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Supported Aqueous-Phase Catalysts

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This work describes a novel family of catalysts denoted supported aqueous-phase catalysts. These catalysts consist of a water-soluble organometallic complex supported in a thin film of water residing on a high-surface-area hydrophilic solid. The catalytic reaction takes place at the water–organic interface where the organic phase contains the reactants and products. Supported aqueous-phase catalysis is demonstrated by liquid-phase hydroformylation. The solid support used here was either CPG-240 or CPG-350; both are porous glasses with narrow pore volume distributions. The catalytic species, $HRh(CO)[m\text{-}P(PhSO_3Na)_3]_3$ was synthesized from $Rh(CO)_2(acac)$ by a new synthetic route and impregnated onto CPG-240. Solution and solid-state ^{31}P NMR data are consistent with a mobile rhodium species in the aqueous phase in hydrated forms of the catalyst. The hydroformylation of oleyl alcohol (OLOH) was accomplished at 100°C and 5.1 MPa of H_2/CO (1/1) using 0.002 g Rh/g OLOH. For example, conversions of up to 96.6% could be achieved in 5.5 h. It is postulated that no significant leaching of Rh occurs, since after filtration to remove the solid catalyst the remaining solution showed no activity for either the hydroformylation of additional OLOH or the hydrogenation of added 1-hexene. The observations that (1) OLOH and its hydroformylation products are not water soluble, (2) the double bond of OLOH is internal, and (3) the Rh does not leach into the organic phase demonstrate the concept of SAP catalysis; the immobilized homogeneous catalyst is active at the interface of two immiscible phases.

INTRODUCTION

The growth of homogeneous catalytic processes is primarily due to their selectivity and activity performance. These qualities satisfy current needs for processes of high efficiency which operate under relatively mild conditions with few by-products (*1*). It has been long recognized that homogeneous processes suffer from the difficulties of separating the catalyst from products and it is for this reason that methods for immobilizing transition metal species have been studied in detail. Techniques used to immobilize homogeneous catalysts have centered on the retention of its structure and properties of its homogeneous counterpart. Comprehensive reviews of immobilization techniques are available (*2*).

In principle, immobilization may be achieved in one of several ways: (i) chemisorption of a metal complex onto a solid support, (ii) physical adsorption of a complex on a support, (iii) entrapment of metal complexes via *in situ* synthesis within zeolites (*3*), (iv) dissolution of a complex in a nonvolatile solvent, and (v) dissolution of a complex in a nonvolatile solvent which is adsorbed onto the surface of a support, i.e. supported liquid phase (SLP) (*4*). At present, the first three of these methods have not provided a commercially viable heterogeneous catalyst. Loss of activity and/or selectivity, often by the leaching or decomposition of the immobilized complex, are the main reasons for this restriction. The immobilization method of partitioning the catalyst and the reactants/products between different phases, represented by (iv) has been more successful. The Rhone–Poulenc hydroformylation process produces butyraldehyde from propylene in water with a water-soluble Rh complex (*5*) and the Union Carbide process

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hydroformylates propylene in high boiling hydrocarbon solvents (*6*). Both of these processes satisfy the condition of an immobilized homogeneous catalyst since reactants and products are phases separate from the catalyst phase under the operating conditions of hydroformylation. The immobilization methods represented by (iv) and (v) above are not able to convert liquid reactants in any fashion sufficient for commercial utilization. The commercial hydroformylation of higher olefins (C_6 or larger) is performed exclusively with cobalt carbonyl-derived catalysts (*7–9*).

It has long been recognized that reactions taking place at an interface differ from those in bulk in the uniform and controlled accessibility and orientation of the reactant molecules (*10*). The interface can lead to an alteration, not only of the rate, but also of the equilibrium position and the selectivity of the reaction. Examples of this kind of reaction are emulsion polymerization and hydrolysis of fats (*10*).

We recently reported a new class of heterogeneous catalysts: supported aqueous-phase (SAP) catalysis (*11*) (see Fig. 1). The catalytic phase, immiscible with the organic phase containing the reactants/products, consists of an aqueous solution of a water-soluble organometallic catalyst. To provide for the necessary interfacial area required for the reaction to proceed at a reasonable rate, the catalyst phase is immobilized in the pores of a high-surface-area solid as shown schematically in Fig. 1. Furthermore, since the catalysis proceeds at the interface between an organic phase containing the reactants and products and an aqueous phase containing the catalytic species, SAP catalysis is usable with liquid reactants. SAP catalysis displays good activity for the hydroformylation of oleyl alcohol (*11*).

Here we report on the physical characterization of the immobilized homogeneous catalyst to support the concept of SAP catalysis. Furthermore, the system is examined as a heterogeneous hydroformylation catalyst for several water-insoluble reactants (*12*).

EXPERIMENTAL

General

Triphenylphosphine (Strem), H_2SO_4 (Fisher), NaOH (Fisher), diethylether (Fisher), SO_3 (Aldrich), tributylphosphate (Aldrich), the controlled pore glasses CPG-240 and CPG-350 (Electronucleonics), and $Rh(acac)(CO)_2$ (Strem) were purchased in their highest purity available and used as received. Unless otherwise stated all manipulations were performed under nitrogen or argon. Fuming sulfuric acid, 71% SO_3 concentration, was prepared by mixing stoichiometric amounts of 30% SO_3 in H_2SO_4 and 99% SO_3. Distilled, deionized water was used in all operations requiring water. All solvents, including water, were degassed by three freeze–pump–thaw cycles.

Catalyst Preparation

Trisodium salt of tri-(m-sulfonphenyl)-phosphine (TPPTS). TPPTS was synthesized via a modification of the patent literature method (*5*). Thus, 8 g of triphenylphosphine (TPP) (30.5 mmol) was placed in a 250-ml round-bottom flask under Ar and cooled to 10°C. Concentrated sulfuric acid (13.7 ml) was then added dropwise while the mixture was stirred vigorously. When all the TPP had dissolved, fuming sulfuric acid (72.7 g–71 wt% SO_3) (645 mmol SO_3) was added dropwise to the solution. The temperature of the reaction flask was allowed to increase to 20.5°C over a 7-h period. After 12 h, the reaction was quenched by cooling to 6°C and adding 200 ml degassed chilled water. The aqueous solution was then extracted two times with 50 g each of tributylphosphate. The tributylphosphate layer was neutralized by vigorous stirring with 50% NaOH in water (dropwise addition in an ice bath). The resultant sludge was washed five times with 100 ml of diethylether per washing and vac-

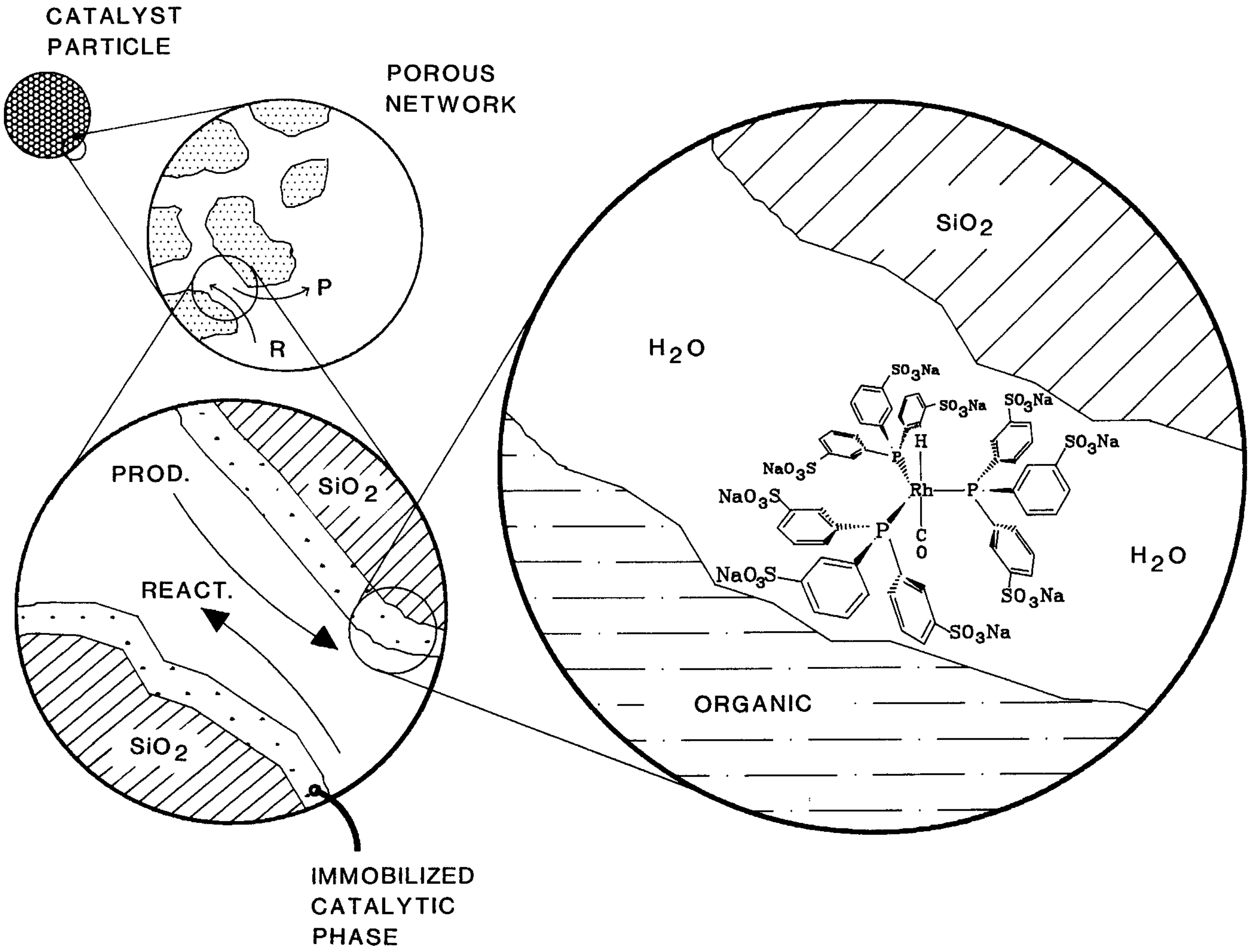


FIG. 1. Schematic representation of a SAP catalyst.

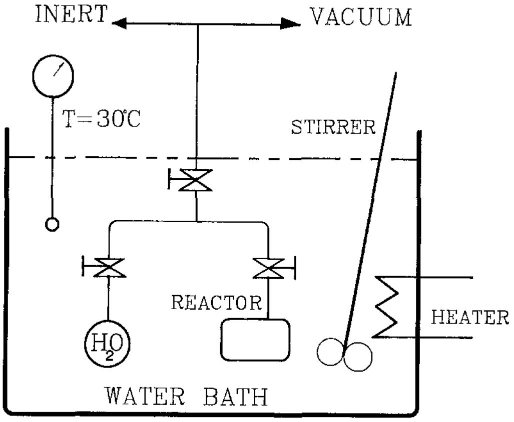


FIG. 2. Schematic of the apparatus used for the introduction of water to the supported catalysts.

uum dried. The sludge was then dissolved in 75 ml of distilled water and 75 ml of absolute methanol was added to yield a brown precipitate. The solid was then removed by filtration. Phosphorus-31 NMR analysis of the solid revealed that it contained a large amount of TPPTS. The mother liquor was evaporated under vacuum to give 5.0 g of TPPTS (29% yield). The ligand was analyzed by ^{13}C and ^{13}P solution NMR.

HRh(CO)(TPPTS)$_3$. A solution of 400 mg TPPTS (0.704 mmol) in 1 ml water was added to 50 mg acetylacetonatedicarbonyl-Rhodium(I),($Rh(CO)_2(acac)$, 0.194 mmol) in a small sidearm flask. The solution was maroon upon dissolution of $RH(CO)_2$ (acac). An atmosphere of H_2/CO (1/1) was introduced to the flask at room temperature and atmospheric pressure. Within 5 min, the color of the solution changed from maroon to yellow. After 6 h, the solution was filtered under nitrogen to remove small amounts of rhodium metal and 8 ml of absolute ethanol saturated with $H_2/CO(1/1)$ was added to yield a yellow precipitate. The solid was collected, washed with absolute ethanol, and vacuum dried; yield, 380 mg $HRh(CO)(TPPTS)_3 \cdot nH_2O$. Thermogravimetric analysis showed a 16% weight loss at 200°C which is attributed to water of solvation. Phosphorus-31 NMR analysis showed no evidence for either phosphine oxide (OTPPTS) or free TPPTS (vide infra).

Impregnation. A 25-ml water solution of 340 mg $HRh(CO)(TPPTS)_3$ and 410 mg TPPTS (pH 10.5) was poured into a flask containing 8.8 g degassed CPG-240. After further degassing the mixture by vacuum boiling, argon was introduced and the slurry was stirred for 1 h. The water was removed under vacuum at room temperature. The final product was a dry, free-flowing yellow powder which was stored under H_2/CO (1/1) at room temperature. The water content was estimated by thermogravimetric analysis to be 2.9 wt%.

Hydration. An aliquot of the supported catalyst was loaded into a reactor which was then immersed into a thermostated bath at 30°C and evacuated. The evacuated catalyst was allowed to adsorb water by exposing the reactor to water vapor from a communicating flask which was also immersed into the thermostated bath (see Fig. 2 for details). Both vessels had been previously evacuated, thus the total pressure in the system was the vapor pressure of water at 30°C (31 Torr). The contact with water vapor was for a period of time, *t*, after which argon was admitted into the system and the reactor immediately closed. The amount of water present in the catalyst was determined by thermogravimetric analysis. By varying the hydration time, *t*, controlled amounts of water could be loaded onto the solid.

Reaction Conditions

The hydroformylation reactor used was a standard batch stainless-steel stirred vessel immersed in a thermostatic oil bath. The H_2/CO ratio used here was always 1/1. The stirring rate and the solvent (cyclohexane) in which the substrates were dissolved were constants for all the experiments. The temperature, pressure, substrate concentration, and hydroformylation time were varied for each substrate. Special care was taken in order to avoid the presence of oxygen at all times.

Analytical Methods

Solution ^{31}P, ^{13}C, and ^{1}H NMR spectra were recorded on a Bruker WP—200 SY spectrometer at 81.02, 50.33, and 200.16 MHz, respectively. Solid-state CPMAS ^{31}P NMR were recorded on a Nicolet NT-150 spectrometer at 60.7 MHz at the Colorado State NMR Center. Proton CRAMPS spectra and dipolar dephasing experiments were recorded at 187 Mz on a modified Nicolet NT-200 spectrometer also at the NMR center at Colorado State. The details of the solid-state NMR experimental procedures used here were the same as those used by Bronnimann *et al.* (*13*). Phosphorus-31 NMR chemical shifts are reported relative to 85% H_3PO_4 (positive values are upfield) and ^{13}C and ^{1}H chemical shifts are reported relative to TMS. Thermogravimetric analyses (TGA) were performed in air on a DuPont 951 thermogravimetric analyzer. Nitrogen adsorption isotherms were recorded on an Omnisorp 100 analyzer. Diffuse reflectance infrared measurements were obtained on an IBM IR/32 FTIR using a Spectra-Tech DRIFTS cell. Transmission infrared measurements were acquired on a Nicolet 5DXB FTIR. Gas chromatography (GC) analysis was performed using a HP 5790A chromatograph. Electron microscopy analysis were obtained using a Phillips 420T STEM and electron microprobe analysis was done in an ARLSEMQ automated electron microprobe at 50 kV with 9 XRD channels.

RESULTS AND DISCUSSION

Catalyst Characterization

The $^{13}C\{^{1}H\}$ ($\{^{1}H\}$ denotes proton decoupling) spectrum of $[HP(m\text{-}PhSO_3H)_3]_2SO_4$ in H_2O (acid form, before neutralization) is shown in Fig. 3. This spectrum confirms that the sulfonate group is in the meta position and that the sulfonation is complete. Also shown in Fig. 3 is the $^{31}P\{^{1}H\}$ spectrum of $[HP(n\text{-}PhSO_3H)_3]_2SO_4$ which consists of a single peak at approximately −5.2 ppm. The corresponding oxide, $P(O)(m\text{-}PhSO_3H)_3$, has a chemical shift of 34.7 ppm; this is virtually absent from the spectrum, which indicates a high purity for the ligand. The solubility of TPPTS was determined in water, glycerin, and ethylene glycol and found to be 0.52–0.85 g TPPTS/g H_2O; 0.11–0.15 g TPPTS/g glycerin; and 0.05–0.08 g TPPTS/g ethylene glycol. The ligand is extremely soluble in water but much less so in either glycerin or ethylene glycol.

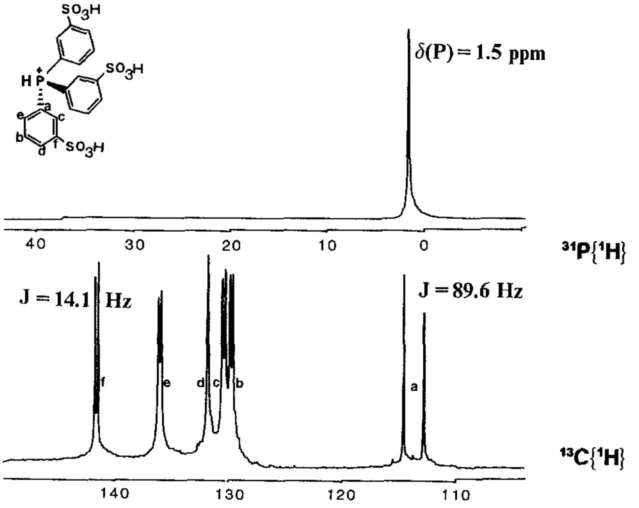


FIG. 3. NMR spectra of $[HP(m\text{-}PhSO_3H)_3]_2SO_4$ in H_2O (acid form of TPPTS).

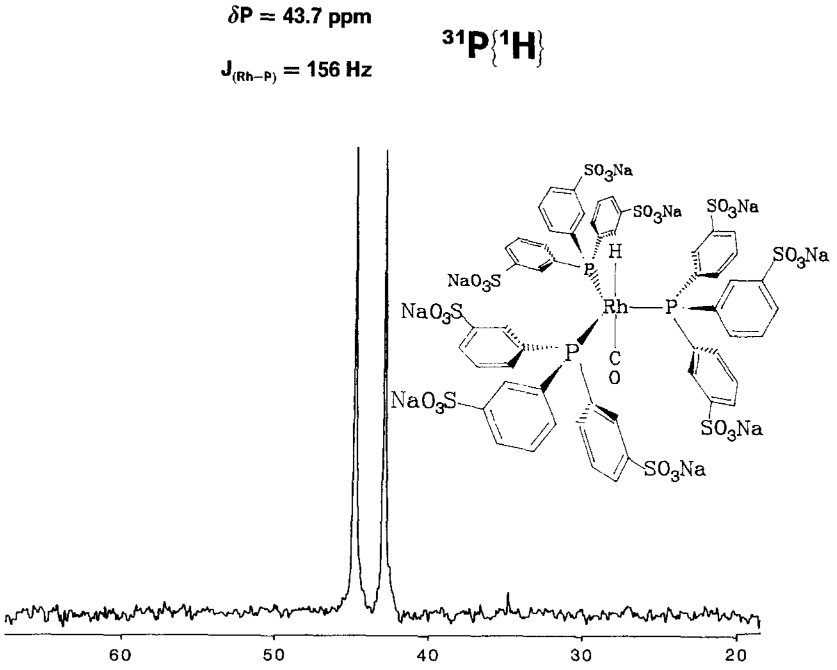


Fig. 4. Phosphorous-31 NMR of $HRh(CO)(TPPTS)_3$ in D_2O and the proposed structure.

The precipitation of $HRh(CO)(TPPTS)_3$ from aqueous solution with ethanol gives an effective purification method since the solubilities of OTPPTS and TPPTS in ethanol are much larger than that of $HRh(CO)(TPPTS)_3$. A TGA of the vacuum-dried $HRh(CO)(TPPTS)_3$ shows a 16% weight loss, which is attributed to water of hydration. Diffuse reflectance FTIR analysis reveals absorptions at 2000 cm^{-1}, assigned as a Rh–H stretch, and at 1921 cm^{-1}, assigned to a carbonyl band by comparison with similar compounds (*14*).

Figure 4 shows the ^{31}P NMR spectrum of $HRh(CO)(TPPTS)_3$ dissolved in D_2O. A doublet at 43.7 ppm with J(Rh–P) = 156 Hz suggests a trigonal bipyramidal structure with the three phosphorus atoms in the equatorial plane and H and CO in axial positions. Independent work by high-pressure NMR is also consistent with this structure (*15*). The ^1H CRAMPS experiments performed on $HRh(CO)(TPPTS)_3$, blank CPG-240, and the corresponding SAPC are shown in Fig. 5. The hydride signal of HRh

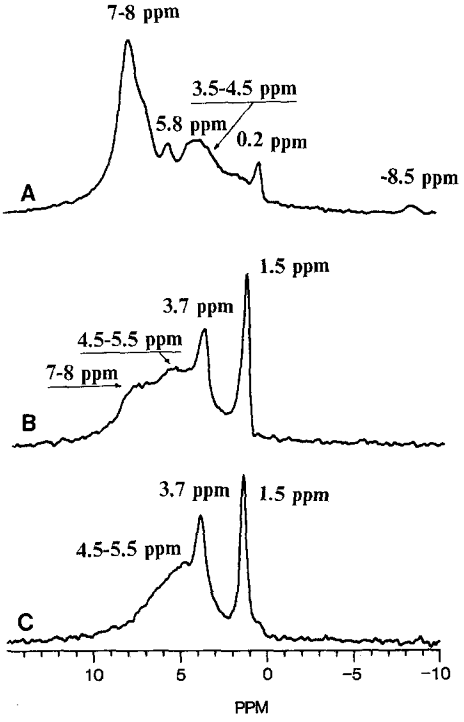


Fig. 5. Proton CRAMPS spectra of (A) $HRh(CO)(TPPTS)_3$, (B) SAP catalyst, and (C) CPG-240.

(CO)(TPPTS)$_3$ is visible at about −8.5 ppm in Fig. 5A. The signals at 0.2 and 5.8 ppm are probably due to residual ethanol from the preparation of RHh(CO)(TPPTS)$_3$. The broad signal at ca. 7.8 ppm is assigned to the aromatic protons of the ligand. Finally, the broad signal at 3.5–4.5 ppm is attributed to water of hydration for the hydrophilic complex.

The ^{1}H CRAMPS spectrum for blank CPG-240 shows signals at 1.5 and 3.7 ppm which are assigned to surface silanol groups and weakly adsorbed water, respectively (Fig. 5C). The broad band at ca. 5 ppm is tentatively assigned to bridged silanols by analogy to results reported for silica gel (*13*). Strongly adsorbed water may also contribute to the signal at 5 ppm. Dipolar dephasing experiments are consistent with two species, one mobile and one static, contributing to the signal at 5 ppm (*16*).

The SAP catalyst derived from CPG-240 and HRh(CO)(TPPS)$_3$ shows signals for surface hydroxyls and adsorbed water, as well as the aromatic protons of the TPPTS ligand (Fig. 5B). The material contains not only coordinated TPPTS but also free TPPTS which is added to enhance the selectivity of the catalyst. A resonance assignable to a hydride is not observed in the SAP catalyst. The failure to observe the hydride is likely due to poor signal-to-noise although abstraction of the hydride cannot be ruled out (*17*).

It has been shown that the dispersion of a catalyst solution in a support with a wide pore volume distribution (PVD) is uneven (*18*). In order to maximize the even distribution of catalyst solution in preparing SAP catalysts, we used the narrow PVD material, CPG-240, as the support. This material, available from Electronucleonics (*19*), has the following properties: mesh size = −120/+200; mean pore diameter = 237 Å; PVD = ±4.3%; pore volume = 0.95 ml/g; surface area = 77.5 m^2/g. It has been reported also that the surface hydroxyl groups of controlled pore glasses in contrast to those of silica gel, are homoenergetic (*20*). The CPG-240 was used as received. From N_2 adsorption–desorption experiments on CPG-240, the values of surface area and dispersion around the mean of the PVD given by the supplier were confirmed.

Thermogravometric analysis performed on the vacuum-dried SAP catalyst shows a 2.9% weight loss attributed to residual water. Electron microprobe analysis of the small SAP catalyst particles shows that the Rh/P ratio is uniform across the particles. Neither diffuse reflectance nor transmission FTIR could detect the infrared bands expected for the complex in the SAP catalyst. The broad silica band at ~1850 cm^{-1}, as well as the low loading, complicate infrared analysis of SAP catalysts.

The CPMAS ^{31}P NMR spectrum of the unhydrated SAP catalyst is shown in Fig. 6. Four phosphorus environments are seen for the unhydrated SAPC sample at 45, 30, −3, and −18 ppm. These have relative integrated areas of 0.30, 0.26, 0.15, and 0.29, respectively. The tentative assignments are HRh(CO)(TPPTS)$_3$, OTPPTS, TPPTS, and TPPTS(ads), respectively.

When the dry supported catalysts are exposed to water it is possible to record a ^{31}P NMR spectrum using normal solution techniques. The solution ^{31}P NMR spectrum for a SAP catalyst containing 40 wt% H_2O is shown in Fig. 7. Four broad signals are seen at 46, 36, 29, and −2 ppm; these are assigned to HRh(CO)(TPPTS)$_3$, OTPPTS, an unidentified species, and free TPPTS, respectively. The presence of OTPPTS arises from the oxidation of TPPTS. Three of these signals, HRh(CO)(TPPTS)$_3$, OTPPTS, and TPPTS are seen in the CPMAS spectrum of the dry catalyst. The signal at −18 ppm in the CPMAS spectrum is absent in the "solution" spectrum. This is consistent with strongly adsorbed TPPTS being solvated by the presence of excess water. The peak of 29 ppm remains unassigned at this time. The fact that solution NMR techniques allow the observation of an NMR spectrum for hydrated SAP cata-

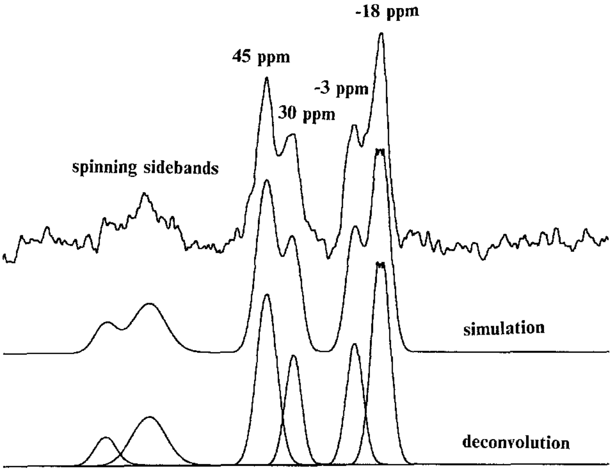


FIG. 6. CP MAS ^{31}P NMR and its deconvolution on unhydrated SAPC.

lyst samples and that CPMAS techniques are necessary for dehydrated samples provide the best evidence that the adsorbed species are mobile when the SAP catalysts are hydrated and static when dehydrated. Further evidence for the static nature of adsorbed species in the dehydrated SAP catalyst samples comes from variable contact time experiments and analysis of spinning sidebands in the CPMAS ^{31}P NMR spectra (*16*).

Hydroformylation Reactions

Hydroformylation of Oleyl Alcohol (OLOH). One of the purposes for developing the SAP materials was to generate heterogeneous catalysts capable of transforming liquid-phase substrates. Since neither oleyl alcohol nor its hydroformylation products are water soluble and the double bond is internal this substrate was chosen to test the concept of SAP catalysis (*11*).

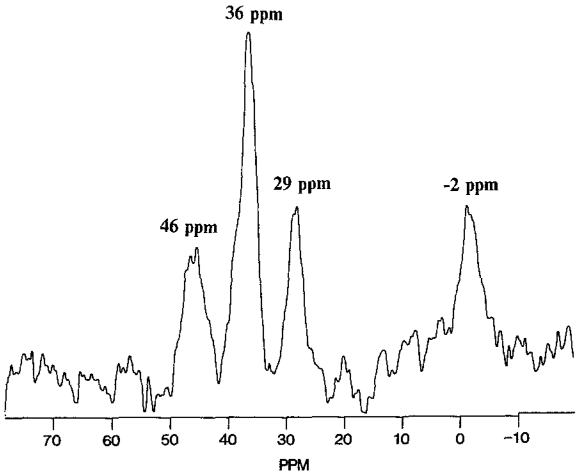


FIG. 7. Liquid state ^{31}P NMR on a SAP catalyst containing 40% H_2O.

Furthermore, in the Rhone–Poulnec water-soluble hydroformylation catalyst system oleyl alcohol can only be hydroformylated when tetraalkyl ammonium salts of tris-sulfonated triphenyl phosphine are used as the ligand (*21*). Under these conditions the catalyst is soluble in hydrocarbon solvents.

We examined a simple two-phase reaction system for comparison with the SAP catalysis results discussed below. Thus when OLOH was charged (26 wt% in cyclohexane) into the hydroformylation reactor along with an aqueous solution of $HRh(CO)(TPPTS)_3$ and TPPTS (weight aqueous phase/weight organic phase = 0.26, moles P/moles Rh = 7.8, weight Rh/weight OLOH = 0.0033) the conversion to aldehydes was below our detection limit (0.1%) after 13 h at 100°C, H_2/CO (1/1), pressure = 6.0 MPa. The aqueous phase, which was yellow at the beginning of the reaction, turned black, indicating decomposition of the catalyst.

The results under SAP catalysis conditions are dramatically improved. When OLOH was charged (26 wt% OLOH in cyclohexane) into the hydroformylation reactor along with an dehydrated sample of the SAP catalyst (weight Rh/weight OLOH = 0.002), the conversion to aldehydes was 96.6% after 5.5 h at 100°C, H_2/CO (1/1) pressure = 5.1 MPa. Significantly the SAP catalyst, which was yellow at the beginning of the reaction, remained yellow. The hydroformylation products of oleyl alcohol were characterized by transmission FTIR and ^1H and ^{13}C NMR. These spectra are consistent with the hydroformylation on the internal double bond of OLOH.

Filtration of the reaction mixture to remove solid catalyst after hydroformylation yielded a colorless solution of products in cyclohexane. Previously, we were unable to detect rhodium in similar colorless solutions by either spectrophotometric or atomic absorption methods (*22*). Thus we tested indirectly for the presence of rhodium by catalytic activity. This is a valid test since rhodium is an effective catalyst at trace concentrations for many reactions. In no case was catalytic activity observed in the filtered solutions. For example, the filtered solutions gave no further conversion of oleyl alcohol (excess oleyl alcohol added to bring concentration to 46 wt%) either at 100°C for 9 h under 5.1 MPa H_2/CO (1/1), or, in a separate test, at 140°C under the same pressure. The inactivity of these solutions suggests that no soluble rhodium species are present in solution.

The possibility that trace amounts of colloidal rhodium could be present in the filtered solutions was examined by testing for hydrogenation activity. Thus, when 1-hexene is added to a filtered solution no hydrogenation is observed after 2 h at 100°C under 0.52 MPa H_2. This suggests that no rhodium is lost through formation of rhodium colloids in the hydrocarbon phase.

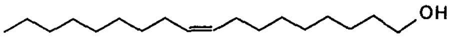
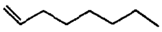
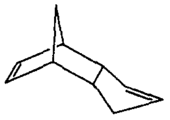
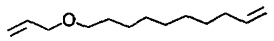
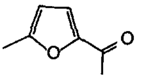
Other supports are available for the preparation of SAP materials. The closely related CPG-350 (*19*) has an average pore diameter of 343 Å and a pore volume of 0.97 ml/g. The surface area of CPG-350 is 67.5 $m^2\ g^{-1}$ vs 77.5 $m^2\ g^{-1}$ for CPG-240.

A catalyst was prepared from CPG-350 such that the amount of rhodium per unit surface area was equal to that of the catalysts prepared with CPG-240. The purpose was to qualitatively examine the influence of surface area on conversion. Under the same reaction conditions similar conversions were obtained when a surface area of the CPG-350 catalyst equivalent to that of the CPG-240 catalyst was used. These results are consistent with the premise that the reaction is occurring at the interface.

Hydroformylation of other substrates. Table 1 summarizes the hydroformylation results for other substrates under SAPC conditions with the CPG-240 catalyst. In all cases shown the water content was 2.9 wt%. A variety of substrates were converted and no surprising selectivities were observed. As described above, the catalysts were tested for rhodium elution when 1-octene was used as the substrate. Again

TABLE 1

Substrates Hydroformylated

OLEYL ALCOHOL	YES		
1-OCTENE	YES	n/i = 2	
DICYCLOPENTADIENE	YES		
ALLYL 9-DECENYL ETHER	YES		
t,t-2,4-HEXANEDIOL	NO		
2-ACETYL-5-METHYLFURAN	NO		

TYPICAL CONDITIONS	
g Rh/g sub.	0.2×10^{3}
H_2/CO	1
P	750 psig
T	100°C
Sub.conc. in sol.	50 %
Reaction time	5 h

no evidence for rhodium loss was observed.

Influence of water content. The weight percentage water in the SAP materials has a dramatic effect on activity. This is evident from the hydroformylation results on 1-octene as a function of water content. The reactivity results are presented in Fig. 8 (reaction conditions: P/Rh = 6.9, wt Rh/wt 1-octene = 0.0005, T = 70°C, H_2/CO = 1, pressure 5.3 MPa, time = 5 h). A substrate solution of 25% octene in cyclohexane was used. Water was reintroduced to the SAP material as described under Experimental for 0, 0.75, 1.5, 3, 6, and 6.5 h. The weight percentage water was determined at 0, 2, and 6 h contact to be 2.9, 7.5, and 31%, respectively. The maximum activity, as determined by conversion, was observed at ~8 wt% water content. The normal-to-branched (*n*/*b*, ratio of aldehyde products) was also dependent on the water content; the observed range was 2.15 to 2.9 for 1-octene. Thus, water content affects the activity and regioselectivity of the catalysts.

It also appears that water content affects the stability of $HRh(CO)(TPPTS)_3$ under SAP catalysis conditions. For example, SAP materials derived from $HRh(CO)(TPPS)_3$ and CPG-240 show progressive darkening with increased temperature and water loading. The effect of temperature and water content upon stability is currently under investigation. In the limit of no solid present, i.e., the simple two-phase reaction described earlier, decomposition of the homogeneous catalyst is observed and no hydroformylation of a water-insoluble substrate is obtained. It is apparent then that the stability of $HRh(CO)(TPPTS)_3$ is enhanced when adsorbed on glass surfaces as in a supported aqueous-phase catalyst.

Three different environments are apparently present in the supported aqueous phase depending on the level of hydration. First, at very low water content the rho-

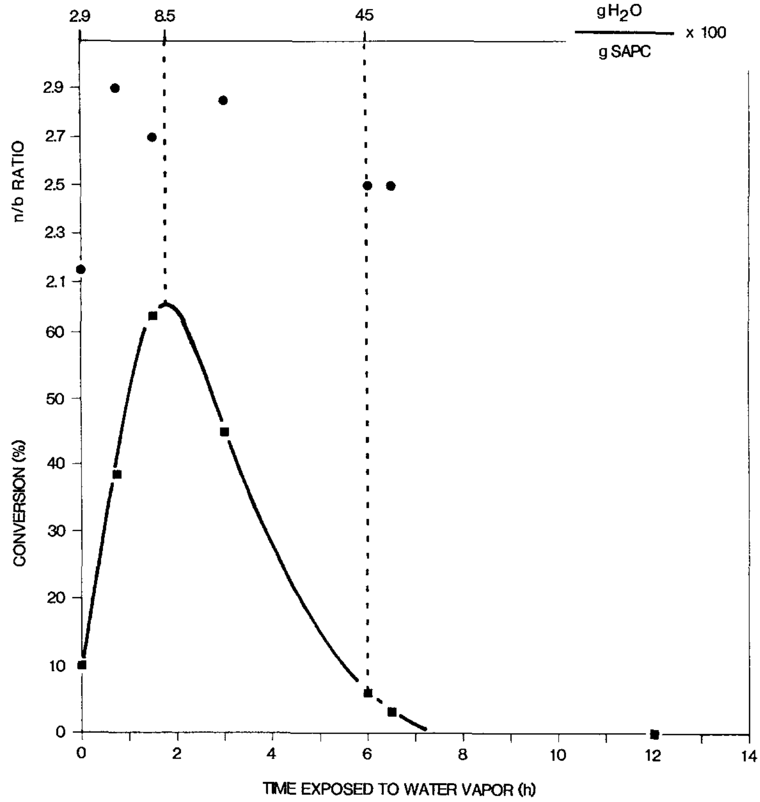


FIG. 8. Influence of H_2O content in a SAP catalyst on the hydroformylation of 1-octene.

dium complex is strongly adsorbed to the surface as evidenced by the lack of mobility seen in the solid-state NMR spectra for the adsorbed complex. The lack of mobility may be responsible for the low catalytic activity observed at low water contents. Furthermore at low water content the catalysts are very stable. Second, at intermediate water contents of 4 to 12 wt% the catalytic activity reaches a maximum while the complex stability is still enhanced. Although NMR data were not obtained in this range of water content it is reasonable that the complex becomes increasingly mobile as the water loading increases. Third, at high water loading, >20 wt%, the SAP materials lose both activity and stability and approach the behavior of the unsupported catalysts.

Influence of excess ligand. A second set of SAP catalysts were prepared from $HRh(CO)(TPPTS)_3$ and excess TPPTS in which the P/Rh ratio was 33 (in the previous examples the ratio was 6.9). Even at this higher P/Rh ratio the *n*/*b* ratio for the aldehyde products from 1-octene hydroformylation (nonanal/2-methyloctanal) was 2.3. This corresponds well with the hydroformylation of 1-alkenes with homogeneous solutions of $HRh(CO)(PPh_3)_3$ at similar P/Rh ratios (*23*). The values obtained in SAP catalysis conditions however are low compared to the results for propylene and 1-hexene hydroformylation with $HRh(CO)(TPPTS)_3$ in aqueous solution. (A direct comparison with the same substrate is not possible since 1-octene is not hydroformylated in a simple two-phase reaction using $HRh(CO)(TPPTS)_3$ as the catalyst; vide supra.)

Hydroformylation with solid, unsupported $HRh(CO)(TPPTS)_3$. The hydride complex, $HRh(CO)(TPPTS)_3$, is isolated as a hydrated solid containing up to 16 wt% water (see Experimental). To some extent then it may be anticipated that the surface of the isolated complex may be similar to the surface of the SAP catalysts. A sample of $HRh(CO)(TPPTS)_3$ powder was examined by STEM and the particles were estimated to have an average diameter of ~180 Å. The surface area is then estimated to be ~100 m^2/g.

When a 25 wt% octene solution in cyclohexane was subjected to hydroformylation conditions in the presence of solid $HRh(CO)(TPPTS)_3$, 98.7% conversion was obtained after 5.2 h at 100°C and H_2/CO (1/1) pressure = 5.2 MPa. The weight Rh/weight 1-octene was 0.014. The specific activity, based on surface rhodium, was remarkably similar to the SAP catalysts; *n*/*b* ratios were also similar. The complex $HRh(CO)(TPPTS)_3$ was completely insoluble in 1-octene/cyclohexane; thus the reaction must occur at the solid–liquid interface.

This result reinforces the idea that the hydroformylation reaction occurs at the interface and involves neither a dissolution of the substrate in the aqueous phase nor a dissolution of the complex in the nonaqueous phase.

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