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Controlled Deposition from the Gas Phase of Surface Species on Amorphous Supports: Preparation of Ruthenium–Bipyridine Catalysts for 1-Hexene Hydroformylation and Water–Gas Shift Reaction

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Controlled stepwise surface reactions were studied to prepare supported ruthenium–bipyridine catalysts. $Ru_3(CO)_{12}$ and 2,2′-bipyridine were introduced onto the support from the gas phase in a fluidized bed reactor. With this method the introduction of the precursors can be carried out independently by successive pulses. The possibilities to control metal content, properties of the surface species, and dispersion were studied by varying the deposition conditions, e.g., temperature and carrier gas. The catalysts were tested in 1-hexene hydroformylation and the water–gas shift reaction. Deposition of the precursors from the gas phase was found to produce active catalysts for both reactions. In the water–gas shift reaction the highest activities were 2–2.5 times greater than those obtained with catalysts prepared by impregnation. © 1994 Academic Press, Inc.

1. INTRODUCTION

Heterogeneous catalysts are widely used industrially in preference to homogeneous ones, since the catalyst materials are often expensive compounds and the separation of them from the reactants and products is economically important. However, the method of preparation can have a strong effect on the activity and selectivity of heterogeneous catalysts. It is therefore important to be able to control the preparation steps.

A main disadvantage in preparing supported heterogeneous catalysts by traditional preparation methods such as impregnation, precipitation, adsorption, or ion-exchange methods is the difficulty of controlling the preparation steps, since the solvent can block adsorption sites on the support and thus the conventionally large surface area of the support cannot be fully employed (1, 2). Furthermore, the relatively low solubility of many desirable catalysts components complicates the use of liquid-phase methods. In order to overcome these disadvantages various gas-phase preparation methods have been developed. Deposition of catalyst components from the gas phase has been shown to lead to deposition deep inside the pores of a porous catalyst support (3). Gas-phase sublimation techniques have been applied in the preparation of supported metal oxides such as SnO_2/SiO_2 (4), MoO_3/Al_2O_3 (5, 6), and $VOPO_4$ (7). Metal carbonyl cluster compounds, e.g., $Co_2(CO)_8$, $Co_4(CO)_{12}$ (8, 9), and $Ru_3(CO)_{12}$ (10), have also been used to prepare metallic particles with high dispersion.

Recently, more advanced thin film preparation methods such as chemical vapor deposition (CVD) (11–19) or atomic layer epitaxy (ALE) (20) have also been applied in the preparation of heterogeneous catalysts. These methods have yielded highly dispersed catalysts with more control of the active surface species than is provided by the conventional liquid-phase methods (15, 16, 19). CVD has also been used to prepare mixed-metal alloys on a glass substrate from the bimetallic carbonyl clusters $HFeCo_3(CO)_{12}$ and $CpFeCo(CO)_6$ (12). Controllable surface reactions have been shown to lead to high selectivity in catalysis, as in the one-atomic-layer preparation of ZrO_2/ZSM-5 catalysts (21).

We have been using controlled stepwise surface reactions to prepare supported ruthenium–bipyridine catalysts from the gas phase in a fluidized bed reactor (22). Ru_3CO_{12} and 2,2′-bipyridine were selected as precursors, since similar catalysts prepared by impregnation have been found to be highly active in the water–gas shift reaction (23, 24) and in alkene hydroformylation (25). Furthermore these reactants have sufficiently low vapour pressures to be deposited from the gas phase.

2. EXPERIMENTAL

2.1. *Reactants*

$Ru_3(CO)_{12}$ was either obtained commercially (Johnson Matthey) and used without further purification or prepared from $RuCl_3 \cdot 3H_2O$ by a standard procedure (26).

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2,2′-bipyridine (99%) was obtained from Aldrich-Chemie and was used without further purification. CO (99.997%, Teknohaus, or 99.0%, Aga) was used as a carrier gas. The catalyst supports were obtained commercially: Silica F22 (Akzo Chemie, 400 m^2g^{-1}, particle size 0.073–0.149 mm), silica gel 60 (Merck, 500 m^2g^{-1}, particle size 0.063–0.200 mm), and alumina (Aldrich-Chemie, 155 m^2g^{-1}, particle size < 0.1 mm).

2.2. *Pretreatment of the Supports*

The supports were pretreated either at 600°C for 18 h in air and cooled in N_2 atmosphere, or they were kept at 300°C *in vacuo* for 18 h in order to remove physisorbed water. At these temperatures the main adsorption centers on silica are either free (isolated) or geminal OH-groups (27).

2.3. *Reactor System for Catalyst Preparation*

Figure 1 shows a schematic presentation of the reactor system, which is a modification of a conventional ALE-reactor made in cooperation with Microchemistry Ltd, Finland. We use a fluidized bed reactor (A) in order to ensure a homogeneous environment for all the support particles and to avoid concentration gradients during the deposition. The reactor system consists of a reactor chamber (B), a gas line for the carrier gas (C), a pump system for gas circulation (D), and a nitrogen glove box (E) for the handling of the air-sensitive reactants. The attached computer can be used to control the heating of the reactor chamber, the reaction times, and the gas flow rates. For analysing the air-sensitive reaction products we have an FTIR spectrometer attached directly to the nitrogen glove box.

2.4. *Methods of Preparation of the Catalysts*

The catalysts were prepared by three different preparation methods. In the first method (method A) $Ru_3(CO)_{12}$ was introduced in a fluidized bed reactor, where the temperature of the bed was lower than that of the reactant supply. These conditions led mostly to physisorbed $Ru_3(CO)_{12}$ on the support surface. This product was then packed into a separate glass shell and mixed with 2,2′-bipyridine. Excess of 2,2′-bipyridine was used in order to ensure a complete reaction. The glass shell was sealed *in vacuo* and the catalyst was activated by heating at 100°C for 72 h, which led to a black product.

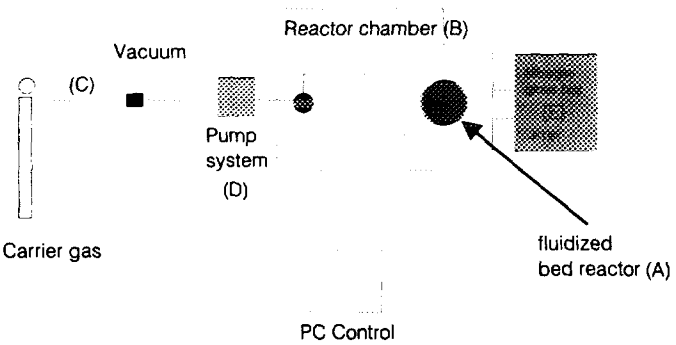

FIG. 1. The fluidized bed reactor system for supported catalyst preparation.

Figure 2 shows a scheme of the second preparation method (method B). In the first step $Ru_3(CO)_{12}$ (reactant A) was introduced onto a clean support with a carrier gas. In the next step this reactant was chemisorbed on the surface sites of the support, since the temperature of the reaction bed was kept equal to or higher than the ruthenium supply to minimize physisorption. The excess of the reactant was removed with the carrier gas. In the next step 2,2′-bipyridine (reactant B) was introduced with the carrier gas and finally the catalyst was formed by the surface reaction between the reactants. Both the gaseous reactants were introduced either with one pulse or with several successive pulses. No further activation was necessary, since the temperature of the bed was high enough (120–145°C) to lead to an activated complex.

Also a mixed preparation method was studied (method C): at first $Ru_3(CO)_{12}$ was chemisorbed onto the support in fluidized bed reactor, as in method B, and 2,2′-bipyridine was added in a sealed glass shell by dry-mixing. Activation was performed as in method A.

2.5. *Characterization of the Catalysts*

The catalysts were characterized by an FTIR spectrometer (Galaxy Series 6020) equipped with a diffuse reflectance accessory (DRIFT technique). Ruthenium content was determined by atomic absorption spectroscopy (AAS) (28). The sample (0.05–0.2 g) was placed in an autoclave with a Teflon liner, and 4 ml of 37% HCl and 50 μl of 65% HNO_3 were added. The autoclave was heated at 240°C for 2 h. The support was filtered and lanthanum sulfate buffer (0.5% w/v La) was added to the solution and diluted with 2% HCl. Calibration curves were obtained with 5–25 ppm solutions of commercial ruthenium atomic absorption standard solution (Sigma Chemical Co., 1005 μg Ru/ml).

With some samples the silica support was removed before the AAS analysis with concentrated HF solution (29). 0.05–0.2 g was weighed into a Teflon disk. Approximately 10 ml of water, 2 ml concentrated H_2SO_4, and an excess of HF were added, and the solution was evaporated on a hot plate. Upon cooling, water and concentrated HCl were added until the final solution was 2% HCl.

2.6. *Catalytic Reactions*

2.6.1. 1-Hexene hydroformylation. 1-Hexene (8 mmol), toluene (5 cm^3), and catalyst (0.5 g) were mixed

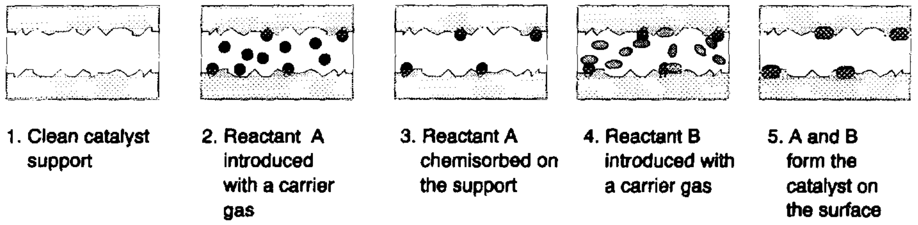

FIG. 2. A scheme for stepwise catalyst preparation via controlled surface reactions between reactants A and B on a porous support material.

in a high pressure autoclave (Berghof 75 ml) under N_2 atmosphere. Benzene (0.2 cm^3) was added as an internal standard. The autoclave was then pressurized with synthesis gas CO_2/H_2 (1 : 1) to a total pressure of 50 bar. The reaction temperature was 150°C and the reaction time 17.5 h. After cooling in liquid nitrogen the autoclave was brought to atmospheric pressure and the solution was separated from the catalyst for analysis.

The hydroformylation products were analysed by capillary gas chromatography on a Hewlett–Packard 5890 instrument equipped with a FID detector, a CP SIL 5 CB column, and a HP 7673 integrator.

2.6.2. Water–gas shift reaction. The reaction was carried out in a continuous flow reactor. The catalyst (1.0 g) was packed into a reactor tube (volume 3.2 cm^3). Carbon monoxide (7 bar) and water vapour (2.7–4.8 bar) were introduced to the tube. The reaction temperature was 150°C and the reaction time typically three to four days. Total flow rate was varied between 10 and 100 cm^3 in order to achieve at least 20–50% conversion. Hydrogen, carbon dioxide, and carbon monoxide were analyzed by gas chromatography using a multi-column system as described previously (30). The activity was determined from the production of H_2 (mol H_2/mol $Ru_3(CO)_{12}$ per 24 h).

3. RESULTS AND DISCUSSION

3.1. Controlling the Ruthenium Content

The major factor affecting the metal content in gas-phase preparation methods is temperature. When the temperature of the fluidized bed is much lower than the temperature of the ruthenium supply, as in method A, the ruthenium content increases linearly with increased deposition time. Figure 3a shows the ruthenium content in wt.% versus deposition time. In this series of experiments the feed temperature was 145°C and the temperature of the fluidized bed was 100–105°C. These conditions led mostly to physisorbed surface species.

Figures 3b and 3c show the ruthenium content when the temperature of the reactor chamber was kept equal to or higher than the feed temperature. In this case the ruthenium content reaches a saturation level. This means that the chemisorbed species are in equilibrium with the surface sites of the support. This equilibirum is also temperature dependent, as can be seen from the two different conditions in Figs. 3b and 3c. In Fig. 3b the temperature of the bed and that of the ruthenium supply were 135°C, whilst in Fig. 3c they were 120°C. The saturation level in the first case was about 1.5 wt.% and in the second case about 1.2 wt.%.

When the catalyst was prepared by successive pulses of both reactants, we again obtained a linear dependence for the ruthenium content versus the number of pulses, as shown in Table 1. Table 1 shows the results for two different pulse lengths and reaction conditions. In the first

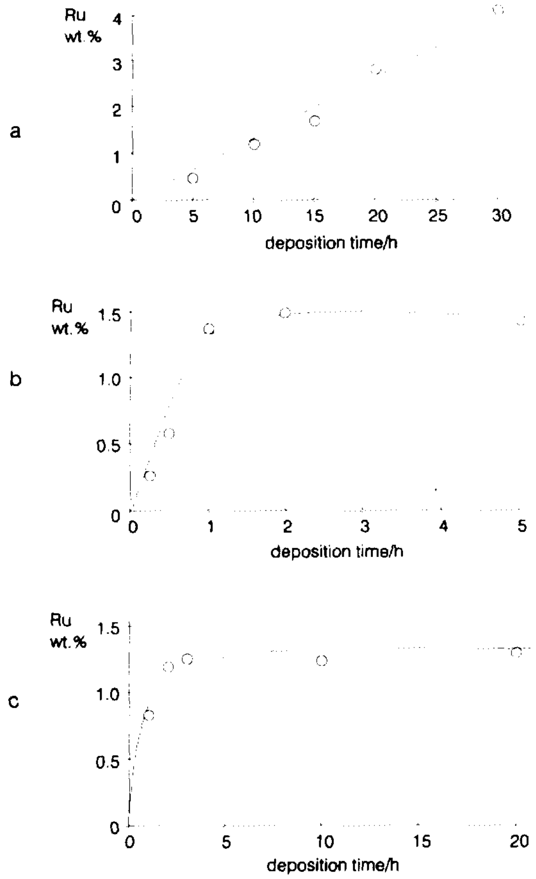

FIG. 3. Ruthenium content (wt.%) on the support versus deposition time with different gas-phase preparation methods. (a) method A, $T(s)$ = 145°C, $T(r)$ = 100–105°C; (b) method C, $T(s)$ = 135°C, $T(r)$ = 135°C; (c) method C, $T(s)$ = 120°C, $T(r)$ = 120°C. For a detailed description of the methods, see the text.

TABLE 1

Ruthenium Content of Ruthenium–Bipyridine Catalysts on Silica Gel 60 Support vs the Number of Pulses in Preparation Method B

	Set 1			Set 2	
Number of pulses	1	7	12	1	7
Calculated[a] Ru wt.%	0.26[b]	1.82	3.12	0.64[c]	4.48
Obtained Ru wt.%	0.26[b]	1.65	3.38	0.64[c]	4.91

Note. Set 1: $t(s) = 0.5$ h, $T(s) = 135°C$, $T(r) = 134–137°C$. Set 2: $t(s) = 2.0$ h, $T(s) = 130°C$, $T(r) = 140°C$.

[a] $n^*[Ru]_1$; n, number of pulses.

[b] Average from three runs, [c] Average from two runs.

set the pulse length $t(s)$ was 0.5 h, the temperature of the feed $T(s)$ was 135°C, and the temperature of the reaction chamber $T(r)$ was 134–137°C. In the second set $t(s)$ was 2 h, $T(s)$ 130°C, and $T(r)$ 140°C. The agreement between calculated and obtained ruthenium content is quite good bearing in mind the possible inaccuracies in the analysis method.

Minor differences to the ruthenium content were obtained with different carrier gas flow rates and different support pretreatment procedures. Although these effects were not fully tested, it can be seen from Table 2 that the ruthenium content of non-pretreated support is three times higher than that of the pretreated ones. This is probably due to an insufficient fluidization of the non-pretreated support. Another explanation could be that the physisorbed water provides different adsorption sites from those on the pretreated supports and thus enhances the ruthenium content.

3.2. Controlling the Surface Species

With conventional catalyst preparation methods such as impregnation it is difficult to control the surface species during the adsorption procedure. Gas-phase methods provide better scope to control and change the properties of surface species, which leads to higher selectivity in catalytic reactions. Furthermore, controlled surface reactions can lead to different active sites from those on conventionally prepared catalysts.

TABLE 2

Effect of Pretreatment Procedures on the Ruthenium Content of Ruthenium Bipyridine Catalysts on Silica Gel 60 with Gas-Phase Preparation Method C

Support	Pretreatment	*t*(s) (h)	*T*(s) (°C)	*T*(r) (°C)	Ru (wt.%)
SG60	Non	1.5	135	135	1.49
SG60	300°C *in vacuo*/18 h	1.5	139	142	0.55
SG60	600°C in air/18 h	1.5	135	136	0.47
SG60	450°C *in vacuo*/18 h	1.5	135	135	0.43
SG60	Ref. methanol/800°C in H_2/18 h	1.5	135	138	0.68

Figure 4 shows the FTIR spectra of the catalysts during different preparation steps. The gas-phase preparation methods lead to physisorbed $Ru_3(CO)_{12}$ and chemisorbed surface species in different proportions depending on the preparation method. Figure 4a shows the carbonyl region spectrum of $Ru_3(CO)_{12}$ deposited on a silica support by preparation method A using CO as a carrier gas. Due to a large amount of physisorbed cluster the absorption bands are broadened. There are also indications of decomposition of the cluster to mononuclear $Ru(CO)_3(OSi)_2$, from which the first signal (2138 m, 2069 s cm^{-1}) is obtained.

Figure 4b shows the FTIR spectrum of $Ru_3(CO)_{12}$ chemisorbed on a silica surface as in preparation method B. This is identical to the FTIR spectrum of $Ru_3(CO)_{12}$

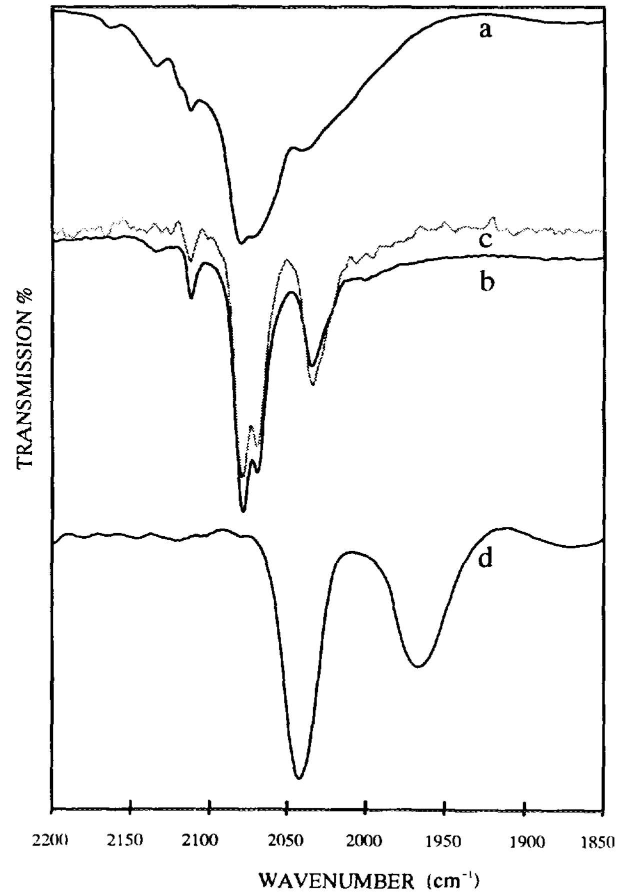

FIG. 4. FTIR spectra of the gas-phase prepared Ru/bipyridine catalysts at different preparation stages. (a) $Ru_3(CO)_{12}$ deposited on silica F22 by method A using CO as carrier gas; (b) $Ru_3(CO)_{12}$ chemisorbed on silica F22 by method C; (c) $Ru_3(CO)_{12}$ impregnated on silica from pentane solution and heated in vacuum; (d) ruthenium/bipyridine/SiO_2 catalyst after activation by heating in vacuum.

impregnated from pentane solution and heated in vacuum. This method has been shown to yield chemisorbed $HRu_3(CO)_{10}(OSi\text{-})$ (31–33). This cluster reforms $Ru_3(CO)_{12}$ cluster in carbon monoxide (34) according to the reaction:

$$Ru_3(CO)_{12} + HOSi\text{-} \rightleftharpoons HRu_3(CO)_{10}(OSi\text{-}) + 2CO.$$

This reaction is reversible, so when the feed of $Ru_3(CO)_{12}$ is interrupted, but the temperature and the CO gas flow are maintained, the chemisorbed species quantitatively reform the physisorbed cluster species, which are carried away from the reactor.

After the surface reaction between the ruthenium surface species and 2,2′-bipyridine and thermal activation of the catalyst, two broad carbonyl signals (2047 and 1970 cm^{-1}) were obtained (Fig. 4d). These do not correspond to any previously known surface species. The shape and relative intensity of the absorption bands indicate a compound with two carbonyl groups. Further spectroscopic work on the active species is in progress and will be published in the near future.

3.3. Controlling the Dispersion

Increased catalytic activity can be accomplished by increasing the surface area of a catalyst material. Thus higher dispersion of an active compound on a large surface area support leads to enhanced catalytic effectivity.

One of the disadvantages of the liquid-phase impregnation method is the difficulty of obtaining high dispersion. The solute blocks the pores and thus the whole surface area of the support cannot be usefully employed. This can be overcome by introducing the reactants from the gas phase in a fluidized bed reactor, where all the support particles have a homogeneous environment and the catalyst precursor compounds can enter the pores of the support. In principle also, when the precursors are chemisorbed onto specific surface sites, this should lead to better dispersion. The choice of the carrier gas was found to have a major effect on the dispersion with $Ru_3(CO)_{12}$ as precursor. The use of nitrogen or argon as carrier gas led to formation of large physisorbed $Ru_3(CO)_{12}$ crystals, but when reactive CO gas was used, no crystals were visible. CO gas could also prevent the thermal decomposition of the ruthenium carbonyl compound and the reaction temperatures could be kept higher than with other carrier gases or vacuum sublimation, and thus the reaction times decreased from weeks to a few hours.

4. CATALYTIC REACTIONS

4.1. 1-Hexene Hydroformylation

The ruthenium–bipyridine catalysts were tested in 1-hexene hydroformylation, since similar catalysts have been found to be highly active when prepared by impregnation (25). The amount of C_7 alcohols vs ruthenium content of the catalysts is shown in Table 3, which summarizes the results for the different preparation methods. It is notable that all the gas-phase preparation methods led to approximately the same activity. This can be explained by the similarity of the active species in hydroformylation. The maximum alcohol yield was between 30 and 40 wt.%. This amount could be reached with a ruthenium content around 1.5 wt.%. Higher ruthenium content did not enhance the amount of alcohols, contrary to impregnation where the highest alcohol yields in the same reaction conditions have been around 90 wt.% (25). On the other hand 1-hexene conversion was good, 95–100 wt.%, and the catalysts were chemospecific in C_7 alcohol formation. One of the main advantages of our catalysts is the reproducibility of the hydroformylation reactions, which has been poor with impregnated ruthenium/bipyridine/SiO_2 catalysts. This also indicates better control in the formation of the active surface species. The results in 1-hexene hydroformylation are in good agreement with the results obtained when ruthenium/bipyridine/SiO_2 catalysts are prepared by the controlled pulse impregnation technique from the liquid phase (35).

TABLE 3

Results for 1-Hexene Hydroformylation with Ruthenium–Bipyridine Catalysts on Silica Prepared by Gas-Phase Methods and Production of C_7 Alcohols vs Ruthenium Content

Preparation method	Ru (wt.%)	C_7 alcohols (wt.%)	C_7 alcohols (n/i)[b]
A	0.46	0	
C	0.47	8	2.6
A	1.09	4	
A	1.17	5	
C	1.19	31	3.6
C	1.24	35	2.7
B	1.29	50	1.9
C	1.35	37	2.6
C	1.49	39	2.7
B	1.65	28	4.3
A	1.68	26	4.2
C	2.00	47	2.8
C	2.10	37	3.3
A	2.14	35	2.9
A	2.36	35	2.5
A	2.47	29	3.1
A	2.80	37	3.5
A	3.90	31	4.2
B	4.91	36	4.7
A	5.51	37	3.6

[a] Reaction conditions: Total pressure = 50 bar, $H_2/CO = 1:1$, reaction time = 17.5 h, 1-hexene 8 mmol, toluene 5 cm^3, catalyst 0.5 g.

[b] n/i is the ratio normal-C_7 to iso-C_7 alcohols.

4.2. *Water-Gas Shift Reaction*

Silica-supported ruthenium–bipyridine catalysts have been found to be highly active in the water–gas shift reaction (23). Our catalysts were tested in a continuous-flow reactor with different flow conditions in order to obtain maximum activity with at least 50 mol.% conversion. The results are shown in Table 4. The highest activities are 2–2.5 times higher than is obtained with catalysts prepared by impregnation. It is notable that these activities can be reached with smaller ruthenium content. This indicates that the surface area of the supports is more effectively used than with conventional impregnation. However, no definitive conclusions can be made about the effect of ruthenium content on the activity.

The effect of preparation method is notable. When the catalyst is made by successive pulses of the two reactants, the activity is poor, even when the ruthenium content is enhanced. This indicates that when $Ru_3(CO)_{12}$ is strongly chemisorbed in the first step, 2,2′-bipyridine cannot react with these surface species effectively enough to produce an active component. The active component in the water–gas shift reaction is thus formed from physisorbed $Ru_3(CO)_{12}$ and 2,2′-bipyridine.

The similarity of the results in Table 4 for different supports is also an indication of rather weak interactions between different surface sites and active surface species. However, with aluminum oxide as support the stability of the catalysts was poorer than with silica F22, and the activity decreased as a function of time.

TABLE 4

Results for the Water–gas Shift Reaction[a] with Supported Ruthenium–Bipyridine Catalysts Prepared by Different Methods

Prep. method	Support	Ru (wt.%)	*A* (max)[b]	Conversion (%)
Subl. $Ru_3(CO)_{12}$[c]	SF22	4.08	30	1
Impregnated[d]	SF22	4.45	7500	98
B	SG60	0.64	1516	5
C	SF22	1.36	2740	18
A	SF22	0.88	3200	9
C	SF22	1.42	4700	30
B	SG60	3.21	5313	48
B	SG60	1.54	5844	36
B	SG60	3.70	6050	58
A	SG60	1.73	10009	40
A	ALU	2.38	10594	60
C	ALU	1.04	11330	66
A	SF22	2.53	11400	64
A	ALU	2.70	11875	72
A	SF22	2.90	13800	98
C	ALU	1.24	16189	74
A	SF22	1.32	16800	84
A	SF22	3.28	19500	72

[a] Reaction conditions: $P(CO) = 7$ bar, $P(H_2O) = 2.7$–4.8 bar, reaction temperature = 150°C, flow rate = 10–100 cm^3/min.

[b] mol H_2/mol $Ru_3(CO)_{12}$ per 24 h.

[c] No 2,2′-bipyridine.

[d] Result from Ref. (23).

5. CONCLUSIONS

The gas-phase preparation methods have been shown to yield active supported ruthenium–bipyridine catalysts for the water–gas shift reaction and 1-hexene hydroformylation. The increased possibilities to control the catalyst preparation steps lead to better dispersion and thus the benefit of the high surface area of the supports can be used more effectively than with the conventional liquid-phase preparation methods.

The fluidized bed reactor system has proved to be efficient in controlling the ruthenium content, the surface species, and the dispersion of the ruthenium–bipyridine catalysts. The control can be achieved by changing the carrier gas or the reactor temperatures or using different support pretreatment procedures. The introduction of two or more reactants in successive pulses permits one to control the surface reactions, which can be very complicated. We believe that this method is very promising for the preparation of supported catalysts.

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