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Preparation of Supported Heterogeneous Catalysts by Pulse Impregnation: Application to $Ru_3(CO)_{12}$/2,2′-Bipyridine/SiO_2 Catalyst

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In this paper we introduce pulse impregnation, a method for preparing supported heterogeneous catalysts by successive impregnation cycles. Pulse impregnation is a method for preparing supported heterogeneous catalysts from the liquid phase. In the pulse-impregnation technique the catalyst surface is grown gradually in consecutive cycles, with each cycle consisting of separate deposition and activation steps. During the deposition step, the catalyst precursor or precursors are deposited onto the support from a suitable solvent. The actual chemically bonded catalyst phase is formed during the activation step (e.g., thermal activation). Pulse impregnation was tested in the separate deposition of 2,2′-bipyridine and $Ru_3(CO)_{12}$ onto a silica support, and in the preparation of $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst, in a column-type reactor system. Macroscopically uniform deposition was achieved with both 2,2′-bipyridine and $Ru_3(CO)_{12}$. Various solvent systems were used to control the amount of solute adsorbed during deposition. In the preparation of the $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst, the ruthenium content increased nearly linearly with the number of preparation cycles. The effect of the preparation method on the catalyst activity was also tested in 1-hexene hydroformylation. © 1994 Academic Press, Inc.

INTRODUCTION

The effectiveness of a supported heterogeneous catalyst depends largely on the surface structure of the catalyst. Even though the chemical nature of the reagents and the interaction between the support and the catalyst precursor essentially determines the surface structure, critical properties such as the amount and distribution of an active component can be effectively modified by proper choice of the catalyst preparation method. Numerous preparation methods exist, each with its advantages and disadvantages. Almost all are multistep processes that typically include pretreatment of a support, adsorption of a precursor, washing, drying, and activation steps. Controlling the adsorption step is the major challenge in catalyst design. Classical liquid-phase methods such as impregnation and precipitation offer only rather limited possibilities to control the formation of the catalyst surface. Direct sublimation can be regarded as a gas-phase analogy to impregnation, and again accurate control of the adsorption step is difficult. With more sophisticated methods it is possible to grow the catalyst surface by using repeated preparation cycles. Step-by-step preparations of thin-layer ZrO_2/ZMS-5, Pd/La_2O_3/ZMS-5, and Pt/Nb/SiO_2 (1/3) provide good examples of controlled formation of the catalyst surface. In chemical vapor deposition (CVD) and atomic layer epitaxy (ALE) derived methods, the catalyst precursor is sublimed in a separate sublimation oven and transferred to the support with a carrier gas. Both methods have their roots in preparation of thin films and thin layer coatings (4, 5). Controlled repetition of preparation steps is easily arranged in both CVD and ALE. CVD has been used, for example, in the preparation of supported V_2O_5, B_2O_3, SnO_2 catalysts (6–10). An ALE-derived method has proven very effective in the preparation of $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst (11, 12).

In this study we introduce pulse impregnation, a liquid-phase method for preparing supported heterogeneous catalysts based on successive impregnations. In pulse impregnation, precursor solution is passed through a support bed in consecutive pulses. Initial adsorption is reversible, so it is possible to shift the adsorption equilibrium and determination the amount of adsorbed precursor by changing the solvent. Initially physisorbed precursor species can be chemisorbed onto the support via a suitable activation step (e.g., thermal activation). The possibility of a continuous repetition of preparation steps offers a controllable way to grow the catalyst surface. In the present work the pulse impregnation method has been studied in the coating of a silica support with $Ru_3(CO)_{12}$ and 2,2′-bipyridine, and in the preparation of $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst.

Principle of the Pulse-Impregnation Method

In pulse impregnation (PI), the catalyst surface is grown gradually in consecutive preparation cycles. A single cy-

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cle consists of deposition and activation steps (Fig. 1). PI is especially suitable for preparing multicomponent catalysts. Catalyst precursors can be deposited onto the support simultaneously from the same solvent or one by one from different solvents. In the latter case the adsorption of each precursor can be affected separately. However, in this case the solvent system must be chosen in such a way that the successive depositions do not remove the formerly deposited precursors. Control of the surface growth in PI is based on the reversible adsorption–desorption (or partition) equilibrium between solvent and support phases. When the precursor (solute) solution is brought into contact with the support, the precursor molecules distribute between solvent and the support according to an adsorption isotherm. In the ideal case the amount of precursor remaining on the support after the solution is removed is the same fraction of molecules as was adsorbed on the support at the equilibrium stage. In PI, a solution of constant solute concentration is continuously fed onto the support. If the adsorption isotherm is linear, the solute concentration on the support phase at the final equilibrium stage is

$$C_s = KC_0, \qquad (1)$$

where C_0 is the original concentration of solute in the solution and K is the distribution coefficient between the support and solvent phases. The amount of the adsorbed solute can now be affected by varying either the solvent or the concentration C_0. In the former case, the distribution coefficient is changed. After the adsorption step precursors are only weakly bonded on the support. The purpose of the adsorption step is merely to deposit the precursors uniformly onto the support. Only during the subsequent activation step do the precursors react with the support and form a chemically bonded catalyst phase. Activation may be a simple thermal treatment. A washing step may also be included in the preparation cycle, to remove any unreacted reagents. Typically the support is not fully covered by the precursor after a single deposition step, which may be advantageous when the free support sites also play an active role in catalysis, or when several precursors are being deposited onto the support. As the preparation cycles are repeated the coverage of the support is increased. Repetition of the cycles may lead either to a fully covered monolayer surface or to multilayer growth, depending on the nature of the adsorption system.

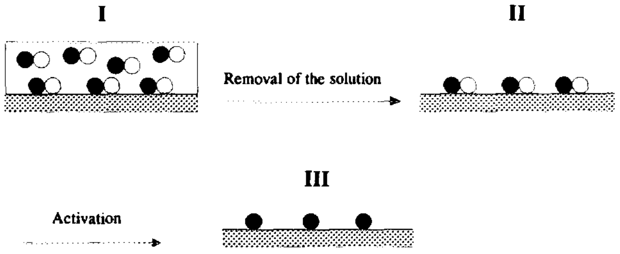

FIG. 1. Schematic representation of a pulse-impregnation cycle. (I, II) Deposition step. Precursor solution is brought into contact with the support. The adsorption–desorption equilibrium is established and the precursor solution is removed. An equilibrium amount of precursor molecules is deposited onto the support. (III) Activation step. Weakly adsorbed precursor molecules react with the surface sites of the support and the active catalyst phase is formed.

The deposition step consists of either direct adsorption onto the solid support or partition between solvent and supported liquid phase (SLP). In the latter case the precursor molecules remain in the supported liquid phase after the deposition solvent is removed. Precursors are then chemisorbed onto the solid surface during the activation. The activation step in the partition system then closely resembles the liquid-phase deposition method used in the preparation of thin metal films (13, 14). SLP itself has also been used as an immobilized liquid phase for homogeneous catalysis (15).

In principle,the PI process can be carried out in a continuously stirred tank or in a column-type reactor such as was used in this work. In the continuously stirred tank all support particles are in a homogeneous solution environment and the amount of adsorbed solute is identical throughout the support material at any time. In a column, uniform adsorbate concentration along the support bed cannot be achieved without sufficiently long pulses. The nonuniform distribution is due to the continuous adsorption, which lowers the solute concentration in the moving phase as it travels through the column. The PI process is, in fact, analogous to chromatographic processes, especially to frontal analysis, where samples are fed into the column continuously. It is thus feasible to analyse the formation and behaviour of a concentration gradient on the support bed in chromatographic terms and apply theories of chromatographic elution to PI.

The simplest way to describe the gradient formation is with the theoretical plate model, which assumes that the adsorbate molecules are in equilibrium with the mobile phase (solvent) and stationary phase (the support) at all times. The column is considered to be composed of N small, equally sized fragments, or theoretical plates, where local equilibrium exists. If the volumes of the stationary and the mobile phase on each theoretical plate are v_s and v_l, the total volume of the mobile phase inside the column is then equal to $Nv_l = V_l$, which is the total free volume in the column. Similarly, the total stationary phase volume is $Nv_s = V_s$. The total porosity and the total free volume of the column can easily be estimated if the density and specific pore volume of the support material are known (16). Even though the concept of true discrete plates in a column is clearly an oversimplification, the simplicity of the plate model makes it a useful method of estimating the gradient behaviour, at least at the qualitative level. To apply the plate model to PI, we need a few additional assumptions: (1) the solution feed consists of sequential, equally sized theoretical pulses, whose volume depends on the size of a theoretical plate; (2) the diffusion between separate pulses is negligible.

There are two methods of developing the elution equation for the chromatographic deposition, one given by Reilley *et al.* (17) and the other given by Said (18). The procedure of Reilley *et al.* assumes that the column can be regarded as a Graigs machine and this leads to a binomial equation

$$n^P_{N_l} = n_0 \sum_{i=1}^{P} \frac{(N+i-2)!}{(N-1)!(i-1)!} \frac{k^{i-1}}{(k+1)^{i+N-1}}, \qquad (2)$$

where k is the solute distribution ratio between stationary and mobile phase ($k = KV_s/V_l$), n_0 is the amount of the solute in an input pulse, and $n^P_{N_l}$ is the amount of solute leaving plate N during the Pth pulse. The amount of solute remaining on stationary phase of plate N after P pulses is then

$$n^P_{N_s} = n_0 \sum_{i=1}^{P} \frac{(N+i-2)!}{(N-1)!(i-1)!} \frac{k^{i}}{(k+1)^{i+N-1}}. \qquad (3)$$

In the binomial model the volume of a single pulse is equal to $V_l/N = v_l$. Said's model, in turn, is derived from a differential material balance around the plate N,

$$C_{N-1}dV - C_N dV = d[(v_l + Kv_s)C_N], \qquad (4)$$

where K is again the distribution coefficient, V is the volume of the mobile phase that has passed from plate $N - 1$ into plate N, C_N is the solute concentration of the mobile phase in plate N, and v_l and v_s are the volumes of the mobile and the stationary phases in a single plate. The deposition equation according to Said is

$$C_{N_l} = C_0 \left(1 - \sum_{i=0}^{N-1} \frac{(aV)^i}{i!} e^{-aV}\right) = C_0 P_N^{aV}, \qquad (5)$$

where C_{N_l} is the solute concentration leaving plate N after volume V is passed through the system, V is the total volume fed, $a = 1/(v_l + Kv_s)$, and P_N^{av} is the Poisson summation distribution function. When Said's model is applied to PI the solute concentration on the stationary phase of the Nth plate after $V/(v_l + Kv_s)$ theoretical pulses can be calculated from the equation

$$C_{N_s} = KC_0 P_N^{aV}. \qquad (6)$$

When theoretical calculations are carried out for a system in which the mobile phase is liquid and the stationary phase solid, it is convenient to replace volumes with masses and molar concentrations with molalities.

The theoretical plate models can also be expanded for multicomponent systems if the interactions between adsorbing components are not severe.

EXPERIMENTAL

Materials

The solvents were p.a. grade and were used without further purification. $Ru_3(CO)_{12}$ (Aldrich Chemicals) and 2,2-bipyridine (Aldrich Chemicals) were used as received. Gases used in 1-hexene hydroformylation were high-purity grade CO (99%) and H_2 (99.997%). Nitrogen used for the manipulation of the air-sensitive $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst was 99.99% pure. Silica gel 60 (Merck, surface area 500 m^2/g, specific pore volume 0.8 ml/g, size range 0.063–0.200 mm) was used for the $Ru_3(CO)_{12}$ and 2,2-bipyridine deposition experiments. $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst was prepared onto the SiO_2 silica grades F-22 (surface area 400 m^2/g, size range 0.074–0.179 mm) obtained from Akzo Chemie.

Deposition of 2,2′-bipyridine onto SiO_2

2,2′-Bipyridine (bpy) pulse impregnations were carried out in a volume-inscribed glass column. The inner diameter of the column was 11 mm and total volume of the support bed was 10 ml. Both formation of the concentration gradient onto the support bed and solvent effects on the 2,2′-bipyridine adsorption were studied. In the gradient experiments, 15-, 30-, 75-, 150-, and 300-ml pulses of 6.40×10^{-3} mol $liter^{-1}$ bpy/CH_2Cl_2 solution were applied. The support bed was prewetted with pure solvent before impregnation. The surface concentration in the column was monitored by dividing the support bed into 10 sample fragments of equal size (ca. 1 ml) and determining the 2,2′-bipyridine concentration of each. Samples were sucked from the column into an analysis bottle by means of a thin glass tube and low vacuum. 2,2′-Bipyridine concentrations were measured both spectrophotometrically and by elemental analysis. In the spectrophotometric method bpy was first extracted with methanol. $FeCl_2 \cdot 3H_2O$/methanol solution was added to the extract and bpy was determined as the Fe(II) complex with a Shimadzu 240 UV–vis spectrophotometer (522 nm).

Solvent effects on adsorption were tested with THF/CH_2Cl_2 mixtures. Solutions with 0, 5, 10, 20, 50, and 100 vol. % (v/v) of THF were used. Pulse lengths were made long enough to achieve a uniform bpy coverage throughout the support bed. Pulses varied from 30 to 90 ml. 2,2′-Bipyridine concentration was held constant at 6.40×10^{-2}

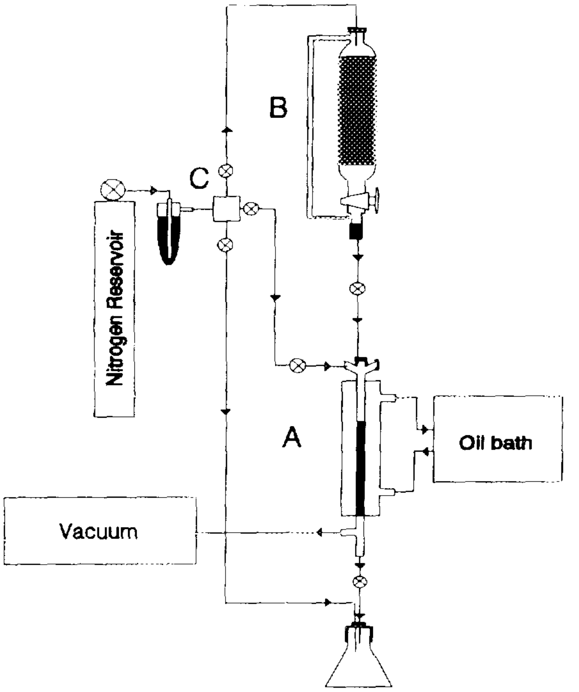

FIG. 2. The pulse-impregnation reactor system used in $Ru_3(CO)_{12}$ depositions (A) Reactor column, (B) solvent vessel, (C) nitrogen line.

mol liter^{-1} in all solutions. Bpy analysis was carried out in the same way as in the gradient experiments.

Deposition of $Ru_3(CO)_{12}$ onto SiO_2

The apparatus for the pulse impregnation of the $Ru_3(CO)_{12}$ is shown in Fig. 2. Silica was calcined for 24 h at 600°C and packed into the reactor column. The inner diameter of the column was 10 mm and total volume of the support bed was 10 ml. Impregnations were carried out from *n*-hexane, dichloromethane, and THF. $Ru_3(CO)_{12}$ concentrations were 2.36×10^{-3} mol liter^{-1} in dichloromethane solutions, 2.35×10^{-3} and 6.26×10^{-3} mol liter^{-1} in THF solutions, and 5.82×10^{-4} mol liter^{-1} in hexane solution. $Ru_3(CO)_{12}$ solutions were tranferred to the solution vessel, after which both metal carbonyl solution and support bed were degassed *in situ*. Degassing of the support was carried out by repeating vacuum–nitrogen cycles in the reactor column. A measured amount of the degassed metal carbonyl solution was pulsed through the support bed in order to achieve a uniform surface concentration. Pulse sizes in dichloromethane and THF impregnations were 100 ml, and in *n*-hexane impregnation, a 400-ml pulse was used. After impregnation, the support was dried under low vacuum (12–16 mbar) at 50–70°C. The ruthenium concentrations were determined by AAS, after dissolving the samples in $HF/H_2SO_4/H_2O$ (19, 20).

Preparation of $Ru_3(CO)_{12}$/2,2'-Bipyridine/SiO_2 Catalyst

$Ru_3(CO)_{12}$2,2'-bipyridine/SiO_2 catalyst was prepared by pulsing $Ru_3(CO)_{12}$ and bpy simultaneously from the THF solution onto silica support under nitrogen atmosphere. The impregnation solution was prepared by dissolving each of 100 mg $Ru_3(CO)_{12}$ and 2,2'-bipyridine in 100 ml THF, after which the solution was transferred to the solution vessel and degassed with N_2. The reactor system shown in Fig. 2 was slightly modified for the preparation of the $Ru_3(CO)_{12}$/2,2'-bipyridine/SiO_2 catalysts. The solvent vessel was placed in an ice–salt bath to prevent reactions between $Ru_3(CO)_{12}$ and 2,2'-bipyridine in the solution. Two grams of the calcined (600°C, 24 h) silica was packed into the column. The impregnation solution was pulsed into the reactor column by applying a slight vacuum to the column and allowing the solution to flow from the solution vessel to the column. After each pulse, the catalyst was activated at 85°C for 5–10 min. After the last activation step, the support was dried under low vacuum. Finally, the reactor column was evacuated and transferred to a glovebox. Ru contents of the catalyst samples (100–300 mg) were determined with AAS after decomposition of the catalysts in the autoclave with 2% HCl/HNO_3 mixture (21) or 2% H_2SO_4. Catalyst activity was tested in 1-hexene hydroformylation carried out according to a method described in the literature (22, 23). Reaction products were analysed by GC.

RESULTS AND DISCUSSION

Formation of a 2,2'-Bipyridine Concentration Gradient on the Silica Bed during Pulse Impregnation

Development of a 2,2'-bipyridine concentration gradient as a function of the pulse length is shown in Fig. 3. Concentration of the supported 2,2'-bipyridine in the first sample fragment increased rapidly with pulse size until

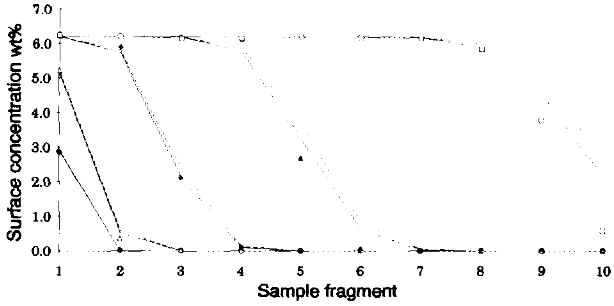

FIG. 3. Development of a 2,2'-bipyridine concentration gradient on the silica support bed. 2,2'-Bipyridine was impregnated from 6.40×10^{-3} mol liter^{-1} dichloromethane solution, using different pulse lengths (volumes). Experimental surface concentrations: (☐) 300-ml pulse, (▲) 150-ml pulse, (◆) 75-ml pulse, (△) 30-ml pulse, (●) 15-ml pulse. Theoretical gradients: (—) Poisson model, (---) binomial model.

the final equilibrium was achieved at ca. 6.2 wt.%. As expected, similar behaviour was repeated on subsequent fragments. Both binomial and Poisson distribution models were fitted to the experimental data. In order to calculate theoretical concentrations distributions, the number of theoretical plates, N, is needed. In principle, N can be determined by similar methods to those used in chromatography, but in this work we used an arbitrarily chosen value, $N = 100$. The distribution coefficient K was determined at the final equilibrium, where the 2,2'-bipyridine concentrations in the mobile and stationary phases were 6.40×10^{-3} mol liter^{-1} and 6.2 wt.%, respectively. The total porosity and the free volume of the support bed were calculated using a cristobalite density 2.32 g/cm^3 and assuming the internal column porosity to be 0.4 (16). With these parameters, the total porosity of the silica bed was calculated to be 0.79. Both distribution models predict the behaviour of the concentration gradient reasonably well. Because of the more or less arbitrary parameters in the theoretical models and the inaccuracy in the experimental sample sizes, theoretical models are still purely qualitative. Nevertheless, distribution models are useful tools in designing the pulse sequences and can be used in the estimation of the pulse sizes required for uniform concentration distribution. Results in Fig. 3 show that when pulses are sufficiently long, at least macroscopically uniform bpy concentration can be achieved throughout the support bed. It should be emphasized that this does not necessarily guarantee uniform microscopic distribution on individual support particles. However, the final dispersion in PI is formed during the activation step when solute molecules react with surface sites. Final dispersion is then determined by the interactions between solute molecules and interactions between solute molecules and the surface sites. If uniform "primary dispersion" after the deposition step is achieved, this further improves the probability to have a well-dispersed final surface phase.

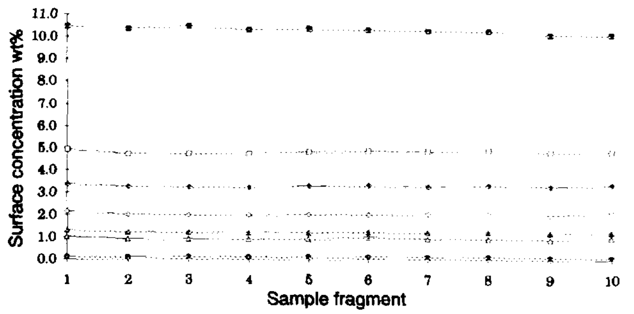

FIG. 4. Solvent effect on 2,2'-bipyridine adsorption onto the noncalcined silica support. Pulse impregnations were carried out from various solvents with 6.40×10^{-2} mol liter^{-1} 2,2'-bipyridine concentration: (■) dichloromethane, (□) 5 vol.% THF/dichloromethane, (◆) 10 vol.% THF/dichloromethane, (◇) 20 vol.% THF/dichloromethane, (▲) 50 vol.% THF/dichloromethane, (△) THF, and (●) from THF solution with 6.40×10^{-3} mol liter^{-1} 2,2'-bipyridine concentration.

Solvent Effects on the Adsorption of 2,2'-Bipyridine

As mentioned above, the amount of solute adsorbed can be controlled by varying the composition of the solvent. The effects of dichloromethane and THF on the adsorption of 2,2'-bipyridine are shown in Fig. 4. The highest average surface concentration (ca. 10.3 wt.%) was achieved with pure CH_2Cl_2 solvent. With an increase in the amount of THF in the solvent, the solvent strength increased and the surface concentration decreased rapidly. Uniform coverage was nevertheless achieved with all solvents. The surface concentration can also be altered by changing the concentration of the impregnation solution. Comparison of the results for 2,2'-bipyridine in dichloromethane show that when the concentration of the impregnation solution was increased tenfold from 6.40×10^{-3} mol liter^{-1} (Fig. 3) to 6.40×10^{-2} mol liter^{-1} (Fig. 4) the surface concentration increased only by a factor of 1.66 (from 6.2 to 10.3 wt.%). Evidently the adsorption isotherm in CH_2Cl_2 is not linear over the concentration range 6.40×10^{-3} to 6.40×10^{-2} mol liter^{-1}. By contrast, when bpy was impregnated from 6.40×10^{-3} mol liter^{-1} THF solution, the average surface concentration was about 0.1 wt.% (Fig. 5), but when concentrated (6.40×10^{-2} mol liter^{-1}) THF solution was used, 0.9 wt.% surface concentration was obtained (Fig. 5). Thus in THF impregnations the correlation between the concentration of the impregnation solution and the surface concentration is nearly linear.

Another factor which has an effect on the bpy adsorption is the pretreatment of the silica. This was tested by depositing 2,2'-bipyridine on calcined silica from 6.490×10^{-2} mol liter^{-1} dichloromethane, from 20 vol.% THF/dichloromethane, and from THF solutions. The final surface concentration in the dichloromethane impregnation

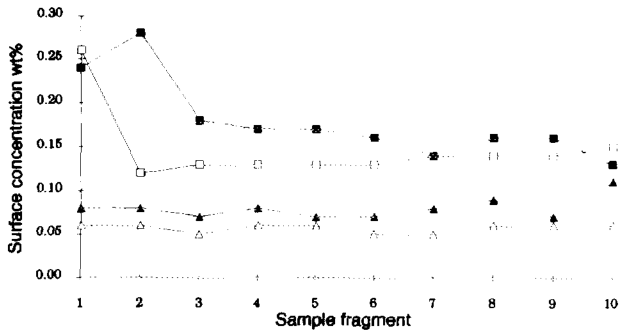

FIG. 5. Solvent effect on $Ru_3(CO)_{12}$ adsorption onto the silica support. Impregnations were carried out from different solvents with different $Ru_3(CO)_{12}$ concentrations: (■) 6.26×10^{-3} mol liter^{-1} THF, (□) 2.36×10^{-3} mol liter^{-1} dichloromethane, (▲) 5.82×10^{-4} mol liter^{-1} n-hexane, (△) 2.35×10^{-3} mol liter^{-1} THF.

was 8.3 wt.%. In the THF/dichloromethane and THF impregnations 1.8 wt.% and 0.9 wt.% surface concentrations were achieved. The surface concentration appears to be lower on calcined silica than on untreated silica (Fig. 4), at least with CH_2Cl_2 and THF/CH_2Cl_2 mixtures. This might be due to the reduced number of the surface OH-groups on the calcined silica, or physisorbed water on the non-calcined support may promote the adsorption of the bpy via increased hydrogen bonding interactions between surface OH groups, physisorbed water molecules, and bpy.

Solvent Effects on Adsorption of the $Ru_3(CO)_{12}$

As shown in Fig. 5, nearly uniform concentration along the silica bed was again achieved. In IR spectra of the adsorbed $Ru_3(CO)_{12}$ the main peaks were at 2064 and 2033–2034 cm^{-1}, which indicate only weak interaction between the adsorbed ruthenium cluster and the SiO_2 surface (24, 25). The concentration peaks in the first sample fragments (taken from the top of the column) are probably due on non-carbonyl Ru species, which apparently effect no changes in the IR spectra of the physisorbed $Ru_3(CO)_{12}$. Non-carbonyl species could arise from partial decomposition of $Ru_3(CO)_{12}$ in the solvent or from impurities in the ruthenium reagent. One advantage of the use of a column reactor in PI is just that strongly adsorbing impurities concentrate in a limited area at the top of the column from which they can be easily removed. In a continuously stirred tank or in conventional impregnation, impurities spread uniformly over the support material and cannot be separated from the product. A precolumn to remove unwanted side products would be a useful addition to the column reactor.

As seen in Fig. 5, the solvent effects on the $Ru_3(CO)_{12}$ adsorption are less pronounced than in bpy adsorption. The final surface concentration varies from about 0.05 to 0.2 wt.%. The ruthenium content nevertheless seems to increase with weakening solvent strength. On the other hand, the poor solubility of $Ru_3(CO)_{12}$ in a weak nonpolar solvent like *n*-hexane limits the concentration of the impregnation solution and thereby the amount of adsorbed $Ru_3(CO)_{12}$.

Preparation of $Ru_3(CO)_{12}$/2,2′-Bipyridine/SiO_2 Catalyst via Pulse Impregnation

$Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst was prepared by pulsing both components simultaneously from the same solvent. THF was chosen because it is a rather strong solvent that can elute both components effectively. With such a strong solvent, only relatively short pulses are needed to achieve uniform coverage. On the other hand, the growth of the catalyst surface per single pulse tends to remain low because of the strong adsorption competition between the solvent molecules and adsorbing precursors. The growth of the ruthenium concentration of the catalyst with number of pulses is shown in Fig. 6 and Table 1. Even though the average ruthenium feed per pulse varied from 2.9 to 5.0 mg, a reasonably steady increase in the Ru concentration was achieved. In long pulse sequences, a dark brown layer formed on the upper part of the support bed. This might have been due to Ru impurities in the impregnation solution or there may have been oxygen residues in the reactor system which caused partial decomposition of the catalyst. This decomposed catalyst was formed only at the top of the column, from which it could easily be separated from the rest of the catalyst material.

Catalytic Activity of $Ru_3(CO)_{12}$/2,2′-Bipyridine/SiO_2

$Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst is known to be active in the water–gas shift reaction (26–29) and in 1-hexene hydroformylation (22, 23, 30). In this study we used hydroformylation as a test reaction for the catalysts prepared with different Ru concentrations. In hydroformylation olefins react with synthesis gas (hydrogen and carbon monoxide) and are converted to aldehydes, which can then be hydrogenated to the corresponding alcohols. It has been found that addition of the amines to the $Ru_3(CO)_{12}$ catalysts tends to favour direct formation of the alcohols (22, 23, 31). In our study, the main catalysis products were C_7-alcohols (mainly 2-methylhexanol and heptanol). With all catalysts, isomerization of the 1-hexene occurred, but no aldehydes were found in the reaction products. The lack of the aldehydes was probably due to the amine effect of 2,2′-bipyridine. The activities of the catalysts vs ruthenium concentration are shown in Table 1 and Fig. 7. With low rutheniunm concentrations (≤ 0.7 wt.%) the catalysts are practically inactive, but between 0.7 and 1.2 wt.% there was an abrupt increase in the activity. With further increase in the ruthenium concentration the activity increased only slightly. Alcohol production seems to level at 30–40 wt.% with higher Ru loadings. These results are in good agreement with the

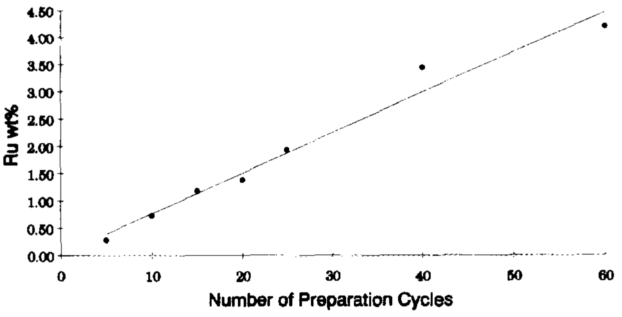

FIG. 6. Increase in the ruthenium content of the $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst with number of pulses.

TABLE 1

Ruthenium Concentration and Activity of the $Ru_3(CO)_{12}$/2,2′-Bipyridine/SiO_2 Catalyst with Number of Preparation Cycles

Number of preparation cycles	Total Ru feed (mg)	Ru/cycle[a] (mg)	Ru surface concentration (wt.%)	Ru concentration growth/cycle[b] (wt.%)	Activity C_7-alcohols[c] (wt.%)	1-Hexene conversion[d] (%)	C_7-Alcohol selectivity (%)
5	24.8	5.0	0.29	0.06	0	12	0
10	38.8	3.9	0.73	0.07	2	43	2
15	52.2	3.5	1.18	0.08	21	98	17
20	71.0	3.6	1.38	0.07	23	95	18
25	89.2	3.6	1.93	0.08	28	98	22
40	133.5	3.3	3.44	0.09	32	98	27
60	174.9	2.9	4.20	0.07	37	98	30

Note. Reaction conditions: pressure = 50 bar, H_2:CO = 1, temperature = 150°C, reaction time = 17 h, 1-hexene = 1 ml (8 mmol), toluene = 5 ml, catalyst = 0.5 g.

[a] Average Ru feed per preparation cycle.

[b] Average increase in the ruthenium concentration of the catalyst per preparation cycle.

[c] C_7-Alcohols produced in 1-hexene hydroformylation.

[d] Total conversion of 1-hexene.

catalytic activity of $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalysts prepared via gas-phase methods (12). Although the $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalysts obtained by pulse impregnation are somewhat less active than conventionally impregnated catalysts (22, 23), reproducibility of the catalyst has clearly been improved. Optimum catalyst loading in conventionally impregnated $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 is found to be 1–1.5 wt.%. The reason for the greater activity of the conventionally impregnated catalysts is not clear. It may have to do with the nonselective formation of several active components during the relatively long impregnations (17 h). On the other hand, the conventional impregnations have been carried out with dichloromethane as solvent and possibly use of the chlorinated solvent leads to a different active component or components than use of the non-chlorinated solvents such as THF.

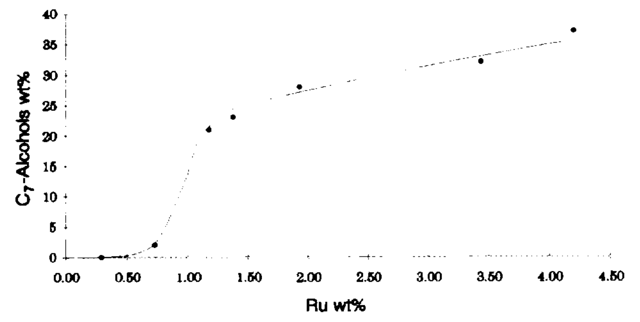

FIG. 7. Effect of the ruthenium concentration of the $Ru_3(CO)_{12}$/2,2′-bipyridine/SiO_2 catalyst on activity in 1-hexene hydroformylation.

CONCLUSIONS

Pulse impregnation offers an alternative method for preparing supported heterogeneous catalysts in the liquid phase. With PI, the catalyst surface can be built in a controlled manner in successive deposition and activation steps. The number of preparation steps can be used to control the coverage of the support and thereby the activity of the catalyst. The growth rate of the catalyst surface can be controlled through the choice of solvent system. A particular advantage of the column-type reactor in PI is that strongly adsorbing impurities or side products in the impregnation solution can easily be separated from the active catalyst. Pulse impregnation is closely related to liquid chromatography, which makes it possible to apply chromatographic elution theories in designing optimum pulse sequences and solvent systems.

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