

Supported Aqueous-Phase, Rhodium Hydroformylation Catalysts

I. New Methods of Preparation

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Improved methods for the preparation of supported aqueous phase (SAP) catalysts are described. An *in situ* preparation of the supported rhodium complex and a more effective hydration procedure are presented. SAP catalysts are also prepared by a self-assembly experiment in which the separated components of a SAP catalyst spontaneously adopt a SAP configuration under reaction conditions. © 1991 Academic Press, Inc.

INTRODUCTION

Recently, we reported on the development of a novel type of catalysis, termed supported aqueous-phase (SAP) catalysis (1, 2). SAP catalysis enables the efficient use of a water-soluble organometallic complex to promote the reaction of substrates soluble only in organic solvents. Specifically for hydroformylation, the water-soluble complex $\text{HRh}(\text{CO})(\text{TPPTS})_3$ (TPPTS = tri-sodium salt of tri-(*m*-sulfophenyl)-phosphine) and H_2O were formulated into a thin film on the hydrophilic porous support CPG-240 (1, 2). The rhodium SAP catalysts proved to be effective in promoting the hydroformylation of water-insoluble olefins. It was determined that the SAP catalysts do not leach significant amounts of Rh into the organic phase by recycling the organic substrate phase and noting the absence of catalytic activity in this phase. It was shown also that the hydroformylation of the olefin most likely takes place at the aqueous-organic interface. The exact nature of this interface is not known. All these characteristics make SAP catalysts unique.

The objective of this work is to develop an improved method for the preparation of SAP catalysts and to test further the stability of the Rh complex in hydroformylation reactions.

EXPERIMENTAL

Materials. Controlled pore glass with an average pore radius of 240 Å (CPG-240) was used as received, except where noted, as the support. $\text{HRh}(\text{CO})(\text{TPPTS})_3$ was prepared as previously described (2). The SAP catalysts, except where noted, contain 0.0208 mmol Rh/g SAP catalyst. The P/Rh ratio, except where noted, is 9.0. Solvent and olefins were purchased in the highest purity available and handled under Ar or N_2 .

SAP catalyst impregnation procedure. Impregnation of the Rh organometallic complex onto CPG-240 was performed by two different techniques: (A) by the previously described procedure (2), and (B) as follows. The Rh^{I} precursor, $\text{Rh}(\text{acac})(\text{CO})_2$, was impregnated onto the support by the incipient wetness technique and the organic solvent (cyclohexane) vacuum evaporated away. Incipient wetness was then used to add an aqueous solution with the desired amount of TPPTS to the glass. During the impregnation the support immediately changed color from white to yellow indicating that ligand

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exchange occurred rapidly (2). Water was removed from the solid under vacuum at room temperature. Exposure of the impregnated solid to a H_2/CO (1:1) mixture at atmospheric pressure and room temperature completed the *in situ* synthesis of the supported complex $HRh(CO)(TPPTS)_3$. This procedure, like (A), yields a dried SAP catalyst although it still contains 2.9% H_2O in this state. The "dried" qualification implies that hydration (as described below) has not occurred. Magic angle spinning ^{31}P NMR of the dry solid shows the presence of $HRh(CO)(TPPTS)_3$, TPPTS, and some oxidized phosphine, $TPPTS=O$.

Hydration procedure. All the hydrated SAP catalysts in this work were hydrated *in situ* under reaction conditions. (In our earlier work (1, 2) the catalysts were hydrated prior to use in catalytic reactions.) Thus, an amount of pure CPG-240, equivalent in weight to 10% of the amount of SAP catalyst to be used in a reaction, was impregnated directly with a desired amount of water. The amount of water added to the CPG was never more than its pore volume. The water was allowed to equilibrate within the pores of the CPG for about half an hour while blending the powder from time to time in a closed container. The wet CPG-240 was then loaded into the reactor. Dry solvent and olefin(s) were immediately loaded into the reactor blanketing the wet CPG. Finally, the dried SAP catalyst (2.9% water) was loaded into the reactor. The reactor was then flushed with H_2/CO and the pressure raised to the desired value. The total amount of water in the system is the sum of the residual water on the dried SAP catalyst (2.9% water) and the water on the wet CPG-240 (19% water). This water distributes over all solid particles and in the organic liquid and vapor phases (*vide infra*) under reaction conditions.

Reaction conditions. The hydroformylation reactors used were standard batch stainless-steel stirred vessels heated either by a thermostatic oil bath or by a thermostatic furnace. A small reactor denoted A

had a usable volume of 0.5 ml and a larger reactor denoted B had a usable volume of 15 ml. Reactor A could not be sampled at different reaction times; its contents were analyzed at the end of the reaction. Also, the stirring rate and the humidity were much more difficult to control in reactor A than in reactor B. Reactor B could be sampled without disturbing the reaction; the very small sample taken was frozen in liquid nitrogen before decompressing it. After the decompression step it was slowly allowed to thaw at atmospheric pressure to avoid flashing. The H_2/CO ratio was always 1/1. The stirring rate (400 rpm, reactor B) and the solvent (cyclohexane) in which the substrates were dissolved were constant for all the experiments. The temperature, pressure, substrate concentration, and hydroformylation time were varied according to the run. All manipulations were carried out under N_2 or Ar which were flushed out with H_2/CO before starting the hydroformylation reaction.

Analytical methods. Solid-state CPMAS ^{31}P NMR were recorded on a Bruker MSL 300 at 121 MHz. ^{31}P NMR chemical shifts are reported relative to 85% H_3PO_4 . The water content of each sample was obtained by thermogravimetric analysis in a manner similar to that reported previously (2). Gas chromatography (GC) analysis were performed on a HP 5790A chromatograph.

RESULTS

Hydroformylations using hydrated SAP catalysts. All the reactions using hydrated SAP catalysts were performed in reactor B. Table 1 shows the results of the simultaneous hydroformylation of 1-heptene, 1-tetradecene, and *t*-7-tetradecene. The reaction was also performed using $HRh(CO)(PPh_3)_3$ as a homogeneous catalyst in order to compare activities and selectivities. The reaction conditions were identical in both cases with the exception of solvent. Toluene was used for the homogeneous reactions. In both cases the molar amount of Rh and phosphine added to the reactor were the same, as well as the molar amounts of olefins and solvent.

TABLE 1

Hydroformylation of Linear Olefins by Hydrated SAP Catalysts (SAPC) or by $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ in Toluene (Homogeneous) $T = 75^\circ\text{C}$, $P = 100$ psig H_2/CO (1/1)

Substrate	TOF ^a (s ⁻¹)	
	Hydrated SAPC ^b	Homogeneous
1-Heptene	2.0E-02 (2.0E-04) ^c	8.4E-02
1-Tetradecene	8.9E-03	4.3E-02
<i>t</i> -7-Tetradecene	1.4E-04	3.2E-03

^a Initial turnover frequency.

^b See text for experimental details.

^c Initial turnover frequency when using a dried SAPC (2.9 wt% water).

In the case of the hydroformylation reaction with the SAP catalyst, the reactor was loaded with 62 mg CPG-240 (19 wt% H_2O), 9.0 ml cyclohexane, 1.0 ml 1-heptene, 1.0 ml 1-tetradecene, 1.0 ml *t*-7-tetradecene, and 0.500 g of dried SAP catalyst (2.9 wt% H_2O). Figure 1 shows the n/b ratios for these reactions as a function of conversion. Table 2 shows the results for the hydroformylation of neat 1-tetradecene with hydrated SAP catalyst at different temperatures. When the

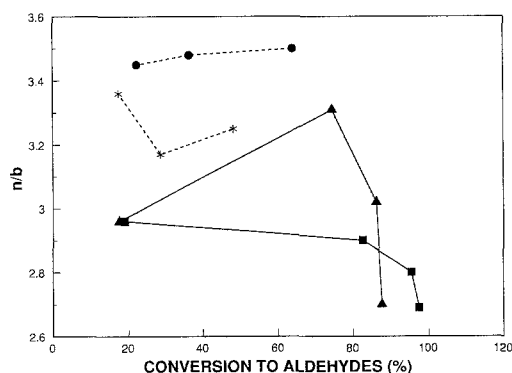


FIG. 1. Normal to branched aldehyde isomer ratio as a function of conversion for 1-heptene and 1-tetradecene. --- hydrated SAP catalyst, ● 1-heptene, * 1-tetradecene; — homogeneous catalysis using $\text{HRh}(\text{CO})(\text{PPh}_3)_3$. ■ 1-heptene, ▲ 1-tetradecene; $T = 75^\circ\text{C}$, $P = 100$ psig; reactor B.

TABLE 2

Hydroformylation of Neat 1-Tetradecene by Hydrated SAPC, 100 psig H_2/CO (1/1)

T ($^\circ\text{C}$)	TOF (s ⁻¹)	n/b
70	0.06	3.9
85	0.10	4.7
100	0.20	5.9

turnover frequencies (TOF) in Table 2 are used to calculate an activation energy, a value of 10 kcal/mol is obtained. This low activation energy implies mass transfer limitations which are not unexpected from highly active heterogeneous catalysts performing liquid phase conversions. Also, the hydrated SAP catalysts are generally 100 times more active than the dried SAP catalysts as illustrated by the data given in Table 1.

Use of other supports for SAP catalysts. Three other supports in addition to as-received CPG-240 were used to prepare SAP catalysts: (A) pretreated CPG-240, (B) Shell Silica Spheres, and (C) high-purity gamma alumina. These three SAP catalysts were tested under the same conditions, namely, 62 mg CPG-240 (19 wt% H_2O), 1-heptene as substrate (3.0 ml), cyclohexane as solvent (9.0 ml), 0.500 g of dried SAP catalyst (2.9% H_2O), $T = 75^\circ\text{C}$, $P = 100$ psig H_2/CO . (A) Pretreated CPG-240 was prepared by washing with water a previously used SAP catalyst. This procedure was used in hope that any possible oxidant present on CPG-240 able to oxidize TPPTS under reaction conditions is likely to be consumed. After removing the previously impregnated complex and excess ligand by washing them off with water, this "pretreated" CPG-240 was used to prepare SAP catalysts as described before (2). The initial turnover frequency obtained using this SAP catalyst was 0.022 s^{-1} and the n/b ratio was 3.75. (B) Shell Silica Spheres (S-970) had a particle size of 2.5 mm and a pore volume of 1.85 cc/g. The TOF obtained with this SAP catalyst was

0.012 s^{-1} and the n/b ratio was 5.6. The particles had disintegrated after the 24-h run due to lack of mechanical stability in the stirred autoclave. (C) With high-purity gamma-alumina as support for SAP catalysis, the TOF was 0.019 s^{-1} and the n/b ratio was 3.65.

Significantly, with pretreated CPG-240 as the support the total amount of phosphine oxide formed during catalyst preparation and catalytic reaction was less than 14% of the total phosphine, without pretreatment, 30% of the total phosphine present is oxide.

Stability studies. These studies were aimed at addressing one of the most important problems with immobilized catalysts, namely the stability of the immobilized catalytic species against deactivation and/or leaching from the support. Many of the tests for leaching were conducted as before (2), i.e., testing for catalytic activity on the filtrate after reaction. The procedure was as follows: after stopping the reaction, the reactor's contents were filtered under a N_2 atmosphere through a MSI,135 filter (teflon, $0.5\text{-}\mu\text{m}$ pores, 25-mm diameter) and 0.4 ml of the filtrate and 0.1 ml 1-hexene were loaded into reactor A and heated at 120°C under 1000 psig H_2/CO for 24 h. The conversion of 1-hexene under these conditions was compared to a blank test which typically yielded a 0.4% conversion of 1-hexene to aldehydes. Changes in the color of the SAP catalyst from its initial bright yellow were taken as indications of likely degradation of the catalyst. Some of the filtrates subjected to the catalytic activity test were also analyzed for Rh (sent to Galbraith laboratories) in order to obtain a quantitative analysis. Selected SAP catalyst samples were also analyzed by solid-state CPMAS ^{31}P NMR before and after reaction to test for degradation of the catalytic species. Finally, another test, denoted the "self-assembly test" was performed to evaluate the possible long term stability of SAP catalysts (vide infra).

Eleven reaction filtrates from different SAP catalysts and/or reaction conditions

(reactor B) were analyzed for hydroformylation catalytic activity. Six of them tested positive for Rh leaching according to the test. These were (i) a run from a hydrated SAP catalyst at 75°C and 100 psig, the apparent amount of leaching was low (1.5% conversion); (ii) the reaction in which the SAP catalyst was the one prepared with gamma-alumina, the apparent amount of leaching was high (8.5% conversion); (iii) a reaction performed with the dried SAP catalyst at 160°C and 100 psig, the apparent extent of leaching was low (1.0% conversion); (iv), (v), and (vi) these catalysts prepared by method B with P/Rh ratios of 3 or less (specifically 3, 2, 0, respectively, for cases (iv), (v), and (vi)). The following five cases gave a 1-hexene conversion on the filtrate at or below the blank level: (vii) dried SAP catalyst, 75°C , 100 psig; (viii) dried SAP catalyst, 120°C , 100 psig; (ix) dried SAP catalyst, 140°C , 100 psig, (x) hydrated SAP catalyst prepared with the pretreated support (vide supra), 75°C , 100 psig; (xi) hydrated SAP catalyst with increased amount of free ligand (P/Rh = 90, 0.0021 mmol Rh/g SAP catalyst).

Four reaction filtrates were assayed for Rh using a graphite furnace Atomic Absorption instrument (Galbraith Laboratories Inc.): none of these showed the presence of rhodium at a sensitivity level of 150 ppb. Three of these filtrates, (ix), (x), and (xi), showed no catalytic activity and the other one, (iii) did. Case (x) was analyzed with an increased sensitivity procedure which also showed no Rh leaching (sensitivity = 46 ppb Rh). Subsequently, repeat experiments similar to those of case (x) have not revealed rhodium loss with a limit of sensitivity of 10 ppb (equivalent to 0.4% of the rhodium charged into the reactor).

In general, the SAP catalysts did not change color after reaction. However, in the few instances when a hydrated SAP catalyst was used at 100 psig and 100°C or higher temperatures, a slight darkening of the catalyst was noticeable (likely indicating degradation). Such was not the case with the dried

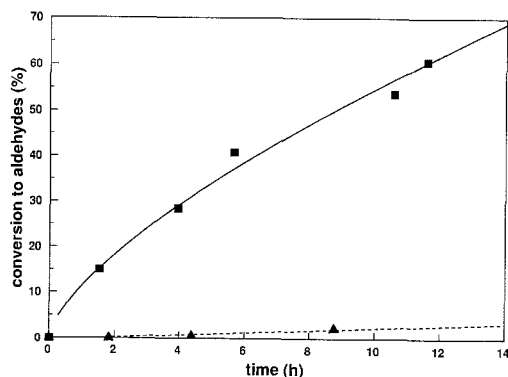


FIG. 2. Conversion to aldehydes as a function of reaction time for the self-assembly test. $T = 100^{\circ}\text{C}$, $P = 1000$ psig, reactor B. —■— CPG-240 added; ---▲--- no CPG-240 added.

SAP catalysts (2.9 wt% H_2O), even at 140°C and 100 psig. In the case of experiment (i) (listed above), where Rh leaching is likely, the SAP catalyst was visibly paler in color. For other runs under the same reaction conditions, no apparent change in color was noted.

Self-assembly test. This experiment was designed to test the possibility of long-term stability of SAP catalysts. The self-assembly test was performed in the following way: 21 mg $\text{HRh}(\text{CO})(\text{TPPTS})_3$ and 37 mg TPPTS were loaded into reactor B and dissolved in 0.060 ml H_2O . An amount of 11.0 ml cyclohexane and 2.5 ml 1-heptene were then added. Finally 0.50 g CPG-240 was added. The reactor was pressurized to 1000 psig with a 1 : 1 mixture of H_2/CO and heated to 100°C with stirring. The reactor was sampled with time and analyzed for conversion. A control experiment was carried out in which exactly the same procedure was followed with exception of no addition of CPG-240. Figure 2 shows results from both the experiment and the control.

High molecular weight products. Analysis of the hydroformylation products from the reaction of 2 ml of 1-heptene at 75°C and 100 psig H_2/CO 1 : 1 using 1.0-g hydrated SAP catalyst revealed that after 22 h the conversion was 80% and the selectivity to

aldehydes was 98%. The percentage of oligomers was estimated to be 0.7% with 85% of those being a dimer. Cyclohexane (9.0 ml) was the solvent and dodecane was used as the internal standard. The analysis was performed with a GC that had been previously calibrated.

DISCUSSION

Preparation of SAP catalysts. The *in situ* synthetic procedure outlined above can be used with any desired P/Rh ratio. The advantages in terms of time consumed and simplicity are obvious with respect to the previously described procedure for the preparation of SAP catalysts (2).

Hydration of SAP catalysts. There are several advantages to the new hydration procedure used in this work instead of the one used in the prior synthesis of SAP catalysts. It was noted previously (2) that SAP catalysts which are hydrated are less stable than the dried versions under the same reaction conditions. In addition, when a liquid state ^{31}P NMR was run on a SAP catalyst containing 40 wt% water, the amount of OTPPTS had increased significantly. By loading the water into SAP catalyst under reaction conditions (H_2/CO , substrate) which can stabilize the Rh complex, it is speculated that the possibilities of degradation of the complex are reduced. The addition of water to the system in the form of hydrated CPG-240 guarantees that the rate of hydration of the rhodium complex in the SAP catalyst will be slow since it must dissolve in the organic phase and diffuse to the solid before hydrating the dried SAP catalyst. The fact that the supported rhodium complex becomes hydrated is demonstrated by the increase in activity of the hydrated catalyst over the dried catalyst. (Previously, we have shown that the catalytic activity of the dried SAP catalysts can be increased by the addition of water (2).)

Table 1 shows the high activity of hydrated SAP catalyst. In the best cases TOFs obtained using SAP catalysis are only a factor of 4 to 5 times slower than the homoge-

neous catalyst under the same conditions. This is remarkable for an immobilized system, especially in light of the fact that it is most likely operating under mass transfer limitations. Figure 1 shows higher n/b ratios for SAP catalysis than for homogeneous catalysis for the same molar amount of Rh and phosphine added to the system. The reasons for this behavior could be twofold: (i) the catalytic species are actually different, and (ii) the effective phosphine concentration is higher in the SAP catalysts than in the homogeneous catalyst because of the reduced amount of solvent for the phosphine. From the results shown in Table 2 a value for the apparent E_a is estimated to be 10 kcal/mol. This value is lower than the value for homogeneous catalysis (3) and is very likely to be due to mass transfer limitations. This is not surprising since the activity of the hydrated SAP catalyst is very high.

Stability studies. The results from the self-assembly test indicate that, under the conditions of the experiment, the individual components of SAP catalysts, i.e., support and aqueous solution of complex and excess ligand, are more stable assembled in a SAP catalyst configuration than separated. This is an important result in the sense that it relates to the thermodynamics of the system. The reverse, i.e., the separation of the solution and complex from the support, is not likely to happen under reaction conditions because it is thermodynamically not favorable. From the studies described here the following conclusions about stability of SAP catalysts can be drawn:

(1) SAP catalysts are not stable with P/Rh values of ≤ 3 . This is reasonable since three phosphine ligands are necessary to form the complex $\text{HRh}(\text{CO})(\text{TPPTS})_3$.

(2) Dried SAP catalysts are more stable than hydrated SAP catalysts at the same T , P , and P/Rh.

(3) Dried SAP catalysts appear to be stable up to temperatures of 140°C under the current experimental conditions.

(4) The use of gamma-alumina as a support for SAP catalysts is not acceptable under the conditions outlined because of Rh leaching.

(5) There is a significant improvement in the stability of SAP catalysts if the support is pretreated.

The upper limit placed on rhodium leaching from the batch reactions performed here is good enough for laboratory reactions and even for some specialty chemicals production at industrial scale. However, for less expensive end products, the only way to ascertain that no significant amount of Rh leaches from the support is to run a continuous flow experiment. A continuous flow experiment has been recently reported by Horvath (4). He finds that after 38 h, water, but not rhodium, has leached from the catalyst.

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