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Expanded Scope of Supported Aqueous Phase Catalysis:

Efficient Rhodium-Catalyzed Hydroformylation of α,β-Unsaturated Esters

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The use of supported aqueous-phase (SAP) catalysts for the rhodium-based hydroformylation of methyl acrylate leads under optimal conditions to much higher activities than those observed under comparable homogeneous and biphasic conditions. The results obtained with a series of acrylic esters are found to be dependent on the water content of the solid support and on the solubility of the functionalized olefin in water. For soluble organic reactants, like methyl acrylate, optimal activities are obtained for fully filled pore volume materials. For less soluble organic reactants, like butyl acrylate, hydroformylations are best achieved with a lower degree of pore filling, strictly dependent on the nature of the functionalized olefin. It is assumed that the reaction of hydrophilic olefins occurs mainly in the homogeneous water film dispersed over the solid support, whilst that of lipophilic olefins takes place at the interface between the organic phase and the aqueous film. The effects of temperature and the nature of the solid support are reported. Experiments are described that indicate that the surface area and the chemical nature of the solid play a major role on the activity of the SAP catalyst, whilst the pore diameter has almost no influence. However, a decrease in the activity of methyl acrylate hydroformylation was observed upon recycling of the SAPC materials, which was attributed to the leaching of rhodium into the organic phase and the gradual dehydration of silica. © 1996 Academic Press, Inc.

INTRODUCTION

Hydroformylation of olefins is an important, well-known commercial process for the production of aldehydes and alcohols. In the case of rhodium-catalyzed hydroformylation of higher olefins, the separation of the catalyst from the reaction products is the major limitation of the process. Indeed, separation of high boiling aldehydes and the catalyst requires generally vigorous distillation conditions which result in degradation of the catalyst with the concomitant loss of rhodium. Due to the rhodium cost, this loss cannot be economically tolerated. To overcome this problem, several attempts to "heterogenize" the homogeneous rhodium catalyst were made. Four major approaches have been developed for the hydroformylation of higher olefins: (i) anchoring of rhodium catalysts to resins, polymeric or mineral supports (1); (ii) homogeneous catalysts with amphiphilic complexes which can be extracted in another phase at the end of the reaction (2); (iii) aqueous–organic biphasic catalysts involving the use of particular ligands (3) or promoters such as a surfactant (4), co-solvent (5), or cyclodextrin (6); and (iv) supported hydrophilic liquid phase catalysis (7, 10–17).

Although supported hydrophilic liquid phase catalysts have not been developed on an industrial scale for hydroformylation, this concept has attracted a great deal of attention during recent years and has even been extended to other reactions such as asymmetric hydrogenation (8) and Wacker oxidation (9). This approach consists of a water-soluble organometallic complex dissolved in a hydrophilic liquid film which is supported on a high surface area hydrophilic support (7). The hydrophilic liquid is immiscible with organic liquids and can be water, ethylene glycol, or polyethylene glycol (10, 11). Among these different liquids, water is the most attractive one from an economic and environmental standpoint.

The systems containing an aqueous phase have been the subject of most of the studies and have been denoted by Davis supported aqueous phase catalysts (SAPC) (10). In the SAPC system, the organometallic complex is solubilized in the supported aqueous phase by using the water-soluble phosphine trisodium tris(*m*-sulfonatophenyl)phosphine (TPPTS) and is assumed to work at the aqueous-organic interface during catalysis (12). The catalytic activity of these SAP catalysts strongly depends on the water content. For example, when l-octene is hydroformylated, the catalytic activity increases by a factor of 6 when the weight percentage of water in the SAP materials increases from 2.9 to 8.5 wt% and decreases rapidly above 8.5 wt% (12). At the maximum catalytic activity,

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Hanson showed from phosphorus-31 spin lattice relaxation times that the adsorbed phosphine TPPTS has mobility similar to that in an aqueous solution (13). The major advantages of the rhodium SAP catalysts on other immobilisation techniques is that rhodium is generally not leached into the organic phase and that the rate of hydroformylation is independent of the size of the higher olefin (12). However, it must be pointed out that continuous-flow experiments performed in a trickle-bed reactor showed that significant amounts of water were lost during the SAP hydroformylation (14). Numerous water soluble complexes, such as $HRh(CO)(TPPTS)_3$ (12), $Co_2(CO)_6(TPPTS)_2$ (15), and $Pt(TPPTS)_2Cl$, $SnCl_3$ (16) have proved to be effective in promoting the SAP hydroformylation of water-insoluble olefins and, recently, it has been reported that the activity of rhodium SAP catalysts can be increased by adding an adequate amount of alkali metal salt (17). Surprisingly, all works devoted to SAP systems have been focused on the hydroformylation of higher olefins and no attention has been given to the hydroformylation of α,β-unsaturated esters such as methyl acrylate. Nevertheless, the hydroformylation of such substrates could give attractive chemical intermediates to make pharmaceuticals and methacrylate esters (18).

Recently, we have investigated the potential application of the SAP rhodium catalyst $HRh(CO)(TPPTS)_3$ to the hydroformylation of such functionalized olefins (19). Indeed, we have reported that SAP catalysis, under suitable experimental conditions, is an effective process for the hydroformylation of methyl acrylate as the turnover frequencies were higher than those obtained with comparable homogeneous single-phase and biphasic systems (19). Now, we wish to describe the effect of various parameters such as the water content and the nature of the support on the activity and selectivity of SAP rhodium catalysts during methyl acrylate hydroformylation. We wish also to report that the scope of the SAP rhodium catalyst can be extended to other α,β-unsaturated esters (Fig. 1).

EXPERIMENTAL

Materials

Methyl acrylate (99%), ethyl acrylate (99%), butyl acrylate (99%), 2-ethylhexyl acrylate (98%), 2-ethoxyethyl acrylate (98%), methyl crotonate (98%), and rhodium(I) dicarbonyl acetylacetonate ($Rh(acac)(CO)_2$, 98%) were purchased in their highest purity available from Aldrich Chemical Co. and were used as received without further purification. Triphenylphosphine (TPP) was obtained from Strem Chemicals (99% pure). The silica gel 60 (pore volume, $V_p = 0.75$ cm^3/g, surface area, $SA = 480$ m^2/g, 70–230 mesh, mean pore diameter, $r_p = 60$ Å) and the silica gel 40 (grade 10180, $V_p = 0.42$ cm^3/g, $SA = 750$ m^2/g, 70–230 mesh, $r_p = 40$ Å) were purchased from Merck. The controlled pore glasses CPG-240 ($V_p = 0.89$ cm^3/g, $SA = 79$ m^2/g, 120–200 mesh, $r_p = 242$ Å) and CPG-350 ($V_p = 0.84$ cm^3/g, $SA = 55$ m^2/g, 120–200 mesh, $r_p = 337$ Å) were obtained as a gift from Electronucleonics. The following supports: Silica gel, Davisil® (grade 710, $V_p = 0.75$ cm^3/g, $SA = 480$ m^2/g, particle size 4–20 μm, $r_p = 60$ Å); silica gel, Davisil® (grade 644, $V_p = 1.15$ cm^3/g, $SA = 300$ m^2/g, 100–200 mesh, $r_p = 150$ Å), and alumina (activated alumina, weakly acid, $SA = 155$ m^2/g, ~150 mesh, $r_p = 58$ Å) were supplied by Aldrich Chemical Co. The glass powder (particle size 40–160 μm) was purchased from Prolabo. Molecular sieve (13X, 8–12 mesh) was obtained from Janssen Chemicals and was ground before use (particle size <200 μm). All supports were dried carefully before use (180°C under vacuum for 18 h). Carbon monoxide and hydrogen were used directly from cylinders (H_2/CO (1:1); >99.9% pure; Air Liquide). Distilled deionized water was used in all the experiments. Reagents and solvents including water were degassed by bubbling nitrogen for 15 min before each use or by freeze-pump-thaw cycles.

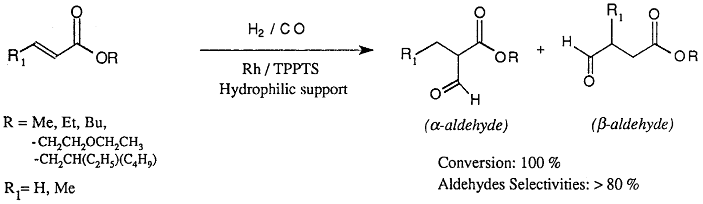

FIG. 1. Hydroformylation of various α-β-unsatured esters catalyzed by supported aqueous phase catalytic systems.

Apparatus and Instrumentation

Unless stated otherwise, all experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. All the hydroformylation experiments were carried out in a 100-ml stainless steel autoclave. The autoclave supplied by Autoclave Engineer was equipped with arrangements for automatic temperature control, pressure regulation, and variable stirrer speed. A safety rupture disk was also fitted to the reactor. Gas liquid chromatography analyses were carried out on a Chrompack apparatus equipped with a CP Sil 5-CB column (25 m × 0.32 mm). Thermogravimetric analyses (TGA) were obtained under air on a Setaram MTB 8 thermogravimetric analyser (Temperature programme: 5°C/min). Rhodium elemental analyses of the reaction filtrates were performed by Laboratories Wolff (Clichy, France).

Synthesis

Trisodium tris(*m*-sulfonatophenyl)phosphine (TPPTS) was synthesized as reported by Gärtner *et al.* (20). The purity of the TPPTS was carefully controlled. In particular, ^{31}P solution NMR indicated that the product was a mixture of TPPTS (ca 98%) and its oxide (ca 2%).

Preparation of the reaction mixtures was carried out as follows: (i) *Homogeneous systems*: under an atmosphere of nitrogen, the rhodium precursor Rh(acac)(CO)$_2$ (0.2 mmol), triphenylphosphine (2 mmol), and the organic reactant (100 mmol) were dissolved in 40 ml of toluene. (ii) *Biphasic systems*: rhodium precursor Rh(acac)(CO)$_2$ (0.2 mmol) and TPPTS (2 mmol) were stirred in 30 ml of water until total dissolution, and then 100 mmol of the organic reactant were added in 40 ml of toluene. (iii) *Supported aqueous phase systems*: the rhodium precursor (0.2 mmol) and TPPTS (2 mmol) were stirred in 20 ml of water until total dissolution, and then added to 9 g of freshly dried support. Water was then partially removed under vacuum until the desired water content, which was precisely determined by gravimetric thermal analysis (Fig. 2).

The resulting powder was mixed with a solution of 100 mmol of the organic reactant in 40 ml of toluene. It must be noticed that we did not systematically study the way of introducing water in the support. Nevertheless, preliminary experiments showed that SAP catalysts prepared either by impregnation with a water solution or by hydration with vapour pressure from a controlled-moisture flask, led to identical results, as previously reported by Davis (12). Due to its simplicity, the first technique was used for the overall study.

Catalytic Runs

A 100-ml stainless steel autoclave was charged under nitrogen with the reaction mixture, then heated at 50°C, and pressurised with 50 atm of CO/H$_2$ (1 : 1). Mechanical stirring (1000 rpm) was then started. The pressure was kept constant throughout the whole reaction time by using a gas reservoir along with a pressure regulator. The reaction was monitored by quantitative gas chromatographic analysis. Products were identified by comparison of GLC retention times and spectral characteristics with authentic samples.

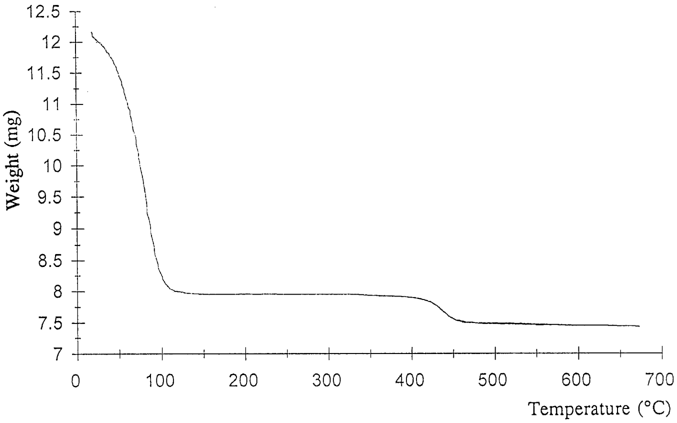

FIG. 2. Thermogravimetric analysis of a SAP catalytic material (water content, 35% weight). Water content = (weight of water in the solid)/(weight of the solid) × 100. In this case, the solid was constituted of 9 g silica gel ($V_p = 0.75$ cm^3/g, $SA = 480$ m^2/g, 70–230 mesh, $r_p = 60$ Å), 5.5 g of water, 1.136 g of TPPTS (2 mmol) and 51.6 mg of Rh(acac)(CO)$_2$ (0.2 mmol). The weight loss at 450°C has been attributed to TPPTS degradation and desorption of chemisorbed water.

Recycling Experiments

The first batch was carried out as described above. After total conversion of methyl acrylate (GLC analysis), the autoclave was cooled to room temperature and the CO/H$_2$ pressure was evacuated. After a 10-min time of decanting, the bulk organic solution was then removed by inverse filtration under the CO/H$_2$ atmosphere, leaving the SAP catalyst in the bottom of the reactor. The latter was washed with toluene (30 ml), and a new reaction mixture containing 100 mmol of methyl acrylate in 40 ml of toluene was introduced. The second batch was carried out using the same procedure as that described above. The overall recycling procedure was then repeated.

RESULTS AND DISCUSSION

Hydroformylation of Methyl Acrylate

In order to make direct comparisons of our SAP catalysts with classical systems, we determined first the activity under comparable homogeneous and biphasic conditions. Thus, when methyl acrylate was charged into the hydroformylation reactor along with a toluene solution of Rh(acac)(CO)$_2$ and triphenylphosphine, the acrylate conversion to aldehydes was completed after 140 min at 50°C, H$_2$/CO pressure = 50 bar (Table 1, entry 1). The reaction profile was linear with an average activity of 3.6 min^{-1} (turnover frequency, TOF, over the whole reaction time) (Fig. 3). The results of the biphasic system Rh(acac)(CO)$_2$ and excess TPPTS in water with methyl acrylate in toluene, under the same reaction conditions, showed a moderate (completion time: 120 min), but surprising increase in the catalytic activity (entry 2) (21). This was particularly the case in the first stage of the reaction (initial TOF = 9.1 min^{-1} vs average activity = 4.2 min^{-1}) (Fig. 3). In both cases, chemoselectivity to aldehydes was high, as only 4.6% and 3.4% of the hydrogenated product, i.e., methyl propionate, were formed, respectively. Regioselectivity of both homogeneous and biphasic systems was almost exclusively directed towards the formation of the branched aldehyde, as classically expected from this type of functionalized olefin (22).

The results of SAP catalysis under proper conditions were dramatically improved. Namely, when a toluene solution of methyl acrylate was charged into the hydroformylation reactor with a SAP catalyst prepared from a 60 Å silica gel ($SA = 500$ m^2/g, $V_p = 0.75$ cm^3/g) containing 37 wt% of water and a combination of Rh(acac)(CO)$_2$ and TPPTS, the conversion to aldehydes was completed within 12 min, under the same conditions as those used for the homogeneous

TABLE 1

Hydroformylation of Methyl Acrylate Using Homogeneous, Biphasic, and SAP Catalyst; Influence of Water Content[a]

Run no.	Catalytic system	Water content		Time[d] (min)	Ald. sel.[e] (mol%)	α/β[f]	Activity (min^{-1})[g]	
		wt%[b]	δ[c]				Initial[h]	Average[i]
1	Homog	—	—	140	95.4	>200	3.7	3.6
2	Biphasic	100	—	120	96.6	128	9.1	4.2
3	SAP	8	0.14	120	97.0	149	11	4.2
4	SAP	17	0.32	80	97.5	158	19	6.3
5	SAP	24	0.50	60	97.1	177	19	8.3
6	SAP	35	0.85	25	96.4	154	39	20
7	SAP	37	0.93	12	94.9	136	75	42
8	SAP	41	1.10	20	94.5	133	63	25
9	SAP	50	1.57	120	93.4	148	6.9	4.2

[a] Conditions: temperature 50°C; pressure 50 bar (1 : 1 H_2/CO); 60 Å silica gel used for the preparation of SAP materials; toluene used as the organic solvent.

[b] Weight% of water = water/(water + silica + TPPTS + Rh precursor).

[c] Degree of pore filling calculated by dividing the volume of aqueous film by the pore volume of the support.

[d] Optimized reaction time for total conversion of methyl acrylate (GC monitoring).

[e] Hydrogenation product (methyl propionate) accounts for the balance.

[f] Ratio of branched to linear aldehyde.

[g] Expressed in mol of substrate transformed per mol of catalyst per minute.

[h] Activity at 10–20% conversion.

[i] Activity calculated over the whole reaction time.

and biphasic systems (entry 7). This SAP material exhibited an average activity (TOF) of 42 min^{-1} but, as illustrated in Fig. 3, the turnover frequency was greatly dependent on the conversion of methyl acrylate. Namely, at the early stage of the reaction, the activity of this catalyst rose to a maximum of 75 min^{-1}, whereas it decreased to 10 min^{-1} in the last two min. Nonetheless, both data demonstrate the superiority of these SAPC over comparable homogeneous and biphasic catalysts.

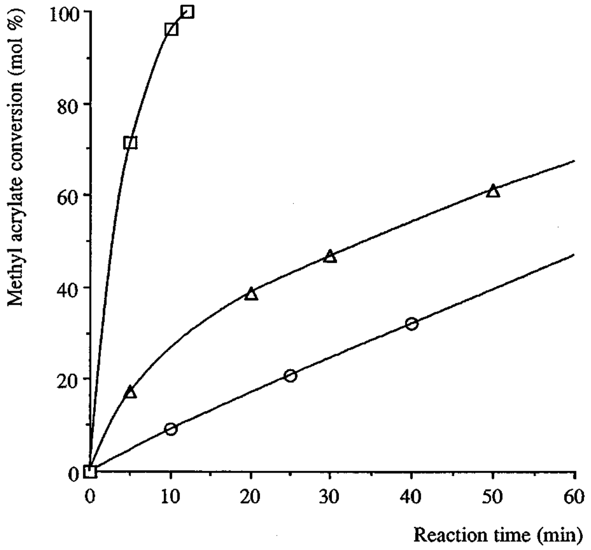

FIG. 3. Methyl acrylate conversion as a function of time for TPP (○), TPPTS (△), and TPPTS/SiO_2 (□) rhodium catalytic systems. SiO_2 (V_p = 0.75 cm^3/g, SA = 480 m^2/g, 70–230 mesh, r_p = 60 Å). See Experimental section for other reaction conditions.

Influence of Water Content

It has been reported by Davis and co-workers that the wt% of water in the SAP material affects considerably the hydroformylating activity of the catalysts (*vide supra*, Introduction) (12). A similar observation was also made for the hydroformylation of 1-hexene with supported hydrophilic polyethylene glycol film catalysts (PEG-SHFC) (11). In this last case, by introducing the degree of pore filling δ, calculated by dividing the volume of the liquid film by the pore volume of the solid, it was found that optimal activities occur for materials with fully filled pore volume ($\delta = 1.00$).

Our SAP catalysts also presented such a behavior, as shown by the reactivity results reported in Table 1 and those depicted in Fig. 4. The aforementioned 60 Å silica gel was used to prepare solid catalysts with various water contents. The maximum activity, as determined by conversion (Fig. 4) and turnover frequency (Table 1), was observed at 37 wt% water, i.e., at $\delta \sim 1.00$ in terms of degree of pore filling. Below this value, at intermediate water contents of 8 to 35 wt% ($0.14 < \delta < 0.90$), the activity increased quite regularly with δ. Yet, further loading of water rapidly resulted in decreased activity. As a matter of fact, at 50 wt% water content ($\delta = 1.60$), the behavior of the SAP material approached that of the biphasic system (compare entries 2 and 9).

The water content of SAP materials sightly affected the selectivity of the reaction. However, a regular increase in

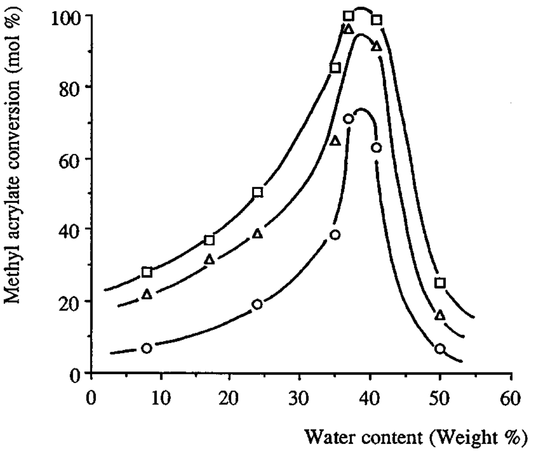

FIG. 4. Methyl acrylate conversion as a function of water content for the supported-aqueous phase system: Rh/TPPTS/SiO$_2$. Reaction times: 5 min (○), 10 min (△), 15 min (□). SiO$_2$ ($V_p = 0.75$ cm^3/g, $SA = 480$ m^2/g, 70–230 mesh, $r_p = 60$ Å), 9 g; Rh, 0.2 mmol; TPPTS, 2 mmol, methyl acrylate, 100 mmol, toluene, 40 ml, T, 50°C, P(CO/H$_2$), 50 bar. Water content: see Fig. 1.

the amount of the hydrogenation product with the water content was observed. In parallel with this, the branched to linear aldehyde ratio α/β was not monotonic since a maximum could be observed at ca 24 wt% water content, but with minute variations. An interesting feature appears once again from the comparison of the biphasic system with the overloaded SAP material ($\delta = 1.60$, entry 9); whilst both catalytic systems exhibited similar activities (*vide supra*), the amount of the hydrogenation product was almost doubled.

Use of Other Supports for SAP Catalysts

In order to know whether all SAP materials exhibit their maximum activity at $\delta = 1$, the use of other supports was investigated.

In the first series of experiments SAP catalyst precursors were prepared from a 40 Å silica gel ($SA = 750$ m^2/g, $V_p = 0.42$ cm^3/g), and a 150 Å silica gel ($SA = 300$ m^2/g, $V_p = 1.15$ cm^3/g). The results obtained for various water contents are reported in Figs. 5a and 5b, and Table 2.

As expected, the results were strikingly dependent on the water content. Figure 5a clearly shows that these silica-based SAP materials exhibited a similar behavior, i.e., a maximum activity could be obtained for a well-determined amount of water, depending on the physical characteristics of the silica used. In fact, as described above for the 60 Å silica gel, the best results for the hydroformylation of methyl acrylate with 40 Å and 150 Å derived SAP materials were obtained when the pores of the solid are totally filled ($\delta \sim 1.00$) (27 wt% and 48 wt% H$_2$O, respectively; entries 10 and 12). This trend appears even more marked in Fig. 5b as the three silicas gave identical activity as a function of the degree of pore filling, δ. This figure also indicates that, at least for these three SAP materials, the catalytic performances seem to be independent of the mean pore diameter and the surface area. Slight deviation from the ideal value ($\delta \sim 1.00$) also resulted in decreased activity. Moreover, the selectivity trend previously described for the 60 Å silica-derived SAP catalyst was found to be general, that is, an increase of hydrogenation with the water content (up to 6.5% for both 40 Å and 150 Å SAPC at 33 wt% and 51 wt%, respectively). Obviously, there was almost no difference in the optimized reaction times and selectivities of these three silica-supported catalysts, despite the differences in the surface area and the mean pore size.

Our results on the water dependence of the catalytic activity are in total agreement with those obtained by Drago *et al.* for the rhodium-based hydroformylation of 1-hexene

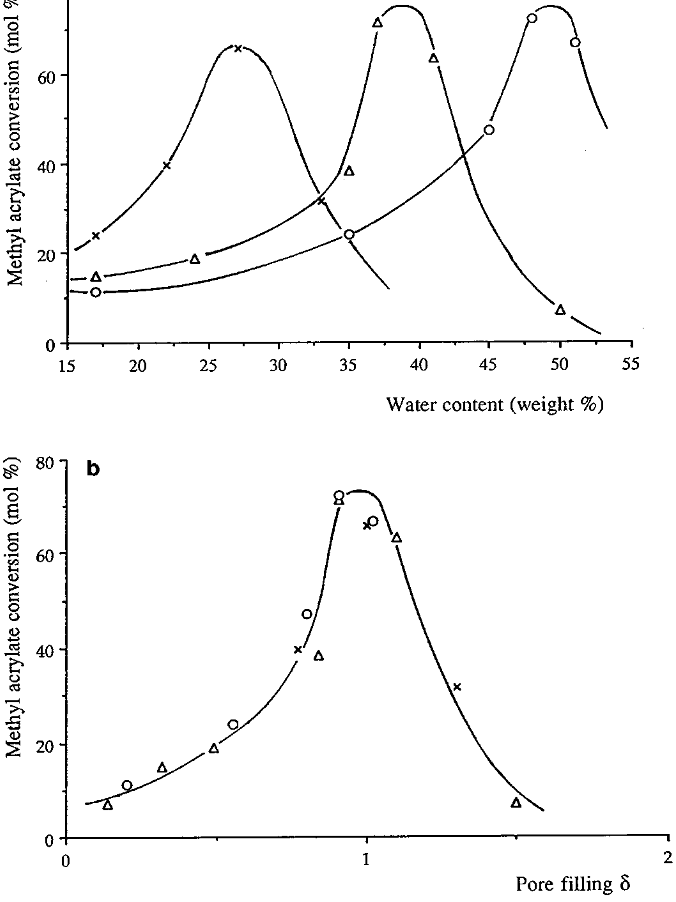

FIG. 5. Methyl acrylate conversion as a function of the nature of silica gel for the supported-aqueous phase system Rh/TPPTS/SiO$_2$ and (a) the water weight content, wt% (see Fig. 1); (b) the degree of pore filling, δ. Silica gel support: (×), $V_p = 0.42$ cm^3/g, $SA = 750$ m^2/g, 70–230 mesh, $r_p = 40$ Å; (△), $V_p = 0.75$ cm^3/g, $SA = 480$ m^2/g, 70–230 mesh, $r_p = 60$ Å; (○), $V_p = 1.15$ cm^3/g, $SA = 300$ m^2/g, 100–200 mesh, $r_p = 150$ Å. SiO$_2$: 9 g; Rh, 0.2 mmol; TPPTS, 2 mmol; methyl acrylate, 100 mmol; toluene, 40 ml, T, 50°C; P(CO/H$_2$), 50 bar. Reaction time, 5 min.

TABLE 2

Hydroformylation of Methyl Acrylate Using SAP Catalysis; Influence of the Support[a]

Run no.	Support	Water content wt%[b]	Water content δ[c]	Time[d] (min)	Ald. sel.[e] (mol%)	α/β[f]	Activity (min^{-1})[g] Initial[h]	Activity (min^{-1})[g] Average[i]
10	SiO_2 40 Å	27	1.00	11	95.0	135	65	45
11	SiO_2 60 Å	37	0.93	12	94.9	136	75	42
12	SiO_2 150 Å	48	0.91	12	96.1	133	72	42
13	CPG 240	44	1.00	20	96.4	94	38	25
14	CPG 350	39	0.90	40	96.1	123	24	12
15	Al_2O_3 58 Å	20	~1.0	20	93.9	74	39	25
16	MS 13 X	12	~1.0	15	96.0	79	53	33

[a] See Table 1 for conditions and footnotes.

using a PEG-silica supported catalyst (11). It was suggested by these authors that the main role of the support is to spread the homogeneous film over the surface of the support and, thus, to provide a film of high surface area in which the reaction occurs (11). It was also proposed that further loading to $\delta > 1.00$ produces droplets of water, thus releasing catalyst into an aqueous phase, where it is less effective than on the surface of the silica (11). Indeed. the shell of the water molecules in the droplets is a stronger barrier to access of the organic reactant to the catalyst than when water is spread in a thin layer of a few molecule thickness on the high surface area of the silica. We can also notice that, at $\delta \ll 1.00$, it is assumed that the mobility of the rhodium catalyst is considerably reduced (12a), and this could also account for the lower activities we observed at low water contents. However, as previously mentioned in the Introduction, ^{31}P NMR experiments conducted by Hanson and co-workers seem to indicate that adsorbed phosphine in SAP material has mobility similar to that in aqueous solution, even at relatively low water content (13).

In a second series of experiments, SAP materials were prepared from CPG-240 silica ($SA = 79$ m^2/g, $V_p = 0.89$ cm^3/g) and CPG-350 silica ($SA = 55$ m^2/g, $V_p = 0.84$ cm^3/g), which were the first supports used in SAP catalysis (10, 12). For the aforementioned reason, the CPG-240 and CPG-350 catalysts were evaluated at $\delta = 1.00$ (Table 2, entries 13 and 14). Astonishingly, the catalytic performances were significantly reduced compared to those of the 40, 60, and 150 Å silica derived SAP materials. This trend is also followed by a decrease in the surface area ($SA = 79$ and 55 m^2/g for the CPG materials vs 300–500 m^2/g for the 40, 60, and 150 Å silica), and the inactivity of a SAP catalyst prepared from a pure glass (very low surface area and pore volume) confirms that, at least to some extent, the activity is also correlated with the specific area of the silica (*vide supra*). It is also noteworthy that with the mechanical stirring used in our experiments, SAP materials were ground during the reaction course. However, we checked that a SAP catalyst prepared from a lower granulometry silica (Davisil®, $r_p = 60$ Å, 4–20 μm) led to identical results.

Finally, we investigated the behavior of chemically different supports. Thus, an alumina ($SA = 150$ m^2/g, $r_p = 58$ Å) (Table 2, entry 15) and a molecular sieve ($SA = 250$ m^2/g, 60–200 μm, $r_p = 10$ Å) (entry 16) were used to prepare SAPC. Once again, the best results in terms of activity were obtained for fully filled pore materials (Fig. 6). The molecular sieve derived catalyst exhibited comparable activities and selectivities than the reference 60 Å silica gel. This is in agreement with the preponderance of the surface area over the pore diameter of the support to prepare efficient SAP catalysts, at least for the hydroformylation of methyl acrylate. In fact, it is most probable that in the first studies devoted to the hydroformylation of higher olefins (10, 12), the use of expensive, mesoporous materials with a narrow pore distribution was not a prerequisite to obtain good results. This was in a way confirmed by Naughton *et al.* who obtained also remarkable results by using an ordinary silica (13). On the other hand, the relatively poor maximum activity of the alumina-based SAP catalyst can also be

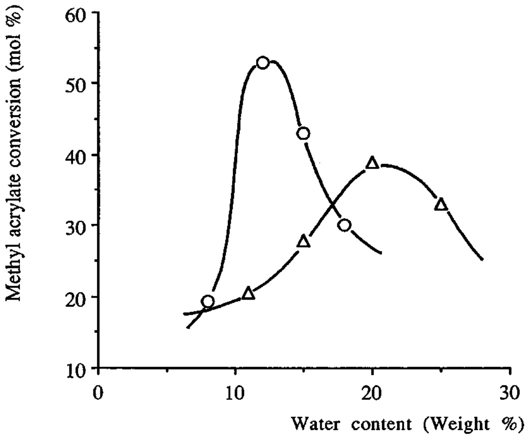

FIG. 6. Methyl acrylate conversion as a function of water content for the supported-aqueous phase systems: Rh/TPPTS/alumina (△) and Rh/TPPTS/molecular sieve (○). Support: 9 g; Rh, 0.2 mmol; TPPTS, 2 mmol; methyl acrylate, 100 mmol; toluene, 40 ml; T, 50°C; P(CO/H_2), 50 bar. Reaction time, 5 min. Water content: see Fig. 1.

attributed to the small surface area of the starting support. Interestingly, the performances of this SAP material were less dependent on the water content than were the other supports previously described. This could be an important factor for the development of such SAP materials, since it is known that the aqueous film leaves the support quite easily during the course of the reaction, thus strongly decreasing the activity of the silica-supported catalyst (12). It must be pointed out that the chemoselectivity into aldehydes was somewhat worse (92.7% with a 25 wt% SAPC vs 98.4% at 11 wt%), although no attempt at optimization was made.

Leaching of the Catalyst and Recycling Experiments

Filtration of the reaction mixture to remove the solid catalyst yielded colourless to slightly reddish toluene solutions, due to the presence of the enolic form of the branched aldehyde, i.e., methyl 2-formyl-acrylate. Elemental analyses of organic solutions from different runs and silicas indicated the presence of variable amounts of rhodium, in the <5 to 10 ppm range (<2 mol% of the initial catalyst). Apparently, there was no obvious relation between the rhodium content in the organic phase and the characteristics of the SAP catalyst used. These results are quite surprising since it has been reported by most authors that generally no leaching occurs under comparable SAP conditions, although extensive leaching could be detected in some cases (12c). It is noteworthy that SAPC systems are closely related to SLPC systems which have proved clear susceptibility to leaching, as other authors have reported (3f). Moreover, the polar nature of the organic reactant may account for this leaching.

An important aspect of SAP catalysis is the possibility to separate easily the catalyst from the reaction medium and to recycle it in further experiments. Figure 7 illustrates some of the results we obtained in such experiments (see experimental section for a typical procedure). A decrease of ca 10–20% in the catalytic activity was observed between each of the five recycling experiments. This decrease in activity is too important to be attributed solely to the rhodium leaching and must also be due to the water leaching as reported by Horvath (14). Indeed, we have previously seen that the activity was strictly related to the water content of the SAP material (Figs. 4 and 5). The loss of water from the silica during our recycling experiments was also evidenced by the progressive decrease of the hydrogenation product (*vide supra*) (94.5% sel into aldehydes for the first batch up to 97.5 for the sixth use).

Influence of Temperature

As expected, SAP catalysts exhibited lower activity with decreased temperature. In the case of the reference 60 Å silica gel SAPC containing 37 wt% water ($\delta \sim 1$), an apparent activation energy of ca 117 kJ/mol was obtained from the temperature dependence of initial turnover frequency by using an Arrhenius plot (Fig. 8). This value is rather high compared to those found by Davis *et al.* for the hydroformylation of 1-heptene, i.e., 40–75 kJ/mol according to the water content of the SAP catalyst (8a). The apparent activation energy obtained here is far too high to represent a mass transfer process, and must, therefore, correspond to a chemical rate determining step (e.g., H_2 oxidative addition (17, 23)).

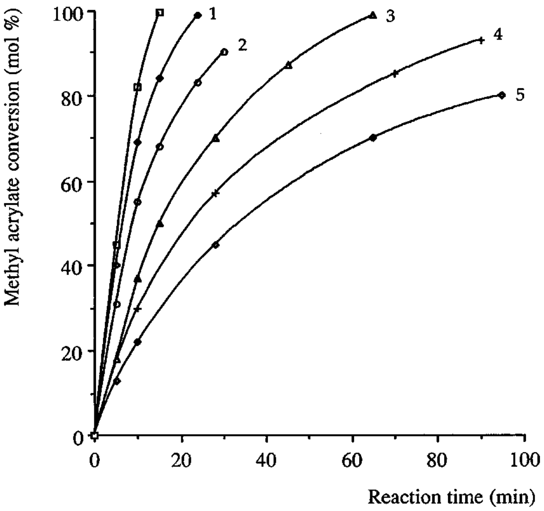

FIG. 7. Methyl acrylate conversion as a function of time and of the recycling of the SAP catalyst: Rh/TPPTS/SiO_2. Initial characteristics: SiO_2 ($V_p = 0.75$ cm^3/g, $SA = 480$ m^2/g, 70–230 mesh, $r_p = 60$ Å): 9 g; water content, 35 wt%; Rh, 0.2 mmol; TPPTS, 2 mmol. Catalytic run: methyl acrylate, 100 mmol, toluene, 40 ml; T: 50°C, P(CO/H_2), 50 bar. Numbered curves refer to recycles.

The stability of the active catalytic species was not affected in this temperature range (25–50°C), as shown by the enduring intense yellow colour of a 37 wt% SAP catalyst throughout the whole reaction time. The loss of activity with decreased temperature was in part balanced by the

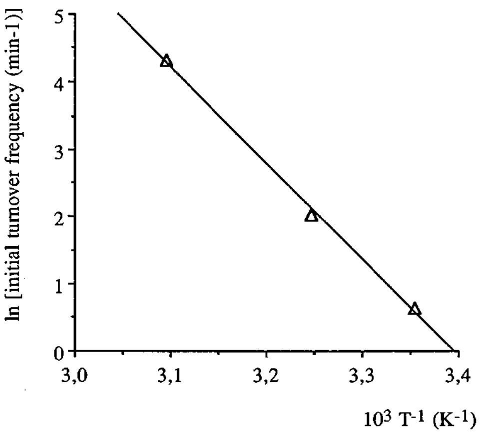

FIG. 8. Dependence of initial turnover frequency on the reaction temperature. SiO_2 ($V_p = 0.75$ cm^3/g, $SA = 480$ m^2/g, 70–230 mesh, $r_p = 60$ Å): 9 g; Rh, 0.2 mmol; TPPTS, 2 mmol, methyl acrylate, 100 mmol; toluene, 40 ml, P(CO/H_2), 50 bar.

TABLE 3

Hydroformylation of Unsaturated Esters and Propene Using SAP Catalysis[a]

Organic reactant	Run no.	System	Time[b] (min)	Ald. sel.[c] (mol%)	α/β[d]	Activity (min^{-1})[e]	
						Initial[f]	Average[g]
Ethyl acrylate	17	Homogeneous	165	93.5	137	2.4	3.0
	18	Biphasic	30	96.6	121	28	17
	19	SAPC 37 wt%	25	96.9	115	36	20
Butyl acrylate	20	Homogeneous	150	95.6	140	3.2	3.3
	21	Biphasic	90	98.2	123	9.1	5.6
	22	SAPC 37 wt%	120	98.0	121	14	4.2
	23	SAPC 30 wt%	100	98.9	128	5.0	5.0
	24	SAPC 26 wt%	80	99.0	101	5.5	6.3
	25	SAPC 19 wt%	120	99.4	114	3.2	4.2
2-Ethylhexyl acrylate	26	Homogeneous	150	93.4	63	3.2	3.3
	27	Biphasic	1200[b]	97.1	59	0.08	0.07
	28	SAPC 37 wt%	1200[h]	93.3	79	0.04	0.42[h]
Ethoxyethyl acrylate	29	Homogeneous	240	86.5	62	1.3	2.1
	30	Biphasic	40	94.0	72	18	12.5
	31	SAPC 37 wt%	40	97.0	103	26	12.5
Methyl crotonate	32	Homogeneous	360	43.8	77	1.4	1.4
	33	Biphasic	720	80.5	>200	1.0	0.7
	34	SAPC 37 wt%	1200[b]	95.8	>200	0.2	0.2
	35	SAPC 6 wt%	1200[b]	98.6	>200	0.4	0.3
Propene (100°C)	36	Homogeneous	<5	>96	0.5	nd	>96
	37	Biphasic	90[b]	nd	0.20	19	4.1
	38	SAPC 37 wt%	90[b]	nd	0.36	14	3.9
	39	SAPC 8 wt%	45	>99	0.43	38	11

[a] Conditions: temperature 50°C (except for propene = 100°C); pressure 50 bar (1 : 1 $\mathrm{H_2/CO}$); homogeneous reaction performed in toluene using $\mathrm{Rh(acac)(CO)_2}$ and TPP; biphasic reaction performed in toluene (30 ml)/water (40 ml) using $\mathrm{Rh(acac)(CO)_2}$ and TPPTS; SAP material prepared from 60 Å silica gel.

[b] Optimized reaction time for total conversion of the substrate (GC monitoring) except for entry 27: 17% conv.; entry 34: 47% conv.; entry 35: 73% conv.; entry 37: 73% conv.; entry 38: 71% conv.

[c] Hydrogenation product accounts for the balance.

[d] Ratio of branched to linear aldehyde.

[e] Expressed in mol of substrate transformed per mol of catalyst per minute.

[f] Activity at 10–20% conversion.

[g] Activity calculated over the whole reaction time.

[h] Non-optimized reaction time and TOF.

significant improvement of the chemoselectivity (aldehydes yield = 98.0% at 35°C; 99.1% at 25°C) and of the regioselectivity ($\alpha/\beta > 200$ at 25°C and 35°C).

Hydroformylation of Related Organic Reactants

In order to gain better insight into the understanding of the behavior of the SAP catalysts, as well as to determine the scope of their efficient utilization, we have examined the reactivity of related organic reactants. Thus, other acrylate esters and the related substrates methyl crotonate and propene were hydroformylated using SAP catalysis. On the basis of the results obtained for methyl acrylate, a 37 wt% SAP material derived from the reference 60 Å silica gel was first investigated, but several catalysts with various water contents were evaluated in a second series. For comparison purposes, all the organic reactants were also tested under homogeneous and biphasic conditions using the same procedures as those used for methyl acrylate. Typical results are summarized in Table 3.

The catalytic activities under SAP conditions for the hydroformylation of ethyl acrylate (Table 3, entry 19) were somewhat lower than those observed with methyl acrylate (Table 1, entry 7), but the performances of the SAP system remained the best compared with the classical ones (Table 3, entries 17 and 18). In the case of butyl acrylate and, above all, for 2-ethylhexyl acrylate, the decrease in the activity of the SAP catalyst was even more drastic (entries 20–28). These results indicate that as the solubility of the organic reactant in the aqueous film decreases (24), the activity of the fully filled pore volume SAP catalyst decreases. The good results of SAP catalysis for the hydroformylation of ethoxyethyl acrylate, an organic reactant quite soluble in water, are in total agreement with this trend (entries 29–31). It is noteworthy that the performances of SAP catalysts for the hydroformylation of olefins or their derivatives, having poor solubility in water, could be significantly improved by decreasing the water content of the silica support. For example, the optimal activity for the hydroformylation of butyl acrylate is obtained for a SAP material containing ca 26 wt% of water ($\delta = 0.70$) (entries 20–25). In the case of propene, a SAP material containing 8 wt% of water ($\delta = 0.14$) exhibited double the activity of a 37 wt% catalyst (entries 38–39), although the performances remained very modest when compared with the homogeneous system (entry 36). These experiments conducted with olefins having poor solubility in water are in total agreement with the results described by Davis and coworkers (12) for the hydroformylation of higher α-olefins, such as 1-octene. Indeed, their best SAP catalysts attained their optimal performances when the degree of filling the available pore volume is low ($\delta \sim 0.1$).

Therefore, it is reasonable to assume that, depending on the solubility of the organic reactant, hydroformylation can occur not only at the interface, but also in the homogeneous liquid film on the support surface, as previously stated for the polyethylene glycol supported homogeneous film catalyst (PEG-SHFC) system (11). Obviously, the surface area of the aqueous film at the surface of the silica increases with the water content; since it is assumed that apolar olefins are hydroformylated at the interface. optimal activities should be obtained at $\delta = 1.0$. Nevertheless, it is noteworthy that at the same time hydrophobic–hydrophilic repulsions between the apolar organic reactant and the aqueous film also increase with the water content. In our opinion, this could be the reason why a compromise must be experimentally found for the water content. Interestingly, it has been reported by Naughton and Drago (11) that the best PEG-SHFC catalysts for the hydroformylation of higher α-olefins are produced for a fully filled pore volume material ($\delta = 1.4$). We assume that these differences in the behavior of SAPC and PEG-SHFC towards organic reactants of low solubility in water arise from the nature of the liquid film on the support and notably from the higher lipophilicity of PEG versus water.

From a selectivity point of view, the results obtained under SAPC conditions for acrylic acid esters, except for 2-ethylhexyl acrylate, were at least equal and generally better than those obtained under biphasic conditions. A significant improvement was also observed in going from the homogeneous to the SAP catalytic system, especially for the hydroformylation of ethoxyethyl acrylate.

In the case of methyl crotonate, the results were strikingly different (Table 3, entries 32–35). As a matter of fact, the highest activities were observed under homogeneous conditions, but along with a very poor selectivity for the formation of aldehydes. The latter was greatly increased with biphasic and, above all, with SAP catalysis; unfortunately, in this case, the turnover frequencies were too low to be of practical use, whatever the water content we used for the support. In fact, it is well known that the hydroformylation of internal olefins is much slower than that of α-olefins.

CONCLUSIONS

We have shown that, under proper SAPC conditions, the hydroformylation reaction of some unsaturated esters can be achieved in high yields and selectivities. According to the nature of the organic reactant, the TOF values were higher still, exceeding those obtainable with the comparable homogeneous single-phase system. Our results suggest that two cases should be distinguished for the hydroformylation reaction using SAP catalysis: (i) for polar organic reactants having high solubility in water (e.g., methyl, ethyl, ethoxyethyl esters of acrylic acid), the best results are obtained for a well-determined water content that fills the pores and spreads the homogeneous catalyst in a high surface area film over the surface of the support; (ii) for organic reactants having quite poor to very low solubility in water (propene, higher olefins), an optimal water content of the support should exist corresponding to a compromise between, on the one hand, the highest surface area of the aqueous film and, on the other hand, the lowest hydrophobic–hydrophilic repulsions between the organic reactant and the aqueous film.

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