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# IMMOBILIZATION OF $HRh(CO)(P(m\text{-}C_6H_4SO_3Na)_3)_3$ ON AN ANION EXCHANGE RESIN FOR THE HYDROFORMYLATION OF HIGHER OLEFINS

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The anion exchange resin Amberlyst, A-26, forms an efficient matrix for the immobilization of the water soluble complex, $HRh(CO)(m\text{-}C_6H_4SO_3Na)_3)_3$. Catalysis proceeds in anhydrous alcohol solvents which allows the conversion of water insoluble olefins to aldehydes. Activities and selectivities are similar to both supported aqueous phase catalysts and to the neutral complex, $HRh(CO)(PPh_3)_3$ in non-aqueous solvents. The catalyst preparation minimizes the quantity of water in the supported catalyst; the lack of water is thought to be responsible for an increase in catalyst stability toward oxidation.

**Keywords:** Water soluble rhodium complex, anion exchange resin catalyst support, immobilization of rhodium complex

The hydroformylation products of lower olefins can be conveniently distilled from homogeneous catalysts [1]; product separation and catalyst recycling is therefore not a problem for these substrates. In the case of higher olefins however, the separation of the aldehyde products cannot be easily accomplished by simple distillation without some decomposition of the homogeneous catalyst although it has been shown that addition of phosphinous acids increases the thermal stability of rhodium phosphine complexes [2].

Catalysis by water soluble transition metal complexes has generated a great deal of interest since the development of a commercial process for the hydroformylation of propylene with $HRh(CO)(TPPTS)_3$,**1**, (TPPTS = trisulfonated triphenylphosphine) as the catalyst [3]. Although the use of water as a solvent has some advantages over the conventional rhodium hydroformylation catalyst in nonaqueous solvents (e.g. higher normal to branched ratios for the hydroformylation of propylene at similar P/Rh ratios, more convenient separation of product aldehydes, and the environmental acceptability of water) it is not applicable to higher olefins. The reason for this is that olefins with seven or more carbons have negligible solubility inw ater [4]. Hydroformylation of higher olefins with complex **1** can be accomplished by the addition of alcohol cosolvents or detergents to make the reaction mixture homogeneous [3,4].

In the novel Supported Aqueous Phase (SAP) catalysts we showed that the water soluble rhodium complex **1** could be efficiently immobilized on a controlled pore glass [5]. Importantly the SAP catalysts allow the use of higher olefins, such as dodecene, as substrates. Furthermore the SAP catalysts can be conveniently separated and recycled [5,6], or used in a continuous mode [7], for hydroformylation. The activity of **1** in SAP catalysts depends critically on the presence of water; optimum water content is 3 to 10 wt%. Water is also implicated in the oxidation of TPPTS by rhodium [8], thus the ultimate lifetime of supported aqueous catalysts that employ phosphines may be limited by the presence of water.

Here we show that a remarkably effective catalyst for the hydroformylation of higher olefins can be generated from the water soluble rhodium complex, **1**, immobilized on the anion exchange resin, Amberlyst, A-26. Importantly these catalysts can be essentially freed from residual water which may allow greater stability of the catalysts towards oxidation while providing good reaction rates.

Complex **1** was prepared as previously described [5b]. The anion exchange resin, Amberlyst-A26, quantitatively extracts **1** and TPPTS from aqueous solutions provided that less than 50% of the exchange capacity of the resin is used. For the results reported here the immobilized catalysts were prepared from 2.0 g Amberlyst, 86 mg **1** and 191 mg TPPTS (R/Rh = 9) in aqueous methanol. This represents 33% of the exchange capacity of the resin under the assumption that each TPPTS displaces three anions from the resin. The exchanged resins were washed with large portions of anhydrous methanol and dried, briefly, under vacuum to remove any non-adsorbed methanol.

Batch catalytic results are summarized in table 1 under various conditions. The results of catalyst recycling experiments in methanol at 80 ° C (fig. 1) and in i-propanol at 100 ° C (fig. 2) demonstate the reproducibility of the catalytic results. After every second cycle in the recycling experiments the reaction solutions were tested for catalytic activity with a different substrate (see below). In nearly every case the reaction solutions showed activity at or below that of the blank reactor.

Two examples of ion exchange resin supported catalysts for hydroformylation have been reported in the literature [9,10]. Also, monosulfonated triphenyl phosphine complexes of rhodium and ruthenium have been immobilized on ion exchange resins and used as hydrogenation catalysts [11]. The catalysts prepared here, however, are unique in several respects. In previous work with cationic substituents on the ligand only one functional group per phosphorus was used [9]. The TPPTS ligand with three anionic groups should bind correspondingly stronger to exchange resins than singly functionalized ligands. Also, in many of the preparations reported by Tang et al. [9] the phosphine is quaternized at phosphorus which facilitates binding to an exchange resin but prevents the phosphine from coordinating to rhodium. We have shown that multiple cationic groups in $[(BDPP\text{-}(NMe_2H)_4Rh]^{5+}$ allows this compound to bind strongly to Nafion and

Table 1[a]

| Entry | Substrate | Solution volume, solvent | Temp (°C) | Pressure (bar) | R. Time (hrs) | Aldehydes (%) | $n/b$ | i-alkenes (%) | other (e.g. acetals) (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | dodecene | 5 ml, MeOH | 80 | 70 | 12 | 16.5 | 2.8 | 2.2 | 0.3 |
| 2 | dodecene | 10 ml, MeOH | 80 | 70 | 12 | 18.7 | 2.9 | 2.8 | 0.2 |
| 3 | dodecene | 5 ml, MeOH | 100 | 70 | 6 | 58.1 | 2.7 | 10.1 | 1.7 |
| 4 | dodecene | 5 ml, MeOH | 120 | 70 | 6 | 28.9 | 2.8 | 42.2 | 27.5 |
| 5 | dodecene | 5 ml, i-propanol | 100 | 70 | 6 | 14.1 | 2.6 | 3.6 | 0.2 |
| 6 | dodecene | 10 ml, i-propanol | 100 | 70 | 6 | 24.1 | 2.8 | 12.4 | 0.2 |
| 7 | dodecene | 5 ml, i-propanol | 100 | 14 | 6 | 8.5 | 4.0 | 4.6 | 0.2 |
| 8 | dodecene | 5 ml, cyclohexane | 80 | 70 | 12 | 4.8 | 2.4 | 1.5 | – |
| 9 | dodecene | 5 ml, cyclohexane | 100 | 70 | 6 | 11.7 | 3.0 | 19.3 | – |
| 10 | dodecene | 5 ml, cyclohexane | 100 | 70 | 12 | 30.3 | 2.4 | 42.5 | – |
| 11 | octene | 5 ml, MeOH | 80 | 70 | 12 | 20.7 | 3.3 | 1.2 | 0.8 |
| 12 | octene | 5 ml, MeOH | 100 | 70 | 6 | 74.4 | 2.5 | 15.3 | 5.8 |
| 13 | octene | 5 ml, n-propanol | 100 | 14 | 12 | 33.1 | 4.3 | 29.2 | 0.7 |
| 14 | octene | 5 ml, i-propanol | 100 | 70 | 6 | 52.9 | 2.9 | 17.9 | 0.5 |
| 15 | tetradecene | 10 ml, MeOH | 100 | 70 | 6 | 15.0 | 3.4 | 1.8 | 0.85 |
| 16 | tetradecene | 10 ml, i-propanol | 100 | 70 | 6 | 16.3 | 2.8 | 11.5 | 0.1 |

[a] 0.0046 mmol Rh/200 mg Amberlyst, P/Rh = 9, Substrate/Rh = 1000.

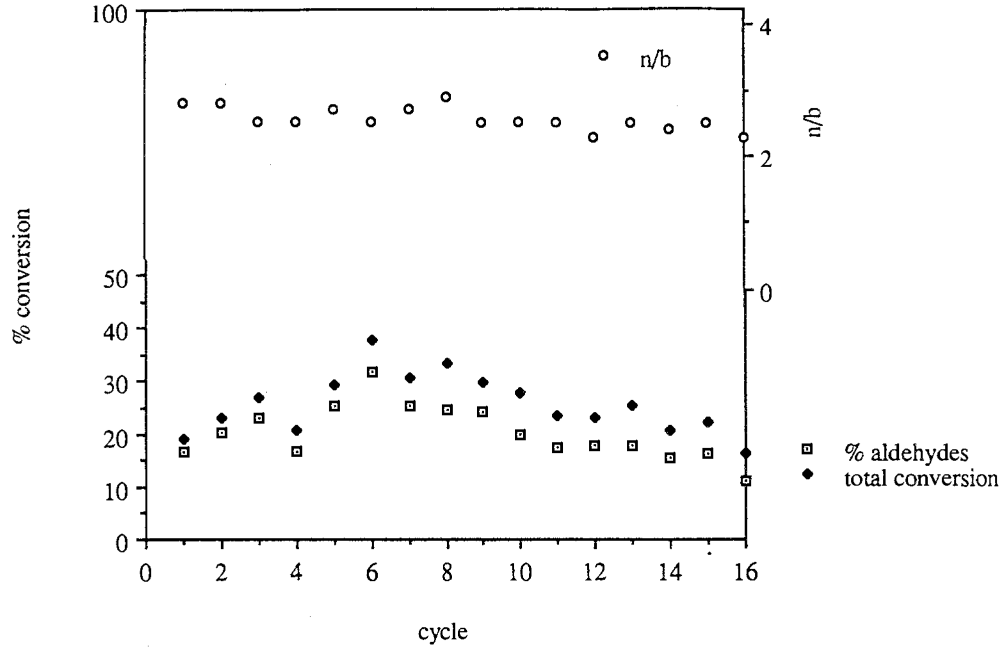

Fig. 1. Recycling in the hydroformylation of 1-dodecene in methanol at 80 °C. Reaction conditions: 0.0046 mmol Rh on 200 mg Amberlyst, P/Rh = 9.0, Substrate/Rh = 1000, 70 bar, $H_2/CO = 1/2$, 12 hours. Total reaction volume 5.0 ml, reactor volume 30 ml.

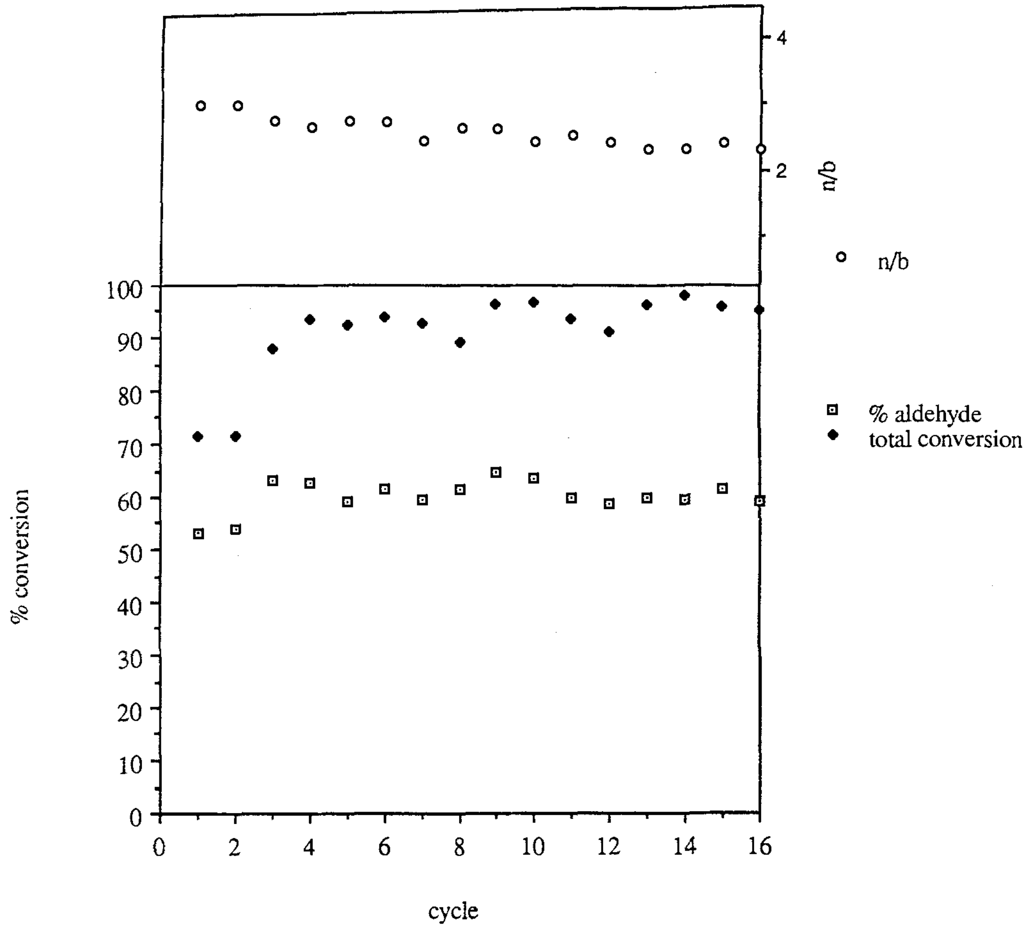

Fig. 2. Recycling in the hydroformylation of 1-octene in i-propanol at 100 ° C. Reaction conditions: 0.0046 mmol Rh on 200 mg Amberlyst, P/Rh = 9, Substrate/Rh = 1000, 70 bar, $H_2/CO = 1/1$, 6 hrs. Total reaction solution volume 5.0 ml, reactor volume 30 ml.

other ion exchange resins where it can function as an effective immobilized asymmetric hydrogenation catalyst [12].

The catalysts reported here are qualitatively like the SAP catalysts under similar reaction conditions. The normal-to-branch ratios at 100 ° C and 70 bar are in the range 2.3–3.4 for the resin supported catalysts. At this pressure and temperature the SAP catalysts also give *n/b* ratios in this range. At lower pressure the *n/b* ratio increases to greater than 4. Temperatures greater than 100 ° C could not be investigated for prolonged periods of time because the resin is thermally unstable at high temperatures.

In those cases when the identical substrate was hydroformylated in different solvents under the same conditions methanol generally gave the best activity and selectivity to hydroformylation products. At higher temperatures with methanol as the solvent a high proportion of aldehyde derivatives, such as acetals, were obtained. These side reactions are minimized in i-propanol. The resin supported catalysts show increasing activity for isomerization with increasing temperature. The highest activity for isomerization was observed with cyclohexane as the solvent; cyclohexane also gave the poorest activity for hydroformylation. This may be attributed to the poor swelling of the exchange resin in cyclohexane; the catalysts are more active in alcohol solvents which swell the resins to a large extent. Slight differences in activity are observed as a function of substrate; these are most likely due to differences in solvent composition since the total volume of solution and the molar substrate to rhodium ratios were kept constant.

Both the catalysts reported here and the SAP catalysts show good activity for olefins $C_8$ and higher; this characteristic is not shared by two-phase (aqueous-organic) catalysis with **1**. As mentioned above under two-phase conditions activity is a function of olefin solubility in the aqueous phase and declines rapidly for olefins $C_7$ and higher [4,7].

The catalyst recycling experiments are significant in determining the long term viability of the catalysts. These were performed with octene and dodecene as the substrates. Typically the reaction solutions were decanted to remove the resin. The resin could then be reused with fresh substrate while the reaction solution was subjected to hydroformylation reaction conditions with a second substrate. Only after the 15th cycle in methanol as the solvent was activity observed in the reaction solution. In i-propanol at 100 ° C activity above the blank level was observed in two cases, specifically the activity was three and two times the blank for the 6th and 9th reaction solutions respectively. In all other cases the activity of the reaction solutions was at or below the blank level (the activity of the blank reactor was 0.9% total conversion at 100 ° C and 6 h). As seen in figs. 1 and 2 the activity of the recycled resin increased in the first few cycles after which it remained essentially constant or dropped slightly. The *n/b* ratio decreases slightly with each cycle consistent with a decrease in P/Rh ratio. Most importantly, like the SAP catalysts, the resin supported catalysts do not show evidence for significant rhodium leaching under batch conditions.

Magic angle spinning $^{31}P$ NMR experiments on the catalysts before and after use revealed some oxidation of the phosphine. Not surprisingly the degree of oxidation increased with further recycling. The as prepared catalysts contained no phosphine oxide. After theree cycles 30% and after 16 cycles at 100 ° C 80% of the phosphine was oxidized. Significantly there was still some free phosphine at the end of 16 cycles. It should be noted that although the catalyst was handled under high purity gases such as Ar, CO, or $H_2$ no special precautions were taken to degas solvents or substrates. After sixteen cycles at 100 ° C a total of ca 15,000 turnovers were achieved. Thus, it is not surprising that oxidation can occur through the presence of adventitious oxygen in the solvents and/or substrate. The recycling of **1** under batch conditions in the presence of water leads to a greater extent of phosphine oxidation. It is predicted that the resin supported catalysts should have good longevity under continuous operation provided the solvents and substrates are well degassed. The P/Rh ratio can also be increased to improve both catalyst lifetime and selectivity.

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