earth-exchanged Y zeolite) collapse with formation of cerium orthovanadate (CeVO_4) whereas HY (hydrogen zeolite Y) collapses with formation of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and silica (tridymite) (2). Mullite formation was also observed in steam-aged V-loaded gels but not in gels containing Ni (2).

Transport experiments have been used to show that in the presence of steam (at 760°C , 1 atm) V impurities on the catalyst surface form volatile compounds (acids such as $\text{H}_4\text{V}_2\text{O}_7$) capable of migrating from catalyst particle to particle (3). This migrating V can be sorbed by adding to the catalyst diluents (such as layered magnesium silicates (3) or aluminas (4)) capable of forming stable vanadates or other heat-stable V-compounds (4).

Addition of antimony organics to cracking catalysts can reduce by 50% gas formation due to metal contaminants, especially nickel (6, 7). Vanadium passivation has not

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been as successful, although tin has been reported capable of reducing the deleterious effects of V contaminants (8–12). The effects of Sn on V-contaminated model catalysts have been recently studied using luminescence experiments (13) and Mössbauer spectroscopy (14). In fact, in two companion papers, it was shown that luminescence experiments can provide useful information on the environment of the rare earth cations present in the zeolite and that it can be used to monitor V-migration between the zeolite and the catalyst matrix even in the presence of Sn (13). Tin-119 Mössbauer spectroscopy has indicated that Sn–V interactions take place only during steam-aging and probably $\text{Sn}^{4+}\text{--O--V}^{5+}$ complexes are formed; V–Sn alloys were not observed (14).

In this paper, electron paramagnetic resonance (EPR) is used to probe the nature of the vanadium species. EPR is sensitive to all oxidation states of vanadium except V^{5+} . It is hoped that by studying these simplified model systems, insight into the more complex metal–surface interactions present in commercial fluid cracking catalysts will be obtained.

EXPERIMENTAL

An $\text{NH}_4\text{--Y}$ sample (supplied by Alfa Ventron) was exchanged with Eu^{3+} cations by stirring 4 g of zeolite in 400 ml of 0.05 M $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at room temperature for 12 h. The product was filtered and washed sparingly with distilled, deionized water and first dried in air at room temperature and then calcined at 575°C. One weight percent of tin and vanadium was loaded onto the zeolite by incipient wetness using toluene solutions containing tetraphenyl tin or vanadyl naphthenate. After slurring the catalyst in the metal solution, excess solvent was volatilized under reduced pressure. Metal loading was followed by a calcination in flowing air at 575°C for 10 h to remove the organic ligands and then by heating at 730°C in a 95% $\text{H}_2\text{O}/5\%$ N_2 mix-

ture with a flow rate of 4 ml water per hour to simulate the aging of fresh FCC.

Three systems were studied: (a) EuY prepared as mentioned above; (b) AAA alumina, which is a 75% $\text{SiO}_2/25\%$ Al_2O_3 amorphous aluminosilicate gel from by Davison (Columbia, MD); and (c) a physical mixture of EuY and AAA alumina formed by grinding a 50/50 mixture of the two with a mortar and pestle. The nomenclature used to describe the various sample preparations is given in detail elsewhere (13). However, an example follows: EuY/AAA (SnCVCS) would refer to an EuY/AAA mixture loaded with 1 wt% tin (Sn), calcined (C), loaded with 1.0 wt% vanadium (V), calcined (C), and finally steamed (S). Higher Sn loadings (1.5 and 2.0 wt%) were also used. In some mixtures, the EuY and the AAA alumina were mixed after loading one metal component in order to monitor metal migration. An example of such a catalyst is EuY(SnAAAC). In this case, EuY has been loaded with tin (Sn), then mixed with AAA alumina, and finally calcined (C).

EPR experiments were performed on a Varian E-3 X-band spectrometer operating at about 9.1 GHz. Samples were loaded into 3-mm-o.d. quartz tubes which were either sealed with air inside or first evacuated before sealing. Spectra were recorded both at room temperature and at 77 K using an external DPPH standard for calibration.

The method used to compare intensities of the EPR signals was the peak height times width squared technique. Comparisons of intensity changes have been made between spectra measured at similar temperatures.

RESULTS

EuY

Figures 1a and 1b show the EPR spectra for vanadyl naphthenate at 77 K and at room temperature, respectively. The vanadyl naphthenate was dissolved in toluene to give a 1 wt% vanadium solution. At room

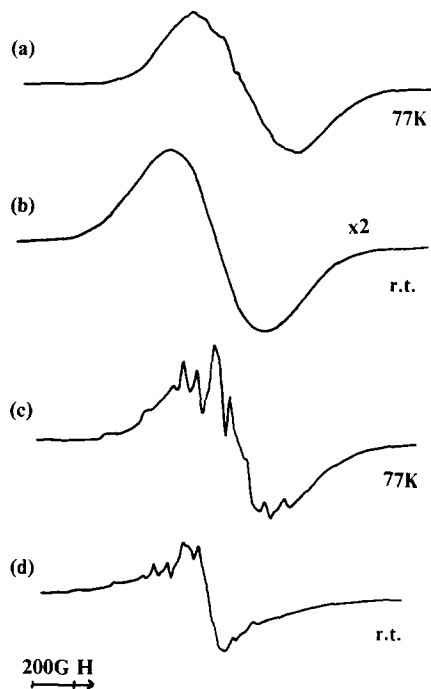


FIG. 1. EPR spectra of 1 wt% solution vanadyl naphthenate in toluene at (a) 77 K, (b) room temperature (RT). EPR spectra of vanadyl naphthenate loaded onto EuY at (c) 77 K, (d) RT.

temperature, a broad isotropic signal with peak-to-peak width (H_{pp}) of 455 G and $g_{iso} = 1.955$ was observed. At 77 K, the spectrum is essentially the same except that a little hyperfine structure is superimposed on the broad isotropic signal. After vanadyl naphthenate deposition, the EuY EPR spectrum exhibited more hyperfine structure, Figs. 1c and 1d. At 77°K, the g_z component could be measured and had EPR parameters $g_z = 1.932$ and $A_z = 182 \times 10^{-4} \text{ cm}^{-1}$ (A represents hyperfine splitting). The perpendicular component was too broad to be deconvoluted accurately. At room temperature, many features of the spectrum were broadened. After calcination at 575°C, the EPR spectrum exhibited the following parameters: $g_x = g_y = g^{\perp} = 1.976$; $A_x = A_y = A^{\perp} = 70 \times 10^{-4} \text{ cm}^{-1}$; $g_z = 1.931$ and $A_z = 185 \times 10^{-4} \text{ cm}^{-1}$ (see Fig. 2a). Linewidths narrowed considerably upon calcination and the gain was correspondingly much

lower in the spectra of the calcined samples (see Figs. 1c and 2a). At room temperature, line broadening was not observed in the spectrum of the calcined sample and the EPR parameters remained unchanged. The EPR spectra of the steamed and vanadium-loaded zeolite decreased in intensity by a factor of 30; some line broadening was also observed (Fig. 2b). The EPR parameters were the same as those for EuY(VC) and the recording temperature had no effect on lineshape.

Tin addition did not change the EuY(VC) EPR spectrum. However, upon calcining this sample, the intensity of the signal decreased by a factor of 20 (Fig. 3a). Reversing the order of tin and vanadium deposition produced a sample with nearly the same EPR spectrum both in terms of intensity and lineshape (Fig. 3b). The EPR parameters for the spectra shown in Figs. 3a and 3b are very similar to those for EuY(VC) although the linewidths are about twice as broad. When vanadium was loaded

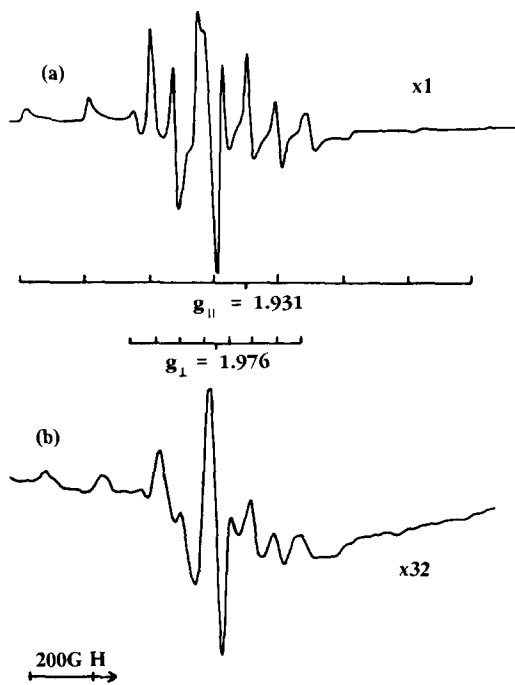


FIG. 2. EPR spectra recorded at 77 K of (a) EuY(VC), (b) EuY(VCS).

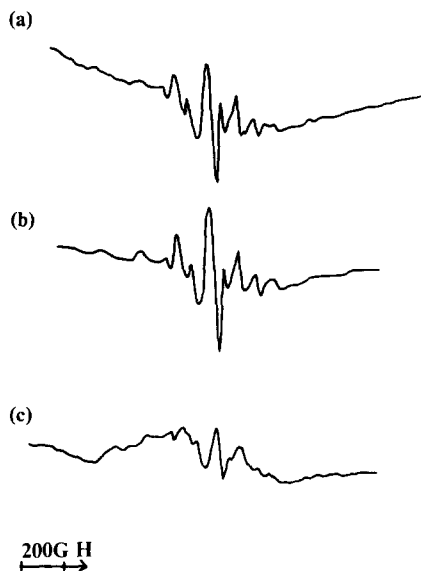


FIG. 3. EPR spectra recorded at 77 K of (a) EuY (VCSnC), (b) EuY(SnCVVC), (c) EuY(SnCVCS).

onto the tin-containing EuY, a broad EPR spectrum similar to that shown in Fig. 1c for EuY(V) was observed. Steaming EuY (SnCVVC), or (VCSnC) decreased the intensity of the EPR signal by another factor of 10 (Fig. 3c). Nevertheless, the EPR parameters of the surviving EPR active species remained unchanged.

Mixing the vanadium-loaded zeolite with AAA alumina followed by calcination produced the same EPR spectrum as that for EuY(V) but with half the intensity. Thus, the presence of the AAA alumina did not affect the V species formed. Similarly, when a V-loaded EuY was mixed with the gel and steamed, EuY(VCAAAS), the intensity and lineshape of the EPR spectrum was similar to that for EuY(VCS). The presence of air in the sample tube had no effect on the EPR spectra of the zeolites tested. When higher concentrations of Sn (1.5 and 2.0 wt%) were used, the EPR spectra had essentially the same lineshapes. However, the intensity of the EPR active species after calcination and steaming remained much higher, decreasing only by a factor of 4 during steaming.

AAA Alumina

Figures 4a and 4b compare EPR spectra, recorded at 77 K, for vanadyl naphthenate before and after deposition on AAA alumina. After deposition, a spectrum with narrow linewidths (~ 25 G) and well-resolved hyperfine splitting was observed (Fig. 4b). This spectrum is temperature independent and has the following EPR parameters: $g_x = g_y = g^{\parallel} = 1.985$; $A_x = A_y = A^{\perp} = 68 \times 10^{-4} \text{ cm}^{-1}$; $g_z = 1.956$ and $A_z = 169 \times 10^{-4} \text{ cm}^{-1}$.

Calcination at 575°C resulted in a species with an EPR spectrum in which the intensity had decreased by a factor of 30 (Fig. 4c). Nevertheless, the EPR parameter g -values and hyperfine splitting remained essentially unchanged. Steaming the vanadium-loaded AAA alumina further increased the broadening of the lines; however, the EPR parameters did not change (see Fig. 4d). Unlike that in EuY, reduction

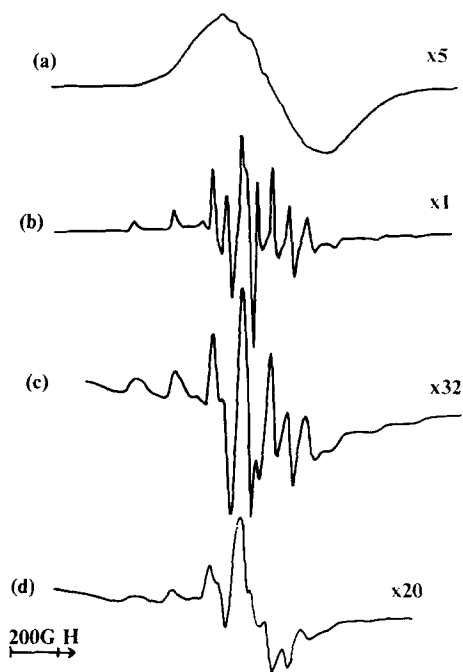


FIG. 4. EPR spectra recorded at 77 K of (a) vanadyl naphthenate, (b) AAA(V), (c) AAA(V), (d) AAA(VCS).

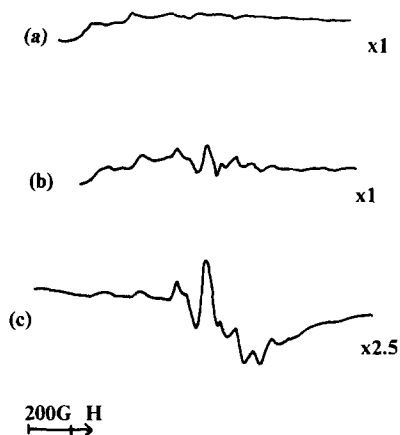


FIG. 5. EPR spectra recorded at 77 K of (a) AAA (VCSn), (b) AAA(SnCVC), (c) AAA(SnCVCS).

in the intensity of the EPR species upon steaming AAA(V) was not observed.

Addition of tin to vanadium-loaded AAA alumina (AAA(VCSn)) gave a species with the same EPR spectrum as that of AAA(V). However, after subsequent calcination, AAA(VCSn), virtually all the vanadium became EPR silent; the remaining weak EPR signal is shown in Fig. 5a. Reversing the order of metal deposition, AAA(SnCVC), gave a slightly stronger EPR signal (Fig. 5b). The EPR spectra of the steamed samples containing both metals have different linewidths for the different orders of deposition (Fig. 5c). When vanadium is deposited first, the linewidths are narrower and comparable to those of AAA(V). When tin is deposited first, the linewidths are larger, very similar to those of AAA(VCS). In all cases, the intensities of the signals are about 25 times weaker than those in AAA alumina loaded with vanadium, AAA(V).

When vanadium-loaded AAA alumina was mixed with EuY, calcination reduced the intensity of the EPR spectrum by a factor of 20. The EPR spectrum for AAA (V, EuY, C) is identical to AAA(V). However, when the V-loaded AAA alumina was mixed with EuY prior to steaming to produce AAA(VCEuY) the resulting spec-

trum more closely resembled that observed for EuY(VCAAAS) than that observed for AAA(VCS).

AAA/EuY Mixtures

When vanadyl naphthenate was deposited on AAA/EuY mixtures, a combination of AAA(V) and EuY(V) spectra was obtained (Figs. 6a and 6b). These spectra show some of the temperature dependence exhibited by V-loaded EuY(V) whereby the lines broadened at room temperature. Also, the hyperfine structure characteristic of AAA(V) is apparent. After calcination at 575°C, the intensity of the EPR signal decreased by a factor of 20 (Fig. 6c). Steaming did not affect the intensity, the linewidth or the lineshape of the EPR spectrum (Fig.

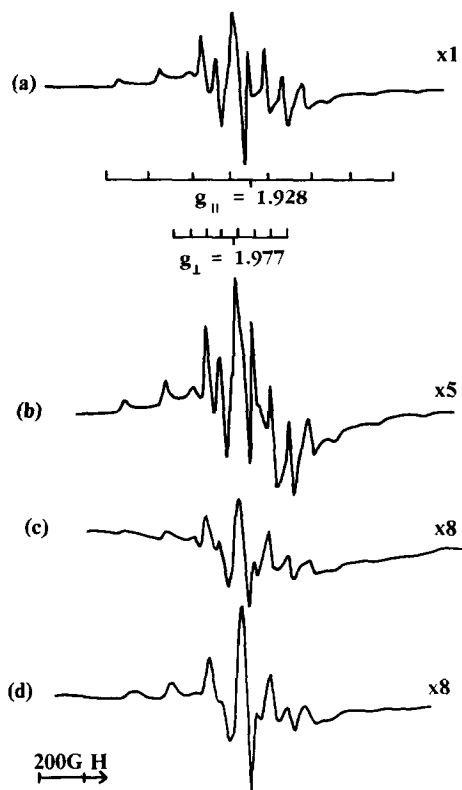


FIG. 6. EPR spectra of (a) AAA/EuY(V) recorded at 77 K, (b) AAA/EuY(V) recorded at RT, (c) AAA/EuY(V) recorded at 77 K, (d) AAA/EuY(VCS) recorded at 77 K.

6d). Addition of both metals followed by calcination produced the same EPR spectrum independent of the order of Sn and V deposition. The spectra were very similar to that for the vanadium-loaded AAA/EuY(VC) mixture. After steaming (in the presence of both metals), the resulting sample exhibited an EPR spectrum which showed features characteristic of both AAA(SnCVCS) and EuY(SnCVCS) crystals.

DISCUSSION

Vanadium is known to form complexes with coordination numbers ranging from 4 to 8 and in oxidation states (0) to (5+). Most of the oxidation states apart from (5+) are EPR active; however, the most easily observed, and best documented, is that of V^{4+} having one $3d$ unpaired electron. This is also the most common oxidation state. The vanadium nucleide is almost entirely ^{51}V ; the spin $\frac{7}{2}$ nucleus and the large gyromagnetic ratio of 0.7×10^{-4} rad G^{-1} ensure a large hyperfine splitting. The hyperfine splittings observed are normally characteristic of a certain stereochemistry and distinguish between vanadium present as V^{4+} ions or as $(V = 0)^{2+}$ ions. The most common coordination for vanadium, as with many transition metal complexes, is octahedral geometry (15).

Some of the largest natural resources of vanadium are certain crudes from Mexico and Venezuela, where it is normally present as vanadyl porphyrins or porphyrin-like complexes. In order to simulate these sources of metal impurities, vanadyl naphthenate dissolved in toluene was used to prepare vanadium-contaminated materials. Figures 1a and 1b show the EPR spectra for a vanadyl naphthenate solution in toluene which, at room temperature, exhibits a broad isotropic line characteristic of rapidly tumbling VO^{2+} cations. At 77 K a small degree of line narrowing permits the observation of hyperfine components in the spectrum. After vanadyl naphthenate impregnation on EuY (and removal of excess

toluene), a considerable degree of line narrowing as well as an axially symmetric environment was observed in the EPR spectrum (Figs. 1c and 1d). The hyperfine parameters measured for the g_x component are characteristic of vanadyl cations in an octahedral environment. The temperature dependence of the spectrum indicates that vanadyl naphthenate species are not strongly absorbed on the zeolite surface at room temperature and that most of the naphthenate ligands are still intact. It is believed that the bulky vanadyl naphthenate will hinder the diffusion of the organometallic complex into the zeolite microstructure. Thus, at this pretreatment stage, it is likely that a large fraction of the vanadyl naphthenate is on the external surface of the zeolite.

Calcination (in air) of the vanadyl naphthenate-loaded zeolite produced the spectrum shown in Fig. 2a. The intensity of the signal indicates that most of the original V^{4+} was not oxidized to V^{5+} . The EPR parameters are characteristic of vanadyl cations in an octahedral environment with tetragonal distortion (16–18). Similar vanadyl species have been observed both in zeolite-type environments and on SiO_2 catalysts (16, 19–21). The slight splitting of the g^1 region into g_x and g_y components is indicative of the orthorhombic nature of the species. This is often found when vanadyl cations are confined in a rigid medium, in this case bounded to the zeolite lattice. The rigidity of the species is evidenced by the fact that there is no change in the EPR spectrum between 77 K and room temperature. The precise coordination of the VO^{2+} cation is not clear; however, the five ligands will probably consist of lattice oxygens and zeolitic water.

Upon steaming the vanadium-loaded EuY, the signal intensity decreased, suggesting that about 95% of the vanadium was converted to V^{5+} and $EuVO_4$ formation occurred. The remaining 5% of the vanadium (V^{4+}) was still present as vanadyl cations in an octahedral environment. However,

some line broadening in the spectrum is possibly due to the presence of vanadyl cations in more than one crystallographic site (as observed in ZSM-5 (20)) or due to dipolar broadening resulting from a concentration of vanadium species. The observed line broadening is unlikely to be from vanadyl cations in a slow tumbling mode (as observed on SiO₂) because the spectral lineshape is temperature independent.

When the vanadium-loaded EuY was calcined in the presence of 1.0 wt% tin, most of the vanadium was no longer stabilized as VO²⁺ cations but was oxidized to V⁵⁺; only about 5% V remained as VO²⁺. However, at higher Sn concentrations (1.5 and 2.0 wt%), more vanadium remained as V⁵⁺; the stereochemistry of the remaining vanadyl cations is still essentially octahedral. From Sn Mössbauer studies (14) on the same systems it has been learned that tin is present as a Sn⁴⁺ species and may form ligands to vanadium through oxygen bridges. This work confirms that any Sn/V complex formed in these samples contains (V⁵⁺-O-Sn⁴⁺) units. Also, it has been shown that without the presence of tin, most of the vanadium on EuY remains in the (4+) oxidation state prior to steaming.

Luminescence studies of EuY-containing vanadium and tin (13) have shown that, after calcination, a small proportion of the europium cations in the zeolite react with vanadium forming europium orthovanadate (EuVO₄). Vanadate concentration increased with Sn levels (13). Therefore, in the calcined EuY (containing both tin and vanadium), there are at least three types of vanadium compounds present: (i) a (V⁵⁺-O-Sn⁴⁺) oxide species, (ii) europium orthovanadate, and (iii) (VO)²⁺ cations in a pseudo-octahedral environment. Luminescence measurements (13) have indicated that the amount of V₂O₅ in these calcined samples is negligible.

From previous work (13), it was found that the worst deleterious effects of vanadium, in terms of degradation of zeolite structure, occurred during the steam aging

step. These results suggest that vanadium (present as free VO²⁺ cations) favors the breakdown of the zeolite lattice and, therefore, elimination of cracking activity. The presence of tin seems to promote the oxidation of vanadium to V⁵⁺ with formation of a vanadium-tin complex that removes VO²⁺-zeolite interactions. The order of deposition of tin and vanadium has little effect on the nature of the resulting species. When tin is deposited first the vanadium is still about 95% in the V⁵⁺ state with the remaining 5% VO²⁺ in an octahedral environment.

When the vanadium-loaded zeolite is mixed with AAA alumina (before calcining and before steaming) the resulting EPR spectra resemble those of EuY. This suggests that the bulk of the EPR active vanadium (i.e., VO²⁺ cations) is remaining on the zeolite. For the calcination procedure alone this accounts for almost all of the vanadium present; V₂O₅ formation was not observed.

The fate of vanadium on the gel is somewhat different from that on the zeolite. Vanadyl naphthenate deposited on the gel generates VO²⁺ ions which in the open three-dimensional macroporosity probably migrate to Al(IV) sites forming -Si-O-Al-OVO²⁺ linkages (1). As a result, VO²⁺ binds strongly with the gel even without calcination, to form pseudo-octahedrally coordinated VO²⁺ cations. The spectrum is well resolved and (unlike that in V-loaded EuY) the lineshape is not temperature dependent (see Fig. 4b). Furthermore, the VO²⁺ ions are not stabilized and after calcination about 95% of the vanadium is oxidized to V⁵⁺. This is reflected by the color of the sample which is yellow/green, suggesting the formation of V₂O₅ which was also verified by luminescence spectroscopy (13). The remaining 5% of the vanadium remains as pseudo-octahedrally coordinated VO²⁺. Steaming resulted in a broadening of the EPR lines without changing the EPR parameters. The lineshape was found to be temperature dependent, suggesting that the

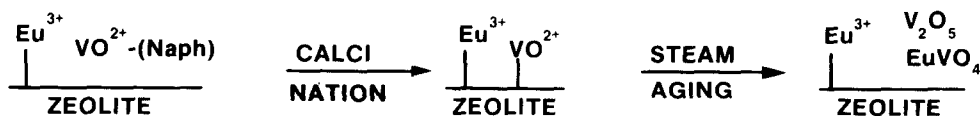
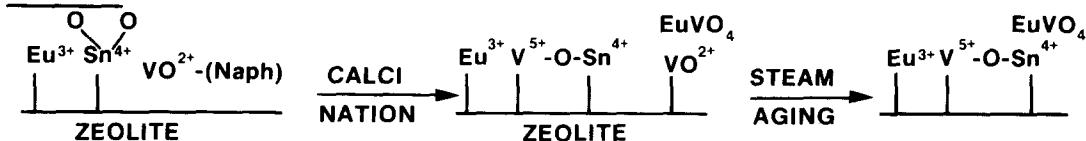
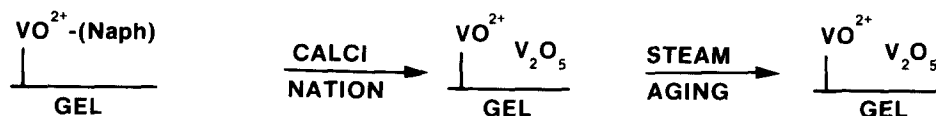
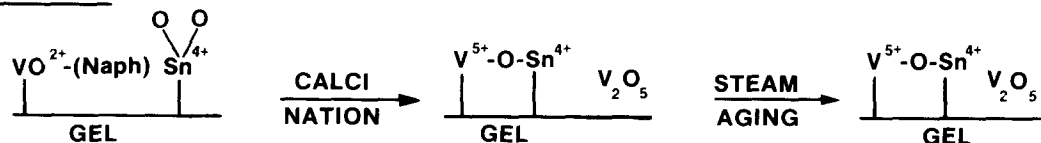
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FIG. 7. Schematic representation of V passivation by Sn in model compounds. The $\text{V}^{5+}\text{-O-Sn}^{4+}$ species is intended to represent vanadium-tin oxide compounds.

broadening may be due either to more than one VO^{2+} species (with slightly different stereochemistries) or to dipolar coupling effects due to a concentration of species. The steamed samples were still yellow/green indicating the presence of V_2O_5 .

When both tin and vanadium were loaded onto the AAA alumina and calcined, virtually all the remaining 5% VO^{2+} cations were converted into V^{5+} EPR silent species. This could also be due to a similar complexation of the vanadium with tin to give $\text{V}^{5+}\text{-O-Sn}^{4+}$ linkages in the gel. The yellow/green

color of the AAA alumina persisted, suggesting that a large proportion of the V_2O_5 remained intact and did not complex with the tin. Because of the lack of an EPR signal, it is impossible to interpret the fate of the vanadium during the steam aging process of the gel. All that may be said is that the color of the calcined AAA alumina did not change upon steaming, suggesting that V_2O_5 is an important species at all stages of treatment. This was previously suggested from luminescence studies of VO^{2+} containing FCCs (22). When the V-loaded gel

was mixed with EuY, prior to calcination there was very little VO^{2+} stabilized on the zeolite. This indirect evidence suggests that during calcination vanadium remained on the matrix. The green color of the sample supported the presence of V on the gel surface.

The EPR spectra of EuY/AAA mixtures loaded with vanadyl naphthenate indicated that vanadium was being deposited on both substrates (Figs. 6a and 6b). The EPR spectra exhibit both the temperature-dependent broad isotropic signal characteristic of VO^{2+} on the zeolites and the sharp well-defined spectrum characteristic of VO^{2+} on the gel. However, after steaming the intensity of the V^{4+} signal is quenched significantly, suggesting that most of the vanadium in the EuY/AAA mixture is sorbed by the gel. On the zeolite, VO^{2+} cations are stabilized and the EPR signal intensity is stronger. This conclusion corroborates previous work (10) where luminescence studies on the same systems also suggested that vanadium was preferentially sorbed on the gel. The vanadium remaining as V^{4+} is divided between the gel and the zeolite and the EPR spectra show features consistent with both substrates. As with the gel spectra, it is difficult to follow the subsequent fate of the vanadium since most of it is EPR silent. A schematic representation of the sequence of events on the different substrates is shown in Fig. 7.

CONCLUSIONS

Analysis of vanadium-loaded model materials by EPR can provide useful information concerning metal oxidation state and stereochemistry. Vanadyl cations, introduced in the form of vanadyl naphthenate, are stabilized in a zeolite with the faujasite structure as pseudo-octahedral VO^{2+} even after calcination at 540°C . Upon steaming, VO^{2+} cations are converted almost entirely to V^{5+} species. The formation of EuVO_4 has been verified but its concentration is never high compared to the total rare earth content of the zeolite.

It is proposed that removal of Eu^{3+} ions from exchange sites in EuY crystals during EuVO_4 formation ($2\text{Eu}^{3+} + \text{V}_2\text{O}_5 + 3\text{H}_2\text{O} = 2\text{EuVO}_4 + 6\text{H}^+$), in addition to destabilization of the faujasite structure, generates protons that perhaps enhance framework dealumination during steaming (2). Destabilization owing to enhanced dealumination and vanadate formation is believed responsible for the rapid structural collapse observed when rare-earth-exchanged zeolite Y crystals are hydrothermally heated at $700\text{--}750^\circ\text{C}/10\text{ h}$ in the presence of small amounts of V (2). The presence of V could also cause oxygen removal from the lattice and promote zeolite destabilization (23).

Tin seems to promote the oxidation of VO^{2+} to V^{5+} during steam aging with formation of $\text{Sn}^{4+}\text{--O--V}^{5+}$ complexes that are believed to minimize V-zeolite interactions, thus preserving zeolite crystallinity. The presence of excess tin seems to minimize oxidation to V^{5+} and promotes the formation of EuVO_4 ; thus excess tin is to be avoided.

On the AAA alumina matrix, vanadium is stabilized, after calcination, mainly in the form of V_2O_5 as verified by its color and by previous luminescence studies (13).

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