

PDF hosted at the Radboud Repository of the Radboud University Nijmegen

The following full text is a publisher's version.

For additional information about this publication click this link.

<http://hdl.handle.net/2066/28521>

Please be advised that this information was generated on 2016-02-03 and may be subject to change.

A Solid State Double Resonance NMR Investigation of Phosphorus-Impregnated γ -Al₂O₃

E. R. H. van Eck and A. P. M. Kentgens

N.S.R. Center for Molecular Design, Synthesis and Structure, Laboratory of Molecular Spectroscopy, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

H. Kraus and R. Prins*

Laboratory of Technical Chemistry, Swiss Federal Institute of Technology, 8092 Zürich, Switzerland

Received: June 6, 1995; In Final Form: August 22, 1995[®]

Solid state double resonance NMR experiments on phosphorus-impregnated γ -Al₂O₃ and amorphous AlPO₄ have been conducted to investigate the interaction between the impregnated phosphorus and the γ -Al₂O₃ surface. The ³¹P–²⁷Al REDOR and TRAPDOR experiments have shown that most phosphorus is in close contact with aluminum, thereby excluding the possibility that stacked phosphate layers or bulk phosphates are formed when more phosphorus is impregnated than is necessary to cover the entire γ -Al₂O₃ surface. The ²⁷Al–³¹P experiments enabled the ²⁷Al spectrum of the aluminum atoms which interact with phosphorus to be separated from the spectrum of the bulk γ -Al₂O₃. These double resonance experiments have shown that a layer of AlPO₄ is indeed formed on the γ -Al₂O₃ surface and that the structure of this layer, although similar, has a slightly higher degree of ordering than the structure of amorphous AlPO₄.

Introduction

The removal of sulfur, nitrogen, oxygen, and metals from oil fractions in so-called hydrotreating processes is of great importance. This removal results in increased storage stability and improved smoke point and octane number and reduces vehicle emissions, a process which benefits the environment. Mixtures of transition metal sulfides dispersed on γ -alumina are typical catalysts used for hydrotreating purposes. The metals are normally molybdenum or tungsten promoted by nickel or cobalt. Many commercial hydrotreating catalysts also contain so-called modifier elements such as phosphorus. Phosphorus is said to enhance the solubility and stability of molybdate in the impregnation solution and to improve the mechanical and thermal stability of the support. In addition, a beneficial effect of phosphorus on the activity for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) has been observed.^{1–3} At present, however, not much is known about the nature of the compounds which originate after the impregnation of the alumina with phosphorus. Most of the work dedicated to catalysts containing phosphorus is concerned with the phosphorus-induced changes of structural and catalytic properties of the active phases.^{4–12} Some authors observed the existence of AlPO₄ compounds after impregnation of alumina with phosphate solutions, especially at high loading (≥ 4 wt % P) and when using phosphoric acid as the phosphorus source.^{13–18} The situation is less clear at lower loading. It is assumed that mono- and polyphosphates are present, which give rise to broad featureless ³¹P MAS NMR lines.¹⁷ The exact type of interaction of these compounds with the alumina surface is still unclear.¹⁸ Furthermore, it is difficult to obtain information about the dispersion of these phases.

In order to investigate the nature of the compounds that are formed after impregnation of the alumina with phosphorus, it would be very useful to separate the ²⁷Al NMR spectra of the aluminum coordinated to phosphorus from the ²⁷Al spectrum of the bulk γ -Al₂O₃ and to investigate the interaction between phosphorus and aluminum. Recently developed solid state

NMR techniques, such as rotational-echo double resonance (REDOR)^{19,20} and transfer of populations in double resonance NMR (TRAPDOR),^{21,22} are able to provide information about phosphorus–aluminum interactions. These solid state NMR techniques combine magic angle spinning (MAS) with a rotor-synchronized pulse sequence. In these experiments, the Hahn-echo spectrum is compared with the REDOR/TRAPDOR spectrum. The application of radio-frequency (rf) pulses on one nucleus (*S*) will effect the signal intensity of the other nucleus (*I*) through the heteronuclear (*I*–*S*) dipolar coupling. If the nuclei under study are close to each other ($< \pm 5$ Å, depending on the type of nuclei), there will be a decrease in echo intensity, whereas if they are far away from each other, no effect on the echo intensity will be observed. The difference between the REDOR/TRAPDOR spectrum and the full echo spectrum gives the spectrum of the *I* spins that are close to the *S* spins. The REDOR technique can be used not only to establish connectivities between nuclei but also to determine the distance between them. For instance, ¹³C–¹⁵N distances have been determined in biological solids.^{23–25} The TRAPDOR technique has been applied to establish connectivities in aluminophosphate molecular sieves and zeolites^{21,26} and in nylon.²² This paper describes the application of aluminum–phosphorus double resonance NMR techniques to investigate phosphorus-impregnated γ -Al₂O₃.

Experimental Section

Samples. The catalyst precursors were prepared by pore volume impregnation of the γ -Al₂O₃ support (Condea, 230 m²/g) with aqueous solutions of (NH₄)H₂PO₄. The catalysts were slowly heated to 110 °C (383 K) and dried for 12 h in ambient air; the samples were not calcined. They are designated as P(*x*)/ γ -Al₂O₃, where *x* is the amount of phosphorus in wt %/g of catalyst. Amorphous AlPO₄ was prepared according to the method of Kehl.^{27,28} The AlPO₄ sample was dried (120 °C, 3 h) and calcined (400 °C, 5 h), and a XRD measurement (Siemens diffractometer D5000) confirmed that the sample was indeed amorphous.

NMR. All experiments were performed on a Bruker CXP-300 spectrometer. A double resonance MAS NMR probe was

[®] Abstract published in *Advance ACS Abstracts*, October 1, 1995.

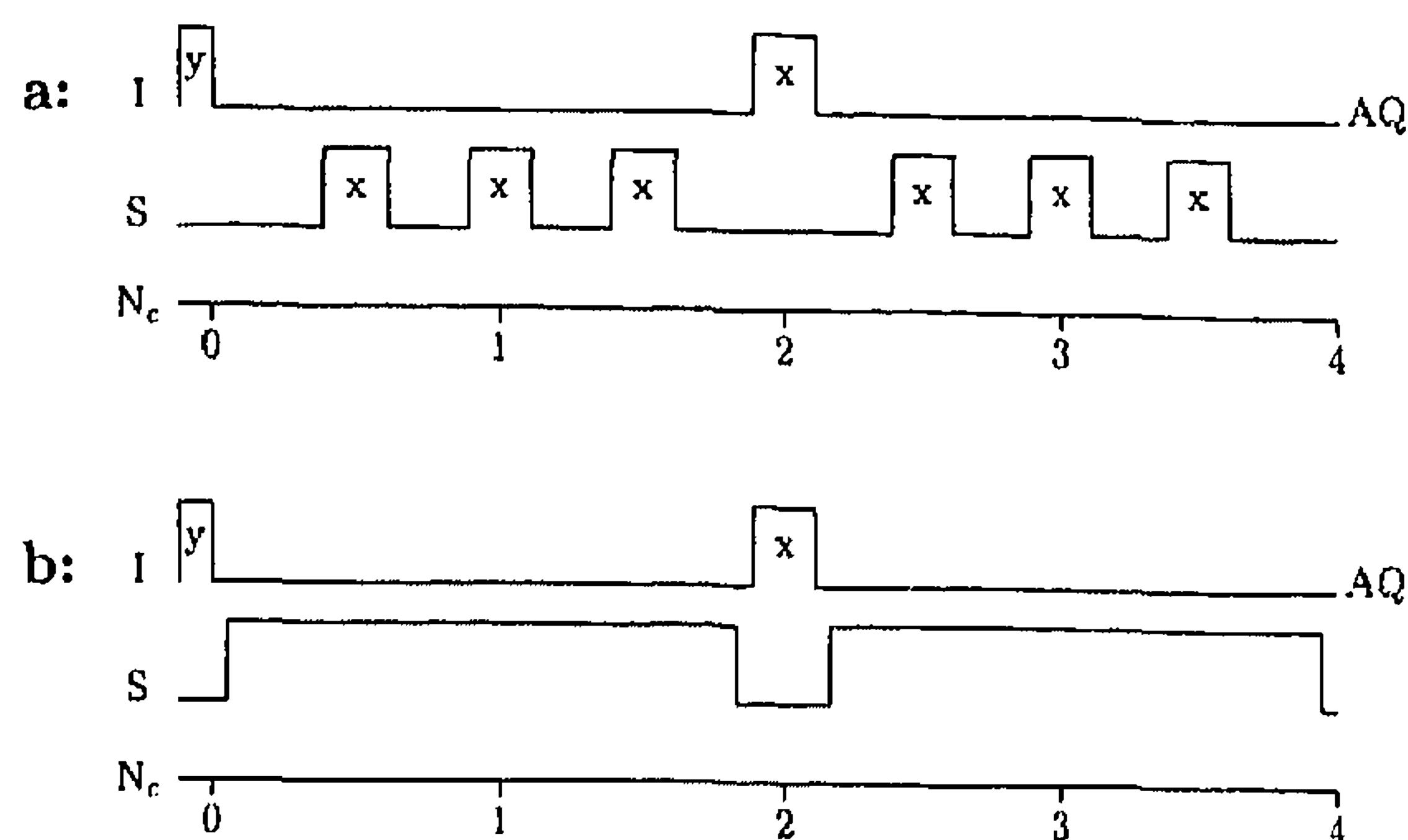


Figure 1. The REDOR pulse sequence (a) and the TRAPDOR pulse sequence (b). The wide blocks represent π -pulses, and the small block represents the $\pi/2$ -pulse. The number of rotor periods (N_c) is indicated below each pulse sequence. In both cases, the I spin magnetization is observed. The REDOR sequence displayed here is a 2,2-REDOR pulse sequence. The quadrupolar S spin is irradiated continuously in the TRAPDOR pulse sequence. Irradiating aluminum during both halves of the echo resulted in a greater loss in intensity, which leads to the conclusion that the level crossings are not perfectly adiabatic, as discussed in the text. The TRAPDOR sequence displayed here is a 2,2-TRAPDOR pulse sequence.

built, which is resonant for ^{27}Al at 78.172 MHz and for ^{31}P at 121.442 MHz. Radio-frequency field strengths of 65 kHz were achieved for aluminum and phosphorus, with power inputs of 250 and 420 W, respectively. A 7 mm Bruker stator with zirconia rotors was used, which reaches spinning speeds of 5.5 kHz. Unfortunately, the highest achievable spinning speeds were insufficient to cancel the spinning sidebands. Chemical shifts are referenced to external $\text{Al}(\text{H}_2\text{O})^{3+}$ in an aqueous solution of AlCl_3 for ^{27}Al (0 ppm) and to 85% H_3PO_4 for ^{31}P (0 ppm). Aluminum and phosphorus T_1 values, measured for AlPO_4 and $\text{P}(10)/\gamma\text{-Al}_2\text{O}_3$, were for aluminum 0.05 s (AlPO_4) and 0.1 s ($\text{P}(10)/\gamma\text{-Al}_2\text{O}_3$) and for phosphorus 13 s (AlPO_4) and 12 s ($\text{P}(10)/\gamma\text{-Al}_2\text{O}_3$). The T_1 values were measured using a saturation recovery pulse sequence. Relaxation delays were set at 0.5 s for aluminum and 64 s for phosphorus. In the ^{27}Al single pulse experiments 512 fid's were accumulated. In the ^{31}P single pulse experiments, the number of scans was increased as the amount of phosphorus decreased.

REDOR Experiments. The REDOR experiment^{19,20} is a rotor-synchronized solid state NMR double resonance experiment in which an echo sequence is applied to one nucleus and its echo is observed, while during the echo period π -pulses are applied on another nucleus at specific positions of the rotor. The difference between the REDOR experiment and a normal spin echo experiment depends on the duration of the echo period and the strength of the heteronuclear dipolar coupling which depends on the distance between the nuclei under investigation. The REDOR pulse sequence is shown in Figure 1a. Because the dipolar coupling becomes time dependent and averages to zero over one rotor period when the sample is rotated around the magic angle, the heteronuclear dipolar coupling has no effect on the echo intensity in a normal rotor-synchronized echo experiment. To reintroduce the effect of the dipolar coupling, π -pulses are applied to the other nucleus which reverse the sign of the dipolar coupling. The dipolar coupling is no longer averaged to zero over one rotor period, and the echo will be attenuated. The signal intensity is described by

$$S(N_c T_r, D) = \int_0^{2\pi} \int_0^\pi \cos\left(\frac{2\sqrt{2}N_c T_r D}{2\pi} \sin 2\beta \sin \alpha\right) \sin \beta \, d\beta \, d\alpha \quad (1)$$

where N_c (the number of rotor periods) times T_r (the rotor period) is the total echo time, and D ($=\gamma_I \gamma_S \hbar / r^3$) is the dipolar coupling

constant. The angles α and β orient the dipolar vector with respect to the spinner axis, and averaging over these angles has to be done when the theoretical REDOR signal intensity of a powder is to be calculated. In general, the closer the nuclei are to each other, the stronger the dipolar coupling and the stronger the echo attenuation will be. In addition, the longer the dipolar coupling is allowed to act upon the spins, the greater the effect on the echo will be. Thus, the REDOR experiment enables us to observe the ^{31}P spectrum of those phosphorus atoms that are in contact with aluminum atoms as well as the ^{27}Al spectrum of those aluminum atoms that are near to phosphorus. These "contact" spectra can provide information about the environment of the phosphorus and aluminum atoms.

The ^{31}P – ^{27}Al REDOR experiments (i.e., where phosphorus is observed) were performed at a spinning speed of 5515 ± 1 Hz. REDOR experiments with two rotor periods (1,1-REDOR) and with four rotor periods (2,2-REDOR) were performed. REDOR experiments with more rotor periods were not carried out since the short phosphorus T_2 greatly reduced signal intensities and the long phosphorus T_1 prevented the use of short recycle delays. The number of scans varied from 128 for AlPO_4 to 640 for $\text{P}(2)/\gamma\text{-Al}_2\text{O}_3$. As ^{27}Al is a quadrupolar nucleus, the REDOR experiment will not be as effective as compared to a spin $1/2$ since the dephasing π -pulses on the aluminum spins will interchange mainly the $\langle 1/2, -1/2 \rangle$ levels, whereas the other quadrupole levels will remain relatively unperturbed.

The ^{27}Al – ^{31}P REDOR experiments were also measured at a spinning speed of 5515 ± 1 Hz. Three REDOR experiments were performed: 1,1-, 2,2-, and 4,4-REDOR. The aluminum T_2 and T_1 permit the longer echo time to be used and thus enable the dipolar coupling to enhance the REDOR effect. The number of scans ranged from 6144 for AlPO_4 to 137 216 for $\text{P}(2)/\gamma\text{-Al}_2\text{O}_3$. The difference in echo intensities is expected to be the greatest for AlPO_4 and the least for $\text{P}(2)/\gamma\text{-Al}_2\text{O}_3$. With only 2 wt % phosphorus and assuming a 1:1 ratio in phosphorus–aluminum contacts, about 3% of the aluminum atoms should be affected by the REDOR pulse sequence. In contrast to ^{31}P – ^{27}Al REDOR, the dephasing π -pulses are applied to phosphorus, and all the phosphorus spins will be flipped by the π -pulses.

TRAPDOR Experiments. The TRAPDOR experiment^{21,22} is based on the same principle as the REDOR experiment, in the respect that the value of the dipolar coupling is actively changed by rf irradiation during the echo but, instead of applying π -pulses, the spins are irradiated continuously. The pulse sequence is displayed in Figure 1b. In order for the TRAPDOR experiment to work, the irradiated nucleus has to be a quadrupolar nucleus. Due to the spinning of the sample, not only does the z component of the dipolar coupling become time dependent but the quadrupolar coupling as well. As the sample is spun about the magic angle and the rf field is applied, level crossings in the rotating frame representation can occur between the different spin levels of the quadrupole nucleus. The state of the spins will change upon level crossing, and therefore the dipolar coupling to the other nucleus changes.²² A more detailed description of the behavior of quadrupolar spins with magic angle spinning and continuous irradiation has been given by Vega.^{29,30} The effectiveness of this process depends on the adiabaticity of the level crossings. The adiabaticity will increase as the rf field strength increases or as the spinning speed and/or quadrupole interaction decreases. At a constant rf field strength and spinning speed, the TRAPDOR effect will increase as the echo time and/or the dipolar coupling increases, just as in the REDOR experiment.

The TRAPDOR experiment is expected to be more effective than the REDOR experiment when the second (not observed) nucleus is a quadrupole nucleus since not only the $\langle 1/2, -1/2 \rangle$

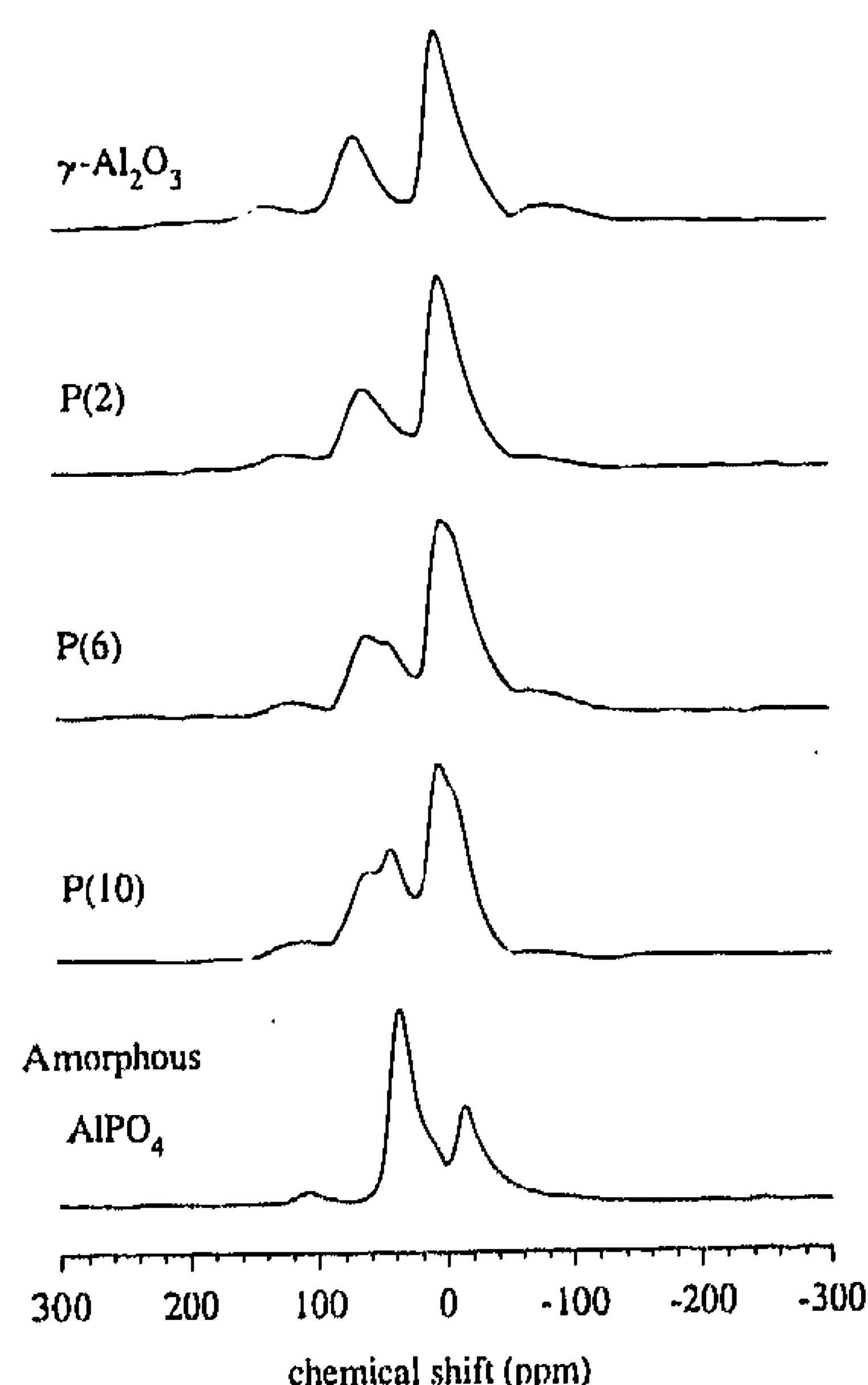


Figure 2. Aluminum single pulse MAS spectra of γ - Al_2O_3 , phosphorus-impregnated γ - Al_2O_3 , and amorphous AlPO_4 .

levels are perturbed but also other quadrupole levels. In fact, the REDOR experiment was developed for spin $1/2$ nuclei but has also been applied to quadrupolar nuclei.²⁶ Very strong quadrupole interactions make the level crossings sudden and, due to limitations in rf field strengths, cannot be made adiabatic. Very small quadrupole couplings render the process highly adiabatic, but the quadrupole starts behaving as a spin $1/2$ and is merely decoupled from the other nucleus. In such a case, a REDOR experiment will be much more effective. Vega²⁹ has defined an adiabatic passage parameter α ($=\omega_{\text{rf}}/\omega_Q\omega_R$, $\omega_Q = 3e^2qQ/2S(2S-1)\hbar$) that gives an indication of the efficiency of the level crossings. Assuming a quadrupole coupling (e^2qQ/h) in the range 3–5 MHz, α would be 1.7–1.0 in our case. While performing ^{27}Al – ^{31}P TRAPDOR experiments we have observed that the experiment is effective in the range of α 's from 0.1 to 5, at least. Furthermore, if the level crossings are perfectly adiabatic, irradiating the quadrupolar spins during the complete echo period would lead to complete refocusing of the echo. Fortunately, however, the level crossings are almost never completely adiabatic.

The ^{31}P – ^{27}Al TRAPDOR experiments were measured at a spinning speed of 5515 ± 1 Hz, with a total of two and four rotor periods (1,1-TRAPDOR and 2,2-TRAPDOR). The rf field strength on both nuclei was 65 kHz. The rf field was applied during the entire echo period and switched off during the refocusing π -pulse on phosphorus and prior to acquisition. Irradiating the entire echo period resulted in the highest difference intensity. Difference spectra will again give the spectra of phosphorus atoms with aluminum neighbors.

Results and Discussion

Single Pulse Experiments. The ^{27}Al single pulse spectra of amorphous AlPO_4 , phosphorus-impregnated γ - Al_2O_3 , and γ - Al_2O_3 are displayed in Figure 2. All ^{27}Al spectra show resonances for tetrahedral and octahedral aluminum atoms. The tetrahedral and octahedral resonances for γ - Al_2O_3 are located at 67.8 and 5.9 ppm, respectively. The tetrahedral and octahedral resonances for amorphous AlPO_4 are located at 37.0 and –13.3 ppm. The shoulder at 11 ppm in the spectrum for amorphous AlPO_4 could be a part of the quadrupole pattern of the tetrahedral resonance, but it is also possible that this is due to five-coordinated aluminum with phosphorus as next-nearest neighbors or to octahedral aluminum which is not coupled to phosphorus. ^{27}Al spectra obtained at higher B_0 field strengths

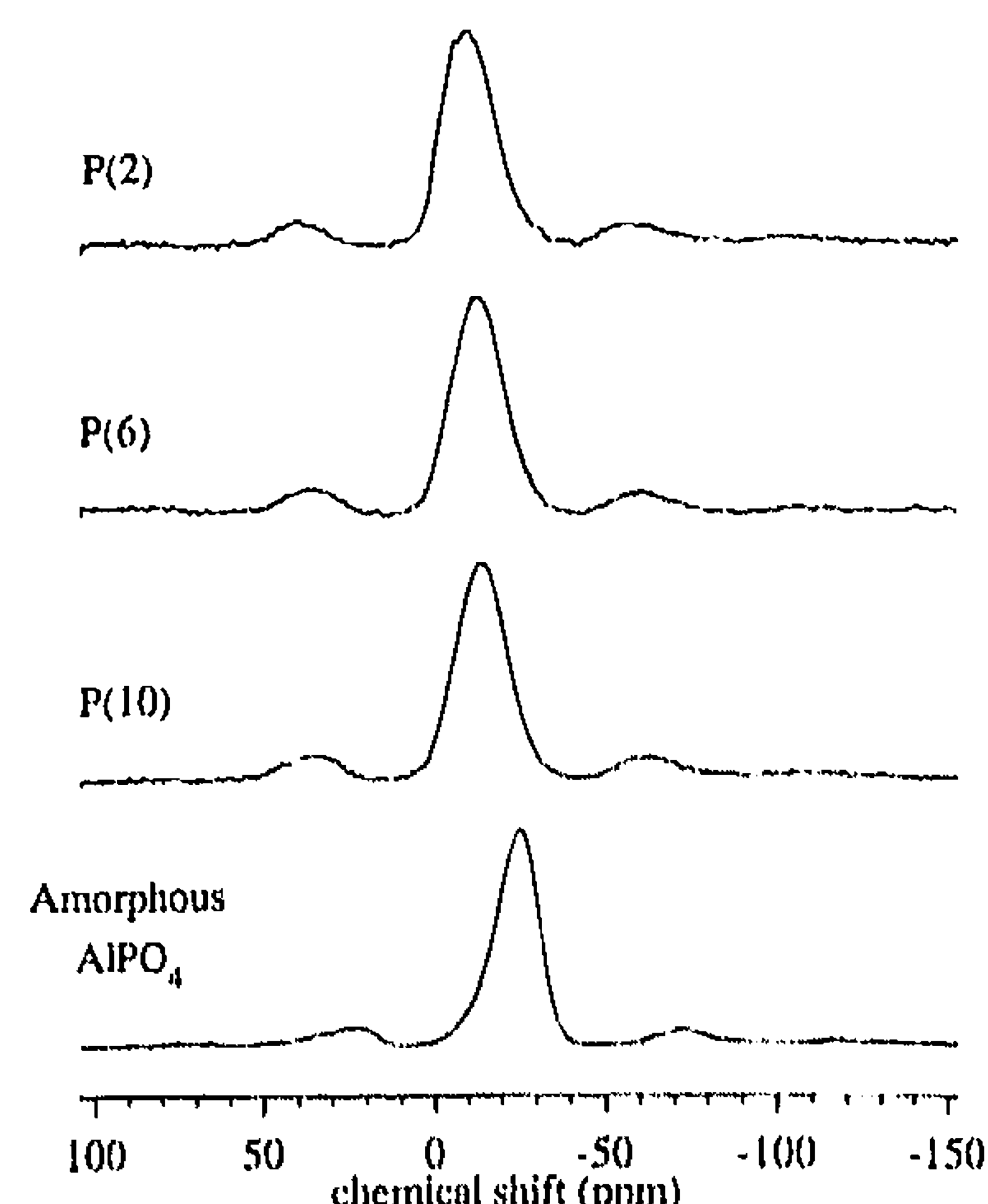


Figure 3. Phosphorus single pulse MAS spectra of phosphorus-impregnated γ - Al_2O_3 and amorphous AlPO_4 .

have shown that the line at 11 ppm is not part of the tetrahedral line. In order to decide between the remaining possibilities, ^{27}Al – ^{31}P REDOR experiments were performed. The spectrum of the P(10)/ γ - Al_2O_3 sample shows not only the γ - Al_2O_3 resonances but also a peak at 42.6 ppm and a shoulder at –6 ppm. These peaks also deform the spectrum of P(6)/ γ - Al_2O_3 with respect to the spectrum of pure γ - Al_2O_3 . The shifts for these peaks fall in the same range as the tetrahedrally and octahedrally coordinated aluminum peaks in AlPO_4 . The spectrum of P(2)/ γ - Al_2O_3 is quite similar to the spectrum of pure γ - Al_2O_3 . The fact that the ^{27}Al spectra of P(10)/ γ - Al_2O_3 and P(6)/ γ - Al_2O_3 are different from the spectrum of pure γ - Al_2O_3 indicates that the impregnated phosphorus interacts with the γ - Al_2O_3 . On the basis of the shifts of the non- γ - Al_2O_3 peaks, one can deduce that the compound formed by phosphorus impregnation is probably an amorphous AlPO_4 phase. No significant change in the ^{27}Al spectrum is observed for the P(2)/ γ - Al_2O_3 sample, but since the phosphorus loading is only 2 wt %, no conclusions can be drawn as to whether the impregnated phosphorus interacts with the γ - Al_2O_3 or not.

Figure 3 shows the ^{31}P single pulse spectra of phosphorus-impregnated γ - Al_2O_3 and amorphous AlPO_4 . All phosphorus spectra show a single broad line. The spectrum of AlPO_4 is asymmetric with a tail to higher ppm values; its maximum value is located at –25.0 ppm. The peak position shifts downfield with lower phosphorus loading. The isotropic shift is –13.3 ppm for P(10)/ γ - Al_2O_3 , –11.7 for P(6)/ γ - Al_2O_3 , and –9.7 ppm for P(2)/ γ - Al_2O_3 . At first glance the phosphorus spectra rule out the possibility that a kind of amorphous AlPO_4 phase is formed upon phosphorus impregnation. However, if an amorphous AlPO_4 phase is formed, it will be on the γ - Al_2O_3 surface which can give rise to phosphorus shifts different from the shift found for the bulk amorphous AlPO_4 sample. For low loadings, a layer of mono- and polyphosphates on the alumina surface will be formed, and the phosphate groups at the surface will be terminated by hydroxyl groups. It is noteworthy that, in the ^{31}P spectrum of amorphous AlPO_4 , the long tail encompasses the range in which the P(x)/ γ - Al_2O_3 phosphorus resonances lie. Furthermore, as the amount of impregnated phosphorus increases, the ^{31}P shifts move toward the AlPO_4 peak maximum. This may indicate that, when the layer thickness of the amorphous AlPO_4 phase increases, the phosphorus environment becomes more similar to that of AlPO_4 . Another possibility may be that the major part of the impregnated phosphorus does not interact with the γ - Al_2O_3 at all. In order to learn more about the interaction between phosphorus and aluminum, REDOR and TRAPDOR experiments were performed.

^{31}P – ^{27}Al REDOR and TRAPDOR Experiments. The echo

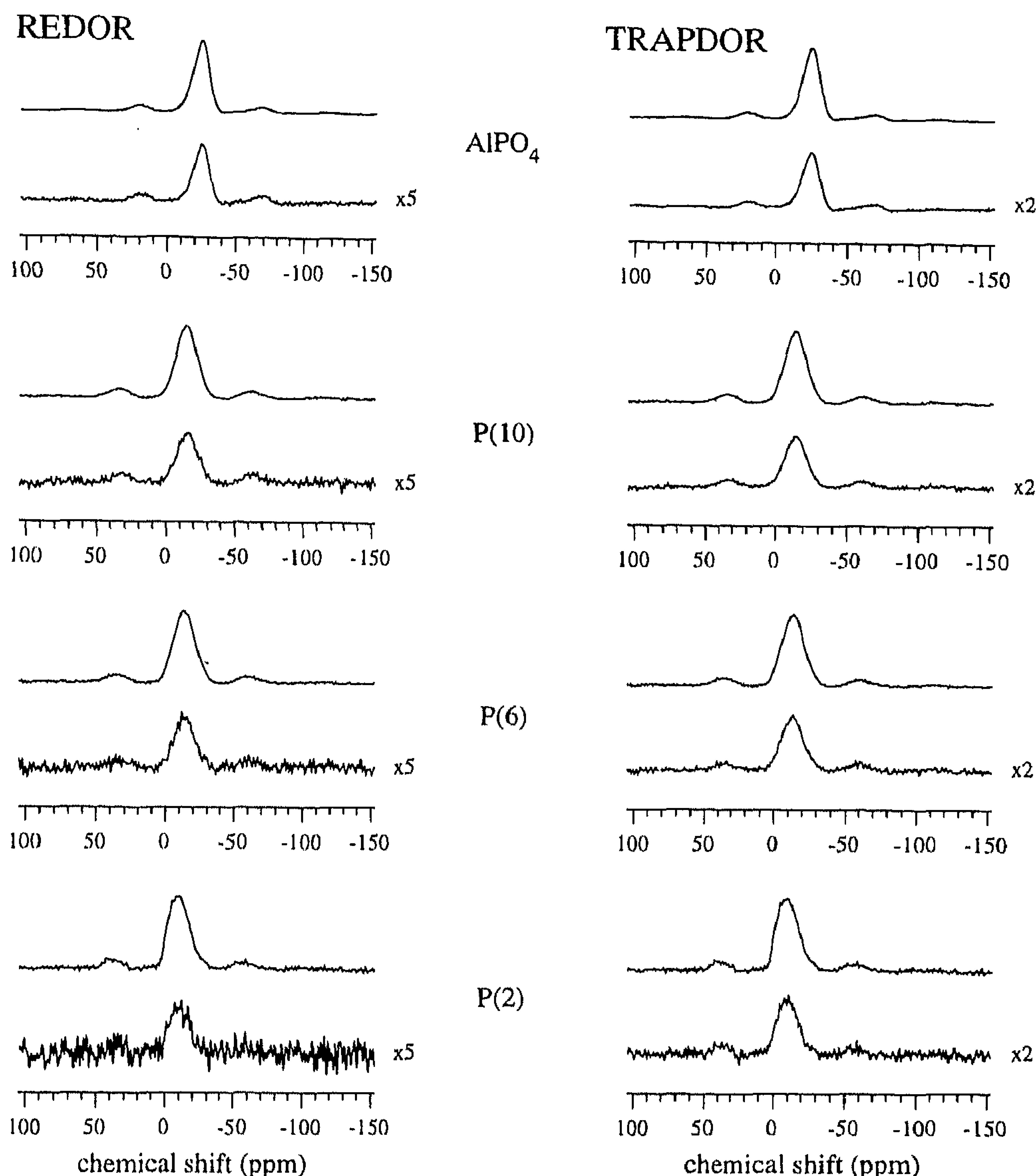


Figure 4. 2,2-REDOR and 2,2-TRAPDOR ^{31}P – ^{27}Al spectra of the samples containing phosphorus. The REDOR spectra are displayed at the left and the TRAPDOR spectra at the right. For each sample and experiment, the original 2,2-echo spectrum is the upper spectrum, and the difference (contact) spectrum is the lower one. The REDOR difference spectra are enlarged 5 times, while the TRAPDOR difference spectra are enlarged 2 times.

spectra and the REDOR and TRAPDOR difference spectra for four rotor periods of all phosphorus-containing compounds are displayed in Figure 4. The difference spectra are the spectra of phosphorus that is in close contact with aluminum. The shifts of the phosphorus resonances of the difference spectra are the same as the shifts found in the echo spectra. The line shapes of the echo spectra and difference spectra are the same. We can, therefore, conclude that most phosphorus atoms are close to aluminum. An interesting observation is that the intensity of the difference spectra is much higher for the TRAPDOR experiment than for the REDOR experiment. This confirms our expectation that the TRAPDOR experiment is more efficient than the REDOR experiment in this case.

Figure 5 shows the relative intensity of the difference spectra $\Delta S/S_0$, the REDOR and TRAPDOR fractions, as a function of the echo time. The difference is largest for the amorphous AlPO_4 sample and the least for $\text{P}(2)/\gamma\text{-Al}_2\text{O}_3$. The general trend is that the difference increases as the echo time increases. This effect is best observed in the TRAPDOR spectra since the difference intensities are higher. For relatively short echo times, in comparison to the time scale of the dipolar coupling, the difference intensity will increase as the dipolar coupling increases. In general, Al – O – P distances lie in the range of 3 Å, resulting in ^{27}Al – ^{31}P dipolar couplings of about 400–500

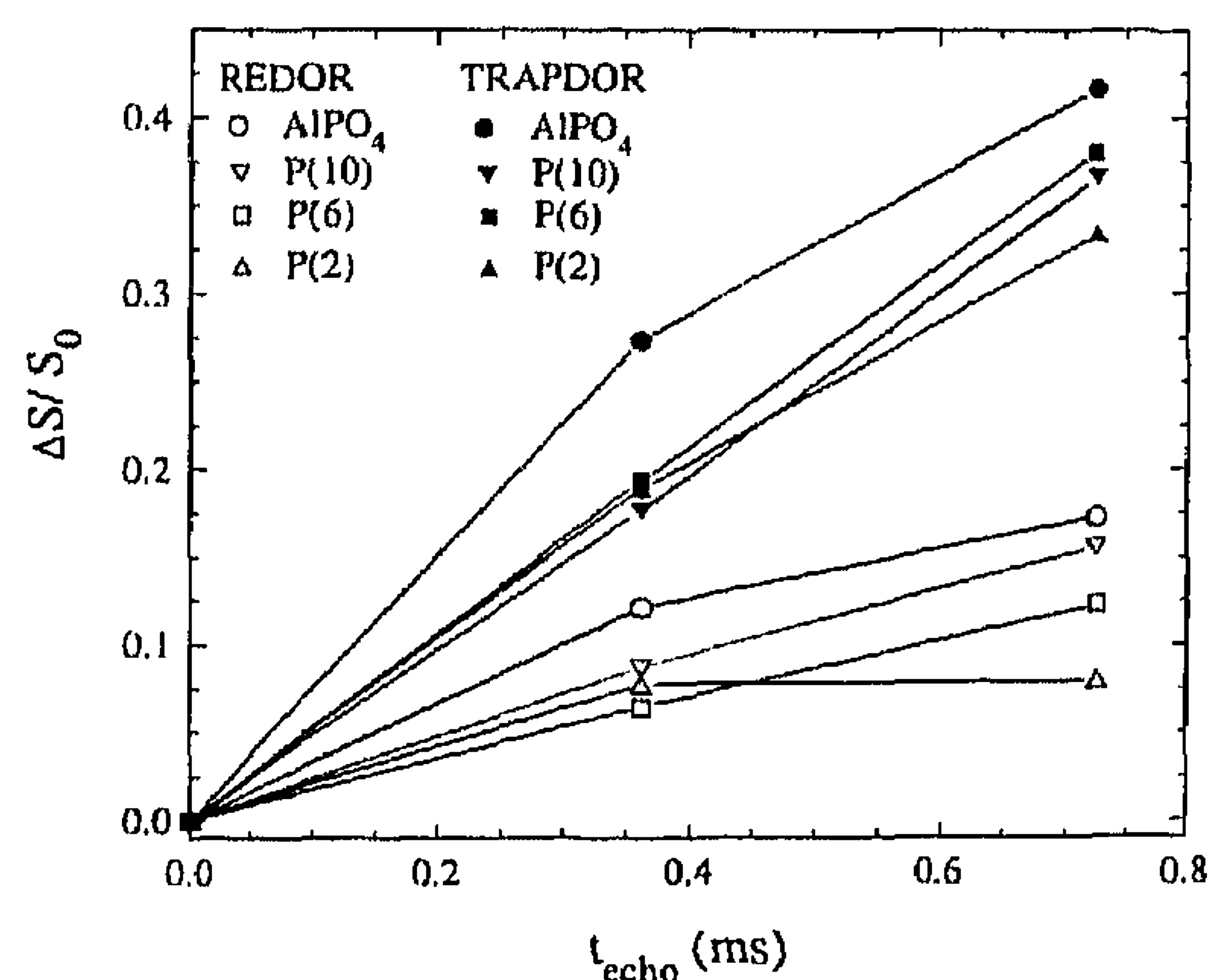


Figure 5. Intensity $\Delta S/S_0$ of the ^{31}P difference spectra relative to the echo intensity, as a function of the echo time. The data points at $t = 0$ are not measured but are zero by definition.

Hz. One could conclude that the difference in intensity between the AlPO_4 sample and the $\text{P}(x)/\gamma\text{-Al}_2\text{O}_3$ samples is caused by a shorter Al – P distance. This is, however, unlikely since Al – P distances in aluminophosphates vary only slightly. A more plausible explanation is that the number of aluminum atoms that coordinate to phosphorus is, on average, larger for

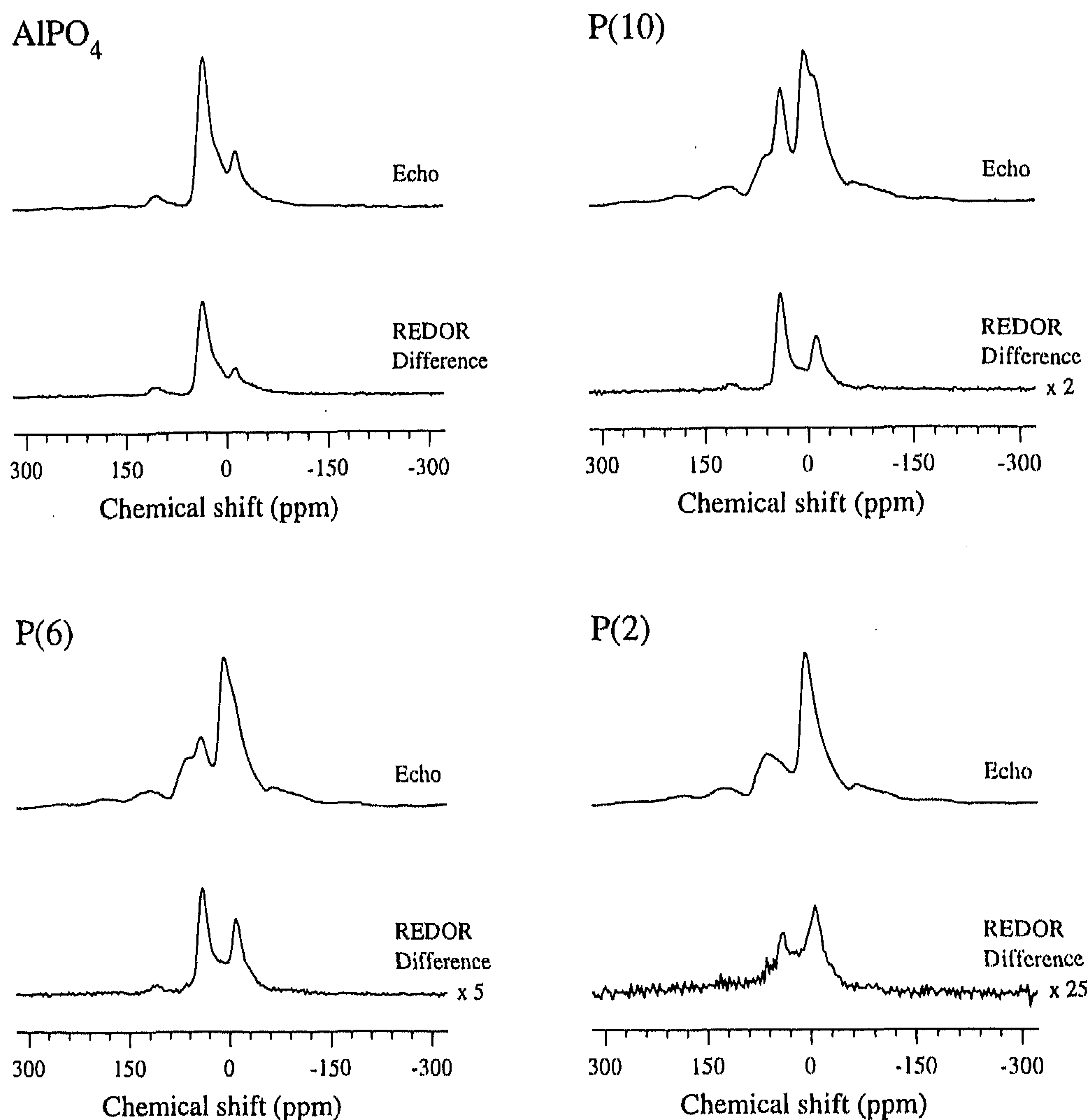


Figure 6. 4,4-REDOR ^{27}Al – ^{31}P spectra of the samples. The full echo spectrum for each sample is the upper spectrum; the difference (contact) spectrum is the lower one. The REDOR difference spectra are enlarged for the phosphorus substituted samples by a factor indicated at the right of each spectrum.

amorphous AlPO_4 than for the $\text{P}(x)/\gamma\text{-Al}_2\text{O}_3$ samples. This seems to be the case for the $\text{P}(2)/\gamma\text{-Al}_2\text{O}_3$ sample where the phosphorus coverage is low and the AlPO_4 phase layer would be the thinnest. It is assumed that surface phosphorus is coordinated to fewer aluminum atoms than phosphorus within a layer of AlPO_4 . The general trend that the relative difference in intensity decreases with a decreasing amount of impregnated phosphorus can be interpreted as a relative increase in the amount of phosphorus at surface sites.

^{27}Al – ^{31}P REDOR Experiments. Figure 6 displays the echo and the REDOR difference spectra of the 4,4-experiments. The difference in signal intensity is the largest in these experiments. The ^{27}Al – ^{31}P REDOR difference spectra show clearly the spectra of the aluminum atoms that are coordinated to phosphorus atoms. The AlPO_4 spectra show that both tetrahedral and octahedral aluminum, located at 36.7 and –13.2 ppm, respectively, are in contact with phosphorus atoms. The shoulder at 11 ppm is also in contact with phosphorus and can therefore be tentatively assigned to five-coordinated aluminum with phosphorus as next-nearest neighbors. The difference spectrum of $\text{P}(10)/\gamma\text{-Al}_2\text{O}_3$ shows a spectrum similar to that of AlPO_4 but with a relatively more intense octahedral aluminum resonance than tetrahedral aluminum resonance. The resonances are located at –10.7 ppm for octahedral aluminum and at 40.5 ppm for tetrahedral aluminum. In the $\text{P}(6)/\gamma\text{-Al}_2\text{O}_3$ difference spectrum, the resonance of six-coordinated aluminum in contact with phosphorus is even more intense. The tetrahedral peak is located at 40.5 ppm, while the octahedral peak is at –8.3 ppm.

In the $\text{P}(2)/\gamma\text{-Al}_2\text{O}_3$ difference spectrum, the positions are 39.2 ppm for tetrahedral aluminum and –6.4 ppm for octahedral aluminum. Here, the contribution of octahedral aluminum to the spectrum is the larger. The relative intensities of the octahedral and tetrahedral aluminum resonances of the $\text{P}(10)/\gamma\text{-Al}_2\text{O}_3$ spectrum are the most similar to the intensities of the amorphous AlPO_4 difference spectrum. For $\text{P}(2)/\gamma\text{-Al}_2\text{O}_3$ the relative intensities are more like those in the $\gamma\text{-Al}_2\text{O}_3$ ^{27}Al spectra, although the shifts differ significantly from the $\gamma\text{-Al}_2\text{O}_3$ shifts. The peak positions of the $\text{P}(x)/\gamma\text{-Al}_2\text{O}_3$ difference spectra are quite similar to the peak positions in the AlPO_4 spectrum, and it seems therefore likely that aluminum and phosphorus form an amorphous AlPO_4 phase that is similar to the synthesized amorphous AlPO_4 , at least at high phosphorus loading.

Figure 7 displays the REDOR difference as a fraction of the echo difference and the full echo intensity. It can be seen that when the phosphorus-to-aluminum ratio becomes smaller, the relative intensity of the aluminum difference spectra decreases with respect to the full echo spectra. This follows from the fact that the maximum number of aluminum atoms with a phosphorus atom in the vicinity decreases. The intensities of the ^{27}Al difference spectra weighed with the amount of phosphorus that is impregnated, of $\text{P}(10)/\gamma\text{-Al}_2\text{O}_3$, $\text{P}(6)/\gamma\text{-Al}_2\text{O}_3$, and $\text{P}(2)/\gamma\text{-Al}_2\text{O}_3$, i.e., dividing the intensities by 10, 6, and 2, respectively, are the same within error limits. The weighed difference intensity of the $\text{P}(2)/\gamma\text{-Al}_2\text{O}_3$ sample is less than that of the other samples, but since the signal-to-noise ratio is also

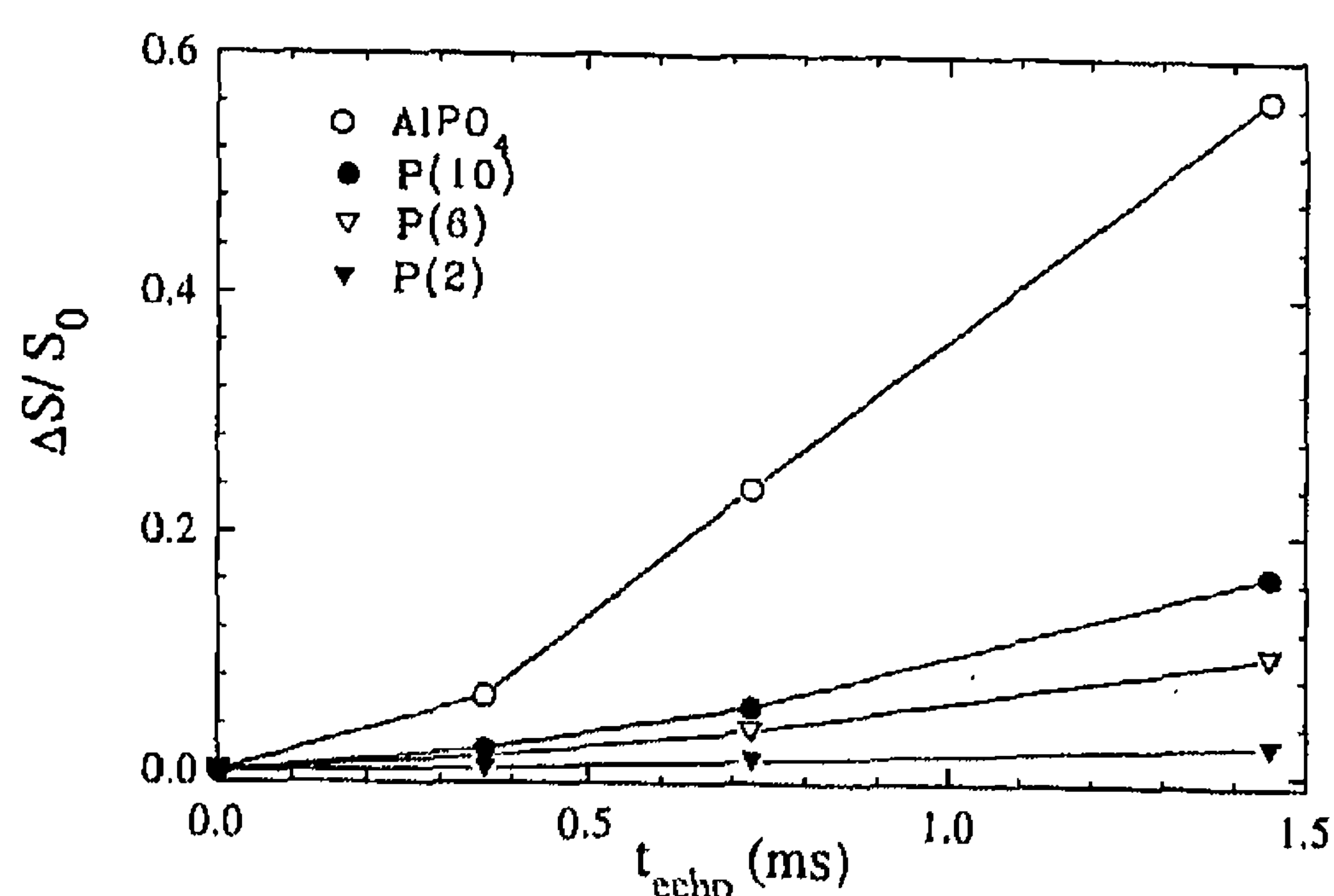


Figure 7. Intensity $\Delta S/S_0$ of the ^{27}Al REDOR difference spectra, relative to the echo intensity, as a function of the echo time. The data points at $t = 0$ are not measured but are zero by definition.

TABLE 1: Peak Positions (ppm) of the Resonances in the Aluminum and Phosphorus Spectra of the Samples under Study^a

sample	$\delta^{27}\text{Al}$ ($B = 7.05$ T)			$\delta^{31}\text{P}$
	Al(IV)	Al(V)	Al(VI)	
AlPO ₄	37.0	11	-13.3	-25.0
P(10)/ γ -Al ₂ O ₃	40.5		-10.7	-13.3
P(6)/ γ -Al ₂ O ₃	40.5		-8.3	-11.7
P(2)/ γ -Al ₂ O ₃	39.2		-6.4	-9.7
γ -Al ₂ O ₃	67.8		5.9	

^a The ^{27}Al shifts of the P(x)/ γ -Al₂O₃ samples are the shifts of the REDOR difference spectra. Note that the assignment of the AlPO₄ resonance at 11 ppm to Al(V) is still tentative.

less than that of the P(10)/ γ -Al₂O₃ and the P(6)/ γ -Al₂O₃ samples the error in the weighed difference intensity has to be taken larger.

For convenience, the shifts of the resonances found in the ^{27}Al single pulse spectra of γ -Al₂O₃ and amorphous AlPO₄ and the REDOR difference spectra of the P(x)/ γ -Al₂O₃ samples as well as the ^{31}P shifts of the single pulse spectra of all phosphorus-containing samples are listed in Table 1.

General Discussion and Conclusions

The impregnation of phosphorus onto γ -Al₂O₃ can lead to different results:

(I) The impregnation is very inhomogeneous, and the phosphorus will form bulk phosphate particles. In this case, phosphorus does not interact with γ -Al₂O₃ at all. This is very unlikely in our case, since the ^{27}Al spectra of the impregnated compounds show an effect of impregnation. The ^{31}P - ^{27}Al REDOR and TRAPDOR results clearly show that phosphorus is in close contact with aluminum. Furthermore, the ^{27}Al - ^{31}P REDOR difference fractions show that the greater the amount of phosphorus which is impregnated, the greater the number of aluminum atoms which are affected by phosphorus.

(II) The phosphorus atoms form a layer of stacked phosphates on the γ -Al₂O₃ surface. If this were true, the amount of aluminum affected by phosphorus would increase until the γ -Al₂O₃ surface would be fully covered and remain approximately constant thereafter. Although one could argue that a layer of stacked phosphates on the γ -Al₂O₃ surface would increase the dephasing effect of the REDOR experiment, this effect would be much smaller than observed since the greater the distance between the nuclei, the smaller the dipolar coupling between them and the smaller the dephasing effect on the echo will be. In the P(6)/ γ -Al₂O₃ and P(10)/ γ -Al₂O₃ samples, the amount of phosphorus is greater than is necessary to form a monolayer on the γ -Al₂O₃ surface. Even so, the number of aluminum atoms that is affected by phosphorus increases by a factor of 10/6, which is equal to the increase in the amount of phosphorus that is impregnated. The same conclusion can be

reached from the ^{31}P - ^{27}Al REDOR and TRAPDOR results. With increasing phosphorus loadings, the REDOR and TRAPDOR fractions would decrease since the amount of phosphorus in the vicinity of aluminum would decrease, relative to the total amount of phosphorus. This is clearly not the case, and we can therefore discard the second possibility.

(III) A layer of AlPO₄ forms on the γ -Al₂O₃ surface at high phosphorus loadings, while at low loadings mono- and polyphosphates connected to surface aluminum atoms (partially) cover the surface. The AlPO₄ layer will be thicker as the amount of phosphorus that is impregnated is increased. The REDOR and TRAPDOR data prove that phosphorus and aluminum atoms are indeed in close proximity. Since the line shape of the ^{31}P - ^{27}Al REDOR and TRAPDOR difference spectra did not alter, all phosphorus atoms are expected to be in contact with aluminum. Furthermore, the ^{27}Al difference spectra, especially of the P(10)/ γ -Al₂O₃ and the P(6)/ γ -Al₂O₃ samples, are quite similar to the ^{27}Al spectrum of amorphous AlPO₄. As was discussed above, the fact that at high phosphorus loadings the intensity of the ^{27}Al difference spectra still increases strongly suggests that a layer of AlPO₄ covers the γ -Al₂O₃ surface and that this layer becomes thicker as phosphorus loadings increase.

The approximate thickness of the AlPO₄ phase can be calculated from the surface area of γ -Al₂O₃ (230 m²/g), the molar mass (121.95 g/mol), and the density of AlPO₄ (2.56 g/cm³). These simple calculations give reasonable results. The layer thicknesses that are calculated this way are 1.3 Å for P(2)/ γ -Al₂O₃, 4.0 Å for P(6)/ γ -Al₂O₃, and 6.7 Å for P(10)/ γ -Al₂O₃. The value for P(2)/ γ -Al₂O₃ is clearly less than the Al-O-P distance in AlPO₄. It is very reasonable that, in this sample, the phosphorus has adsorbed mainly monomerically on the alumina surface, since there is insufficient phosphorus to cover the whole surface. Most of the phosphorus atoms are connected to one aluminum atom only, whereas the other bonds are terminated by phosphorus hydroxyl groups. This is also reflected in the value of the phosphorus shift of this sample. When more phosphorus is impregnated, polyphosphates are formed. They also contain internal and terminal phosphate groups which resonate upfield of the monophosphate resonances.³¹ This polyphosphate monolayer can still form phosphorus hydroxyl groups. At even higher loadings, when no more phosphorus can be accommodated in a phosphate monolayer, the first layer of aluminum atoms at the γ -Al₂O₃ surface starts to react with the phosphorus to form an amorphous AlPO₄ layer. This layer can have a slightly different structure compared to the bulk amorphous AlPO₄. It can be expected that the formation of the AlPO₄ layer occurs during drying of the samples as a condensation reaction when water is removed. At the surface of this layer further phosphorus can be adsorbed as mono- or polyphosphates. The fact that the ^{31}P shifts of the P(x)/ γ -Al₂O₃ samples move toward the value for amorphous AlPO₄ at higher loadings can be explained by the fact that the phosphorus atoms inside the layer have an environment that becomes more similar to the environment of phosphorus in AlPO₄ with an increasing thickness of the AlPO₄ layer.

The aluminum difference spectra show both octahedral and tetrahedral resonances with shifts that are close to the shifts of the amorphous AlPO₄ sample. The higher the phosphorus loading is, the greater is the shift of the octahedral aluminum resonance toward the value of amorphous AlPO₄. It is also clear that the relative intensity of the octahedral resonance decreases as the amount of impregnated phosphorus increases. At low phosphorus content, the intensities may reflect the actual number of aluminum atoms that are coordinated to phosphorus, assuming that one surface aluminum atom coordinates to one

phosphorus. It is also possible that the octahedral aluminum atoms at the surface coordinate to two or more phosphorus atoms, while the surface tetrahedral aluminum atoms coordinate to one phosphorus only. This would also give rise to an increased intensity of the octahedral aluminum resonance, since the average dipolar coupling to phosphorus is larger, thus increasing the effect of the REDOR experiment. However, IR investigations of alumina surfaces³² have only revealed aluminum ions coordinated to one hydroxyl group. The intensity of the resonances are therefore considered to be a rough measure of the number of aluminum atoms coordinated to phosphorus. The relative intensities must be weighed with the T_2 of the respective resonances, but since the T_2 's of the octahedral and tetrahedral resonance do not differ very much, this is of little consequence to the relative intensities. For the P(2)/ γ - Al_2O_3 sample, the ratio of octahedral to tetrahedral resonance of aluminum that is coordinated to phosphorus is similar to that of γ - Al_2O_3 . Since less phosphorus is impregnated than is needed for a monolayer, the phosphorus reacts with the γ - Al_2O_3 surface, and the ratio of octahedral and tetrahedral aluminum reflects the ratio of the atoms that are in contact with the phosphate layer. When the amount of phosphorus is increased, a layer of AlPO_4 is formed in which the relative occurrence of tetrahedral and octahedral aluminum sites becomes more similar to the relative occurrence of these sites in amorphous AlPO_4 . The ^{27}Al line widths of the difference spectra of the P(10)/ γ - Al_2O_3 and the P(6)/ γ - Al_2O_3 samples are notably smaller than those of the amorphous AlPO_4 sample. Furthermore, the broad shoulder at 11 ppm, which is present in the spectrum of the amorphous AlPO_4 sample, is less pronounced for the P(10)/ γ - Al_2O_3 and P(6)/ γ - Al_2O_3 samples. This indicates that the structure of the AlPO_4 layer on the γ - Al_2O_3 surface is better defined than the structure of the amorphous AlPO_4 sample. The reason for this could be that the γ - Al_2O_3 surface acts as a template for the formation of the AlPO_4 layer which forces the AlPO_4 phase to have a better defined structure than the amorphous AlPO_4 . The possibility of different amorphous "transition states" in the formation of AlPO_4 has been suggested before.³³

Sometimes, in the ^{27}Al spectra of aluminas, not all aluminum atoms are observed.³⁴ This raises the question as to whether we observe all the aluminum atoms that are in contact with phosphorus in the ^{27}Al - ^{31}P REDOR spectra. Huggins and Ellis³⁵ have shown that the amount of so-called invisible aluminum that is present in aluminas decreases as the temperature is lowered. They concluded that the fact that some of the aluminum atoms are not observed is due to dynamic processes of protons which migrate on the surface and provide an efficient quadrupolar relaxation mechanism. When phosphorus is impregnated on the γ - Al_2O_3 surface it will react with the surface aluminum hydroxyls and Lewis sites. An aluminum atom that is coordinated to phosphorus is no longer available for proton migration. Thus, this relaxation mechanism of this aluminum atom no longer functions and the aluminum becomes "visible". As soon as the whole surface is covered with a monolayer of phosphorus, there are no more aluminum sites available for proton migration. It is therefore likely that all the aluminum that is in contact with phosphorus is observed.

The double resonance techniques have provided valuable information about the phosphorus impregnation of γ - Al_2O_3 . Upon impregnation of γ - Al_2O_3 with phosphorus, the surface of γ - Al_2O_3 will be partially covered with a monolayer of mono- and polyphosphates at lower loadings. When the amount of phosphorus increases, the impregnation results in a layer of AlPO_4 on the γ - Al_2O_3 surface. The structure of the AlPO_4 layer seems to be better defined than the structure of the amorphous

AlPO_4 sample. The double resonance solid state NMR experiments have proven to be suitable for distinguishing surface phases from the bulk phase of the catalyst support. These experiments are therefore very useful for studying the interaction of catalyst supports with the active phases.

Acknowledgment. The authors acknowledge J. W. M. van Os and J. W. G. Janssen for their technical support. W. S. Veeman, C. P. Grey, and B. H. Meier are recognized for their helpful suggestions and comments.

References and Notes

- (1) Fitz Jr., C. W.; Rase, H. F. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 40-44.
- (2) Tischer, R. E.; Narain, N. R.; Stiegel, G. J.; Cillo, D. L. *Ind. Eng. Chem. Res.* **1987**, *26*, 422-426.
- (3) Eijsbouts, S.; van Gestel, J. N. M.; van Veen, J. A. R.; de Beer, V. H. J.; Prins, R. J. *Catal.* **1991**, *131*, 412-432.
- (4) Stanislaus, A.; Absi-Halabi, M.; Al-Dolama, K. *Appl. Catal.* **1988**, *39*, 239-253.
- (5) Gishti, K.; Iannibello, A.; Marengo, S.; Morelli, G.; Tittarelli, P. *Appl. Catal.* **1984**, *12*, 381-393.
- (6) López Cordero, R.; Esquivel, N.; Lázaro, J.; Fierro, J. L. G.; López Agudo, A. *Appl. Catal.* **1989**, *48*, 341-352.
- (7) Fierro, J. L. G.; López Agudo, A.; Esquivel, N.; López Cordero, R. *Appl. Catal.* **1989**, *48*, 353-363.
- (8) Spojakina, A.; Damyanova, S.; Petrov, L.; Vit, Z. *Appl. Catal.* **1989**, *56*, 163-176.
- (9) López Cordero, R.; López Guerra, S.; Fierro, J. L. G.; López Agudo, A. *J. Catal.* **1990**, *126*, 8-12.
- (10) Kim, S. L.; Woo, S. I. *J. Catal.* **1992**, *133*, 124-135.
- (11) Lewis, J. M.; Kydd, R. A. *J. Catal.* **1992**, *136*, 478-486.
- (12) Ramírez, J.; Castaño, V. M.; Leclercq, C.; López Agudo, A. *Appl. Catal.* **1992**, *A83*, 251-261.
- (13) McMillan, M.; Brinen, J. S.; Haller, G. L. *J. Catal.* **1986**, *97*, 243-247.
- (14) Mangnus, P. J.; van Veen, J. A. R.; Eijsbouts, S.; Beer, V. H. J.; Moulijn, L. A. *Appl. Catal.* **1990**, *61*, 99-122.
- (15) Han, O. H.; Lin, C. Y.; Haller, G. L. *Catal. Lett.* **1992**, *14*, 1-9.
- (16) Han, O. H.; Lin, C. Y.; Sustache, N.; McMillan, M.; Carruthers, J. D.; Zilm, K. W.; Haller, G. L. *Appl. Catal. A* **1993**, *98*, 195-210.
- (17) DeCanio, E. C.; Edwards, J. C.; Scalzo, T. R.; Storm, D. A.; Bruno, J. W. *J. Catal.* **1991**, *132*, 498.
- (18) van Veen, J. A. R.; Hendriks, P. A. J. M.; Andréa, R. R.; Romers, E. J. G. M.; Wilson, A. E. *J. Phys. Chem.* **1990**, *94*, 5382-5285.
- (19) Gullion, T.; Schaefer, J. *Advances in Magnetic Resonance*; Academic Press: San Diego, 1989; Vol. 13, pp 57-83.
- (20) Gullion, T.; Schaefer, J. *J. Magn. Reson.* **1989**, *81*, 196-200.
- (21) van Eck, E. R. H.; Janssen, R.; Maas, W. E. J. R.; Veeman, W. S. *Chem. Phys. Lett.* **1990**, *174*, 428-432.
- (22) Grey, C. P.; Veeman, W. S.; Vega, A. J. *J. Chem. Phys.* **1993**, *98*, 7711-7724.
- (23) McDowell, L. M.; Holl, S. M.; Qian, S.; Li, E.; Schaefer, J. *Biochemistry* **1993**, *32*, 4560-4563.
- (24) Christensen, A. M.; Schaefer, J. *Biochemistry* **1993**, *32*, 2868-2873.
- (25) Garbow, J. R.; McWherter, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 238-244.
- (26) Fyfe, C. A.; Mueller, K. T.; Grondley, H.; Wong-Moon, K. C. *J. Phys. Chem.* **1993**, *97*, 13484-13495.
- (27) Kehl, W. C. U.S. Patent 4080311, 1978.
- (28) Marcelin, G.; Vogel, R. F.; Swift, H. E. *J. Catal.* **1983**, *83*, 42-49.
- (29) Vega, A. J. *J. Magn. Reson.* **1992**, *96*, 50-68.
- (30) Vega, A. J. *Solid State Nucl. Magn. Reson.* **1992**, *1*, 17-32.
- (31) Grimmer, A. R.; Haubenreisser, U. *Chem. Phys. Lett.* **1983**, *99*, 487-490.
- (32) Knözinger, H.; Ratnasamy, P. *Catal. Rev.—Sci. Eng.* **1978**, *17*, 31-70.
- (33) Müller, D.; Grunze, I.; Hallas, E.; Ladwig, G. *Z. Anorg. Allg. Chem.* **1983**, *500*, 80-88.
- (34) O'Reilly, D. E. *Adv. Catal.* **1960**, *12*, 31.
- (35) Huggins, B. A.; Ellis, P. D. *J. Am. Chem. Soc.* **1992**, *114*, 2098-2108.