

Hydroformylation of 1-hexene on Rh/C and Co/SiO₂ catalysts

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Received 20 July 1996; accepted 27 November 1996

Abstract

The effect of the support for rhodium on activated carbon, and the effect of precursor for cobalt on silica, were studied in the liquid phase hydroformylation of 1-hexene. At best the activities of the heterogeneous catalysts were similar to their homogeneous counterparts. The activity of the Rh/C catalysts correlated with the support; the larger the pores the better the mass transfer, and the higher the activity. In the case of Co/SiO₂, the effect of precursor on the activity of the catalysts was diverse, and the activities remained lower than that of the homogeneous cobalt carbonyl. Some metal was, however, dissolved from the supports, and consequently the activity was mainly due to the dissolved catalytic species rather than the heterogeneous catalyst. The dissolution of the metal from the support was due to both synthesis gas mediated formation of soluble active species, and reaction product effectuated dissolution. Yet, the heterogeneous functionality of the active carbon support was revealed by the formation of C₂₁ acetals, which were only formed on a support with acidic character and large enough pores. The acidic character of the active carbon supports was also shown by the formation of C₁₄ condensation products, which were only formed in traces for homogeneous rhodium.

Keywords: 1-hexene hydroformylation; Heterogeneous catalysts; Rhodium/cobalt catalysts; Activated carbon support; Stability

1. Introduction

The most important industrial applications of hydroformylation are the manufacture of *n*-butanal from propene, the synthesis of long chain alcohols from olefins such as 1-octene and higher, and the hydroformylation of ethene to propanal [1]. Cobalt-based processes still govern the majority of higher olefin hydroformylations, whereas more than 90% of the propene hydroformylation processes involves rhodium catalysis [2].

Homogeneous hydroformylation catalysts

have been heterogenized on different supports, such as inorganic and polymer carriers. However, under typical hydroformylation conditions, the active metal has been leached from the polymer supports [3–6], whereas the oxidic supports have appeared more stable [7,8]. Hydroformylation catalysts have been supported on silica [6–9], alumina [8,9], magnesia [8] and zeolite [9–14]. The catalysts have been found to be active in the liquid phase, although some leaching of the active component has been observed, particularly in conjunction with ion exchanged zeolites [10,11]. The metal elution from the support has also been correlated with the amount of aldehyde products in the liquid phase [5,15].

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In the gaseous phase, $\text{Co}_2(\text{CO})_8/\text{SiO}_2$ has been a promising catalyst for the conversion of ethene [16]. Reinikainen [16] assumed that linear CO adsorbed on isolated metal sites was essential for the CO insertion. In accordance, the activity of the supported rhodium catalysts in the gas phase hydroformylation has been related to isolated, positively charged, active sites [17–20]. The formation of these sites is facilitated on highly dispersed metallic rhodium particles through the oxidation of Rh by surface OH^- [21]. Huang et al. [21] suggested, however, that the linear CO on Rh^0 was uniquely responsible for the heterogeneously catalyzed hydroformylation on Rh/SiO_2 . Thus, the carbonyl precursors appear beneficial for the preparation of catalysts for hydroformylation, since the carbonyl based preparations have typically produced more highly dispersed catalysts than the conventional impregnations [22–24]. The extent of reduction on the surface of the $\text{Co}_2(\text{CO})_8$ based catalyst has also been surprisingly low (15%), facilitating the presence of highly dispersed partially reduced active sites suitable for the insertion of CO [24].

Although the superior performance of rhodium and cobalt in hydroformylation has been widely reported [1,25–28], the literature regarding rhodium or cobalt on activated carbon is scarce. However, the activated carbon supported rhodium catalysts have been shown to be promising heterogeneous catalysts for methanol carbonylation [29–31] — a reaction also commonly carried out in homogeneous mode [32]. Consistently, in the liquid phase, under conditions typical for a homogeneous hydrocarbonylation reaction, the activity of the Rh/C catalysts has been, in fact, of homogeneous origin, i.e. due to the amount of metal leached from the support [33]. In the vapor phase, however, exceptional selectivities have been obtained with the same Rh/C preparations [34], suggesting that the catalysts merit further studies with a more moderate reaction medium, such as hydroformylation.

The present studies concentrate on 1-hexene

hydroformylation on heterogeneous Co/SiO_2 of carbonyl and nitrate origin, and Rh/C with different types of activated carbon support. The cobalt catalysts were chosen for study due to their extraordinary activity in gaseous phase hydroformylation [16], and the rhodium catalysts due to their promising performance in methanol hydrocarbonylation [33,34]. The studies were performed in the liquid phase to determine the activity and stability of the studied catalysts in terms of their potential application in heterogeneous hydroformylation.

2. Experimental

2.1. Catalyst preparation

For the 3 or 5 wt% Rh/C catalysts, denoted as $\text{Rh}(3)/\text{C}$ and $\text{Rh}(5)/\text{C}$ respectively, C(N) stands for peat based Norit Rox 0.8, C(T) for wood based Japanese Takeda Shirasagi, and C(C) for coconut based activated carbon from Johnson Matthey. Homogeneous $\text{Rh}(\text{NO}_3)_3$ is denoted as $\text{Rh}(\text{N})$. The Rh/C catalysts were prepared by incipient wetness impregnation using an aqueous solution of $\text{Rh}(\text{N})$ as reported previously in more detail [33]. A commercially available catalyst, $\text{Rh}/\text{C}(\text{COMM})$, and homogeneous $\text{Rh}(\text{N})$ were tested as reference catalysts. The Rh/C catalysts were reduced under hydrogen at 400°C ($5^\circ\text{C}/\text{min}$) for 1 h before use. Some characteristics of the Rh/C catalysts are shown in Table 1 [33,35].

The Co/SiO_2 catalysts were prepared using different precursors, and the abbreviations are as follows. For the 4 or 5 wt% Co/SiO_2 catalysts, Co(N) stands for $\text{Co}(\text{NO}_3)_2$, $2\text{Co}(\text{CO})$ for $\text{Co}_2(\text{CO})_8$ and $4\text{Co}(\text{CO})$ for $\text{Co}_4(\text{CO})_{12}$. The carbonyl catalysts were prepared by incipient wetness impregnation using dichloromethane (dcm) or *n*-pentane (p) as a solvent. In the case of $2\text{Co}(\text{CO})/\text{SiO}_2$ catalysts, the batch number is shown in brackets, e.g. a catalyst from the first batch prepared from the dichloromethane solution of $\text{Co}_2(\text{CO})_8$ is denoted as

Table 1
Characteristics of Rh/C catalysts

	Rh(3)/C(C)	Rh(5)/C(C)	Rh(3)/C(N)	Rh(5)/C(N)	Rh(3)/C(T)	Rh(5)/C(COMM)
Support particle size (mm)	0.3–0.75	2–5	0.3–0.75	0.8	0.3–0.75	1–2
Surface area ^{a,b} (m ² /g)	1140	1223	1075	—	1480	1142
Pore volume ^a (cm ³ /g)	0.506	—	0.583	—	0.708	0.525
Volume of pores ^a (<i>r</i> > 1 nm (cm ³ /g))	0.047	—	0.174	—	0.104	0.066
Fraction of pores (<i>r</i> > 1 nm (%))	9.3	—	29.8	—	14.7	12.6
H ₂ uptake ^c (μmol/g _{cat})	19.2	49.4	3.6	13.9	6.7	66.3
Rh particle size ^c (nm)	9.0	4.8 ^d	41	15 ^d	23	4.0 ^d
Dispersion ^c (%)	12.0	22.7	2.6	7.1	4.6	27.3
XPS: C/O atom ratio	—	10.3	—	8.5	—	4.0
XPS: C/O atom ratio ^e	8.3	8.3	14.9	14.9	10.4	—

^a Physisorption measurements.

^b BET isotherm (0.001–1).

^c H₂ chemisorption measurements based on irreversible hydrogen uptake at 25°C.

^d X-ray amorphous, determined by XRD.

^e Active carbon support.

2Co(CO)(dcm1)/SiO₂. For the homogeneous catalysts, Co(N) stands for cobalt nitrate and 2Co(CO) for Co₂(CO)₈. The silica support was dehydroxylated at 600°C under vacuum. The carbonyl catalysts were reduced under hydrogen flow at 300°C (5°C/min) for 7 h. All stages of the preparation of the carbonyl catalysts were carried out under an inert atmosphere.

The Co(N)/SiO₂ catalyst was prepared by incipient wetness impregnation using an aqueous solution of Co(N). The support was wetted with a water–ethanol solution (1:1), dried at 120°C overnight and under vacuum at 200–400 Pa and 200°C for 2 h. After impregnation, the catalyst was dried in a rotary evaporator at 200–400 Pa and 60°C, calcined in air flow at 300°C for 12 h, and reduced under hydrogen at

400°C (5°C/min) for 1 h. The characteristics of the cobalt catalysts are shown in Table 2 [24,36]. The metal contents of the cobalt and rhodium catalysts were determined before and after the reaction by atomic absorption spectroscopy.

2.2. Catalyst activity testing

The experiments were carried out in a 250 ml AISI316 magnetically stirred autoclave, equipped with a separate zirconium or teflon vessel. The reduced catalyst and 1-hexene were packed into the reaction vessel in a glove box under a nitrogen atmosphere, and then transferred to the autoclave. The amount of catalyst was 0.5 g, and that of 1-hexene, 25 ml. The autoclave was pressure tested with nitrogen at

Table 2
The characteristics of Co/SiO₂ catalysts after reduction by hydrogen

Catalyst	H ₂ uptake ^a μmol/g _{cat}	Reduction (%) XPS	Dispersion (%)	Size (nm) chemisorption	Size (nm) XRD
Co(N)/SiO ₂	12.5	42	7.1	13	14
2Co(CO)(dcm)/SiO ₂	46.2	15	80	1.22	2.3 ^b
2Co(CO)(p1)/SiO ₂	72.1	—	—	—	—
4Co(CO)(dcm)/SiO ₂	52.2	41	32	3.0	3.4 ^b

^a Total H₂ adsorption.

^b Upper limit estimate only, since the sample was oxidized at 573 K prior to measurement.

120 bar, and thereafter pressurized with synthesis gas ($\text{CO:H}_2 = 1:1$ mol/mol) to the initial pressure of 73 bar. The reaction time was 4 h including the heating period for all the catalysts, except for Rh(5)/C(N) which was reacted for 3 h. In the blank test, the pressure was 100 bar at the reaction temperature, 150°C. At the end of the experiment, the autoclave was cooled to room temperature and depressurized. The products were diluted with tetrahydrofuran (THF) and analyzed by a HP 5890 series gas chromatograph, using a polar DB WAX capillary column and a flame ionization detector. The surface areas of the peaks were divided by sensitivity factors [37] and normalized to obtain the distribution of the products in weight percentages.

Extraction experiments were carried out on the Co(N)/SiO₂ catalyst to elucidate the dissolution mechanism of cobalt from the support. 1-Hexene was replaced by the aldehyde product (1-heptanal), and the reaction atmosphere was synthesis gas, nitrogen or hydrogen.

3. Results and discussion

3.1. Rh/C

For the Rh/C catalysts the conversion of 1-hexene was 48–92%, whereas conversion for the homogeneous Rh(N) was 90%, see Fig. 1. Thus, the activity of Rh/C(N) was comparable to homogeneous rhodium (25 mg Rh). The normal to branched ratio was between 0.5–0.6 for C₇ aldehydes and between 0.7–0.9 for C₇ alcohols for the Rh catalysts tested. The higher *n/i* ratio for alcohols compared to aldehydes is in accordance with the results of Alvila [9] on Co₂Rh₂(CO)₁₂/Al₂O₃/Et₃N catalyst at 100°C and 50 bar. In fact, at temperatures from 30 to 50°C, the *n/i* ratios were almost equal for both aldehydes and alcohols, but at higher temperatures the *n/i* ratios for C₇ alcohols exceeded those for C₇ aldehydes. Alvila [9] also reported an increase in the isomerization of 1-hexene at a

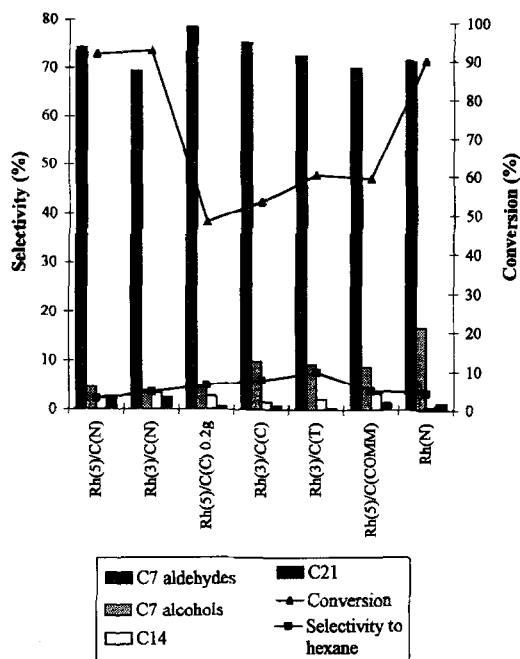


Fig. 1. The conversion and selectivity on Rh catalysts.

rise of temperature from 85°C to 110°C at 50 bar, which was indicated by the appearance of 2-ethyl-pentanal. The result is in accordance with the results of Lazzaroni et al. [38] for Rh₄(CO)₁₂ catalyzed hydroformylation of 1-hexene at the pressure of 100 bar. The quite low *n/i* ratios, i.e. below 1, might be explained by the rather high temperature, 150°C [9,38], and the rather low CO pressure [39]. For aldehydes, the selectivity towards different isomers decreased in the order 2-methyl-hexanal > heptanal > 2-ethyl-pentanal. The isomerization activity was affected by the reaction conditions rather than the Rh/C catalysts used, because selectivity towards 2-ethyl-pentanal was 13–14% for all the Rh catalysts tested.

However, the Rh/C catalysts were not stable during the reaction, and the amount of metal leached from the support is presented in Table 3. The amount of Rh in solution was greatest for the most active catalyst Rh(5)/C(N) (8 mg), and 5 mg or less of Rh for the other heterogeneous Rh/C catalysts. The results also show that the metal content in solution was not directly related to the activity, contrary to our

Table 3
The amount of dissolved metal from Rh/C and Co/SiO₂ catalysts

Catalyst	Fresh catalyst (wt%)	Dissolved amount ^a (%)
Rh(5)/C(C) (0.2 g)	4.5	31
Rh(3)/C(C)	3.3	32
Rh(5)/C(N)	4.2	40
Rh(3)/C(N)	2.9	37
Rh(3)/C(T)	3.0	33
Rh(5)/C(COMM)	5	20
Co(N)/SiO ₂	4.4	49
2Co(CO)(p1)/SiO ₂	5.1	52
2Co(CO)(p2)/SiO ₂	5.0	47
2Co(CO)(dcm1)/SiO ₂	4.2	39
2Co(CO)(dcm2)/SiO ₂	4.9	40
4Co(CO)(dcm)/SiO ₂	4.0	39

^a Determined from the used catalyst.

findings for methanol hydrocarbonylation [33], see Fig. 2. In addition, the order of activity was different in these two reactions: Rh/C(N), which had the lowest activity in liquid phase methanol hydrocarbonylation, was the most active catalyst in hydroformylation. Thus, most of the activity apparently originated from the dissolved species, but the remainder may be assigned to the heterogeneous catalyst.

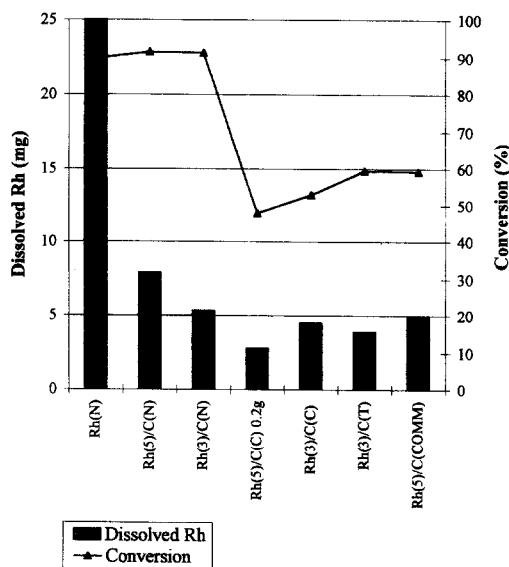


Fig. 2. The conversion, and the dissolved amount of metal on Rh/C catalysts.

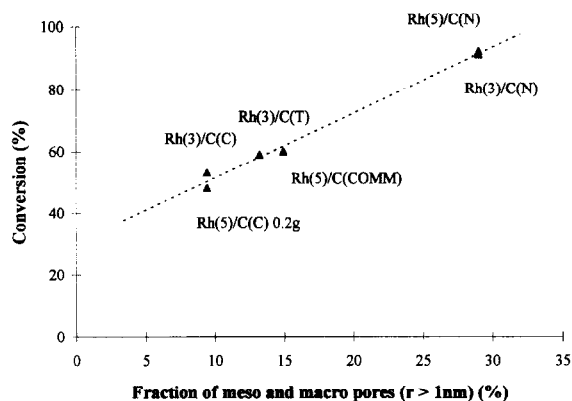
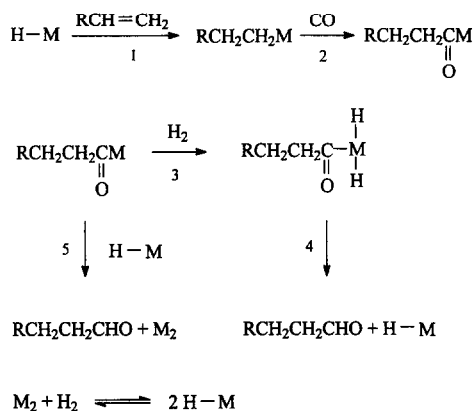


Fig. 3. Conversion versus fraction of meso and macro pores ($r > 1$ nm) on Rh/C catalysts.

We observed a linear correlation between the pore size distribution and the activity — the higher the fraction of meso and macro pores ($r > 1$ nm) the higher the activity, see Fig. 3. For the most active catalyst, Rh/C(N), 30% of the pores were greater than 2 nm in diameter. On the other hand, the dispersion of the catalysts prepared on the C(N) support was low. Therefore, rhodium elution from Rh/C(N) with large pores and large metal particles was more probable than from the other catalysts with smaller pores and better dispersed metal, see Table 3. However, large pores are also beneficial with regard to the heterogeneous reaction pathway, because in micro pores the mass transfer may be limited.

The amount of heterogeneous activity cannot easily be determined from the present data. However, the in situ IR characterizations of Chuang and Pien [40] have provided evidence for the adsorbed acyl species on the Rh/SiO₂ catalyst, indicating that a CO insertion step may take place on the heterogeneous catalyst during ethene hydroformylation at 393–573 K and at a pressure of 1.01 MPa. The temperature-programmed reaction study revealed that the acyl species can be hydrogenated to form propanal. Also, Balakos and Chuang [41] have studied propanal formation on Rh/SiO₂ by a transient isotopic method at 0.1–0.5 MPa and 503 K. They [41] showed that propanal may be formed



Scheme 1. Generally agreed course of the hydroformylation of a terminal olefin. For the sake of clarity, $(\text{CO})_m$ and L_n ligands are omitted; it is understood that the insertions of olefin and of CO are preceded by the coordination of these molecules to the metal center.

via the insertion of CO into the adsorbed ethyl species to form the acyl intermediate, which may then be hydrogenated to produce adsorbed propanal. Thus, the results suggest that both the homogeneous and truly heterogeneous routes may function on our catalysts simultaneously, and result in the formation of similar products.

Since the activity of the heterogeneous catalysts originated in part from the true heterogeneous catalysis, it is essential to consider in detail the formation of products through the homogeneous and heterogeneous reaction pathways. Scheme 1 shows the generally agreed course of the hydroformylation of a terminal olefin. Although the reaction steps for cobalt and rhodium catalyzed hydroformylation are substantially the same, the relative rates of the individual steps appear to be different for the two catalysts. The rate-limiting step varies not only with the catalyst used but also with the reactivity of the olefin substrate and the CO partial pressure [25]. Two possible routes have been discussed in the literature for the last step, the transformation of the acyl-metal species to the aldehyde: hydrogenolysis after oxidative addition of a H_2 molecule (steps 3 and 4), or reaction with a second catalyst species (step 5). This is often the rate-determining step in alde-

hyde synthesis. Henrici-Olivé and Olivé [28] have suggested that the decisive difference between the homogeneous and the heterogeneous process is the availability of a free, mobile, very reactive hydrido-metal species in solution. This makes step 5 the only important mode of reaction for the acyl-metal species in the homogeneous system. In the heterogeneous system, however, the M-H species are fixed at their surface sites and cannot encounter any acyl-metal species, also fixed at the surface. Therefore, the oxidative addition of molecular hydrogen to an acyl metal species is the only means of formation of the aldehyde.

In the case of an acyl complex, $\text{C}_2\text{H}_5\text{O}(\text{CO})\text{Co}(\text{CO})_3$, the rate constant for the reaction with H_2 is an order of magnitude lower than that of the reaction with $\text{HCo}(\text{CO})_4$ [28]. Although the model compound does not represent exactly the active species in the catalytic cycle, the trend evidently supports the hypothesis that in homogeneous media acyl-complexes react mainly with hydride complexes and not with H_2 [28]. Thus, the homogeneous reaction path is probably much faster and may therefore conceal the heterogeneous route on our catalysts. Also, the selectivities of the two routes might differ, since side reactions of the reactive intermediates on the heterogeneous catalyst become more probable due to the slower last step of the reaction.

In the light of these mechanistic considerations, we accurately determined the differences in the product distributions between the homogeneous and heterogeneous systems, and indeed observed distinct products. First of all, the selectivity towards alcohols for the heterogeneous Rh/C catalysts differed from homogeneous Rh(N), see Fig. 1. The results indicated that hydrogenation of an aldehyde was easier on homogeneous Rh(N) than on heterogeneous Rh/C. In accordance, on homogeneous Rh(N) the main secondary products were C_{21} acetals; condensation products of C_7 aldehydes with two C_7 alcohol molecules. C_{21} products were formed mainly on heterogeneous Rh/C(N) and

Rh/C(COMM). In addition, on the heterogeneous Rh/C catalysts, C₁₄ products were formed, whereas on homogeneous Rh(N) they were formed only in traces. The C₁₄ compounds were aldol condensation products formed of two C₇ aldehydes, and hemiacetals formed of C₇ aldehyde and C₇ alcohol. When examining the hydrogenation activity towards hexane, see Fig. 1, there was almost no difference between the catalysts at the higher conversion level. Also, although selectivities towards hexane were higher at the lower conversion level, the differences between the catalysts were minor.

Acetal formation is catalyzed by a trace of strong acid [42], and the aldol condensation may also proceed as an acid catalyzed reaction [43]. This is why we studied the nature of the surface of the active carbon supports in more detail, in order to determine the amount of oxygen containing functional groups responsible for the acidity. The C/O atom ratio of the carbon surfaces was determined by X-ray photoelectron spectroscopy [35], and the decomposition of the surface groups to carbon monoxide and carbon dioxide was evaluated by TPD [35]. The XPS data for the C/O atom ratio for the supports alone and the reduced catalysts was somewhat diverse [35], but the TPD results indicated that the acidic character of the supports decreases in the order C(N) > C(C) > C(T). The acid catalyzed formation of dimethylether decreases in gas phase methanol hydrocarbonylation in the order Rh/C(C) > Rh/C(N) >> Rh/C(T) [33], i.e. the acidic character of the supports decreases in the same respective order. Thus, the highest fraction of meso and macro pores (good mass transfer), together with the acidity, might be responsible for the formation of C₂₁ acetals on Rh/C(N). In the case of more microporous supports, the more acidic character of Rh/C(COMM) catalyst compared to Rh/C(C) was demonstrated by the greater amount of C₂₁ acetal formation. Also, the formation of C₁₄ condensation products on heterogeneous Rh/C catalysts is explained by the acidic character of the active carbon support. In summary, the pore

size distribution and the nature of the support were related to the activity and selectivity of the heterogeneous rhodium catalysts.

The heterogeneous functionality of the catalysts in terms of product selectivity has increased in the gas phase methanol hydrocarbonylation reaction compared to the liquid phase reaction [34]. Thus, it is highly likely that the heterogeneous function will also be enhanced in gas phase hydroformylation, since the free and reactive hydrido-metal species required for the homogeneous route is absent in the gas phase. Accordingly, further studies will be carried out in the gas phase in the near future.

3.2. Co/SiO₂

Homogeneous 2Co(CO) was extremely active in hydroformylation; the conversion of 1-hexene to products was 96%, whereas it was only 73% for homogeneous cobalt nitrate, see Fig. 4. Although selectivity towards alcohols was similar for the two catalysts, the selectivity

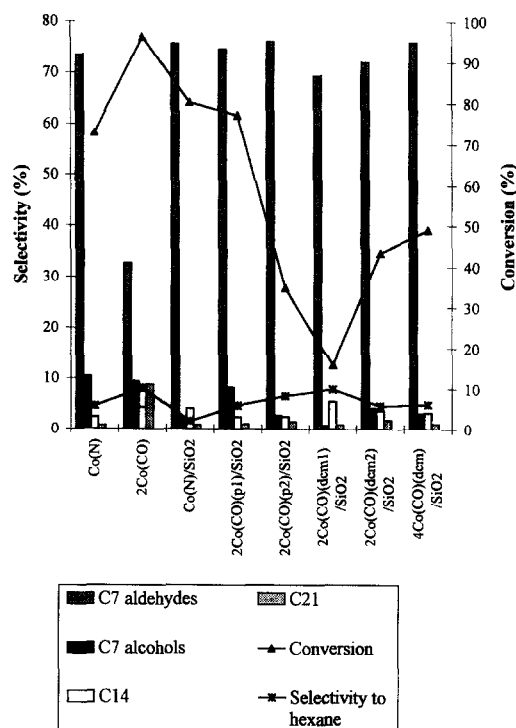


Fig. 4. The conversion and selectivity on Co catalysts.

towards C_{21} products was clearly higher for $2Co(CO)$ precursor, i.e. the hydrogenation to alcohols was originally higher with $2Co(CO)$ precursor. The difference in activity and selectivity is related to the ease of formation of the catalytically active cobalt carbonyl species. Cobalt nitrate has to be first transformed to $Co_2(CO)_8$ and further to $HCo(CO)_4$, whereas this transformation takes place more readily from $2Co(CO)$ [44]. The solubility of $Co(N)$ into the reaction medium was low, and the formation of $Co_2(CO)_8$ required a certain minimal CO pressure. This results in a lower concentration of $Co_2(CO)_8$ in the case of $Co(N)$ and further in the activity and selectivity differences between the homogeneous precursors. The strong acidic character of $HCo(CO)_4$ [25] compared to $HRh(CO)_4$ was evidenced by the high selectivity towards C_{21} acetals on homogeneous $2Co(CO)$. For homogeneous Co precursors the selectivity towards C_7 alcohols surpassed that of the respective heterogeneous catalysts, which resembles the selectivity differences between the homogeneous and heterogeneous Rh catalysts. Also, the hydrogenation of 1-hexene to hexane was higher on homogeneous cobalt precursors than on the respective heterogeneous catalysts, see Fig. 4.

At best, the activity of the $Co(N)/SiO_2$ and $2Co(CO)(p1)/SiO_2$ catalysts was comparable to the homogeneous nitrate precursor, whereas the activities of the other catalysts were clearly lower, see Fig. 4. The excellent result with $2Co(CO)(p1)/SiO_2$ catalyst could not, however, be reproduced, a subsequent preparation, $2Co(CO)(p_2)/SiO_2$, producing different results. The activity was not related to the impregnation solvent either, since $2Co(CO)(dcm1)/SiO_2$ and $2Co(CO)(dcm2)/SiO_2$ differed from each other, and from the other two catalysts. Possibly, the differences originate from the catalyst preparation and handling procedure, making it very difficult to determine the effect of precursor on the activity. Also, an uncontrolled equilibria between dormant and active species might be responsible for the differences, because the CO

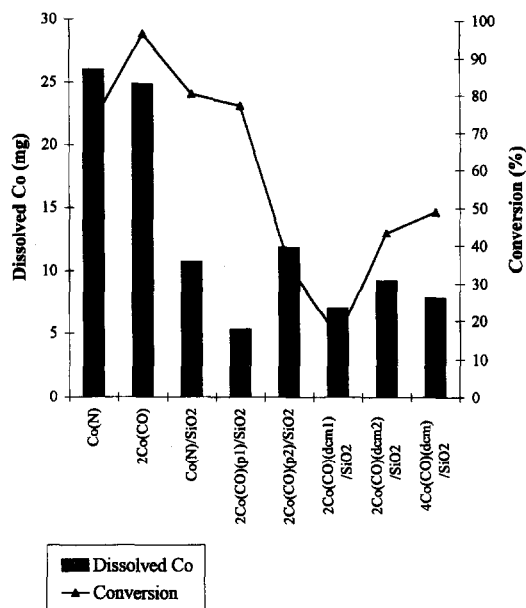


Fig. 5. The conversion, and the dissolved amount of metal on Co/SiO_2 catalysts.

pressure required to maintain active cobalt carbonyl species stable in solution at the temperature of $150^\circ C$ is more than 40 bar [26]. In the case of Rh catalysts, however, the reaction conditions were in the stable region, and accordingly, the experiments were repeatable from run to run.

The analyses of the catalysts after reaction, see Table 3, revealed that during the reaction some soluble cobalt species had formed. This observation is, in fact, in accordance with the literature [26,27,44,45]. Homogeneous and heterogeneous activity were difficult to distinguish, due to the batch to batch variations in catalytic performance. It is apparent, however, that most of the activity originated from homogeneous catalyst, although the activity was not directly related to the amount of dissolved species, as illustrated in Fig. 5. Furthermore, the dissolution of the catalytic metal was not affected by dispersion, but rather by the reaction conditions [26].

The most active $Co(N)/SiO_2$ catalyst was extracted with the aldehyde product (1-heptanal) to elucidate, in more detail, the dissolution of

Table 4
The amount of cobalt on Co(N)/SiO₂ before and after the extraction experiment with 1-heptanal.

Reaction atmosphere	Fresh catalyst (wt%)	Used catalyst (wt%)	Dissolved Co (%)
CO:H ₂ = 1:1	4.5	1.0	77
N ₂	4.5	2.9	35
H ₂	4.5	3.1	31

the active metal. The results showed that the catalyst was not stable, even in a nitrogen or hydrogen atmosphere. In the synthesis gas atmosphere, 77% of the metal was leached from the support, whereas in the absence of CO, i.e. in a nitrogen or hydrogen atmosphere, 35% and 31% of the metal was eluted from the support, see Table 4. This result is extraordinary, since metallic or oxidic cobalt is not soluble in aldehydes or alcohols. In the literature, the metal elution from the support has been correlated with the aldehyde or alcohol products in the solution in the case of rhodium carbonyl based tertiary amine catalysts [5], and Ru₃(CO)₁₂/2,2'-bipyridine based oxidic catalysts [15], but the dissolution mechanism has not been discussed. In a hydrogen atmosphere, the aldehyde product reacted to heptanol and

C₂₁ products, whereas in a nitrogen atmosphere C₁₄ products were formed, see Fig. 6. In a synthesis gas atmosphere, 1-heptanal reacted to heptanol and both C₁₄ and C₂₁ products. Moreover, we did not detect significant amounts of acidic components, which could dissolve cobalt. It remains speculative whether some heavy hydrocarbons were retained in the pores of the catalysts, thereby increasing the sample weight and resulting in erroneous analyses.

In all, the synthesis gas mediated formation of soluble species and the reaction product effected leaching, both contributed to the instability of the catalysts in the liquid phase. Accordingly, the stability of the catalysts might be enhanced under less severe reaction conditions, i.e. in gas phase hydroformylation, when leaching by liquid products would also be avoided.

4. Summary and conclusions

In the liquid phase hydroformylation of 1-hexene, we studied the effect of support and precursor on the activity and stability of Rh/C and Co/SiO₂ catalysts.

At best the activity of the heterogeneous catalysts was similar to their homogeneous counterparts. Some metal was dissolved from the support, but the activity of the heterogeneous catalysts was not directly related to the amount of dissolved metal. Instead, the activity of Rh/C appeared to correlate with the support, i.e. the larger the pores, the better the mass transfer of the reactants and products, and the higher the activity. The Rh/C catalysts also exhibited heterogeneous functionality in terms of selectivity: part of the activity clearly originated from the heterogeneous catalysts. On Rh/C(N), the acidic character of the support was revealed by the formation of C₂₁ acetals, i.e. a reaction of C₇ aldehyde with two C₇ alcohols. The acidic character of the active carbon support was also demonstrated by the formation of C₁₄ condensation products, which were only formed in traces on homogeneous

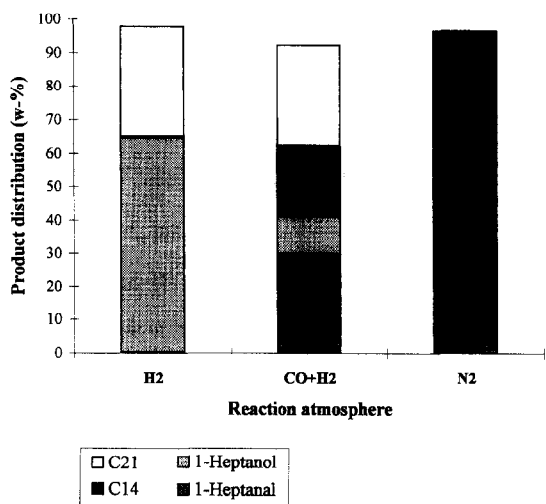


Fig. 6. The product on extraction experiments with 1-heptanal on Co(N)/SiO₂ catalysts.

rhodium. C_{21} acetal formation on homogeneous rhodium was in accordance with the good alcohol selectivity.

The strong acidic character of $HCo(CO)_4$ was shown by the good selectivity towards C_{21} acetals on homogeneous $Co_2(CO)_8$. In the case of Co/SiO_2 , the activity was not directly related to the precursor in terms of dispersion, and neither was the amount of metal lost from the support. Furthermore, the activity of the catalysts cannot entirely be explained by the dissolved cobalt species. The best activity of the heterogeneous cobalt catalysts of carbonyl origin was, however, associated with problems regarding the repeatable preparation of the catalyst.

In summary, in the liquid phase under conditions typical for the homogeneous reaction, the activity of the heterogeneous catalysts was mainly of homogeneous origin, i.e. due to the syngas mediated formation of soluble metal species, as well as product effectuated dissolution of the metals. Nevertheless, the heterogeneous functionality was also observed both in terms of activity, and selectivity. The catalysts merit further studies under vapor phase hydroformylation, since under more moderate conditions the heterogeneous functionality will be enhanced.

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