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IS-T--1454

DE92 001692

Studies of Vanadium-phosphorus-oxygen Selective Oxidation

catalysts by ^{31}P and ^{51}V NMR Spin-echo and Volume

Susceptibility Measurements

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M.S. thesis submitted to Iowa State University

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Date Transmitted: October 1991

Prepared for the U. S. Department of Energy

Under contract no. W-7405-eng-82.

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INTRODUCTION

Industrially, the selective oxidation of butane or butene to maleic anhydride is achieved with the aid of vanadium phosphorus oxide catalysts. Maleic anhydride (2,5-furandione) is used principally in the manufacture of unsaturated polyester resins, agriculture chemicals, food additives, lubricating oil additives and pharmaceuticals^{1,2,3}. Among the more significant potential new uses is its conversion to butanediol via hydrogenation of maleic acid. This chemistry may become economically more favorable than the present acetylene-based chemistry by 1990s^{4,5,6}. The first commercial process for maleic anhydride production appeared in 1928. This process, developed by National Aniline and Chemical, used benzene as a feedstock⁷. Since then alternative process technologies and alternative feedstocks (butane or butene feedstock) have been commercialized. The earliest patents appeared in the late 1950s, but commercial production via C-4 hydrocarbon route began to seriously rival the older route based on benzene oxidation, in terms of tonnage, at the beginning of the 1980s. In recent years, high oil prices have made benzene increasingly expensive, and required usage of unleaded gasoline for environmental protection has increased the demand for aromatics, which made of the use of benzene

as a feedstock less economically desirable⁸ . The other reason of benzene being replaced by butane as a feedstock (all production in the U.S. is butane-based) is that butane is a lower cost and environmentally more desirable raw material, and butane oxidation produces a cleaner product stream, forming mainly maleic anhydride and carbon oxides.

In recent years, maleic anhydride has been produced with a world wide capacity of about 1300 million pounds⁹ . In the 1970s, more than 70 patents related to the oxidation of butane to maleic anhydride were issued¹⁰ . The catalysts reported most often were vanadium-phosphorous oxides, either alone or mixed with activating modifiers (some transition metals). In the process, a four-carbon hydrocarbon is converted to a four-carbon product. The selectivities to maleic anhydride (MA) until now have been relatively low (50% ~ 60%), which has resulted in a strong incentive to develop improved catalyst systems¹¹ . Studies of selective oxidation of n-butane and butene to maleic anhydride over V-P-O catalysts have focused on the unsupported mixed oxide with no modifiers. Commercial catalyst formulations have included P-to-V ratios of 0.9 to 1.2 with the highest activity apparent for P/V=1.0 to 1.1^{12,13,14} . The exact effect of the P/V atomic ratio on the activity depends on the method of synthesis, including the reducing medium (organic or aqueous), and calcination temperature, duration

and atmosphere^{15,16} . There exist a wide variety of V-P-O catalysts, but one phase in particular, vanadyl Pyrophosphate, is the most important one. It seems that this particular phase, in one form or another, is involved in a type of Mars and Van Krevelan¹⁷ oxidation/reduction catalysis with the V(IV) of the pyrophosphate being oxidized to some form of V(V) ¹⁸ . As a result, the vanadyl pyrophosphate and its various oxidized forms, vanadyl phosphates, have been the subject of many investigations.

Activation of n-butane can be divided into two types: C-H bond activation and C-C bond activation. Since C-C bond activation would lead to cracking and non-selective products, most work would focus on activation of the C-H bonds. Several mechanisms of selective oxidation of n-butane have been proposed. In more recent work, Centi and Trifiro¹⁹ propose the fairly detailed mechanism presented below:

n-butane $\longrightarrow$ [1-butene $\longrightarrow$ 1,3-butadiene $\longrightarrow$ dihydrofuran $\longrightarrow$ furan] $\longrightarrow$ maleic anhydride.

The first coherent description of the structure of vanadium-phosphorus-oxygen (V-P-O) catalysts was proposed by Nakamura et al.²⁰. These workers envisaged a structure featuring aggregates of V^{4+} ions, present in a phosphate matrix on which oxygen adsorption readily occurred. Another structure model was proposed by Bordes and Courtine²¹ , and

Bordes²² based on the detection of microdomains and antiphase boundaries in used V-P-O catalysts which comprised mostly $(VO)_2P_2O_7$. They proposed a structure on which microdomains of $VOPO_4$ existed within larger domains of $(VO)_2P_2O_7$. Numerous early reports on industrial catalysts, almost all of which concentrated on V-P-O catalysts which had been prepared in aqueous media, emphasized the role of the P:V ratio in determining the final oxidation state of the catalysts^{23,24}. Starting from a reduced precursor, catalysts with high P:V ratios, i.e., >1 , tend to be resistant to oxidation during calcination in air, whereas those with low P:V ratios, i.e., <1 , tend to be easily oxidized. The phosphorus present in excess of the 1.1 ratio plays the role of inhibiting the movement of lattice oxygen through the V-P-O structure^{25,26}. The most recent studies of V-P-O catalysts have concentrated on preparations using organic media. The catalyst prepared from organic media with P:V of 1 was roughly twice as active as a catalyst with P:V of 1.1, but selectivities were similar. Most recent work has focused on correlating activity and selectivity with various preparations and techniques of activation. Of particular interest has been catalyst morphology, P/V ratio and oxidation and reduction characteristics.

The purpose of this work is to characterize the vanadium-phosphorous oxide (V-P-O) catalysts for the selective oxidation of n-butane and 1-butene to maleic

anhydride. The utility of solid state nuclear magnetic resonance as an analytical tool in this investigation lies in its sensitivity to the electronic environment surrounding the phosphorous and vanadium nuclei, and proximity of paramagnetic species. Spin-echo mapping NMR of ^{31}P and ^{51}V and volume magnetic susceptibility measurements were used as local microscopic probes of the presence of V^{5+} , V^{4+} , V^{3+} species in the model compounds: $\beta\text{-VOPO}_4$, $\beta\text{-VOPO}_4$ treated with n-butane/1-butene, $(\text{VO})_2\text{P}_2\text{O}_7$, $(\text{VO})_2\text{P}_2\text{O}_7$ treated with n-butane/1-butene; and industrial catalysts with P/V (phosphorus to vanadium) ratio of 0.9, 1.0 and 1.1, before and after treatment with n-butane and 1-butene. The NMR spectra provide a picture of how the oxidation states of vanadium are distributed in these catalysts.

REVIEW OF PREVIOUS WORK

Despite the commercial importance of this catalytic process, there remains much uncertainty concerning the mechanism of the selective oxidation of butane/butene to maleic anhydride catalysis. V-P-O catalysts are characterized by facile formation of a number of crystalline phases. The structure of the active phase must be discussed in term of factors such as oxidation state, phosphorus-to-vanadium ratio and crystal phase transformation under reactant atmospheres. Many workers have made efforts to study the oxidation states of vanadium and changes of oxidation states during catalytic reactions.

In the 1960s and 1970s, and even during the first half of the 1980s, oxidation states of vanadium were studied by chemical titration methods. Titration is easy and cheap, but not suitable for insoluble catalysts. In recent years, instrumental methods of chemical analysis which are convenient, quick and capable of being coupled with catalytic reaction systems have been sought as analytical tools.

Vanadium-phosphorous oxide catalysts have been characterized using a large number of instrumental

techniques. X-ray diffraction, infrared spectroscopy and X-ray photoelectron spectroscopy have been widely applied. However, many catalysts are sufficiently complex that the existence of several crystalline phases or amorphous phases has made identification of the active phase difficult. Application of laser raman spectroscopy²⁷ has been reported, permitting the stability of specific model catalysts to be examined under *in situ* conditions. The technique of solid electrolyte potentiometry (SEP) was recently applied to follow the oxygen activity in V-P-O catalysts during the catalytic oxidation of butene²⁸. The SEP data about the oxygen activity could be coupled with reaction rate data to help elucidate the behavior of V-P-O catalysts. The use of electron spin resonance and catalytic reaction tests²⁹ was also reported to determine the mechanism of n-butane oxidation on V-P-O catalysts. It was found that oxidation of n-butane involved the $V^{5+} \longrightarrow V^{4+}$ and $V^{4+} \longrightarrow V^{3+}$ transitions, the latter of which was accompanied by dissociation of the vanadyl bond. Reflectance UV-Visible spectroscopy coupled with electron spin resonance was used by Curilla and coworkers³⁰ to investigate the electronic structure of V-P-O catalysts. The studies are concluded that (1) the transformation of precursor into the catalytically active form of the catalyst in a nonoxidizing medium involved generation of V^{3+} ions; (2) the oxidation of

V^{3+} to V^{4+} by oxygen at temperature close to the temperature used for oxidation of n-butane (770 K) is possible; and (3) the V-P-O catalyst occurs in a partially reduced form after its interaction with n-butane oxygen mixture as well as after catalytic oxidation of n-butane to maleic anhydride.

Nuclear magnetic resonance was first used by Dr. Russel D. Walker³¹ (previous student of the Chemistry Department in the group) to investigate the oxidation states of vanadium in V-P-O catalysts in 1985. Unfortunately, results were not definitive and reasonable, which prompted the present further study. The previous work was done in a broad band homebuilt pulse NMR spectrometer³² operating at 220 MHz for 1H . Single pulse excitation was used for both ^{31}P and ^{51}V NMR experiments. The far shifted peak at 2500 ppm of ^{31}P NMR was not observed by Walker for the model compound $\beta\text{-VOPO}_4$ treated with butane and butene, $(VO)_2P_2O_7$ treated with butane and butene, and the industrial catalyst with $P/V=0.9$. No ^{31}P NMR signals were observed by Walker for the catalysts with $P/V=1.0$ and 1.1 treated by butane. The possible reasons for missing these information are limited band width of the probe in broadcasting and receiving, and not moving the carrier frequency far enough to make sure no more signals. The common chemical shift range of ^{31}P NMR is 250~461 ppm³³ relative to ^{31}P in 85% H_3PO_4 for diamagnetic compounds. The peak of ^{31}P NMR at 2500 ppm down field from phosphoric acid observed for ^{31}P in

$(VO)_2P_2O_7$ is an incredible large shift, but not surprising for the V-P-O catalysts which contain paramagnetic species. Some spectra of ^{51}V NMR done by Walker exhibit a poor signal-to-noise ratio which may be a result of poor sensitivity of the NMR spectrometer used and paramagnetic V(IV) and V(III) relaxing too rapidly.

NMR OF ^{31}P SPIN-ECHO MAPPING

General Information

^{31}P NMR

Phosphorus-31 has spin quantum number $1/2$, 100% natural abundance and relatively high sensitivity. It is an easy nucleus to observe by NMR. Even prior to 1970, a great deal of information had been obtained for simple compounds using continuous wave instruments. The advent of pulse NMR has greatly accelerated development of the field (especially in coordination chemistry and biochemistry), and ^{31}P is now one of most common of all NMR tags.

The reported chemical shifts of ^{31}P NMR are known over 250~461 ppm, but the range depends on the oxidation state. Chemical shifts found for P(V) compounds cover a much smaller range (50~100) ppm in general. If the chemical shift is far beyond that range, the effect of paramagnetic centers should be considered. The recently reported phosphorus compounds exhibit a very wide range of shielding, from the highly deshielded phosphinidene bridge in $\text{BuP}\{\text{Cr}(\text{CO})\}_2$, +1362 ppm³⁴, to the highly shielded P_4 molecule, -461 ppm³⁵. The ranges of chemical shifts are very much larger for two and three coordinate compounds

where the phosphorus atom has lone pairs of electrons than they are for four, five and six coordination where all the phosphorus electrons are involved in bonding. There is a general tendency to increased shielding of the phosphorus as the coordination increases from 2 to 6. To a first approximation, the shielding is determined by the number and type of directly bonded atoms and is relatively less affected by considerations of charge and structure. For metal complex compounds, the shift may occasionally be very large (the published record is probably -291 ppm for $\text{Cr}(\text{CO})_5(\text{PI}_3)^{36}$), and there are also many cases of erratic variations between seemingly similar ligands. In addition to the nature of the metal, its oxidation state and geometry also affect the chemical shift of phosphorus. The situation is very complex and correlations do not exist from which to make accurate predictions of chemical shifts for individual complexes. No satisfactory theory exists to predict the chemical shift of ^{31}P . Studies assume that chemical shift of phosphorus due to heavy atoms arise primarily from variations in the paramagnetic contribution from electrons in valence orbitals and attempts to account for the chemical shifts use three contributions: substituent electronegativity, bond angles, and the extent of π bonding.

The coupling constants involving ^{31}P have been studied for most of the magnetically active nuclei³⁷. The

couplings are very sensitive to the phosphorus substituents, hybridization and oxidation states, and generally increase in magnitude with substituent electronegativity and show an algebraic increase in reduced coupling constant from P^{III} to P^V . The coupling constants between directly bonded phosphorus atoms cover a very wide range, from +766 Hz in $P_2F_2O_4^{2-}$ to -451 Hz in P_2Bu_4 . The coupling constants between P-P atoms largely depend on stereochemistry, related especially to rotation about the P-P bond when lone pairs are present. The P-E-P coupling (E = nonmetal) is expected to vary with oxidation states of phosphorus atoms, the electronegativity and steric bulk of the substituents, and the degree of rotation about the P-E bonds. Any π bonding between P and E and the interbond angles at E could also be important. The most extensive studies on this kind of coupling is P-N-P linkage compounds. Couplings via oxygen are usually of small magnitude (< 35 Hz) in both P^{III} and P^V derivatives, and even with very electronegative substituents, although a few large couplings (up to 111 Hz) have been reported^{38,39}. Measurement of phosphorus-phosphorus coupling in P-M-P (M = metal) type compounds is very interesting in the study of stereochemistry of complexes. The large variation of coupling constant depends on the complex geometry, the nature of the metal, and the nature of the substituent on phosphorus. In general, this

type of coupling is in the range of a few Hz to near one thousand Hz. Coupling of P-V-P via vanadium is not reported.

General characteristics of NMR in paramagnetic systems

Paramagnetic species affect NMR spectra strongly. NMR spectra of paramagnetic samples differ from spectra of diamagnetic samples in two notable ways. First, owing to the large magnetic moments of unpaired electrons, the chemical shift scale is greatly expanded. For this reason it is often necessary to modify standard NMR spectra to extend their chemical shift ranges. That is to move the carrier frequency far beyond the normal chemical shift ranges of diamagnetic samples and retune the probe when it is required. In addition to the large resonance shifts, there is generally more or less spectral line broadening. In many cases this broadening is so severe as to obscure multiplet structure arising from spin-spin splitting. Extensive broadening is not invariably found. Another general feature of NMR spectra of paramagnetic molecules is their marked temperature dependence. Quite often isotropic shifts will be linear in $1/T$ reflecting Curie or near Curie behavior.

NMR spin-echo

In FT-NMR experiments, the FID (free induction decay) is observed following a 90 degree pulse. Initially the magnetization is at equilibrium parallel to the direction of the stationary magnetic field (z axis). The magnetic moment is then nutated by applying a 90 degree pulse so that, after the pulse, all of the individual magnetic spins are aligned along the y axis (see Figure 1), giving a non-zero value to the transverse component of the magnetization. Then the component commences to decay because of T_2 relaxation processes and inhomogeneities in the magnetic field. The larmor frequencies of different portions of sample differ slightly as a result of field inhomogeneities (or differences in chemical shifts), and in axes rotating at the mean larmor frequency, the magnetization vectors of these different portions slowly fan out and signal decays, which results in a loss of phase coherence of the individual spins. If, after a time τ , a 180°_y (note the phase change) pulse is applied, the spins will be flipped 180 degrees (see (c) in Figure 1).

Figure 1. The spin-echo effect, (a) a 90°_x pulse puts M_0 into the y direction, (b) the spin isochromates fan out, (c) a 180°_y pulse interchanges slow and fast spin at time τ , (d) refocusing occurs, (e) the echo at time 2τ

Because the individual spins are still precessing at their same individual frequencies as before, and move in the same direction, after a further time of 2τ , the magnetization again in phase in the y direction producing a signal called spin-echo. The pulse sequence for spin-echo is $90^\circ_x - \tau - 180^\circ_y - \tau - \text{acquire}$.

The advantages of using the NMR spin-echo technique is that (1) the dead time problem is avoided, (2) there is no phase distortion if precise triggering is used, (3) broad lines are observable, and (4) spurious signals are eliminated.

Experimental Procedures

Sample preparation

The preparation of model compounds β -VOPO₄ and (VO)₂P₂O₇ has been described elsewhere⁴⁰. Most catalyst samples were prepared by Mark Lashier of Dr. Glenn Schrader's research group. The industrial catalysts with composition ranges of starting materials of phosphorus to vanadium ratio P/V=0.9, 1.0 and 1.1 were also prepared⁴¹ by Lashier. During treatment with hydrocarbons (n-butane and 1-butene), the samples were exposed to a stream of 1.5 % n-butane or 1-butene in air at 450°C for 18 hours. The samples were cooled in the reactive gas and sealed under vacuum in a glass tube with quartz wool plugs at either end.

³¹P spin-echo mapping

The ³¹P NMR experiments were performed at a resonance frequency near 121.5 MHz in Bruker MSL-300 nuclear magnetic resonance spectrometer. Due to paramagnetism of V-P-O catalysts, very broad NMR signals and large shifts were observed. In order to record all real signals from the samples, a spin-echo mapping method was used at the static (nonspinning) condition. The pulse sequence of spin-echo is 90°_x - τ - 180°_y - τ - acquire. The 90 degree pulse width

was 3.3 μ s with $\tau = 20 \mu$ s. The carrier frequency was changed by 50 KHz increments to both positive and negative sides of resonance respectively. Mapping was applied until no signal was observed. The spectra (see Figures 3, 5-8) are a superposition of the spectra obtained at all offset frequencies. The time average signals at fixed offset was Fourier transformed and plotted on an absolute scale. The transient was digitized at a rate of 5 MHz. The shifts of ^{31}P are reported relative to an external standard of ^{31}P in 85% of H_3PO_4 on the δ scale with higher frequency (down field) being more positive. The model compound $\beta\text{-VOPO}_4$ before and after butane and butene treatment had relatively stronger signals and longer spin lattice relaxation times than the other samples. The model compound $(\text{VO})_2\text{P}_2\text{O}_7$, precipitated (precursor) catalysts, industrial catalysts (calcined catalysts) of P/V=0.9, 1.0 and 1.1 before and after treatment with butane and butene contain more paramagnetic species exhibit weak signals and shorter T_1 .

Results

The ^{31}P NMR spectra of the model compound $\beta\text{-VOPO}_4$, and after treatment with n-butane and 1-butene are shown in

Figure 3. The spectrum of vanadyl phosphate β -VOPO₄ is a single peak with full width at half maximum (FWHM) of 110 ppm, centered at 0 ppm which is almost the same chemical shift as ³¹P in phosphoric acid H₃PO₄. From the structure of β -VOPO₄⁴² (see Figure 2), phosphorus is believed to reside only in PO₄ tetrahedra.

Figure 2. Idealized structure of β -VOPO₄, (a) a three dimensional structure, (b) the structure of β -VOPO₄ is projected onto the ac plane

Figure 3. ^{31}P NMR spin-echo mapping spectra of $\beta\text{-VOPO}_4$, $\beta\text{-VOPO}_4$ -butane, and $\beta\text{-VOPO}_4$ -butene

The individual P-O distances range from 1.519(5) to 1.514(7) Å, but do not differ significantly from each other. The PO₄ groups share their oxygen atoms with four separate VO₆ groups. All phosphorus in β-VOPO₄ (mainly V⁵⁺) experience the nonparamagnetic environment which gives a single peak in the ³¹P NMR. However, after β-VOPO₄ is treated with n-butane, the peak at 0 ppm is broadened to 160 ppm (FWHM) wide and a distinct peak appears at 2500 ppm (down field) with FWHM of 850 ppm. The fraction of intensity under the peak at 0 ppm is 60%. After β-VOPO₄ is treated with 1-butene, a similar result as for butane treatment was obtained, but the peak near 2600 ppm is broader (FWHM about 1000 ppm) and of lower intensity (34 % of total intensity). The appearance of the second peak shifted down field gives the evidence that vanadium V⁵⁺ in β-VOPO₄ is partially reduced to a lower oxidation state, V⁴⁺, after treatment with hydrocarbons, by comparison with ³¹P NMR spectrum of the model compound (VO)₂P₂O₇ (mainly V⁴⁺ component) (*vide infra*) in Figure 5.

The NMR spectra of ³¹P in the model compound (VO)₂P₂O₇, before and after treatment with n-butane and 1-butene are shown in Figure 5. The major feature in the spectrum of ³¹P for vanadyl pyrophosphate, (VO)₂P₂O₇, is a broad peak with a maximum intensity at 2500 ppm, which contributes 94% of the total area. The FWHM of the peak is about 900 ppm. The peak at 2500 ppm is the characteristic NMR signal of ³¹P in

microscopic proximity to V^{4+} . In addition to the peak at 2500 ppm, another two small peaks are observed at about 0 ppm and 800 ppm respectively, which are believed to be a small amount of defect structures, or a small amount of partially amorphous phases. The signal at 0 ppm is from a small amount of defect containing V^{5+} , and signal at 800 ppm may be from ^{31}P in partially amorphous states. An idealized structure of vanadyl pyrophosphate^{43,44} is shown

Figure 4. Idealized $(VO)_2P_2O_7$ structure, (a) only vanadyl group, (b) projection along the (020) plane

in Figure 4. The vanadium octahedra are linked in pair through a common edge, forming double chains in this direction.

Figure 5. ^{31}P NMR spin-echo mapping spectra of $(\text{VO})_2\text{P}_2\text{O}_7$, $(\text{VO})_2\text{P}_2\text{O}_7$ -butane, and $(\text{VO})_2\text{P}_2\text{O}_7$ -butene

Each phosphorus of the pyrophosphate groups is a tridentate bridge between the vanadium atoms from three double chains and is linked by two oxygen atoms with vanadium atoms from two chains and by one oxygen atom from a third chain. After the sample is treated with n-butane and 1-butene, the peak positions and line widths exhibit no obvious change. Reducing a small amount of V^{4+} to V^{3+} on the $(VO)_2P_2O_7$ surface is possible during catalytic process. However, a sufficiently small amount of V^{3+} produced would not be observed from the ^{31}P NMR signal.

The model compound of mixed valent vanadium, $V_2(VO)(P_2O_7)_2$, contains V^{4+} and V^{3+} , and has two strong signals of ^{31}P at 1500 ppm and 4500 ppm respectively (see Figure 6). The peak at 1500 ppm is the ^{31}P near V^{4+} and the peak at 4500 ppm is one near V^{3+} . The structure of this new model was determined by single crystal X-ray diffraction and is shown in Figure 5. The structure consists of vanadium trimers linked together by $P_2O_7^{4-}$ groups. There are two trivalent vanadium atoms and one tetravalent vanadyl group in each trimer. The trivalent vanadium atoms are octahedrally coordinated by oxygen atoms while the central tetravalent vanadium atom is in a square pyramidal environment with a tightly bound, unshared oxygen atom at apex. The vanadium (IV) square pyramid shares opposite edges with each of the vanadium (III) octahedra to form a linear trimer.

Figure 6. The crystal structure of $V_2(VO)(P_2O_7)_2$

The ^{31}P NMR spectra of the industrial catalyst with preparation stoichiometry, phosphorus to vanadium molar ratio of 0.9, are shown in Figure 8. The precipitated catalyst (precatalyst) shows an intense peak at 1800 ppm. However, after air calcination, the catalyst with $P/V = 0.9$ develops two peaks with some overlap, one having maximum intensity at 0 ppm and the other one at 2500 ppm. After treatment with n-butane, the catalyst $P/V=0.9$ shows a broad peak with maximum intensity at 2500 ppm and broad base from 0 ppm to 4000 ppm (see Figure 8). The catalyst with $P/V=0.9$ treated with 1-butene exhibits two overlapping peaks, one

with maximum at 2500 ppm which is broader and highest intensity. The other one is centered at 0 ppm. Comparing the spectra of catalyst P/V=0.9 with catalyst P/V=0.9/butane, and with catalyst P/V=0.9/butene in Figure 8, it is clearly seen that the peak at 0 ppm in the untreated catalyst disappears after butane treatment, and is decreased greatly by butene treatment. Using the observed chemical shifts of ^{31}P in the model compounds $\beta\text{-VOPO}_4$ and $(\text{VO})_2\text{P}_2\text{O}_7$, V^{5+} in the catalyst with P/V=0.9 is partially or totally reduced to V^{4+} by treatment with hydrocarbons.

The ^{31}P NMR spectra of the industrial catalyst with preparation stoichiometry P/V=1.0, before and after treatment with n-butane and 1-butene are shown in Figure 9. The spectrum of precipitated, uncalcined catalyst shows a major peak at 1800 ppm. The spectrum of the catalyst with P/V=1.0 exhibits two peaks, one at 0 ppm and the other one with similar intensity at 2500 ppm which is broader. After treatment with butane, the spectrum spreads between 0 and 4000 ppm with a maximum at 2500 ppm. After treatment with butene, the catalyst exhibits a wide peak with maximum at 2500 ppm. The results are similar to those of the catalyst with P/V=0.9 treated with butane and butene, but the reduction of V^{5+} to V^{4+} is quantitatively different.

The NMR spectra of ^{31}P in the industrial catalyst with preparation stoichiometry P/V=1.1, before and after treatment with n-butane and 1-butene are shown in Figure 10.

The precipitated catalyst has a major peak at 1800 ppm which is the same as the other industrial catalysts with $P/V=0.9$ and $P/V=1.0$. The catalyst with $P/V=1.1$ shows two overlapping peaks, the most intense peak being at 2500 ppm and the other centered one at 0 ppm. After treatment with butane, this catalyst exhibits a broad spectrum with major intensity at 2500 ppm. A low intensity region develops between 0 ppm and 2000 ppm. After treatment with butene, the situation is similar to that with treatment by butane, but the spectrum shows a stronger intensity at 2500 ppm and lower intensity at 0 ppm. The 0 ppm peak in the catalyst with $P/V=1.1$ disappears after treatment with hydrocarbons, giving evidence of reduction of V^{5+} to V^{4+} .

Figure 7. ^{31}P NMR spectrum of spin-echo mapping of $\text{V}_2(\text{VO})(\text{P}_2\text{O}_7)_2$

Figure 8. ^{31}P NMR spectra of spin-echo mapping of precatalyst $\text{P/V} = 0.9$, catalyst $\text{P/V} = 0.9$, catalyst $\text{P/V} = 0.9$ -butane, and catalyst $\text{P/V} = 0.9$ -butene

Figure 9. ^{31}P NMR spectra of spin-echo mapping of precatalyst P/V=1.0, catalyst P/V=1.0, catalyst P/V=1.0-butane, and catalyst P/V=1.0-butene

Figure 10. ^{31}P NMR spectra of spin-echo mapping of precatal. $P/V=1.1$, catal. $P/V=1.1$, catal. $P/V=1.1$ -butane, and catalyst $P/V=1.1$ -butene

NMR OF VANADIUM-51

General Information

Vanadium in vanadium-phosphorus-oxygen catalysts has an important catalytic function. The oxidation state of the vanadium in the catalysts is a critical factor in the mechanism of oxidation of butane or butene to maleic anhydride. Vanadium-51 is a favorable nucleus for NMR observation. Because of its natural abundance of 100% and fairly high magnetogyric ratio of 1.12 KHz/Gauss, achieving suitability of signal-to-noise ratio is well within the capability of current NMR instrumentation.

Unlike the spin 1/2 nucleus ^{31}P , vanadium-51 has spin quantum number of 7/2, and quadrupole moment of $0.3 \times 10^{-28} \text{ cm}^2$ putting it in the category of medium quadrupole coupling constant, where NMR signal widths are highly sensitive to electric field gradient at the nucleus^{45,46}. An electric quadrupole moment arises from an asymmetry of the distribution of the electric charge in the nucleus and does not depend on the net charge. It is often viewed as two electric dipoles displaced from one another and pointing in opposite directions. It has the unit of charge times area although it is usually given in unit of cm^2 , the electric charge having been divided out. The electric quadrupole

moment becomes important only when the nucleus is in an electric field gradient (EFG)^{47,48} either static or dynamic. Any environment that does not have cubic symmetry will provide such EFG. In any case, the quadrupole moment of vanadium-51 is small enough that in most samples the quadrupole broadening will not be so severe that the signal will be broadened into the baseline. In a stationary EFG, the quadrupole interaction shifts the Zeeman levels. The NMR signal of ^{51}V , is supposed (theoretically) to split into seven peaks to first order in the perturbation treatment of the effect of the quadrupolar interaction on an Zeeman levels (see Figure 11).

Figure 11. First order powder pattern of a quadrupolar interaction for a nucleus with $I = 7/2$

The splitting can be large compared to NMR broadcasting and receiving bandwidths, and the irradiation and the detection of such transitions can be difficult. The most intense peak corresponding to the central transition remains at about the frequency at which the nucleus would resonate in the absence of a quadrupole interaction and it is this peak that is observed with single pulse NMR experiments.

Some of the samples studied here involved V^{3+} and V^{4+} which contain unpaired electrons. These paramagnetic species in the sample sometimes give rise to difficulties in detection of NMR measurements. The electron has a very large magnetic moment. Therefore if an unpaired electron is present in the sample, e.g., in the form of a free radical or paramagnetic ion, it will have a dramatic effect on the NMR spectrum. First, the nuclei and the electron will undergo scalar coupling (the magnitude is represented as A), or s-state hyperfine coupling. Therefore the coupling to the electron spins must be averaged over the electron spin orientations of many electrons. In the absence of an external field, there is no preferential orientation for electron spins, and thus there is zero average magnetic coupling to the nuclei. On the other hand, the application of a static field polarizes the electron spins, giving a nonvanishing coupling. Second, there will be a dipole-dipole interaction which may also provide an efficient relaxation mechanism for the nucleus. The consequences of

these two effects depend initially on the electron relaxation time (T_1^e). If this is comparable with A, $(T_1^e)^{-1} \sim A \sim \text{MHz}$, as is normally the case in free radicals, then the NMR spectrum is so broadened by T_1 relaxation that it is unobservable. If, as is quite often the case in paramagnetic complexes (T_1^e) $\gg$ A, then sharp lines are observed in the NMR spectra which show large shifts^{49,50}.

Experimental

Single pulse experiment

⁵¹V NMR experiments were performed on Bruker MSL-300 spectrometer at about 78.86 MHz. A 3.0 μ seconds pulse width maximized the signals. A recycle time of 2 seconds was used to avoid saturation. Samples were measured under static (nonspinning) conditions. 988 number of scans were used for all samples. V_2O_5 (the spectrum is shown in Figure 13) was used as an external reference for chemical shift scale. In Figure 19, all spectra were taken under the same experimental conditions in order to be able to compare signal intensities. The plots are on an absolute intensity scale.

^{51}V NMR spin-echo studies

To obtain better signal intensities for the samples which give very weak ^{51}V NMR signals like $(\text{VO})_2\text{P}_2\text{O}_7$, the spin-echo mapping experiment was applied. All spectra are obtained on Bruker MSL-300 spectrometer under static conditions. A 5.6 μs of pulse width which maximize the NMR signal was used. A 15 μs delay follows the first pulse. Then a 11.2 μs of pulse which gives no signal was applied. The 5.6 μs pulse and 11.2 μs pulse are equivalent to 90 degree and 180 degree pulse, respectively, in the situation of nuclear with spin quantum number of $I = 1/2$. The acquisition was started at 17 μs after the second pulse. The spectra of each sample were composed of many spectral lines in different probe tuning and carrier (broadcast) frequencies. The frequency of 50 KHz was shifted for each probe tuning and broadcasting. V_2O_5 was used as an external reference. A recycle time of 4 seconds and 100 scans was used for the model compound VOPO_4 , VOPO_4 -butane and VOPO_4 -butene. The other samples contained paramagnetic species, and a relatively short recycle time of 0.4 seconds and 1400 scans were used. The spectra were plotted in absolute scale (scale 1). The spectra of $(\text{VO})_2\text{P}_2\text{O}_7$, $(\text{VO})_2\text{P}_2\text{O}_7$ -butane, $(\text{VO})_2\text{P}_2\text{O}_7$ -butene and catalyst $\text{P/V}=1.1$

treated with butene were plotted in absolute scale (scale 8, means that spectra are enlarged by eight times of scale 1).

Results

Single pulse experiment

The ^{51}V NMR signals for the samples VOPO_4 , VOPO_4 treated with butane, catalyst $\text{P/V}=0.9$, pretreated catalyst $\text{P/V}=0.9$, catalyst $\text{P/V}=1.0$ (spectra in Figures 14, 16 and 17) were clearly observed at 0 Hz, the same shift as model compound V_2O_5 (0 Hz single peak for central transition of vanadium $I=7/2$, $1/2 \rightarrow -1/2$, see Figure 13). The NMR signal for the catalyst $\text{P/V}=0.9$ treated with butane is very weak. The samples $(\text{VO})_2\text{P}_2\text{O}_7$, catalyst $\text{P/V}=1.0$ treated with butane, catalyst $\text{P/V}=1.1$ and catalyst $\text{P/V}=1.1$ treated with butane (see Figures 15, 17 and 18) showed very weak signals near 0 Hz. The signals are very hard to distinguish from background, and no signal were observed at other offset frequencies. Although the signals for all the samples appeared at the same positions (about 0 Hz), they showed different line width and intensity in the same experimental conditions. In Figure 17, all spectra are plotted together

in order to compare the signal intensities. The NMR signal of the model compound V_2O_5 shows that the peak at 0 Hz represents the V^{5+} signal, since V_2O_5 contains primarily V^{5+} , and only small amounts of V^{4+} exist as defects. The structure of the model compound V_2O_5 is shown in Figure 12.

Figure 12. Idealized structure of V_2O_5 , (a) viewed perpendicular to a layer, (b) viewed end on to a layer (the longer V-O bonds have been omitted)

Each vanadium atom in V_2O_5 forms five bonds to oxygen atoms, one at 1.585 Å which is roughly perpendicular to the plane, while the other four equatorial V-O bond lengths are 1.80 Å, two 1.88 Å, and 2.02 Å⁵¹. No signals from V^{4+} or V^{3+} in the model catalyst $(VO)_2P_2O_7$ and other catalyst samples were

observed by single pulse ^{51}V NMR. The ^{51}V NMR spin-echo studies (*vide infra*) showed that all spectra from the samples which give signals had similar line shapes. It is reasonable to presume that the integrated area of NMR peak from these catalysts are comparable. The Table 1 includes integrated area for per gram of catalyst, which gives the relative amount of observable Vanadium in the samples.

Table 1. Relative amounts of vanadium observed by ^{51}V single pulse NMR in the catalysts

Sample	NMR peak area per gram of sample
V_2O_5	1000
$\beta\text{-VOPO}_4$	202
$\beta\text{-VOPO}_4\text{-butane}$	84
$(\text{VO})_2\text{P}_2\text{O}_7$	0
Precatalyst P/V=0.9	44
Catalyst P/V=0.9	81
Catalyst P/V=0.9-butane	29
Catalyst P/V=1.0	36
Catalyst P/V=1.0-butane	0
Catalyst P/V=1.1	0
Catalyst P/V=1.1-butane	0

Figure 13. ^{51}V single pulse NMR spectrum of V_2O_5

Figure 14. 51v single pulse NMR spectra, (a) $\beta\text{-VOPO}_4$
(b) $\beta\text{-VOPO}_4$ treated with butane

Figure 15. ^{51}V single pulse NMR spectra,
(a) empty probe-background (b) $(\text{VO})_2\text{P}_2\text{O}_7$

Figure 16. ^{51}V single pulse NMR spectra,
(a) catalyst $P/V=0.9$
(b) pretreated catalyst $P/V=0.9$,
(c) catalyst $P/V=0.9$ treated by butane

Figure 17. 51v single pulse NMR spectra,
(a) catalyst P/V=1.0
(b) catalyst P/V=1.0 treated by butane

Figure 18. 51v single pulse NMR spectra,
(a) catalyst P/V=1.1
(b) catalyst P/V=1.1 treated by butane

Figure 19. ^{51}V single pulse NMR spectra. All spectra are taken under same experimental conditions and plotted in absolute scale. Same amount of the samples was used. (a) $\beta\text{-VOPO}_4$, (b) catal. $\text{P/V}=0.9$, (c) $\beta\text{-VOPO}_4$ -butane, (d) catal. $\text{P/V}=1.0$, (e) $\text{P/V}=1.1$, (f) precatal. $\text{P/V}=0.9$, (g) catal. $\text{P/V}=1.1$ -butane, (h) catal. $\text{P/V}=0.9$ -butane, (i) catal. $\text{P/V}=1.0$ -butane

^{51}V NMR spin-echo mapping

The ^{51}V NMR spin-echo mapping of the model compound VO_2 (V_2O_4) was done on the Bruker MSL-300 under static conditions. The spectrum of VO_2 exhibits a first order quadrupole powder pattern (see Figure 21). The central transition ($-1/2 \rightarrow +1/2$) of ^{51}V ($I = 7/2$) stays about 2500 ppm relative to V_2O_5 as external standard. Seven peaks (represent seven transitions) spread 20000 ppm wide. The signal of ^{63}Cu appears at 10400 ppm down field which overlaps with

Figure 20. Structure of VO_2 , (a) three-dimensional structure, (b) Projection of the structure on (010) plane

Figure 21. NMR spin-echo mapping spectrum of ^{51}V of VO_2

one of the ^{51}V transition ($-7/2 \rightarrow -5/2$). VO_2 is composed of V^{4+} and oxygen with V-O distances ranging from 1.76 to 2.05 Å in deformed rutile structure⁵². Figure 20 shows a three dimensional and projection structure of VO_2 . V^{4+} in VO_2 stays in the center of distorted octahedra joined by edges to form strings. VO_6 octahedra are mutually connected by corners to form a three dimensional network.

The spectra of the model compound $\beta\text{-VOPO}_4$, before and after treatment with n-butane and 1-butene are shown in Figure 22. $\beta\text{-VOPO}_4$ (sample weight 0.1903 grams) exhibits a broad peak from 2000 ppm to -2000 ppm wide with center at 0 ppm. After treatment with butane ($\beta\text{-VOPO}_4$ -butane, sample 0.2124 g) and butene ($\beta\text{-VOPO}_4$ -butene, sample 0.1916 g), the samples show a peak at the same position as those untreated, but with broader width and different intensity. The intensity ratio (area ratio) of $\beta\text{-VOPO}_4$: $\beta\text{-VOPO}_4$ -butane : $\beta\text{-VOPO}_4$ -butene is 1 : 0.53 : 0.66. The peak observed at 0 ppm represents the amount of observable V^{5+} in the samples. The above results of ^{51}V NMR provide the evidence that V^{5+} on the surface or near surface layers of $\beta\text{-VOPO}_4$ is reduced after hydrocarbon treatment, which is also proved by results of ^{31}P NMR (see previous part: NMR of ^{31}P spin-echo mapping).

The spectra of $(\text{VO})_2\text{P}_2\text{O}_7$, before and after treatment with butane and butene are shown in Figure 23. These spectra exhibit low signal-to-noise ratio because $(\text{VO})_2\text{P}_2\text{O}_7$

which contains V^{4+} is a paramagnetic (d^1) compound. One peak was observed at about 0 ppm for these three samples with different line widths and intensities. The intensity ratio of $(VO)_2P_2O_7$ (sample weight 0.1933 g) : $(VO)_2P_2O_7$ - butane (0.3371 g) : $(VO)_2P_2O_7$ - butene (0.3171 g) is 1 : 0.89 : 0.97. There is a small decrease in peak area after treatment with butane and butene. The decrease of amount of observable vanadium may be caused by production of V^{3+} in the sample after treatment with hydrocarbons. The peak at 0 ppm in these three samples is believed to be the NMR signal of $V(V)$. There is no V^{4+} NMR signal (with first order quadrupole interaction) observed in VO_2 and a very weak intensity of the broad peak observed from -2000 to -2000 ppm. It is clear that electron-nuclear interactions in $(VO)_2P_2O_7$ broaden the V^{4+} NMR signal beyond observation. There is no ^{51}V NMR signal observed for the model compound $V_2(VO)(P_2O_7)_2$ under conditions of 2542 scans and 0.2 s recycle time.

The spectrum of the calcined industrial catalyst with phosphorus to vanadium ratio $P/V=0.9$ is shown in Figure 24 (sample weight 0.0709 g). The spectrum of the uncalcined catalyst (precursor catalyst) with $P/V=0.9$ is shown in Figure 25 (0.1019 g). The catalyst with $P/V=0.9$ treated by butane (0.1131 g) and butene (0.1084 g) in Figure 26 exhibit a peak at 0 ppm, the same position as the model compounds.

But the peaks of different samples have different intensities and line widths. The intensity ratio of P/V=0.9 catalyst : precatalyst : P/V=0.9-butane : P/V=0.9-butene is 1 : 0.63 : 0.22 : 0.55. The decrease of the peak area means the decrease of amount of observable V^{5+} in the samples, which provides the evidence of reduction of V^{5+} to V^{4+} in the samples after treatment with butane and butene. The amount of V^{5+} in P/V=0.9-butene is more than that in P/V=0.9-butane. The results of ^{51}V NMR nicely complement with the results of the NMR ^{31}P spin-echo mapping.

The industrial catalyst (calcined catalyst) with P/V=1.0 (sample weight 0.0806 g), precipitated (uncalcined) catalyst with P/V=1.0 (0.1061 g), and the catalysts treated with butane (0.0706 g) and with butene (0.0898 g) in Figure 27 show single peaks at 0 ppm with different intensities and line widths. The area ratios of catalyst P/V=1.0 : precatalyst : P/V=1.0-butane : P/V=1.0-butene is 1 : 0.097 : 0.25 : 0.26. The decrease in amount of V^{5+} in the catalyst with P/V=1.0 after treatment with hydrocarbon supports the inference from spin-echo mapping NMR of ^{31}P , that V^{5+} on surface of catalyst is reduced to V^{4+} or V^{3+} after reaction.

The NMR spectra of the industrial catalyst with P/V=1.1 (sample weight 0.1036 g) and the catalysts treated with butane (0.1050 g) are shown in Figure 28, and with butene (sample weight 0.1163 g) in Figure 29. The spectrum in

Figure 29 was enlarged by eight times when plotting. Weak signals are exhibited at 0 ppm. The precipitated catalyst with $P/V=1.1$ (0.1009 g) did not show an obvious signal within the range of -5000 ppm to +5000 ppm at 1400 scans. The intensity ratio of the peak centered at 0 ppm is 1 : 0 : 0.69 : 0.14 for the catalyst with $P/V=1.1$: precatalyst : $P/V=1.1$ -butane : $P/V=1.1$ -butene. The peak intensities of the samples treated with hydrocarbons are largely decreased, which means that the catalyst (V^{5+}) is reduced after treatment with butane and butene. The same inference is obtained by spin-echo mapping studies of NMR ^{31}P .

Table 2 includes the relative NMR signal intensities of observable vanadium per gram of model compound and per mole of vanadium present. The Table 3 includes relative NMR intensities of observable vanadium per gram of industrial catalysts and equal moles of vanadium present.

Table 2. Relative intensities of vanadium in
model compounds
(Results of ^{51}V NMR spin-echo mapping)

Sample	Intensity (per gram)	Intensity (per mole V)
V_2O_5	100	100
$\beta\text{-VOPO}_4$	20.2	36
$\beta\text{-VOPO}_4\text{-butane}$	10	19
$\beta\text{-VOPO}_4\text{-butene}$	13	23
$(\text{VO})_2\text{P}_2\text{O}_7$	0.15	0.5
$(\text{VO})_2\text{P}_2\text{O}_7\text{-butane}$	0.13	0.45
$(\text{VO})_2\text{P}_2\text{O}_7\text{-butene}$	0.14	0.48
$\text{V}_2(\text{VO})(\text{P}_2\text{O}_7)_2$	0	0

Table 3. Relative intensities of vanadium
in industrial catalysts
(Results of ^{51}V NMR spin-echo mapping)

Sample	Intensity (per gram)	Intensity ^a (equal mole of V)
$\beta\text{-VOPO}_4$	100	100
Catalyst P/V=0.9	25.3	22.8
Catalyst P/V=0.9-butane	5.5	4.9
Catalyst P/V=0.9-butene	14.0	12.6
Precatalyst P/V=0.9	16.0	14.4
Catalyst P/V=1.0	20.8	20.8
Catalyst P/V=1.0-butane	5.3	5.3
Catalyst P/V=1.0-butene	5.5	5.5
Precatalyst P/V=1.0	2.0	2.0
Catalyst P/V=1.1	6.6	7.3
Catalyst P/V=1.1-butane	4.5	4.9
Catalyst P/V=1.1-butene	0.94	1.0
Precatalyst P/V=1.1	0	0

^aThe intensities per mole of V are calculated by the intensities per gram times the P/V ratios.

Figure 22. ^{51}V NMR spin-echo mapping spectra, (a) $\beta\text{-VOPO}_4$, (b) $\beta\text{-VOPO}_4$ -butane, (c) $\beta\text{-VOPO}_4$ -butene

Figure 23. ^{51}V NMR spin-echo mapping spectra
 (a) $(\text{VO})_2\text{P}_2\text{O}_7$, (b) $(\text{VO})_2\text{P}_2\text{O}_7$ -butane
 (c) $(\text{VO})_2\text{P}_2\text{O}_7$ -butene

Figure 24. ^{51}V NMR spin-echo mapping spectrum of catalyst P/V=0.9

Figure 26. ^{51}V NMR spin-echo mapping spectra
(a) catalyst P/V=0.9 - butene
(b) catalyst P/V=0.9 - butane

Figure 25. ^{51}V NMR spin-echo mapping spectrum of precatalyst P/V=0.9

Figure 27. ^{51}V NMR spin-echo mapping spectra,
(a) catal. P/V=1.0, (b) precatal. P/V=1.0,
(c) catalyst P/V=1.0 - butene
(d) catalyst P/V=1.0 - butane

Figure 28. ^{51}V NMR spin-echo mapping spectra,
(a) precatalyst $\text{P}/\text{V}=1.1$,
(b) catalyst $\text{P}/\text{V}=1.1$ -butane, (c) catalyst $\text{P}/\text{V}=1.1$

Figure 29. ^{51}V NMR spin-echo mapping spectrum of catalyst P/V=1.1 treated with butene

VOLUME SUSCEPTIBILITY

General Information

Molecules may be thought of as being composed of electrons moving around nuclei, so it is easy to see how molecules might possess classical magnetic dipole moments. The situation is complicated by the fact that electrons also possess an intrinsic magnetic dipole moment, which is independent of its ordinary orbital motion, and the total magnetic moment of the molecule is a sum of orbital and intrinsic moments. The magnetic properties of bulk samples are largely determined by the orbital electron, electron spin, and field induced molecular moments. In a uniform electric field, molecules may experience a net force. This is because positive and negative charges do exist and ionized molecules are not electrically neutral. A molecule may experience a torque in a uniform magnetic field, for its energy can depend upon its orientation in the field. This torque arises from the interaction of the field and a molecule magnetic dipole moment. We consider a magnetic dipole as arising from a current loop formed by a rotation charge (see Figure 30). As indicated in Figure 30, a relatively large magnetic moment, counter to the applied

field, is induced via a ring current when the plane of the benzene ring is

Figure 30. Qualitative view of the diamagnetic ring current effect for benzene

perpendicular to the applied field. The magnetic lines of force so induced reinforce the applied field for the in-plane hydrogens. An analogous situation occurs for magnetically paramagnetic complexes (see Figure 31). When an average over all possible orientations is taken for paramagnetic molecules, the situation in bulk solids, a down field shift will result in the NMR signal.

When a magnetic dipole is placed in a magnetic field, it experiences a turning effect, which is proportional to a specific character termed the magnetic moment. The magnetization can be defined as magnetic moment per unit volume. The intensity of magnetization I induced at any

point in a body is proportional to the strength of the applied field H , $I = \kappa H$, where κ is a constant of proportionality depending on the material of the body. It is called the magnetic susceptibility per unit volume (volume susceptibility), and may be defined qualitatively as the extent to which a material is susceptible to induced magnetization. For an isotropic body the susceptibility is the same in all directions. However, for anisotropic crystals the susceptibility along the three principal axes are different, and measurement on their powdered samples give the average of the three values. The present study is based on the principle that the chemical shift $\Delta H/H$ depends on the volume susceptibility of the sample. $\Delta H/H$ is proportional to $\Delta \kappa$, where $\Delta \kappa$ is the change in volume susceptibility.

Figure 31. Qualitative picture of the effect of paramagnetic anisotropy ($\chi_{||} > \chi_{\perp}$)

Experimental

The volume susceptibility measurements⁵³ were performed on a 220 MHz (^1H) homebuilt spectrometer described elsewhere³². The arrangement of the NMR tube for susceptibility measurements is shown in Figure 32.

Figure 32. NMR tube used in susceptibility measurement

A small tube of water is surrounded by a paramagnetic sample. The proton resonance in water is then shifted down field, as a result of the increase magnetic induction at the protons due to the bulk susceptibility of surrounding medium. Thirty scans were taken for each sample. In order to shorten the spin lattice relaxation time of protons, the distilled water in the center capillary tube was doped with about 1% CuSO_4 . Each measurement was kept in the same

volume and same experimental conditions. The reported paramagnetic shifts of all samples are relative to the shift of water in the center tube without sample present.

Results

The theoretical volume susceptibility of Gd_2O_3 can be obtained from Curies Law (Formula 1)

$$\kappa = 2Ng^2\beta^2S(S+1) / 3kTV \quad (1)$$

with temperature at 298K. A molar volume of $233 \text{ cm}^3\text{mol}^{-1}$ is assumed to be same for all the samples studied here. The values of volume susceptibility of all samples are calculated by using the following formula (2).

$$\kappa_u = \kappa_s (\Delta H_u / \Delta H_s) = (2.26 \times 10^{-4} / 20928\text{Hz}) \Delta H_u \quad (2)$$

Here κ_u is the volume susceptibility of unknown samples. κ_s is theoretical volume susceptibility of Gd_2O_3 , which is equal to 2.26×10^{-4} calculated by using formula (1). ΔH_u and ΔH_s are the paramagnetic shifts of unknown samples and standard sample (Gd_2O_3 , 20928Hz) relative to the shifts of water in units of Hertz. The paramagnetic shifts observed by NMR, and results of volume susceptibility for model compounds, industrial catalysts, and those treated with butane and butene are presented in Table 4.

Table 4. Results of volume susceptibility measurements

Sample	Shift (Hz) ΔH	Volume Susceptibility κ (c.g.s.)
H ₂ O	0	
Gd ₂ O ₃	20928	$2.26 * 10^{-4}$
β -VOPO ₄	4	$4.3 * 10^{-8}$
β -VOPO ₄ -butane	67	$7.2 * 10^{-7}$
β -VOPO ₄ -butene	264	$2.8 * 10^{-6}$
(VO) ₂ P ₂ O ₇	688	$7.4 * 10^{-6}$
(VO) ₂ P ₂ O ₇ -butane	1023	$1.1 * 10^{-5}$
(VO) ₂ P ₂ O ₇ -butene	1030	$1.1 * 10^{-5}$
Precatalyst P/V=0.9	181	$1.9 * 10^{-6}$
Precatalyst P/V=1.0	261	$2.8 * 10^{-6}$
Precatalyst P/V=1.1	303	$3.3 * 10^{-6}$
Catalyst P/V=0.9	56	$6.0 * 10^{-7}$
Catalyst P/V=1.0	70	$7.5 * 10^{-7}$
Catalyst P/V=1.1	264	$2.8 * 10^{-6}$
Catalyst P/V=0.9-butane	386	$4.2 * 10^{-6}$
Catalyst P/V=0.9-butene	365	$3.9 * 10^{-6}$
Catalyst P/V=1.0-butane	353	$3.8 * 10^{-6}$
Catalyst P/V=1.0-butene	390	$4.2 * 10^{-6}$
Catalyst P/V=1.1-butane	427	$4.6 * 10^{-6}$
Catalyst P/V=1.1-butene	439	$4.7 * 10^{-6}$
V ₂ (VO)(P ₂ O ₇) ₂	1440	$1.6 * 10^{-5}$

The resonance frequency of a proton in the magnetic field is a linear function of the magnetic induction at the nucleus. The magnetic induction depends on the magnetic field intensity and static magnetic susceptibility of the medium surrounding the nucleus. The model compounds β -VOPO₄ and (VO)₂P₂O₇ treated with butane and butene exhibit larger shifts than untreated samples. The values of volume susceptibility increase with increase of phosphorus to vanadium ratio in catalysts, which means the susceptibility of catalysts exhibit the trend: $P/V=1.1 > P/V=1.0 > P/V=0.9$. All industrial catalysts show an increase of susceptibility after treatment with butane and butene. These results are in accord with the trends observed in the spin-echo mapping of ³¹P NMR and ⁵¹V NMR.

WET CHEMICAL ANALYSIS

Experimental

Determination of the oxidation state of vanadium was attempted for model compounds: VO_2 (V_2O_4), V_2O_5 , $\beta\text{-VOPO}_4$, $(\text{VO})_2\text{P}_2\text{O}_7$ and $\text{V}_2(\text{VO})(\text{P}_2\text{O}_7)_2$, and some industrial catalysts: precursor catalysts $\text{P/V}=0.9$ and 1.0 , catalysts $\text{P/V}=0.9$, 1.0 and 1.1 , and catalyst $\text{P/V}=0.9$ treated with butane. The dissolution procedure⁵⁴ was to place about 0.1 grams of a sample into 17.0 ml of $12\text{ M H}_3\text{PO}_4$ and to boil the resulting solution until completely dissolved. The model compounds dissolved relatively easier than the industrial catalysts. For some industrial catalysts, continuous boiling about 1 hour (even four hours) did not result in complete dissolution.

The clear solutions of completely dissolved samples were added into a water solution in which 10 ml of concentrated sulfuric acid had been added in advance, and diluted to a total volume of 250 ml. The average oxidation number of vanadium was determined by a redox titration procedure similar to that employed by Nakamura et al.⁵⁵. All vanadium ions (V^{4+} and V^{3+}) were oxidized to pentavalent ions by titration with KMnO_4 solution and pentavalent ions were reduced to V^{4+} by a subsequent titration with standard

FeSO_4 solution using diphenyl amine dissolved in concentrated phosphoric acid as an indicator.

Results

The model compounds were dissolved completely into solutions within a relatively short period of time. The average oxidation states of vanadium in model compounds were obtained by redox titration. The results of titration of model compounds yield oxidation states of vanadium calculated from stoichiometry, indicating that this method works well for model compounds. The results of titrations for model compounds are shown in Table 5. However, some industrial catalysts do not completely dissolve into 12 M phosphoric acid within a relatively short period of time, which results in failure to determine the oxidation states of vanadium in these industrial catalysts. The weights of samples, the boiling time and results of dissolution for industrial catalysts are listed in Table 6.

Another dissolution method⁵⁶ was also tried. About 0.1 to 0.2 grams of unsupported industrial catalysts were placed into a mixture of 10 ml of 18 N sulfuric acid and 4 ml of 46 % hydrofluoric acid. All the model compounds and industrial catalysts do not dissolve, even with heating the solution to boiling.

Table 5. Oxidation states of vanadium in model compounds
determined by titration vs. calculated from
stoichiometry

Compound	Oxidation State from Titration	Oxidation State from Stoichiometry
V_2O_5	5.0	5.0
VO_2	4.0	4.0
$\beta\text{-VOPO}_4$	4.9	5.0
$(VO)_2P_2O_7$	3.9	4.0
$V_2(VO)(P_2O_7)_2$	3.5	3.3

Table 6. Dissolution results of industrial catalysts

Sample	Weight (g)	Boiling Time	Dissolution Results
Precat. P/V=0.9	0.0520	10 min.	Partially dissolved green color solution. Suspensions remain.
Precat. P/V=1.0	0.0769	20 min.	Same results as precat. P/V=0.9
Catalyst P/V=0.9	0.0447	5 min.	Completely dissolved green yellowish color solution.
Catalyst P/V=1.0	0.0784	20 min.	Clear green color solution. Some small Black particles remain.
Catalyst P/V=1.1	0.0476	4 hrs.	Light blue color solution. Many black particles remain.
Catalyst P/V=0.9 treated with butane	0.0690	1 hrs.	Green color solution. Many fine black particles remain.

SUMMARY OF RESULTS FROM ^{31}P , ^{51}V NMR AND SUSCEPTIBILITY

Table 7. Summary of model compounds

Sample	^{31}P NMR Peak Position (ppm)	^{51}V NMR (Intensity)	Volume Susceptibility
V_2O_5	no signal	100%	
$\beta\text{-VOPO}_4$			
untreated	one at 0	36%	4.3×10^{-8}
C_4H_{10} -treated	major at 0 weak at 2500	19%	7.2×10^{-7}
C_4H_8 -treated	major at 0 weak at 2500	23%	2.8×10^{-6}
$(\text{VO})_2\text{P}_2\text{O}_7$			
untreated	major at 2500 very weak at 0	0.5%	7.4×10^{-6}
C_4H_{10} -treated	same as untreated	0.45%	1.1×10^{-5}
C_4H_8 -treated	same as untreated	0.48%	1.1×10^{-5}
$\text{V}_2(\text{VO})(\text{P}_2\text{O}_7)_2$	stronger at 1500 weaker at 4500	0 %	1.6×10^{-5}

Table 8. Summary of industrial catalysts

Sample	^{31}P NMR Peak Position (ppm)	^{51}V NMR (Intensity)	Volume Susceptibility
V_2O_5		100%	
$P/V=0.9$			
Catalyst	one at 2500 a little stronger at 0	10%	6.0×10^{-7}
C_4H_{10} -treated	one broad at 2500	2.2%	4.2×10^{-6}
C_4H_8 -treated	strong at 2500 overlap weak one at 0	5.6%	3.9×10^{-6}
Precatalyst	one at 1800	6.4%	1.9×10^{-6}
$P/V=1.0$			
Catalyst	one at 2500 equal one at 0	7.5%	7.5×10^{-7}
C_4H_{10} -treated	broad peak spread - from 0 to 3500	1.9%	3.8×10^{-6}
C_4H_8 -treated	strong at 2500	2.0%	4.2×10^{-6}
Precatalyst	one at 1800	0.7%	2.8×10^{-6}

Table 8 (Continued)

Sample	³¹ P NMR Peak Position (ppm)	⁵¹ V NMR (Intensity)	Volume Susceptibility
P/V=1.1			
Catalyst	stronger one at 2500 weaker one at 0	2.2%	2.8×10^{-6}
C ₄ H ₁₀ -treated	major one at 2500 weak flat part -from 0 to 1700	1.5%	4.6×10^{-6}
C ₄ H ₈ -treated	one at 2500	0.3%	4.7×10^{-6}
Precatalyst	one at 1800	0 %	3.3×10^{-6}

DISCUSSION

The proximity of unpaired electron spins to nuclei being observed has important effects on an NMR spectrum^{56,57}. In some cases, the presence of paramagnetic ions even affects the NMR signal of neighboring nuclei, which is the situation observed in present study. These effects often lead to an increase in the line width of the NMR signal by magnetic dipolar interactions, a decrease in relaxation time by hyperfine coupling between the unpaired electron spin and the nuclear spin, and larger chemical shifts than in diamagnetic compounds. The NMR line width could be broadened beyond observability if the width is wider than the bandwidth of the NMR spectrometer. Another problem with a broad signal is that the wider the signal, the lower the intensity. The vanadium ions, i.e., V(IV) and V(III) having $3d^1$ and $3d^2$ configurations respectively, contain unpaired electrons and affect the NMR signals of ^{51}V and ^{31}P in the model compounds: untreated, and butane and butene treated $(\text{VO})_2\text{P}_2\text{O}_7$, and $\text{V}_2(\text{VO})(\text{P}_2\text{O}_7)_2$; and in industrial catalysts: untreated, and butane and butene treated catalysts with $\text{P}/\text{V}=0.9, 1.0, 1.1$. The paramagnetic effects cause chemical shifts of ^{31}P in these samples beyond

the normal range (up to 2500 ppm, even 4500 ppm in $V_2(VO)(P_2O_7)_2$) and failure in observation of V(IV) and V(III) NMR signals which is the case for the ^{51}V NMR of $(VO)_2P_2O_7$ and $V_2(VO)(P_2O_7)_2$.

β -VOPO₄ contains almost all V(V) and has magnetic volume susceptibility of order of 10^{-8} , which reflects it being diamagnetic. The one symmetrical peak of ^{31}P NMR at 0 ppm for β -VOPO₄ (see Figure 3) exhibits the same chemical shift as ^{31}P in phosphoric acid. The position and shape of the peak of ^{31}P NMR are consistent with the results reported for other orthophosphates⁵⁸. ^{51}V NMR of β -VOPO₄ exhibits a broad peak centered at 0 ppm (see Figure 20) with full width about 4000 ppm, and does not obviously show a first order quadrupolar powder pattern with axial symmetry. The broad peak might be the overlapping of all first order transitions or a few transitions, or only central transition. The signal intensity of ^{51}V NMR in β -VOPO₄ is low relative to that of vanadium present in V_2O_5 , which means that not all the vanadium in β -VOPO₄ gives an observable ^{51}V NMR signal. The result of the redox titration shows that the average oxidation number of β -VOPO₄ is 4.9 instead of 5.0 (see Table 5). The result of ESR measurements³¹ for β -VOPO₄ show a small concentration of V(IV) present, which is believed to reduce the observable vanadium signal. But, the vanadium

(IV) concentration is low enough that it has no apparent effect on the ^{31}P spectrum.

After treatment with n-butane, the ^{31}P NMR in $\beta\text{-VOPO}_4$ exhibits another small peak at 2500 ppm in addition to the main peak still at 0 ppm (see Figure 3). The result is interpreted to indicate that about 34% of V(V) is reduced to V(IV) while n-butane is oxidized to maleic anhydride. It is obvious by comparing with the spectrum of ^{31}P NMR in $(\text{VO})_2\text{P}_2\text{O}_7$ (see Figure 5 on page 22) with mainly V(IV). The large changes in oxidation states of vanadium is believed to occur on the catalyst surface and near surface layers, as pointed out by Hodnett⁵⁹. The ^{51}V NMR of $\beta\text{-VOPO}_4$ treated with butane shows a signal at the same position as for the untreated sample, but with much lower intensity than that of untreated one. More than 45% of the intensity drop in the observable vanadium from untreated $\beta\text{-VOPO}_4$, combined with increase of volume susceptibility from 4.3×10^{-8} (untreated $\beta\text{-VOPO}_4$) to 7.2×10^{-7} (butane treated sample), provides the evidence that the oxidation state of vanadium is changed to a lower state [V(IV) and V(III)] occurring during catalytic process. The laser Raman spectroscopy and X-ray diffraction and X-ray photoelectron spectroscopy studies²⁷ indicated that during butane oxidation, some reduction occurs on the $\beta\text{-VOPO}_4$ catalyst, but not throughout the entire bulk

structure of the catalyst.

β -VOPO₄ treated with 1-butene gave a similar ³¹P NMR spectrum as the butane treated sample, but the peak at 2500 ppm was broader, which correlates with the greater value of volume susceptibility of β -VOPO₄ treated with butene than the value of β -VOPO₄ treated with butane. ⁵¹V NMR of β -VOPO₄ treated with butene exhibits a broad peak at 0 ppm which has intensity lowered by about 36% relative to untreated β -VOPO₄. This indicates that paramagnetic species are produced after the catalyst is oxidized by hydrocarbon. The more observable vanadium and greater value of bulk volume susceptibility in 1-butene-treated β -VOPO₄ than in n-butane-treated β -VOPO₄ suggest that total amount of reduced vanadium is smaller, but the degree of reduction is greater in the butene-treated sample than in that of the butane-treated one. It is possible that some V(III) is generated during oxidation of 1-butene. Centi et al.⁹ pointed out that when n-butane is oxidized under the same conditions, the degree of catalyst reduction is less than that observed with 1-butene. A partial phase transformation from β -VOPO₄ to (VO)₂P₂O₇ is also possible during 1-butene oxidation²⁷.

(VO)₂P₂O₇, with primarily V(IV), shows a major ³¹P NMR signal at 2500 ppm. This characterizes the NMR signal of phosphorus near V(IV). This chemical shift is beyond the

normal ^{31}P NMR chemical shift range for diamagnetic compounds⁶⁰. In view of the structure (see Figure 4), each phosphorus atom shares three oxygens with vanadium atoms in three different chains, and all phosphorus atoms remain in an equal chemical environment, it is easy to understand the presence of one ^{31}P NMR peak. However, two other small peaks (approximately 6% of total intensity) were observed near 0 ppm and 800 ppm, respectively. These signals are attributed to defects in $(\text{VO})_2\text{P}_2\text{O}_7$ crystallites^{61,62}, which is a result of sample preparation. The possible presence of disorder in the crystalline structure of vanadyl pyrophosphate was also confirmed by Johnston's measurements⁶³. The volume susceptibility (7.2×10^{-6}) of $(\text{VO})_2\text{P}_2\text{O}_7$ is roughly expected for paramagnetic component of V(IV) at 298K by calculation using Curies Law. The ^{51}V NMR of $(\text{VO})_2\text{P}_2\text{O}_7$ shows a very weak signal at 0 ppm, which basically comes from defect vanadium V(V). There is no $^{51}\text{V}(\text{IV})$ signal observed, because the dipolar interactions between the unpaired d^1 electron in V(IV) and the ^{51}V nucleus leads to T_1 relaxation so rapid that NMR cannot be detected on the time scale of our measurements.

After treatment with n-butane and 1-butene, $(\text{VO})_2\text{P}_2\text{O}_7$ (see Figure 5 on page 22) does not exhibit an obvious change in NMR spectra of ^{31}P . The bulk chemical environment of

phosphorus may remain unchanged after hydrocarbon oxidation. The topotactic nature of the redox cycle⁶⁴ between $(VO)_2P_2O_7$ and the β' -phase $((VO)^{2+}(VO)^{3+}_{2n-1}(P_2O_7)^{4-}(PO_4)^{3-}_{2n})$, here n is 1,2,4,8, ----,) is suggested for the oxidation of butane to maleic anhydride. The structure of the β' -phase in the ac plane is topologically similar to that of $(VO)_2P_2O_7$. ^{51}V NMR results of $(VO)_2P_2O_7$ treated with butane and butene show peaks at the same positions (centered at 0 ppm) as, but with slightly lower intensities than for the untreated sample. The 10% and 4% of intensity decrease respectively for butane and butene treated $(VO)_2P_2O_7$, together with the increase of volume susceptibility, suggest that there is a surface reduction. However, only a very small amount of vanadium, which is not enough to be able to produce a shifted ^{31}P NMR signal which can be seen, is reduced. NMR is a relatively insensitive technique for the measurements of low concentrations. The amount of V(III) produced during n-butane oxidation depends on the relative gas concentration of oxygen in n-butane⁶⁵. In high oxygen and low n-butane concentrations, a small amount of V(III) is produced as evidenced by the magnetic susceptibility results.

With the above results, and model in mind, the NMR of ^{31}P , ^{51}V and volume susceptibility measurements on the precursor catalyst, n-butane and 1-butene treated and

untreated catalysts form a coherent picture which may be used to infer information about local structures present in the industrial vanadium-phosphorus-oxygen catalysts. The NMR of ^{31}P in precursor catalysts with atomic ratio of phosphorus to vanadium $\text{P/V}=0.9$, 1.0 and 1.1 in the starting materials exhibit the main peak at 1800 ppm (^{31}P near V(IV) at 2500 ppm and near V(V) at 0 ppm) which with the observed value of volume susceptibility is taken to be indicative of microscopically mixed oxidation states of V(V) and V(IV) being present (see Figures 8, 9, 10). ^{51}V NMR spectra of precipitated catalysts demonstrate the increasingly important effects of unpaired electron spins at high values of P/V . There is about 6.4% of observable vanadium in precipitated catalyst with $\text{P/V}=0.9$ and 0.7% in $\text{P/V}=1.0$, which indicate only small amounts of relatively unaffected vanadium. There is no ^{51}V NMR signal observed for precipitated catalyst with $\text{P/V}=1.1$. This suggests that all vanadium atoms present are paramagnetic. The chemical structure and composition of precipitated catalysts are very complex. Each the three precipitated catalysts showed an X-ray diffraction pattern characteristic⁴⁰ of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$. The preparation conditions have a pronounced effect on microstructure^{62,66}, i.e., on the morphology, solid state reactivity, and the presence of disorder in the stacking

fold of crystalline planes of its layered structure, of precipitated catalysts. The nonstoichiometry is easily accommodated as evidenced by preparation of compounds with atomic ratio of $P/V=0.9-1.2$ ⁶⁷. The presence of water, containing protons 1H , will add heteronuclear dipolar interactions and complicate the NMR spectrum.

After calcination, the ^{31}P NMR spectra of these catalysts change considerably. The lone peak of precipitated catalysts are separated into two overlapping peaks, one with maximum at 0 ppm and the other at 2500 ppm (see Figures 8, 9, 10 on pages 28, 29, 30). There are different peak intensities for different P/V ratios. The peak intensity at 2500 ppm increases, and at 0 ppm decreases, with increasing the P/V ratio. A possible explanation for the results is that both $\beta\text{-VOPO}_4$ and $(VO)_2P_2O_7$ phases are present in air calcined catalysts, but vary in relative amounts. Bergeret et al.⁶⁷ found that low P/V ratios favored the formation of $\beta\text{-VOPO}_4$ with vanadium oxidation states close to +5, and that high P/V ratios favored the formation of a β or B phase with vanadium oxidation states +4. A decrease of crystallinity of the catalysts was also noticed with the increase of the P/V ratio. The diffuse reflectance studies⁶⁶ showed that the presence of both V(IV) and V(V) on the surface of the

catalyst, and the fresh catalyst is a vanadium(IV) with a certain percent of vanadium(V). The amount of V(IV) increases from $P/V=0.9$ to $P/V=1.1$, which supports the inference that excess phosphorus stabilizes V(IV) in the catalysts^{68,69,70}. The peak intensities of ^{51}V NMR of these catalysts decrease and the volume susceptibility increases with increasing the P/V ratio, which is consistent with the results of ^{31}P NMR. The ESR spin counting measurement also showed the trend of increasing electron spin with P/V ³¹. The study of Cavani and coworker⁶⁸ supports the observation that V(IV) is more concentrated in catalysts with higher phosphorus to vanadium ratio. There is more V(V) than V(IV) in the catalyst with $P/V=0.9$, because it was determined to have semicrystalline V_2O_5 in a nearly amorphous phase of the oxidized hemihydrate⁴⁰. The change from precursor to active catalyst involves the change from face-share to edge-share vanadium octahedra in converting the hemihydrate to the pyrophosphate results in a small expansion of one axis, but the other in-plane dimension shows little change according to the pseudomorphic relations between the two crystalline structures⁷¹. This indicated a topotactic mechanism of transformation, and which has been confirmed with scanning electron microscopy^{72,73}.

After treatment with n-butane and 1-butene, the catalyst with $P/V=0.9$ (see Figure 8 on page 28) shows dramatic changes in the ^{31}P NMR spectra. The peak intensities at 0 ppm decrease and at 2500 ppm increase greatly relative to the untreated catalysts, which indicate that more paramagnetic $\{\text{V(IV)}\}$ species are produced after treatment with hydrocarbons. For the catalyst with $P/V=0.9$ treated by butane, the ^{31}P NMR spectrum exhibits a broad peak at 2500 ppm, which indicates that the large percent of V(V) are reduced to lower oxidation states when butane is oxidized to maleic anhydride. The catalyst with $P/V=0.9$ treated by 1-butene shows a small peak at 0 ppm in addition to a main peak at 2500 ppm, which indicates less reduction of vanadium than for the butane treated sample. The result of more reduction in butane-treated sample than butene-treated one is unexpected, but it is supported by ^{51}V NMR and volume susceptibility measurements. ^{51}V NMR results exhibit 2.2% and 5.6% of observable vanadium respectively for $P/V=0.9$ treated with butane and butene relative to 100% of observable vanadium in V_2O_5 . The less observable vanadium means more paramagnetic species, i.e., more V(IV) in butane-treated $P/V=0.9$ than in the butene-treated sample. The results of volume susceptibility are 4.2×10^{-6} for the catalyst with $P/V=0.9$ treated with butane and 3.9×10^{-6} for

that treated with butene.

The ^{31}P NMR results on the catalyst with $\text{P/V}=1.0$ treated by butane (see Figure 9) shows very broad feature spread between 0 ppm and 4000 ppm. Several structures and phases are possibly present. These include mixed valence compounds (V(V) and V(IV) in microscopically isolated regions), microscopic mixture of phases, defects, a partly amorphous phase (which can be described as small groups of corner sharing VO_6 octahedra surrounded by numerous corner-linked PO_4 tetrahedra and a crystalline core⁶⁸), and interface between surface and bulk. After treatment with butene, the ^{31}P NMR spectrum of the catalyst with $\text{P/V}=1.0$ shows a peak centered at 2500 ppm, and a very low intensity NMR signal near 0 ppm. The V(V) (maybe a $\beta\text{-VOPO}_4$ phase or mixed with a little amorphous V_2O_5) in the untreated catalyst with $\text{P/V}=1.0$ is greatly reduced to lower oxidation states which might be V(IV) or a small amount of V(III) after treatment. ^{51}V NMR results of the hydrocarbon-treated catalyst with $\text{P/V}=1.0$ indicate a low percentage (only about 2%) of observable vanadium. This suggests a large amount of paramagnetic species being present. The value of the magnetic volume susceptibilities of the butane and butene treated catalysts are relatively large compared with the untreated sample. According to previous studies⁴⁰, the

catalyst with $P/V=1.0$ after treatment with butane becomes a mixture of $\beta\text{-VOPO}_4$ and $(\text{VO})_2\text{P}_2\text{O}_7$. The present studies correlate with this conclusion, but indicate that the situation in the butane-treated catalyst with $P/V=1.0$ is more complicated than just mixture of two phases. The catalyst with $P/V=1.0$ treated with butene may be a mixture of $\beta\text{-VOPO}_4$ and $(\text{VO})_2\text{P}_2\text{O}_7$ phases, but $(\text{VO})_2\text{P}_2\text{O}_7$ is predominant. Perhaps or a small amount of V(III) is formed on the catalyst surface.

The industrially active catalyst with $P/V=1.1$ treated by butane shows a broad peak at 2500 ppm and a very low intensity at 0 ppm of ^{31}P NMR spectrum (see Figure 10). ^{51}V NMR of butane-treated catalyst with $P/V=1.1$ exhibits that the intensity of observable vanadium decreases to 32% of the untreated catalyst with $P/V=1.1$. The volume susceptibility increases from 2.8×10^{-6} for the untreated sample to 4.6×10^{-6} after treatment with butane. This evidence suggests that V(IV) or V(III) species are generated after treatment with hydrocarbons. The previous study³⁰ indicated that the V-P-O catalyst is in a partially reduced form after its reaction with a mixture of n-butane-oxygen as well as after catalytic oxidation of n-butane to maleic anhydride. The amount of V(III) produced during the catalytic process depends on the gas mixture of butane and oxygen⁶⁶. More butane and less

oxygen in the mixture will produce more V(III). The samples used in the present studies are treated by 1.5% of n-butane (or 1.5% 1-butene) and 22% of oxygen. In this case, if there is any V(III) produced, it will be a small amount on the surface which is not detectable by NMR of ^{31}P . The catalyst with $\text{P/V}=1.1$ shows a strong peak at 2500 ppm and near zero intensity at 0 ppm (stronger intensity at 0 ppm for butane-treated $\text{P/V}=1.1$), which indicates more reduction of vanadium in butene-treated sample than in the one treated with butane. ^{51}V NMR measurements also show lower intensity (0.3%) of observable vanadium than that of butane-treated $\text{P/V}=1.1$ (1.5%). The results of magnetic volume susceptibility also agree with the above results by providing a slightly higher value of 4.7×10^{-6} for butene-treated $\text{P/V}=1.1$ than that of 4.6×10^{-6} for butane-treated $\text{P/V}=1.1$.

A summary of the observed changes in these materials, from industrial active catalysts to n-butane and 1-butene treated catalysts, in view of the information inferred from NMR of ^{31}P and ^{51}V , and volume susceptibility measurement in the model compounds $\beta\text{-VOPO}_4$ and $(\text{VO})_2\text{P}_2\text{O}_7$ before and after oxidation of butane and butene is as follows:

- (1) The ^{31}P NMR spectra of $\beta\text{-VOPO}_4$ and $(\text{VO})_2\text{P}_2\text{O}_7$ indicated that NMR markers of ^{31}P in the neighborhood of V(V) and

V(IV) are species resonating at 0 ppm and 2500 ppm respectively.

- (2) Intensity between these two marker locations is taken to be indicative of ^{31}P microscopically in the neighborhood of both V(V) and V(IV), or in partially amorphous state, or in defect states, or in the interface between bulk [e.g., V(V)] and surface [e.g., V(IV)].
- (3) The catalysts with the initial preparation of P/V=0.9, 1.0 and 1.1 treated by butane and butene, appear to be reduced to a lower oxidation states of vanadium, primarily in V(IV) (may have V(III) which depends on the gas mixture concentration of hydrocarbon and oxygen).
- (4) From the ^{51}V NMR results, the smaller number of intensity of observable vanadium indicates more paramagnetic species [V(IV) or V(III)] in the sample.
- (5) The larger volume susceptibility indicates more paramagnetic species in the sample.

The conclusions of present study are summarized as follows:

- (1) NMR spin-echo mapping of ^{31}P and ^{51}V provide a new analytical tool to monitor the oxidation states of vanadium in catalysts.

- (2) The active catalysts contain both V(V) (β -VOPO₄ phase) and V(IV) [(VO)₂P₂O₇ phase], may have small amount of partially amorphous phase or defect.
- (3) The relative amounts of V(V) and V(IV) in the catalysts depends on the phosphorus to vanadium ratio. The amount of V(IV) increases with P/V ratio, i.e., the excess phosphorus in the catalysts stabilizes V(IV).
- (4) Vanadium in the catalysts is reduced to a lower oxidation state after n-butane and 1-butene are oxidized to maleic anhydride. V(V) on the catalyst surface is reduced to V(IV), and a small amount of V(IV) on the catalyst surface may be reduced to V(III).
- (5) The catalyst with higher P/V ratio shows more reduction after treatment with n-butane or 1-butene. The catalyst with P/V=1.1 shows more paramagnetic species than P/V=1.0 and P/V=0.9 after treatment.
- (6) The catalyst with P/V=1.1 is the most active catalyst for oxidation of n-butane and 1-butene to maleic anhydride in the three catalysts of present study. It is even more active for butene oxidation.

ACKNOWLEDGEMENTS

This work was performed at Ames Laboratory under contract No. W-7045-ENG-82 with the U.S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1454 to this thesis.

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