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# Multifactorial analysis in the study of hydroformylation of oct-1-ene using supported aqueous phase catalysis

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## Abstract

The influence of the hydration and the surface characteristics of five supports in the hydroformylation of oct-1-ene by supported aqueous phase catalysis (SAPC) using $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ as catalyst was studied. The results confirm that the size of the pores and the amounts of water were found to be the determining factors contributing to the SAPC. According to the size of pores there is a critical value for which the SAPC takes place either in the classical model or in conditions where the pores are filled. When the pores are fully filled the SAPC can operate efficiently onto the external surface, stabilising the conversion in a relatively wide range of support hydration. © 2001 Published by Elsevier Science B.V.

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## 1. Introduction

Since the pioneering work of Arhancet et al. [1] on supported aqueous phase catalysis (SAPC), many researches have been devoted to the hydroformylation, hydroxycarbonylation, oxidation and allylation reactions of heavy alkenes and other compounds [2–12]. In SAPC, the catalytic phase, immiscible with the organic phase containing the reactant/products, consists of an aqueous solution of a water-soluble organometallic catalyst. To provide the necessary interfacial area required for the reaction to proceed at a reasonable rate, the catalyst phase is immobilised in the pores of a high-surface-area hydrophilic support, such as controlled-pore glasses or silica. Then, the catalysis proceeds at the interface between an organic phase containing the reactants and products and an aqueous phase containing the catalytic species [1]. For each catalytic system, the usual parameters like pressure, temperature, amounts of free phosphine have been clearly optimised, and hydration was found to be very important.

Although SAPC is very perspective due to its high capacity in the conversion, the selectivity and also the easy recovery of the catalyst from the organic phase, and thus is economically and ecologically advantageous, it still remains to solve the important problem of the very high dependence of the conversion with the hydration rate of the support. In this sense, Arhancet et al. [2] and Horváth [13] tried to explain the mechanisms of SAPC. Therefore, the optimum hydration yielding the best conversion was found to be very narrow. Nobody succeeded in stabilising this high dependence; only Dos Santos et al. [12] recently

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reported conditions allowing to stabilise the conversion of an SAPC system in a larger range of hydration. But the authors did not give any explanation of this unusual result.

Thus, in this study, we were interested in finding conditions to stabilise the conversion of an SAPC system, and also in understanding the influence of the physical properties of the support. Taking into account that SAPC occurs onto the surface of the support, several parameters could play an important role in the improvement of the process like the total porous volume, the specific surface area or the mean size of the pores of the support.

We present here the influence of the hydration and the surface characteristics of five silica supports for the hydroformylation of oct-1-ene using $[Rh_2(\mu\text{-S}^tBu)_2(CO)_2(TPPTS)_2]$ as catalyst.

## 2. Experimental

Reagents and solvents were purchased from Aldrich and SDS, and used without further purification. Rhodium trichloride trihydrated is a generous loan from Engelhardt-Comptoir Lyon-Alemand-Louyot. Tris(*m*-sodiumsulphonatophenyl)phosphine (TPPTS) is a generous gift from Hoechst (Ruhrchemie). Distilled, deionised water was used in all operations requiring water. All solvents, including water, were degassed by three freeze-pump-thaw cycles. The complex $[Rh_2(\mu\text{-S}^tBu)_2(CO)_2(TPPTS)_2]$ was prepared as described by Kalck et al. [14]. Unless otherwise stated, all manipulations were performed under nitrogen or argon. The structure and purity of $[Rh_2(\mu\text{-S}^tBu)_2(CO)_2(TPPTS)_2]$ and TPPTS were verified by NMR spectroscopy. Liquid phase $^{31}P$ NMR spectra were recorded on a Brüker AM 250 spectrometer (101.26 MHz) and on a Brüker AMX 400 (161.99 MHz) calibrated with $H_3PO_4$ as the external standard. Liquid phase $^1H$ and $^{13}C$ were recorded on a Brüker AM 250 spectrometer (250.13 MHz for $^1H$ spectra and 62.90 MHz for $^{13}C$ spectra) and on a Brüker AMX 400 (400.14 MHz for $^1H$ spectra and 100.62 MHz for $^{13}C$ spectra) calibrated with TMS as external standard.

Five supports were used to prepare SAPC catalysts: the Sipernat silica samples DS22 and DS50 (a generous gift from Degussa); one SDS silica sample (S200) and glass beads (GB1 and GB2). The characterisation of the supports was accomplished (Table 1). For determining the BET surface, total porous volume and mean diameter of the pores, nitrogen adsorption isotherms were recorded on a Nova 1000 QuantaChrome analyser. Particle size measurements were obtained on a Mastersizer MALVERN S. The water content of each sample was obtained by thermogravimetric analysis in helium on a Setaram CS 92 apparatus.

Catalytic tests were carried out in a 150 ml stainless steel stirred autoclave heated by a thermostatic oil bath. In a typical run, except where noted, 0.0141 g ($2.27 \times 10^{-4}$ mol) of TPPTS, 0.038 g ($2.26 \times 10^{-5}$ mol) of $[Rh_2(\mu\text{-S}^tBu)_2(CO)_2(TPPTS)_2]$ and 2.3 g of the support were placed in the autoclave. The solids were covered with 57 ml of toluene. Then, 2.86 g ($2.55 \times 10^{-2}$ mol) of oct-1-ene and the quantity of permuted water necessary to reach the desired hydration percentage were added before closing the autoclave. The reactor was pressurised three times with 2 bar of an equivalent mixture of hydrogen and carbon monoxide. After these operations, the autoclave was pressurised with 2 bar of the same gas mixture, then the reactor was heated to 80°C at 1870 rpm. When this temperature was reached, the reactor was pressurised

Table 1
Characteristics of the supports

| | DS22 | DS50 | S200 | GB1 | GB2 |
|---|---|---|---|---|---|
| BET surface ($m^2/g$) | 173 | 488 | 317 | 0.07 | 0.01 |
| Total porous volume (ml/g) | 0.19 | 0.73 | 0.58 | [a] | [a] |
| Mean diameter of the pores (Å) | 45 | 59 | 74 | [a] | [a] |
| Mean size of the particles (μm) | 119 | 53 | 442 | 93 | 583 |
| Water content (%) | 11.8 | 8.5 | 6.7 | 0.04 | 0.04 |

[a] Non-porous.

with 5 bar of gas mixture. During the catalytic test, the pressure was kept constant at 5 bar inside the reactor. After 3 h, except where noted, the gas mixture feed was stopped and the reactor was cooled to room temperature. Then, the reactor was decompressed and the liquid and solid phases were separated by filtration. The organic phase was analysed by gas phase chromatography on a Carlo Erba HRGC 5160 chromatograph equipped with a flame ionisation detector and a capillary column Alltech Econopac FFAP (30 m; 0.53 mm; 1.2μm), $T_{\mathrm{det}} = 200°\mathrm{C}$, $P_{\mathrm{H}_2} = 0.45$ bar.

## 3. Results and discussion

In a previous work, using the DS22 silica, the influence of the temperature and the pressure on the conversion of oct-1-ene in the SAPC hydroformylation was studied [15]. The best results were obtained at 80°C and 5 bar. Under these conditions, we investigated the influence of the P/Rh molar ratio. The complex $[\mathrm{Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2}]$ under a CO pressure is in equilibrium with an inactive tetracarbonyl complex [16]. Hence, for avoiding the formation of this inactive species, an excess of phosphine is needed in the system. Fig. 1 shows that increasing the P/Rh ratio an optimum was found at P/Rh = 6. Above this value, the ligand competes with the alkene for the coordination to the metal centre.

Then the influence of the hydration degree was studied by measurement of the catalytic performances for the sample silica DS22 (Fig. 2). We could not notice any sharp enhancement of the yield at low hydration degree as found usually in SAPC, but a maximum of activity (yield around 90%) could be reached for a hydration degree of silica of ca. 24 wt.%. Moreover, high conversions could be observed in a wide range of water contents (19–44 wt.%).

From 14.3 wt.%, the mobility of the catalyst seems to be sufficient enough to allow a better contact with the substrate. The high improvement of the conversion begins with the total filling of the pores (corresponding to 16.5 wt.%) and then, the excess of water allows the catalyst to have enough mobility on the surface to improve consequently the yield on a very large interval ranging from 19 to 44 wt.%. This point is of a crucial importance because an appreciable variation of the quantity of water does not lead to any notable variation in the yield. The conversion dramatically decreased above 44 wt.%, because the excess of water was found to form droplets which leave the surface giving a leaching of catalyst into the organic phase.

On the other hand, the linearity of the product changes in a range from 74.4 to 89.3%. This important change must be associated to the environment of the catalyst. It has been shown, that a reaction occurring in a pure aqueous phase gives a linearity of ca. 98%, whereas at the interface water/organic solvent a linearity ca. 85–88% and in pure organic solvent a linearity of ca. 75% are obtained [17]. Then, it can be thought that, for the best conversion, which corresponds to the lower values of linear isomer, the reaction occurs in a more organic medium, nearer to the organic phase, what means at the surface of

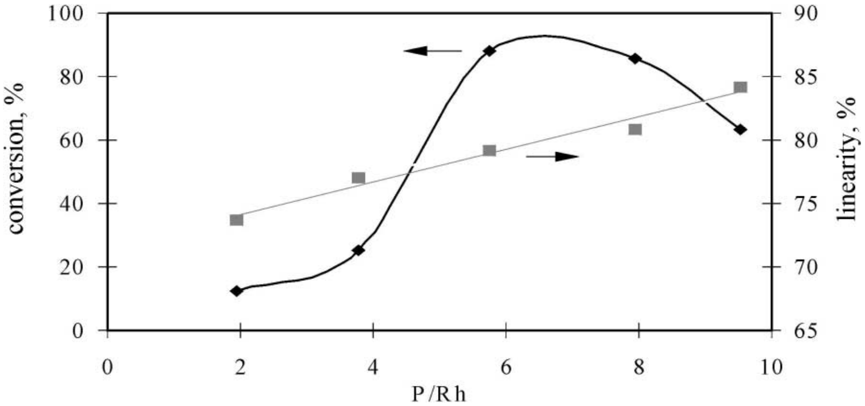

Fig. 1. Influence of the P/Rh molar ratio on the conversion ($t = 18$ h).

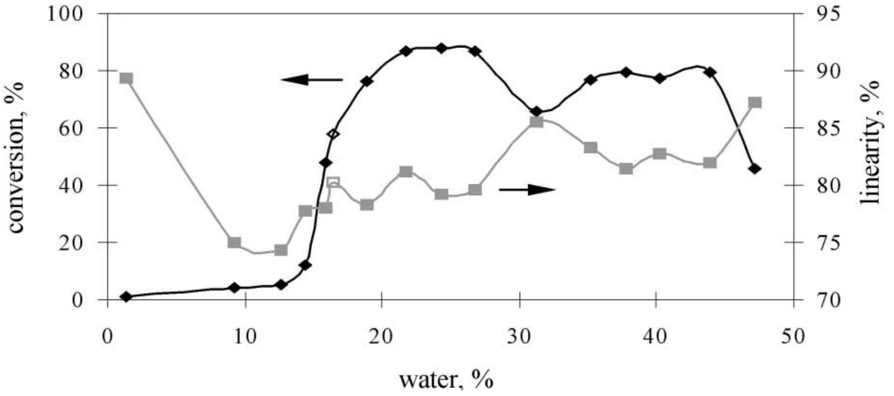

Fig. 2. Influence of the hydration rate on the conversion and the linearity for the DS22 silica sample ($t = 18$ h). The points in blank correspond to the fully filling of the pores.

the support. That would explain the great conversion observed because of a higher mass transfer.

These results suggest two possible explanations:

1. The total porous surface does not play any role in the process and then only the exterior surface of the solid is important.
2. For supports with relatively small pores, the classical SAPC model is no longer valid: the catalyst has not enough place in the pores to produce the active intermediate species so that the porous volume only stores the TPPTS ligands and the catalyst. The active species are produced at the external surface of the particles.

To test the first possible explanation, we used two different non-porous glass beads (GB1 and GB2) and varied the operating conditions. We never observed any catalytic activity but a leaching of rhodium into the organic phase. Then, it can be clearly stated the necessity of a porous volume for SAPC.

In order to verify the second explanation, the dependence of the conversion versus the hydration rate was studied using as support the S200 silica which has larger pores diameters than DS22 (Table 1). A multifactorial study involving two different silica samples was accomplished too (Table 2).

The curve obtained with S200 silica (Fig. 3) exhibits two parts in agreement with the classical model for the SAPC. Before the filling of the pores, a maximum of conversion is observed as it was reported in precedent works [2–7,9,18]. This behaviour is in total accordance with the model proposed by Horváth [13]. When the

Table 2
Variation of the yield in aldehyde in function of the variation of the different parameters

| No. | Support | Water (%) | Mass of support (g) | BET surface (m$^2$) | Porous volume (μl) | External surface (m$^2$) | External water (μl) | Yield in aldehyde (%) | Linearity (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | DS22 | 24.4 | 2.30 | 398 | 447 | 0.048 | 283 | 32.1 | 79.2 |
| 2 | DS50 | 25.8 | 2.30 | 1123 | 1669 | 0.123 | 0 | 2.9 | 78.9 |
| 3 | DS50 | 49.5 | 0.82 | 398 | 592 | 0.044 | 139 | 12.9 | 89.9 |
| 4 | DS50 | 56.5 | 0.62 | 301 | 447 | 0.033 | 283 | 2.5 | 91.5 |
| 5 | DS50 | 47.0 | 0.90 | 440 | 654 | 0.048 | 77 | 22.3 | 86.3 |
| 6 | S200 | 25.4 | 2.30 | 728 | 1339 | 0.012 | 0 | 37.1 | 83.9 |
| 7 | S200 | 38.4 | 1.26 | 398 | 732 | 0.007 | 0 | 19.8 | 88.5 |
| 8 | S200 | 50.5 | 0.77 | 243 | 447 | 0.041 | 283 | 2.6 | 90.7 |
| 9 | S200 | 7.9 | 9.08 | 2873 | 5282 | 0.048 | 0 | 8.4 | 81.6 |
| 10 | S200 | 39.7 | 9.08 | 2873 | 5282 | 0.048 | 283 | 14.2 | 76.0 |

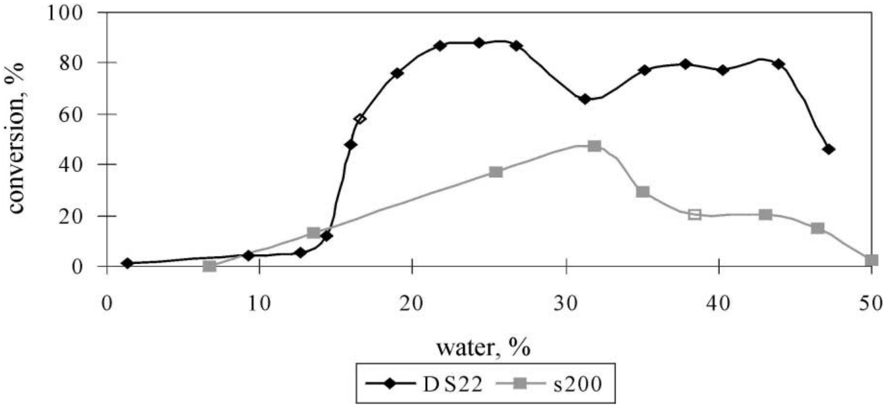

Fig. 3. Influence of the hydration rate on the conversion for the DS22 ($\Delta t = 18\,h$) and S200 ($\Delta t = 3\,h$). The points in blank correspond to the fully filling of the pores.

pores have been filled, the catalytic activity decreases due to an impossibility for the organic phase to penetrate into the pores avoiding an efficient contact between the catalyst and the substrate. Like in the precedent case with DS22, the conversion is stabilised just in a small range after the filling of the pores. Then, when the amount of water is further increased, a decrease in conversion and a leaching of rhodium are observed.

Table 2 shows the influence of two main parameters (hydration and mass of support) on the conversion. For S200, the comparison of Table 2 and Fig. 3 (obtained with a constant mass of support) shows clearly that the main factor which governs the catalysis is the hydration degree.

In the case of the DS50 silica, the first observation is that the filling of the pores is essential for the conversion in correspondence with its small pore size. In run 2, for which the pores are not filled, the conversion is very poor, indicating that an efficient contact between the catalyst and the substrate could not occur. When the pores are filled (run 5) the maximum value for the conversion was obtained. However, above a water content near to 55% (run 4), the conversion drops dramatically. Droplets have been observed in the solution, as previously for DS22. It has been checked by atomic adsorption spectrometry that a leaching of rhodium occurs in these drops. In run 3, a significant decrease occurs giving a conversion of 12.9%. It seems that DS50, having pore diameters between DS22 and S200, has a behaviour intermediate between these two supports.

## 4. Conclusions

The results confirm that the size of the pores and the amounts of water are the key factors in SAPC. According to the size of pores SAPC could take place either at the surface of the pores (according to the classical model) or at the external surface of the particle with a storage of TPPTS and catalytic complex in the filled pores. When the pores are fully filled the SAPC can operate efficiently onto the external surface, stabilising the conversion in a relatively wide range of support hydration.

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