

## Phosphorus Poisoning of the Three-Way Catalyst Studied by $^{31}\text{P}$ NMR

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Magic angle spinning  $^{31}\text{P}$  NMR spectroscopy is shown to be an informative technique for the study of the extent and chemistry of phosphorus poisoning of the three-way catalyst (TWC) used to control auto emissions. The NMR study of both used and fresh catalysts indicates that phosphorus is extraneous to the fresh catalyst and probably associated with the reduced catalytic activity of the aged converter. At least three different types of phosphorus compounds are observed and tentatively assigned. © 1988 Academic Press, Inc.

The platinum-rhodium (Pt-Rh) three-way catalyst (TWC) employed for the simultaneous removal of nitrogen oxides, CO, and hydrocarbons from light-duty auto emissions is prone to deactivation by lead, sulfur, and phosphorus chemical poisoning (1-5). Recently, it has been found that use of zinc dialkyldithiophosphate (ZDTP, a common antiwear oil additive) in engine oils results in the formation of a glassy glaze on the surface of the catalyst (6), substantially reducing catalytic activity. Surface characterization techniques have shown that the glaze, which covers the noble metal particles and hinders the flow of gases through the catalytic converter, is possibly zinc pyrophosphate ( $\text{Zn}_2\text{P}_2\text{O}_7$ ) (6).

To elucidate further the chemical nature of the glaze on the TWC that results from the use of ZDTP in engine oils, magic angle spinning (MAS)  $^{31}\text{P}$  NMR experiments have been performed on powdered samples of deactivated and fresh Pt-Rh TWCs. NMR is unique in its ability to identify and quantify chemical species and to ascertain local molecular structure, such as amorphous versus crystalline nature. This note presents preliminary results on the types of phosphorus compounds found on poisoned TWCs.

### EXPERIMENTAL

Phosphorus-31 MASNMR spectra were acquired at 120.5 MHz on a Bruker MSL300 spectrometer. The Bruker MAS probe uses a Lowe-type double air-bearing alumina rotor and requires 300 mg of sample. Nonspinning spectra were acquired by means of a Bruker broad-band solids probe. Pulse sequences for creation of the free induction decay (FID) were either a single  $90^\circ$  pulse followed by data acquisition (ACQ) or a spin echo sequence,  $90^\circ-\tau-180^\circ-\tau$ -ACQ (7). Initially, acquisition was accompanied by high-power proton decoupling (7) to remove  $^{31}\text{P}$ - $^1\text{H}$  dipolar coupling along with the usual cross-polarization (CP) techniques (8) for signal enhancement. The FID was processed by standard Fourier transformation and phasing (7). Chemical shifts are expressed with respect to 85%  $\text{H}_3\text{PO}_4$  at 0 ppm. Negative shift values are upfield.

### SAMPLE

The TWC had a precious metal loading of  $1.77 \times 10^3 \text{ g/m}^3$  at Pt/Rh = 9/1 and was a 5-in.-long honeycombed monolith (2). The deactivated catalyst was aged in service on a neat-methanol-fueled 2.3-liter Ford Pinto

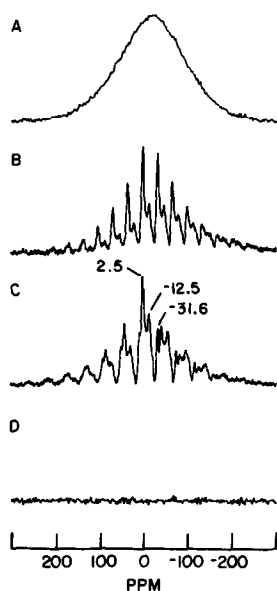


FIG. 1. Phosphorus-31 NMR spectra of the first  $\frac{1}{4}$  in. of the methanol fuel aged TWC. (a) Nonspinning, liquid echo,  $\tau = 20 \mu\text{sec}$ , 2600 acquisitions; (b) 4 kHz MAS, single  $90^\circ$  pulse, 26,800; (c) 5 kHz, single  $90^\circ$  pulse, 31,500; (d) 5 kHz, single  $90^\circ$  pulse, 28,000.

and was removed from the vehicle after it showed high emissions (2).

For the MASNMR, approximately 1 g of material was chipped from the first  $\frac{1}{4}$  in. of the catalyst on the face that was closest to the engine. This part of the catalyst was discolored from its normal brownish color. The sample was ground in an agate mortar and approximately 300 mg was packed into the MAS rotor. One gram of sample was used to obtain the nonspinning spectrum.

## RESULTS

The  $^{31}\text{P}$  NMR spectrum illustrated in Figure 1A was acquired from a nonspinning sample by means of the spin echo sequence without proton decoupling. Data acquisition was initiated at the top of the echo. This technique was used to avoid the probe and spectrometer ringdown transient observable in the FID under single pulse-conditions. The lineshape of this spectrum is similar to the shapes often observed for resonances severely broadened by proton

dipolar coupling (9). However, spectra acquired with or without proton decoupling of greater than 80 kHz were identical. Although this sample also gave a broad, intense proton resonance, there appears to be no hydrogen in the phosphorus-containing species. The lack of  $^1\text{H}$ - $^{31}\text{P}$  coupling also explains why the CP technique, which requires this interaction (8), was unusable.

Further information about the nature of the phosphorus species in the catalyst comes from the MASNMR experiment. Spectra for spinning speeds of 4 and 5 kHz, acquired with a single  $90^\circ$  pulse, are illustrated in Figs. 1B and 1C, respectively. These examples demonstrate the typical features seen in MASNMR spectra. The broad resonance of Fig. 1A has been broken up into a series of sidebands that flank to both high and low frequency the line located at the position of the isotropic chemical shift. In the 4-kHz spectrum, two series of sidebands are observed, one approximately twice the height of the other. On going to 5 kHz, however, where the separation of the lines increases, it is seen that there are actually three series. The isotropic chemical shifts, whose positions are independent of the rotor frequency, are indicated in Fig. 1C by numbers that give their shifts in ppm. As may be concluded from the theory of MASNMR (10), the three isotropic chemical shifts represent three distinct, nonequivalent species of phosphorus in the catalyst. The presence of at least three species (and perhaps others, see below) whose MAS-averaged resonances are broad explains why the nonspun spectrum shows none of the sharp features characteristic of the anisotropic chemical shift powder pattern spectrum of a single species (9). No phosphorus signal was observed from a fresh, but otherwise similar catalyst (Fig. 1D), indicating that the three compounds are foreign to the TWC. It may not be concluded, however, that all of the phosphorus compounds are located on the surface of the catalyst since the NMR

technique cannot *a priori* discriminate between surface and bulk phosphorus.

The isotropic chemical shift values seen for the phosphorus species fall within the range normally observed from phosphate compounds (11). More specifically, the resonances at 2.5 and  $-12.5$  ppm are within the subrange of the end phosphate group (12), a phosphorus with three terminal and one bridging oxygens (13). The third line at  $-31.6$  ppm falls on the border of the ranges for middle and branching phosphates. Middle phosphates have two terminal and two bridging oxygens while branching phosphates have one terminal and three bridging oxygens. These ranges overlap to an extent (14).

#### DISCUSSION

At least three phosphate species have been mentioned in relation to the problem of ZDTP poisoning of the TWC (4). One of these, ZDTP itself, is not observed on the catalyst. The  $^{31}\text{P}$  MASNMR spectrum of ZDTP is a doublet with the isotropic shifts at 95 and 90 ppm, well outside of the values observed for the species on the catalyst.  $\text{AlPO}_4$ , at  $-27$  ppm, is upfield of the range commonly expected for the orthophosphates (11). This species cannot, however, account for any of the catalyst species. Electron probe analysis has indicated the presence of zinc on the catalysts, possibly in the form of zinc pyrophosphate (4). Zinc pyrophosphate has two equivalent end phosphate groups, which may account for one of the end groups seen by the NMR. A sample of  $\text{Zn}_2\text{P}_4\text{O}_7$  was prepared by precipitation from a solution of  $\text{ZnCl}_2$  and  $\text{Na}_4\text{P}_2\text{O}_7$  and showed a broad (full width at half height of 4 ppm) peak at  $-7$  ppm. This does not correspond to any of the catalyst's peaks. Nevertheless, the shifts observed in the catalyst are not far from those for  $\text{AlPO}_4$  and  $\text{Zn}_2\text{P}_4\text{O}_7$ . It is possible that these species are indeed present but that their shifts are perturbed by the complex environment of the catalyst's surface.

The existence of additional types of

phosphate compounds cannot be ruled out. The linewidths of the MAS-averaged resonances of Figs. 1B and 1C are still broad enough to mask the presence of other similar, but distinct phosphate groups whose resonances overlap. Two effects will contribute to the spectral linewidths of the individual  $^{31}\text{P}$  resonances. The first of these is P-P dipolar coupling, which goes as the inverse cube of the distance between two phosphorus atoms (9). For zinc pyrophosphate, phosphorus dipolar coupling will contribute roughly 2 kHz (15 ppm) to the nonspinning linewidth. Under MAS conditions, the broadening due to this interaction will be markedly reduced if not eliminated. Broadening also results if the material is noncrystalline. If a material is amorphous, characterized by a distribution of environments, its isotropic chemical shifts will be dispersed, as observed in the MAS experiment. Linewidths observed for phosphorus in the TWC, taking into account the possibility of MAS-averaged P-P dipolar coupling, are consistent with amorphous phosphorus compounds. This observation further supports the notion that the glassy material observed by scanning electron microscopy (1) is indeed one of the phosphorus species.

The NMR can measure the percentage of phosphorus in the TWC by comparison of the integrated signal intensity against that from a known sample such as  $\text{KH}_2\text{PO}_4(\text{s})$ . This comparison indicated that the TWC was approximately 2% P by weight, in agreement with a previous determination by x-ray fluorescence (2). It is possible, therefore, to observe a  $^{31}\text{P}$  NMR signal from a sample with 0.1% phosphorus by weight. From a practical point of view, the observability of a small weight percentage of phosphorus and the inherent selectivity of  $^{31}\text{P}$  NMR makes this an informative alternate technique to x-ray fluorescence to determine (a) whether a catalyst has been poisoned by phosphorus, (b) the extent of this poisoning, and (c) the chemical nature of the poisoning species.

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