Fisher-Tropsch synthesis catalysed by cobalt-rhodium and cobalt-ruthenium carbonyl clusters on silica

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ABSTRACT

A systematic study was made of the use of tetranuclear $Co_{4-n}Ru_nH_n(CO)_{12}$ (n = 0-4), $Co_2Ru_2(CO)_{13}$ and $Co_{4-n}Rh_n(CO)_{12}$ (n = 0,1,2 or 4) clusters as catalyst precursors. Catalysts were characterized by temperature-programmed reduction and Fourier-transform infrared spectroscopy techniques, and their activity and selectivity in Fischer-Tropsch synthesis were determined, as well as the effect on their performance of reaction temperature, pretreatment atmosphere and method of preparation.

Monometallic Co_4/SiO_2 and Ru_4/SiO_2 catalysts were very active and all rhodium-containing $Co_{4-n}Rh_n(CO)_{12}/SiO_2$ catalysts were fairly weakly active in Fischer-Tropsch synthesis. Deactivation was associated with the bimetallic sites on cobalt-rhodium catalysts and with ruthenium on cobalt-ruthenium catalysts.

The effect of temperature on the catalysts followed a characteristic trend: when the temperature increased, product selectivity shifted to lighter molecular mass compounds and selectivity for oxygenates mainly decreased.

Per metal atom, refluxed catalysts tended to show higher activity in Fischer-Tropsch synthesis than did the corresponding impregnated catalysts. However, since the metal content of the refluxed catalysts was significantly lower than that of impregnated ones, the overall reaction rates over refluxed catalysts were slower.

In the bimetallic catalysts, the interaction between cluster and support probably occurred between the rhodium species and silica, and between ruthenium species and silica, not between cobalt and silica. Evidently rhodium and ruthenium interact more strongly with silica than cobalt does.

ACKNOWLEDGEMENTS

LIST OF PUBLICATIONS

This thesis is based on the following publications, which are referred to in the text by the corresponding Roman numerals:

PUBLICATIONS

I   Kiviaho, J., Reinikainen, M., Niemelä, M. K., Kataja, K. and Jääskeläinen, S. The activity of carbonyl cluster derived Co-Ru/SiO$_2$ and Co-Rh/SiO$_2$ catalysts in CO hydrogenation. **J. Mol. Catal. A: Chemical 106** (1996) 187.

II   Reinikainen, M., Kiviaho, J., Kröger, M., Niemelä, M. K. and Jääskeläinen, S. CO hydrogenation activity of carbonyl cluster derived Co-Ru/SiO$_2$ catalysts prepared by reflux method. Accepted to **J. Mol. Catal. A: Chemical.**

III   Kiviaho, J., Niemelä, M. K., Morioka, Y. and Kataja, K. TPR and FT-IR studies on carbonyl cluster derived Co-Rh/SiO$_2$ catalysts. **Appl. Catal. 144** (1996) 93.

IV   Kiviaho, J., Niemelä, M. K., Reinikainen, M. and Pakkanen, T. A. TPR and FT-IR studies on carbonyl cluster derived Co-Ru/SiO$_2$ catalysts. Accepted to **Appl. Catal.**

APPENDIX

V   Kiviaho, J., Niemelä, M. K., Reinikainen, M., Vaara, T. and Pakkanen, T. A. The effect of decomposition atmosphere on the activity and selectivity of the carbonyl cluster derived Co/SiO$_2$ and Rh/SiO$_2$ catalysts. Submitted to **J. Mol. Catal A: Chemical** (1996).

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CONTENTS

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ABBREVIATIONS

Co_4	$Co_4(CO)_{12}$
Co_3Ru	$Co_3RuH(CO)_{12}$
$Co_2Ru_2(I)$	$Co_2Ru_2H_2(CO)_{12}$
$Co_2Ru_2(II)$	$Co_2Ru_2(CO)_{13}$
$CoRu_3$	$CoRu_3H_3(CO)_{12}$
Ru_4	$Ru_4H_4(CO)_{12}$
Co_3Rh	$Co_3Rh(CO)_{12}$
Co_2Rh_2	$Co_2Rh_2(CO)_{12}$
Rh_4	$Rh_4(CO)_{12}$
(Co_4+Ru_4)	$Co_4(CO)_{12} + Ru_4H_4(CO)_{12}$
(Co_4+Rh_4)	$Co_4(CO)_{12} + Rh_4(CO)_{12}$
TPR	Temperature-programmed reduction
FT-IR	Fourier-transform infrared spectrometry
DRIFTS	Diffuse reflectance infrared Fourier-transform spectroscopy
KBr	Potassium bromide
CO	Carbon monoxide
GHSV	Gas hourly space velocity
α	Chain-growth probability
C-%	Carbon efficiency
C_i	Steady state conversion
C_t	Conversion at time t

1 INTRODUCTION

1.1 INDUSTRIAL AND HISTORICAL ASPECTS

Crude oil is a superior chemical feedstock for producing gasoline and other chemicals because the hydrocarbons are present in liquid form. The crude oil itself is a highly complex mixture of hydrocarbons, requiring fractionation, cracking, isomerization and aromatization for sufficient amounts of high qualilty gasoline to be obtained. Another route to gasoline, as well as other hydrocarbons and their oxygenated derivates, is Fischer-Tropsch synthesis, where synthesis gas ($CO + H_2$) is passed over an appropriate catalyst. Synthesis gas is obtained from the gasification of coal [1].

Resources of coal are estimated to be ten times larger than those of crude oil. Thus, in the long run, production of coal will exceed that of oil and processes for hydrocarbon synthesis will have to be based on coal. The economic feasibility of these processes is dependent on the oil-to-coal price ratio, and the date of their commercial realization is difficult to predict for the moment. The high price of coal in most countries ensures that the synthesis of gasoline or other liquid fuels by Fischer-Tropsch processes is not yet economically viable. However, the synthesis of selected compounds of high value to the chemical industry would make the process more attractive. Such compounds would include C_2-C_4 olefins, linear alcohols, linear α- or β-olefins with medium or long chains and waxes [2].

The first reports on heterogeneous CO hydrogenation over nickel catalysts were made in 1902 by Satier and Senders [3] and the first patent for the synthesis of liquid hydrocarbons was taken out in 1913 by BASF [4]. The classical experiments date back to 1922 when CO hydrogenation over alkalized iron catalysts at high temperatures and pressures yielded oxygen-containing products [5]. Iron-zinc catalysts made it possible to produce liquid and solid hydrocarbons under low pressure conditions, but the catalysts were rapidly deactivated. Further investigation led to the cobalt-based catalyst for the normal pressure synthesis of mainly saturated hydrocarbons at temperatures below 200 °C [6].

Just before Word War II, Germany, which has no significant crude oil sources, built nine plants to convert synthesis gas from coal to liquid fuels [3]. Fischer-Tropsch synthesis was also carried out before 1945 in one plant in France, four plants in Japan and one plant in Manchuria. When the war ended, most of these plants were dismantled [2]. During the 1950s the Fischer-Tropsch process became generally uneconomical because of

plentiful supplies of crude oil. By the 1980s, only South Africa had an operating Fischer-Tropsch process. South Africa has large coal reserves but essentially no crude oil, and roughly 40 % of the motor fuels consumed in South Africa were produced by this process [7]. A few commercial Fischer-Tropsch processes continue to operate in South Africa and there also is one in Malesia [8].

1.2 FISCHER-TROPSCH SYNTHESIS

Fischer-Tropsch synthesis can be defined as a reductive oligomerization of carbon monoxide over a heterogeneous catalyst [2]:

$$n\,CO + m\,H_2 \quad \text{---(catalyst)---} \, C_xH_yO_z \qquad (1)$$
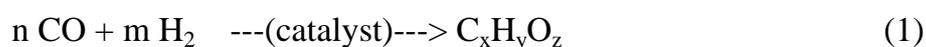
The reaction yields paraffins, olefins and oxygenated products such as alcohols, aldehydes, ketones, acids and esters.As is usual for an oligimerization, a more or less complicated product mixture has to be expected rather than the selective formation of individual products [2]. The probability of formation decreases in the order paraffins > olefins > oxygenated products. Within the group of n-alkanes, the probability of formation decreases with chain length, while in the group of n-olefins this order is reversed [9]. Also, variation in catalyst composition, temperature, pressure and type of reactor will markedly affect the average molecular weight of the products [7].

1.3 TRANSITION-METAL CLUSTERS IN CATALYSIS

A metal cluster can be defined as a compound consisting of three or more metal atoms, each of which is chemically bonded to at least two other metals of the group [9, 10]. Carbonyls are by far the most common ligands for organometallic clusters, and appear to stabilize the M-M bonds [10].

Because of their potential both as models for the catalytic metal surface and as catalysts in their own right, transition-metal clusters have been under intensive investigation [11]. The application of multimetallic cluster catalysts has also attracted much interest because their catalytic activity and selectivity have often differed significantly from that of the monometallic systems of the constituent metals [12]. Mixed transition-metal clusters are expected to find important applications in heterogeneous catalysts since a suitable combination of metals should permit more efficient interaction with

substrates than is obtained with mononuclear metal complexes or monometallic clusters [13]. With mixed transition-metal clusters as precursors, highly dispersed metal particles and a uniform metal composition as well as a specific structure of the two metal components manageable at the molecular level can be achieved in oxide-supported catalysts [14, 15].

Fischer-Tropsch synthesis has been one of the most intriguing topics in the field of heterogeneous catalysis by transition metals. In the Fischer-Tropsch synthesis the selectivity for hydrocarbons and alcohols is constrained by the Schulz-Flory distribution of the products, and tremendous efforts have been directed towards finding catalysts that are more selective, particularly for oxygenated compounds [16 - 22]. A number of reports have suggested that the size of the metal particles in the catalysts may have a significant effect on the product distribution [20, 22, 23]. Transition-metal clusters have been used as precursors to obtain high metal dispersion with particles smaller than 10 Å [20, 22]. Transition-metal carbonyl clusters, moreover, have provided zero-valent metal particles at lower reduction temperatures than have conventional precursors [24]. Catalysts prepared from metal carbonyl clusters also are free from contamination by residual materials such as Cl^- and NO_3^-. In particular, residual Cl^- is often strongly bound with the basic sites of oxide supports, thereby inhibiting the activation of CO by metals [16].

Cobalt [20] and ruthenium [25] are two of the most active metals for Fischer-Tropsch synthesis and have been considered for the production of long chain hydrocarbons through CO hydrogenation owing to their high activity for carbon monoxide dissociation and carbon-carbon bond formation. Bimetallic cobalt-ruthenium clusters on silica produce still larger amount of oxygenates than the corresponding monometallic cluster catalysts or conventional cobalt-ruthenium salt catalysts, though in all cases yields have been quite small [14,18, 26]. Rhodium on silica is known to be a good catalyst for selective production of oxygenated compounds [27, 28], but improvement in the activity and selectivity is necessary before a new process can be developed [29]. In the bimetallic system, cobalt is considered to promote the formation of C-C bonding in the synthesis of higher alcohols [20, 30 - 32].

1.4. SCOPE OF THE RESEARCH

Mono- and bimetallic clusters are of great potential for the preparation of novel active and selective catalysts. Under well-controlled conditions it is

possible to prepare heterogeneous catalysts that possess a high and uniform metal dispersion and good catalytic properties. The primary objective of the present work was to study, systematically, the use of tetranuclear $Co_{4-n}Ru_nH_n(CO)_{12}$ (n = 0-4), $Co_2Ru_2(CO)_{13}$ and $Co_{4-n}Rh_n(CO)_{12}$ (n = 0,1,2 or 4) clusters as catalyst precursors. Figure 1 shows the schematic structures and metal composition of the clusters used in catalyst preparation [33].

The activity and selectivity of the catalysts in Fischer-Tropsch synthesis were studied, and the effects of reaction temperature, pretreatment atmosphere and method of preparation of catalysts were investigated.
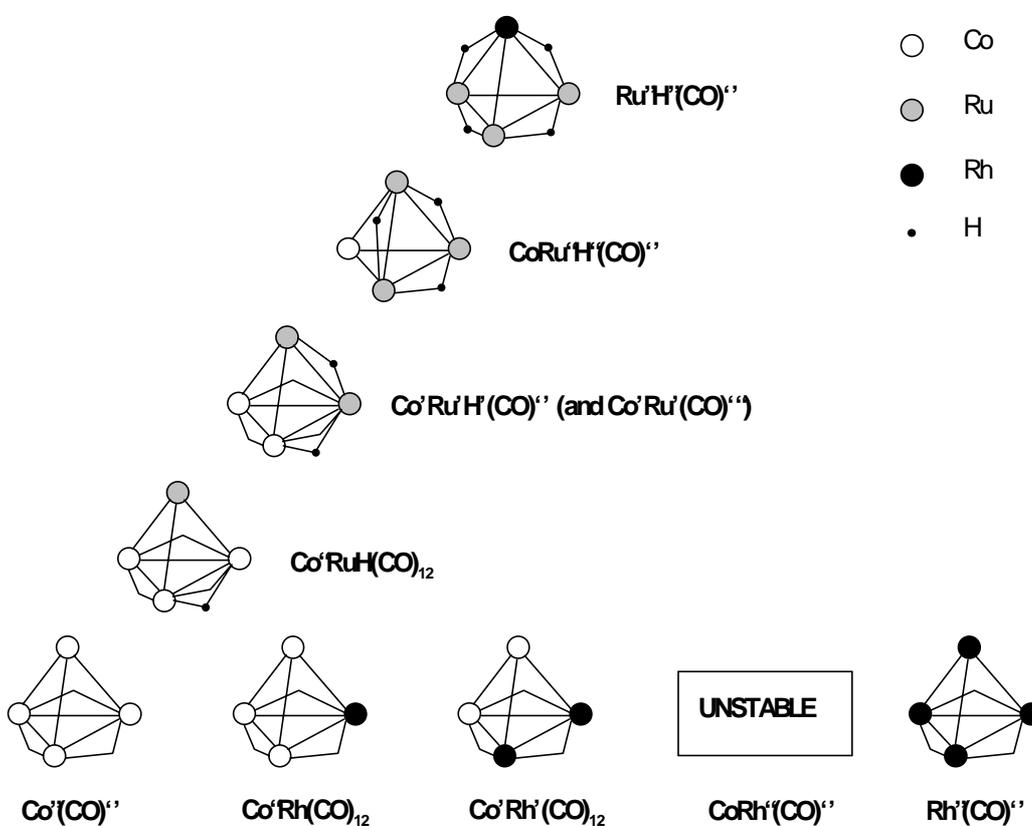

Figure 1. Cobalt-rhodium and cobalt-ruthenium carbonyl clusters used as catalyst precursors [33]. The terminal carbonyls are omitted for clarity.

2 PREPARATION AND CHARACTERIZATION OF CATALYSTS

2.1 PREPARATION OF THE CATALYSTS [I, II]

Except for the Co_4 and Rh_4 clusters, which were commercially available, all metal carbonyl clusters were prepared by published methods [13, 34 - 38]. The mono- and bimetallic carbonyl clusters were impregnated into Grace 432 silica (dried under vacuum at 600 °C/2h) in nitrogenated dichloromethane under deoxygenated atmosphere and the catalysts were dried slowly under vacuum at room temperature. The metal loading of all catalysts was 0.9 mmol/1 g SiO_2. To ensure that there was no contact with air, every step in the preparation was carried out using a glove box and vacuum line.

The refluxed catalysts used in the experiments investigating the effect of preparation method were prepared by using the same amounts of carbonyl clusters as in the preparation of impregnated catalysts. Carbonyl cluster and silica were refluxed in dried oxygen-free n-hexane under nitrogen atmosphere for 5 h. After cooling to room temperature, excess solvent was removed, and the catalyst was washed 5 - 10 times with n-hexane by means of a filter cannula until the solvent remained clear.

2.2 CHARACTERIZATION BY TEMPERATURE-PROGRAMMED REDUCTION TECHNIQUE [III, IV]

In the temperature-programmed reduction technique (TPR), a chemical reaction is monitored while temperature increases linearly in time. The technique can be applied to real catalysts and has the advantage of being experimentally simple and inexpensive in comparison with many of the spectroscopic techniques. Interpretation on a qualitative basis is rather straightforward. The first useful information that TPR provides is the temperature needed for the complete reduction of a catalyst [39]. Our TPR studies dealt with the decomposition of clusters on silica and with the properties of the catalysts.

During catalyst preparation at room temperature, precursors lose some of their carbonyl groups through ligand exchange with the hydroxyl groups of the support surface. The decarbonylation at room temperature depends on the stability of the precursor itself, as well as on the interaction of the precursor with the support. Since the precursors under study seems to be

stable at room temperature under inert atmosphere [34], the decarbonylation must be due to transformation of the cluster to hexanuclear form, or to the degradation of the cluster to subcarbonyls or metal through cluster-support interaction.

2.2.1 Experimental

TPR studies were carried out using a down-flow tubular quartz microreactor connected to a Balzers quadrupole mass spectrometer. Fresh impregnated catalyst was studied under flow of 3% H_2 in argon, and the temperature was ramped at a linear rate of 3 °C/min from 25 °C to 450 °C. The decomposition of clusters, occuring by the reaction shown in equation 2, was measured by the formation of carbon monoxide, carbon dioxide, methane and water and by the consumption of hydrogen

$$M'(CO)''/SiO' \xrightarrow{\;H' + \triangle\;} M^{0-II)}/SiO' + \begin{cases} \bullet\ CO \\ \bullet\ CH' (+ > C') \\ \bullet\ CO' \\ \bullet\ H'O \\ \bullet\ (Oxygenates) \end{cases} \qquad (2)$$
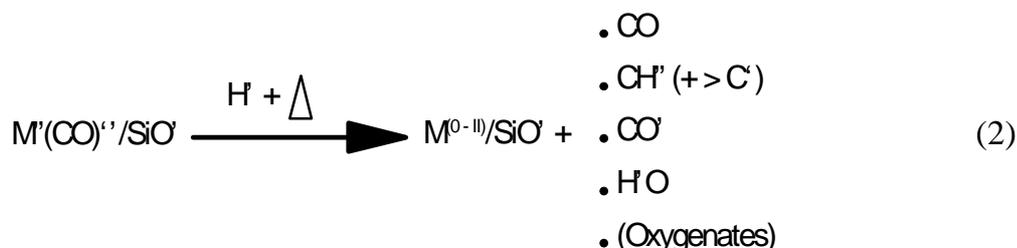
2.2.2 Cobalt -rhodium carbonyl clusters on silica [III]

The main reaction of all cobalt-rhodium catalysts was the decarbonylation of the clusters (Figure 2).

The amount and temperature of decarbonylation varied with the precursor: the amount of decarbonylation was greatest for Co_4 and least for Rh_4, and the peak maxima increased in temperature as follows: $Co_2Rh_2 = 123$ °C, $Co_3Rh = 125$ °C, $(Co_4+Rh_4) = 135$ °C, $Co_4 = 137$ °C and $Rh_4 = 178$ °C.

The degree of interaction between silica and the clusters determines the amount of decarbonylation occurring at higher temperatures [40]; when the interaction is weak, the decarbonylation is weak during preparation and occurs mainly later, above room temperature [41]. Since, as can be seen in Figure 2, the extent of decarbonylation above room temperature was greatest for Co_4/SiO_2, and less and similar for the other catalysts, we can

deduce that Co_4 interacts more weakly with the support than Rh_4 and bimetallic clusters do.
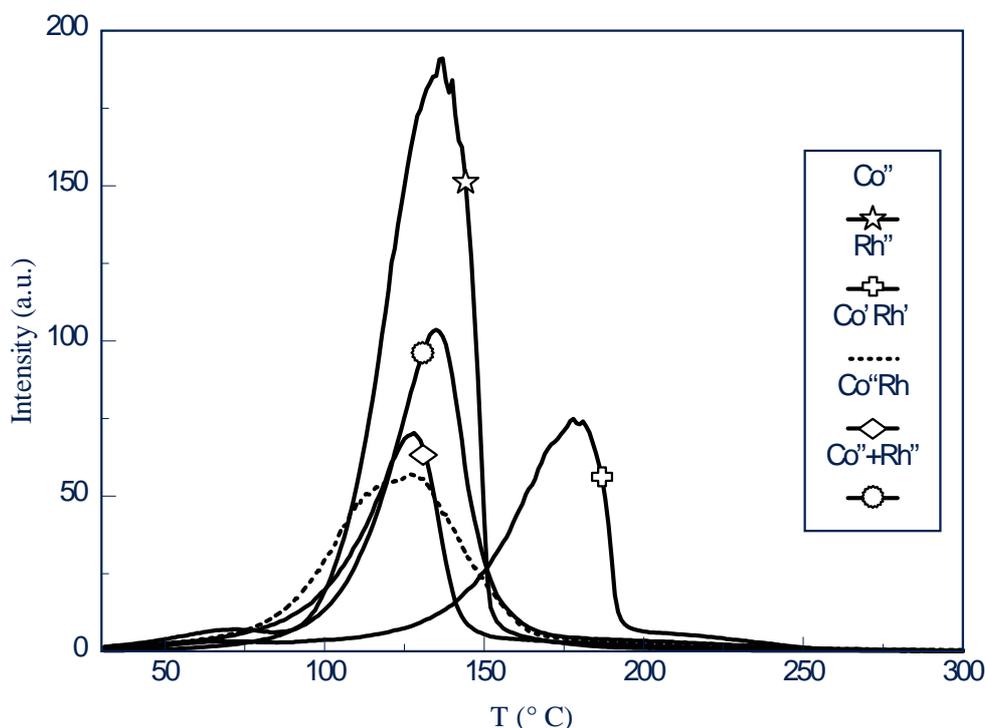
Figure 2. *Desorption of carbon monoxide during TPR of $Co_{4-n}Rh_n(CO)_{12}$ clusters on silica (r = 3 °C/min, T = 25 - 450 °, H_2/Ar = 3%) [III].*

In the bimetallic catalysts, the interaction between precursor and support occurred between rhodium species and silica, not between cobalt and silica. This means that most of the carbonyls bound to rhodium would have been lost during the preparation, at room temperature, leaving the carbonyl groups bound to cobalt species to be released above room temperature. Evidently rhodium has enriched on the surface of the silica and cobalt in the outer layer of the catalyst, in accordance with the results of van't Blik et al. [42]. A supporting conclusion is suggested by the significantly lower decarbonylation temperature for Co_4 and the bimetallic clusters than for Rh_4. Evidently the desorbed carbonyls are similar in nature for all cobalt-rhodium clusters on silica except Rh_4.

2.2.3 Cobalt-ruthenium carbonyl clusters on silica [IV]

The main reaction during the TPR of cobalt-ruthenium catalysts was decarbonylation of the cluster at well below 230 °C (Figure 3); the peak maxima were as follows: (Co_4+Ru_4) = 123 °C, $CoRu_3$ = 127 °C, $Co_2Ru_2(II)$

= 133 °C, Co_4 = 137 °C, $Co_2Ru_2(I)$ = 144 °C, Co_3Ru = 148 °C and Ru_4 = 185 °C.
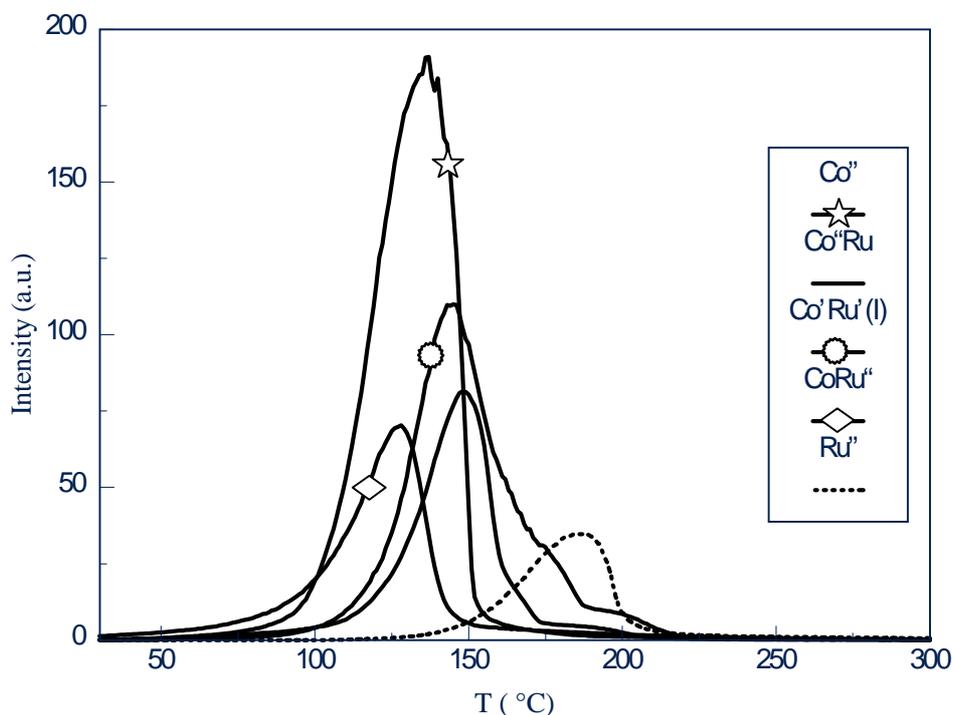
Figure 3. Desorption of carbon monoxide during TPR of $Co_{4-n}Ru_nH_n(CO)_{12}$ clusters on silica (r = 3 °C/min, T = 25 - 450 °, H_2/Ar = 3 %) [IV].

The decarbonylation of Ru_4/SiO_2 occurred at significantly higher temperature than the decarbonylation of Co_4/SiO_2 and the bimetallic catalysts, but at almost the same temperature as that of the Rh_4/SiO_2 catalyst. Thus, the stability of the Rh and Ru carbonyl species on the silica was similar, and greater than that of the cobalt carbonyl, in agreement with the results of Bor [43]. The temperature of decarbonylation of the bimetallic catalysts was not directly related to the amount of cobalt or ruthenium, and catalysts with equal metal ratio, $(Co_4+Ru_4)/SiO_2$, $Co_2Ru_2(I)/SiO_2$ and $Co_2Ru_2(II)/SiO_2$, decarbonylated at different temperatures.

At elevated temperatures the amount of decarbonylation was greatest for Co_4/SiO_2 and lowest for Ru_4/SiO_2, while for the other catalysts it was more or less similar. Since the clusters are fairly stable in solid form under inert atmosphere at room temperature, it would seem that ruthenium, like rhodium, interacts more strongly with silica than cobalt does.

2.3 CHARACTERIZATION BY FOURIER-TRANSFORM INFRARED SPECTROMETRY [III, IV]

One great advantage of infrared spectroscopy is that the technique can be used to study catalysts in situ. In the diffuse reflectance mode, samples can be measured as loose powders, so that not only is the tedious preparation of wafers unnecessary but, also, diffusion limitations associated with tightly pressed samples are avoided [39]. Thus, diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) is a suitable technique for studying heterogeneous catalysts in powder form.

Carbon monoxide on metals is the most thoroughly studied adsorption system in vibrational spectroscopy. The C-O stretching frequency is highly informative about the direct environment of the molecules and an excellent indicator of the way CO is bound to the substrate. However, the precise absorption frequency depends on the substrate metal, its surface structure and the CO coverage [39].

2.3.1 Experimental

The IR spectra were recorded with a Perkin Elmer model 1760X FT-IR spectrometer to which an in situ diffuse reflectance cell was coupled. To obtain better quality spectra, the samples were prepared by grinding a mixture of KBr and the catalysts. The spectra were measured by 100 scans (resolution 2 cm^{-1}) at intervals of 10 °C between 30 °C and 250 °C under flowing hydrogen or carbon monoxide. A background spectrum was recorded at each temperature from SiO_2 diluted with KBr, and this was subtracted from the absorption spectrum of the sample. The interfering bands of gas phase carbon monoxide were eliminated by subtracting the spectrum of gaseous CO on the SiO_2/KBr sample. Thus, the calculated spectra represent the absorbance of metal carbonyls supported on silica, or the absorbance of the species adsorbed on the metals. The spectra were converted to Kubelka-Munk units.

2.3.2 Cobalt-rhodium carbonyl clusters on silica [III]

Except for Rh_4, the bands observed for $Co_{4-n}Rh_n(CO)_{12}$ clusters on silica at room temperature agreed well with the bands of the clusters alone. In accordance with earlier findings [44], the Rh_4 cluster transformed almost completely to $Rh_6(CO)_{16}$ upon contact with silica. In addition, all bimetallic catalysts containing rhodium exhibited a band characteristic of the

hexanuclear cluster $Co_{6-n}Rh_n(CO)_{16}$ (n = 0 - 6) at approx. 1800 cm^{-1}, indicating that partial transformation had occurred.

When the catalysts were stored at room temperature under argon atmosphere, all clusters began to decompose to metal via the hexanuclear $Co_{6-n}Rh_n(CO)_{16}$ framework. The total rate of decomposition decreased in the order Rh_4 > bimetallic > Co_4. Transformation of Rh_4 to $Rh_6(CO)_{16}$ was very fast, but decomposition to metal took considerably more time, because only after 150 days was a new band, characteristic of CO coordinated to metal particles [44], found at 1860 cm^{-1}. In comparison, for the Co_4 cluster the transformation was extremely slow: after 290 days the band at 1795 cm^{-1} characteristic of $Co_6(CO)_{16}$ [45] was still very weak.

The thermal decomposition of $Co_{4-n}Rh_n(CO)_{12}$ clusters on silica was carried out under hydrogen. The complete loss and decomposition of Co_4 occurred well below 120 °C. The decomposition of the other clusters occurred similarly, but above 120 °C, as shown for Co_2Rh_2 in Figure 4, two weak bands could be observed at 2026 - 2037 cm^{-1} and 1723 - 1750 cm^{-1}, both of them typical for metal covered with a layer of CO. The higher band was assigned to terminal and the lower one to bridged-type CO.
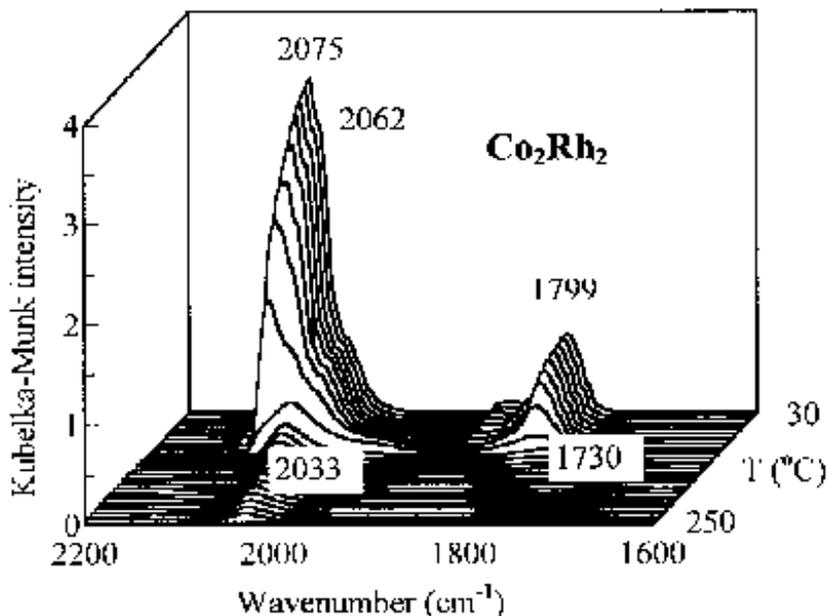

Figure 4. The decomposition of Co₂Rh₂ cluster on silica under hydrogen atmosphere [III].

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The results suggest that the thermal decomposition of $Co_{4-n}Rh_n(CO)_{12}$ clusters on silica takes place at approx. 120 - 150 °C. This is slightly lower temperature than suggested by the TPR experiments, but the difference probably is due to the different experimental procedure, the rate of heating for example.

Thermal decomposition of Co_4 and Rh_4 on silica was also carried out under carbon monoxide. The stability of the clusters was clearly enhanced in the presence of CO, and the original bands were well retained up to a much higher temperature than under hydrogen. Huang et al. [46] have also found that the original structure of the cluster is more stable under CO than under hydrogen.

2.3.3. Cobalt-ruthenium carbonyl clusters on silica [IV]

IR spectra showed most of the $Co_{4-n}Ru_nH_n(CO)_{12}$ and $Co_2Ru_2(CO)_{13}$ clusters to have lost weak bands during catalyst preparation, while retaining the strong ones at the original wavenumbers or slightly shifted. It is noteworthy, however, that many bands in the spectra of the catalysts were quite wide, because several different surface species may exist simultaneously, and the spectrum is a composite of the superimposed spectra of several unknown species.

When the Co_4/SiO_2 catalyst was stored at room temperature under argon atmosphere the Co_4 on the surface slowly transformed to $Co_6(CO)_{16}$, which then decomposed in minor amount to metallic cobalt covered by CO. In contrast to the Co_4 and other $Co_{4-n}Rh_n(CO)_{12}$ clusters, the ageing of $Co_{4-n}Ru_nH_n(CO)_{12}$ and $Co_2Ru_2(CO)_{13}$ clusters on silica did not proceed through hexanuclear intermediates. The Ru_4, $CoRu_3$ and Co_3Ru clusters on silica retained their original spectra during ageing, which means that they were stable and no decomposition occurred. In contrast, the spectra of catalysts $Co_2Ru_2(I)/SiO_2$, $Co_2Ru_2(II)/SiO_2$ and $(Co_4+Ru_4)/SiO_2$ decayed fast, indicating the decomposition of clusters. Because the original band positions were retained, however, part of the clusters may have remained unaffected, and the decomposition products may have covered the clusters and in this way reduced the band intensities.

The thermal decomposition of $Co_{4-n}Ru_nH_n(CO)_{12}$ and $Co_2Ru_2(CO)_{13}$ clusters on silica was carried out under hydrogen. In the case of Co_3Ru/SiO_2, band intensities decreased smoothly, and then more rapidly at approx. 140 °C in accordance with the TPR result. Finally, at 250 °C only small and broad bands in the linear (2011 cm^{-1} and 1977 cm^{-1}) and bridged (1860 cm^{-1}) region were detected.

The thermal decomposition of the $Co_2Ru_2(I)$, $Co_2Ru_2(II)$ and (Co_4+Ru_4) clusters on silica occurred fairly smoothly and slowly and all bands almost disappeared at 250 °C, leaving only a weak single band at 2012 - 2017. This single band could be assigned to linear CO adsorption on a fully reduced mono- or bimetallic particle on the surface [47].

The thermal decomposition of $CoRu_3$ and Ru_4 clusters on silica was much more complicated than the decomposition of other clusters. In the case of $CoRu_3/SiO_2$ catalyst (Figure 5), when the temperature rose towards 130 °C the band intensities increased rapidly and drastically, indicating the formation of oxidized ruthenium species such as $[Ru^{2+}(CO)_2]$, $[Ru^{2+}(CO)_2]_n$ and $[Ru^{2+}(CO)_3]_n$, as suggested by Asakura et al. [48]. The intensity of the bands suddenly decreased again at 140 °C, and thereafter decreased smoothly with increasing temperature until finally only two bands were left, at 2069 cm^{-1} and 2006 cm^{-1}, assigned to $[Ru^{2+}(CO)_2]$ species. In the case of Ru_4/SiO_2 catalyst, bands reached a maximum at 150 °C indicating the existence of $[Ru^{2+}(CO)_2]$ and $[Ru^{2+}(CO)_2]_n$ species. The bands prevalent at 150 °C were also detected at 250 °C, although the intensities were considerably reduced. In addition, thermal decomposition of $CoRu_3$ and Ru_4 clusters on silica appears to be only partial since the final band intensities at 250 °C were quite strong.
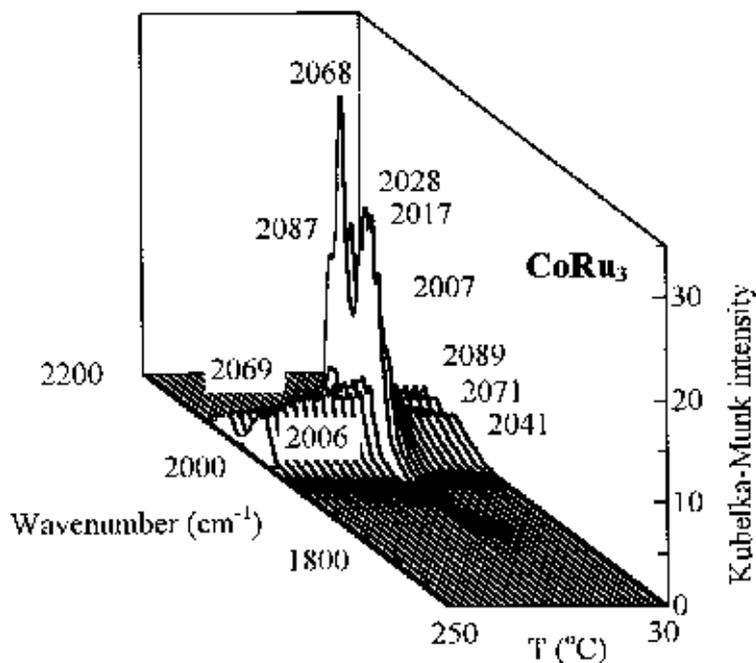

Figure 5. Decomposition of the CoRu₃ cluster on silica under hydrogen atmosphere [IV].

3 FISCHER-TROPSCH SYNTHESIS

3.1. EXPERIMENTAL [I]

Fischer-Tropsch synthesis was carried out in a modified Sotelem LCT-570 continuous flow fixed bed tubular reactor equipped with an on-line analysing system. The catalyst was loaded into the reactor in a glove box under deoxygenated and dried argon atmosphere. The amount of catalyst used in reaction tests was 1.0 g (2.75 ml). The reactor was connected to the reactor system without contact with air. Just before use, the catalyst was reduced in situ under flowing hydrogen at 300 °C/2h (r = 2 °C/min). After reduction, the catalyst was slowly cooled to 190 °C under hydrogen. The reaction was initiated by changing the gas flow to synthesis gas and by increasing the pressure of the reactant gas ($CO/H_2/Ar = 3/6/1$) to the desired reaction pressure. The reaction pressure was kept constant at 2.1 MPa, while the flow rate of the synthesis gas was varied between 2 l/h and 40 l/h. The typical reaction temperature was 233 °C. However, the temperature dependence of the activity and selectivity was studied by varying the temperature between 190 °C and 290 °C.

3.2. ACTIVITY AND SELECTIVITY OF CATALYSTS

3.2.1. Cobalt-ruthenium carbonyl clusters on silica [I]

All the $Co_{4-n}Ru_nH_n(CO)_{12}$ and $Co_2Ru_2(CO)_{13}$ clusters on silica were active in Fischer-Tropsch synthesis at 233 °C and 2.1 MPa pressure (Figure 6), but the activity decreased in the cluster order $Ru_4 > Co_4 = Co_2Ru_2(II) > CoRu_3 > Co_3Ru > Co_2Ru_2(I) > (Co_4+Ru_4)$. The monometallic Ru_4/SiO_2 and Co_4/SiO_2 catalysts tended to exhibit higher activity than the bimetallic ones, and the activity passed through a minimum when the Co/Ru ratio was 1:1. These results differ from those of Xiao et al. [14]. In their experiments the activity of the bimetallic catalysts increased with the increasing molar ratio of Co/Ru, and the monometallic cobalt and ruthenium catalysts were the least active. The primary reason for this difference is the pretreatment of the catalysts. Namely, Xiao et al. [14] oxidized their catalysts under O_2 before in situ reduction, whereas in the present study catalysts were decomposed under hydrogen. In addition, the activity of $Co_2Ru_2(II)/SiO_2$ was exceptional in being equal to that of Co_4/SiO_2 and much higher than that of the corresponding $Co_2Ru_2(I)/SiO_2$ catalyst. This extraordinary behaviour may have something to do with the composition of the cluster: all $Co_{4-n}Ru_nH_4(CO)_{12}$ clusters have an equal number of hydrogen and ruthenium atoms in their molecular structure, but in $Co_2Ru_2(II)$, two hydrogen atoms are replaced by a carbonyl group [35]. This lack of

hydrogen in the molecular structure of the cluster may cause cobalt to enrich on the surface in the $Co_2Ru_2(II)/SiO_2$ catalyst [IV].
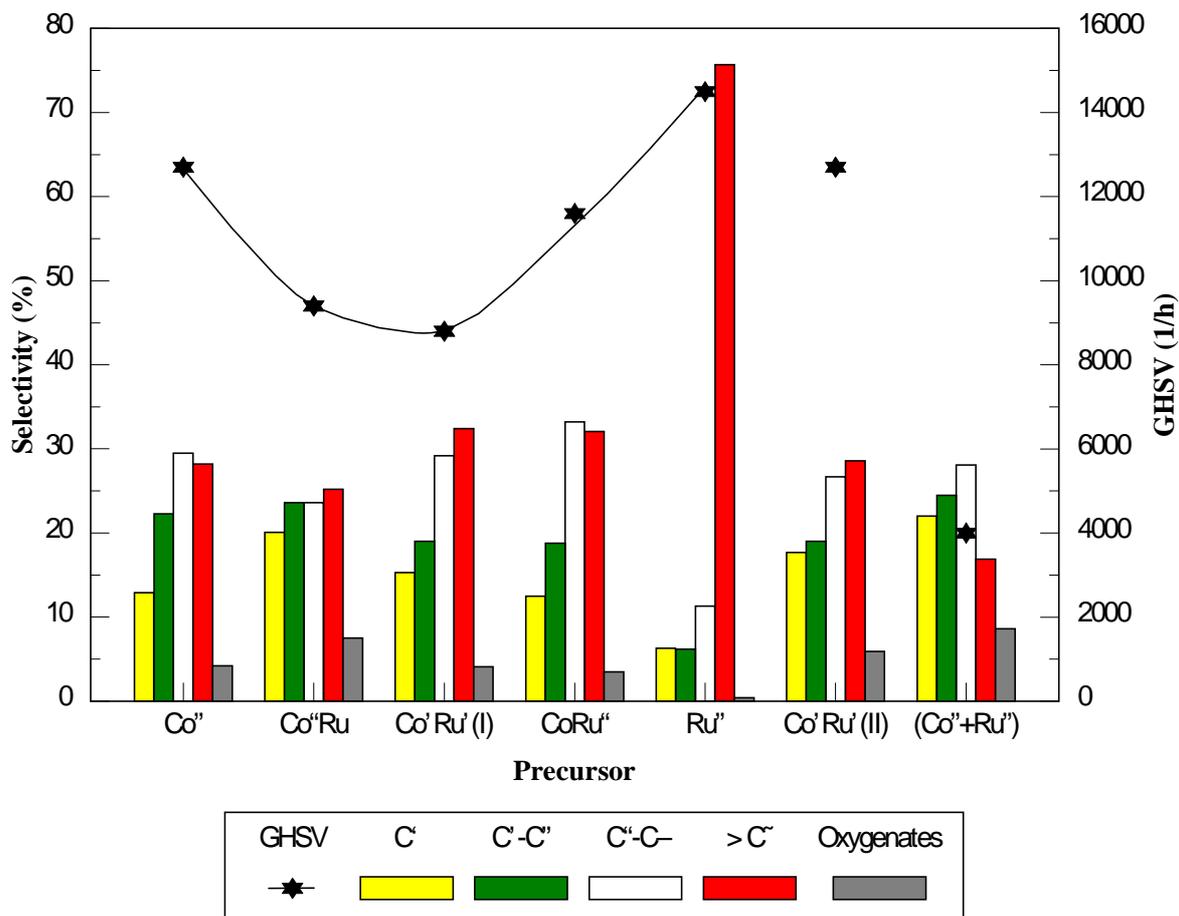
Figure 6. Activities and selectivities of $Co_{4-n}Ru_nH_n(CO)_{12}$ and $Co_2Ru_2(CO)_{13}$ clusters on silica in Fischer-Tropsch synthesis.

All catalysts had a clear tendency to produce hydrocarbons and in all cases the selectivity for hydrocarbons was more than 90 %. The chain-growth probability α was within 0.72 - 0.82 for all $Co_{4-n}Ru_nH_n(CO)_{12}$ and $Co_2Ru_2(CO)_{13}$ clusters on silica except Ru_4, for which α was 0.91. The Shulz-Flory equation, which says that the maximum mass selectivity for the C_5 - C_{11} cut is 48 % [49], holds fairly well for the $Co_{4-n}Ru_nH_n(CO)_{12}/SiO_2$ and $Co_2Ru_2(CO)_{13}/SiO_2$ catalysts.

The $Co_{4-n}Ru_nH_n(CO)_{12}/SiO_2$ and $Co_2Ru_2(CO)_{13}/SiO_2$ catalysts formed only small amounts of oxygenates, less than 10 % in every case. The selectivity for oxygenates was highest when the Co/Ru ratio in the cluster was 3:1 (7.5 C-%) and lowest when the cluster contained only ruthenium (0.4 C-%). However, the $(Co_4+Ru_4)/SiO_2$ catalyst prepared from two monometallic clusters had the highest selectivity of all for oxygenated compounds (8.6 C-%) whereas the catalysts prepared from one cluster with equal metal ratio,

$Co_2Ru_2(I)/SiO_2$ and $Co_2Ru_2(II)/SiO_2$, had much lower selectivity, 4.1 and 5.9 C-%, respectively. Apparently the selectivity of Co-Ru catalysts is influenced by both the metal ratio of the catalysts and the internal nature of the cluster.

3.2.2. Cobalt-rhodium carbonyl clusters on silica [I]

All rhodium-containing $Co_{4-n}Rh_n(CO)_{12}$ clusters on silica have fairly weak activity in Fischer-Tropsch synthesis at 233 °C and 2.1 MPa pressure (Figure 7) and the activity decreases in the order $Co_4 > Co_3Rh > Rh_4 > Co_2Rh_2 \geq (Co_4+Rh_4)$. The activities of the bimetallic catalysts did not lie between those of the monometallic Co_4/SiO_2 and Rh_4/SiO_2, and the least active catalysts were those with Co/Rh ratio 1:1. These results differ from the findings of Ceriotti et al. [29], who found the Co_2Rh_2/Al_2O_3 catalyst to be more active than Rh_4/Al_2O_3. The difference in the results may be due to the different metal loading and support as well as the lower reaction pressure used in their experiments.
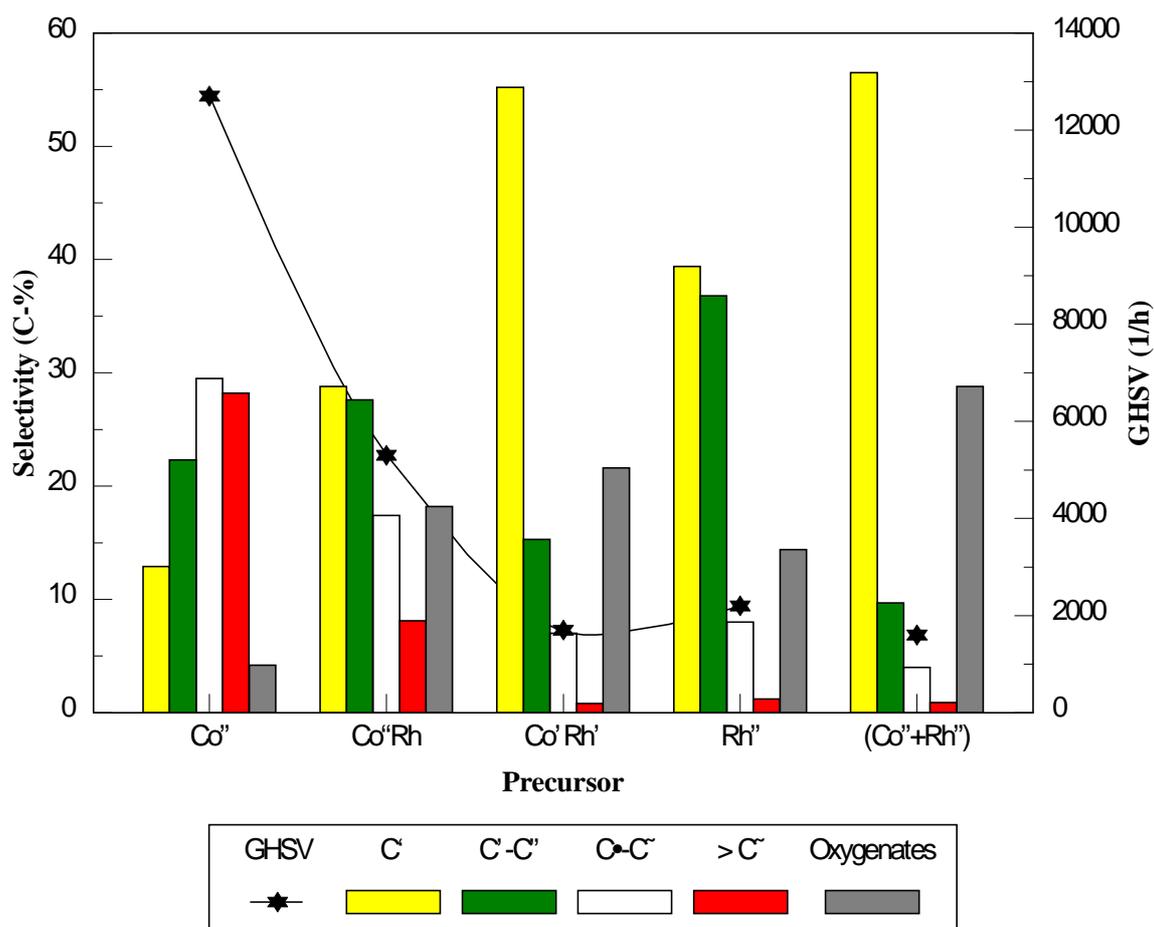

Figure 7. Activities and selectivities of $Co_{4-n}Rh_n(CO)_{12}$ clusters on silica in Fischer-Tropsch synthesis.

All $Co_{4-n}Rh_n(CO)_{12}$ clusters on SiO_2, except Co_4, have a strong tendency to produce methane as well as other light hydrocarbons. The chain-growth probability α decreased with the decreasing number of cobalt atoms in the cluster, i.e. it correlated very well with the number of cobalt atoms. The selectivity for oxygenates was relatively high, and here the bimetallic catalysts produced more oxygenated compounds than the monometallic ones, with the maximum produced with a 1:1 ratio of Co/Rh. It should be noted, however, that as the selectivity for oxygenates increased, the activity of the catalyst decreased.

In addition, the product distribution of oxygenates was sensitive to the Co/Rh ratio in the catalysts. Only ethanol was present in significant amount in all runs, and selectivity for it changed drastically with the number of rhodium atoms in the cluster. The maximum selectivity for ethanol was obtained with the Co_2Rh_2/SiO_2 and $(Co_4+Rh_4)/SiO_2$ catalysts. Formation of methanol was also greatest for the bimetallic than the monometallic catalysts. The Rh_4/SiO_2 catalyst produced a lot of acetic acid and ethyl acetate, whereas the other catalysts produced them in much smaller amount or not at all. Evidently the yield of oxygenates and product distribution do not solely depend on the metal ratio of the catalyst, because Co_2Rh_2/SiO_2 and $(Co_4+Rh_4)/SiO_2$ catalysts with equal metal ratio behaved differently: $(Co_4+Rh_4)/SiO_2$ produced more oxygenates and especially higher alcohols.

3.3. CATALYST DEACTIVATION [I, II]

A clean catalyst surface begins to deactivate as soon as it encounters reactant molecules. Usually, this initial deactivation occurs too fast to be detected by a conventional reactor system such as used in these studies. However, a steady state is achieved after the deactivation of the most unstable active sites, which play no further role in the catalysis [50]. The decay of relative activity (C_t/C_i where C_i = steady state conversion and C_t is conversion at time t) demonstrates the amount of deactivation.

After 75 hours of reaction the order of the relative activity of $Co_{4-n}Rh_n(CO)_{12}$ clusters impregnated on silica was the following: $Co_4 = Rh_4 > (Co_4+Rh_4) > Co_2Rh_2 > Co_3Rh$ (Figure 8). The monometallic catalysts were the most resistant to deactivation and the bimetallic catalysts deactivated rapidly; for example, after 75 reaction hours only 43 % of the initial activity of the Co_3Rh/SiO_2 catalysts remained. The activation is probably caused by coking and the combined sites of cobalt and rhodium appear to play an important role in the deactivation process.

The degree of deactivation of $Co_{4-n}Ru_nH_n(CO)_{12}/SiO_2$ catalysts prepared by impregnation methods [I] decreased in the precursor order $Ru_4 > Co_2Ru_2(I) > CoRu_3 \approx Co_3Ru \approx (Co_4+Ru_4) > Co_4$ (Figure 8). Initial deactivation was relatively fast, but further deactivation within 25 and 75 h of reaction was moderate. The least resistant against deactivation was Ru_4/SiO_2, and its activity declined most dramatically; after 25 h reaction time only 40 % of the initial activity remained. Most resistant against deactivation was Co_4/SiO_2, and all bimetallic cobalt-ruthenium catalysts fell in between the monometallic catalysts in terms of deactivation. These results indicate that the deactivation process is closely related to the presence of ruthenium, and probably the high hydrocarbons, such as waxes, plugged the small pores and blocked the active metal inside the pores. It is well known that when catalysts operate under wax-producing conditions the pores of the catalyst are likely to fill with wax very fast and, for example, in the SASOL fixed bed reactors about 50 % of the hydrocarbon product inside the reactor is in liquid state. The liquid waxes slow down the rate of diffusion of the reactant within the catalyst pores and so slow down the rate of reaction [49].
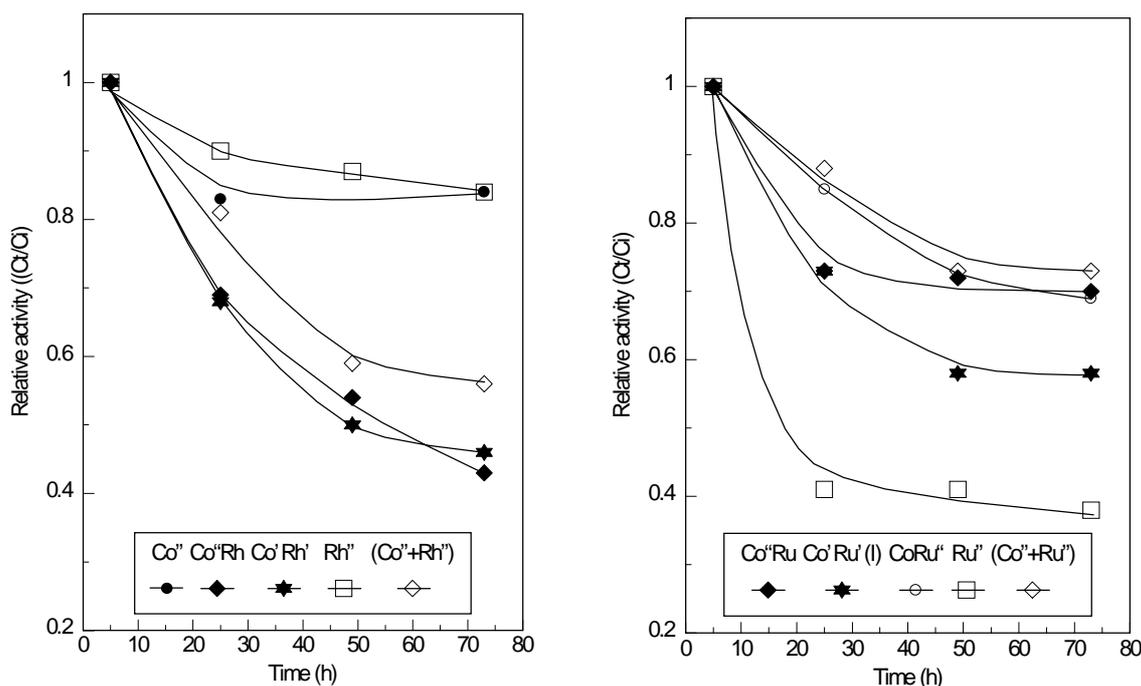
Figure 8. Deactivation of $Co_{4-n}Rh_n(CO)_{12}$ and $Co_{4-n}Ru_nH_n(CO)_{12}$ clusters on silica at 233 °C and 2.1 MPa in Fischer-Tropsch synthesis [I].

After 75 h reaction time, the order of relative activity of $Co_{4-n}Ru_nH_n(CO)_{12}/SiO_2$ and $Co_2Ru_2(CO)_{13}/SiO_2$ catalysts prepared by reflux methods [II] was in cluster order $CoRu_3 > (Co_4+Ru_4) > Co_2Ru_2(I) \approx Co_3Ru > Ru_4 > Co_2Ru_2(II)$. In contrast to the impregnated catalysts, the deactivation of refluxed catalysts was smooth and a state of more or less

constant activity was not obtained during the test. However, even though the deactivation rate is different, the mechanism of deactivation is probably the same as for the impregnated catalysts; heavy hydrocarbons plugged some of the active sites of the catalysts.

3.4. EFFECT OF REACTION TEMPERATURE [I]

Typically, when the reaction temperature increases, the product selectivity shifts to lighter molecular mass compounds and at the same time selectivity for oxygenates mainly decrease [49]. In the present studies the effect of reaction temperature on activities and selectivites was determined at 190 - 290 °C and constant pressure (2.1 MPa).

The effect of reaction temperature on activity and selectivity for $Co_{4-n}Rh_n(CO)_{12}$ clusters impregnated on silica was fairly small until 250 °C, but above 260 °C the activity increased sharply with temperature as shown by the example in Figure 9. Selectivity for methane and oxygenates depended strongly on temperature: with higher temperatures, selectivity for methane increased and selectivity for oxygenates decreased, as pointed out in the literature [49].
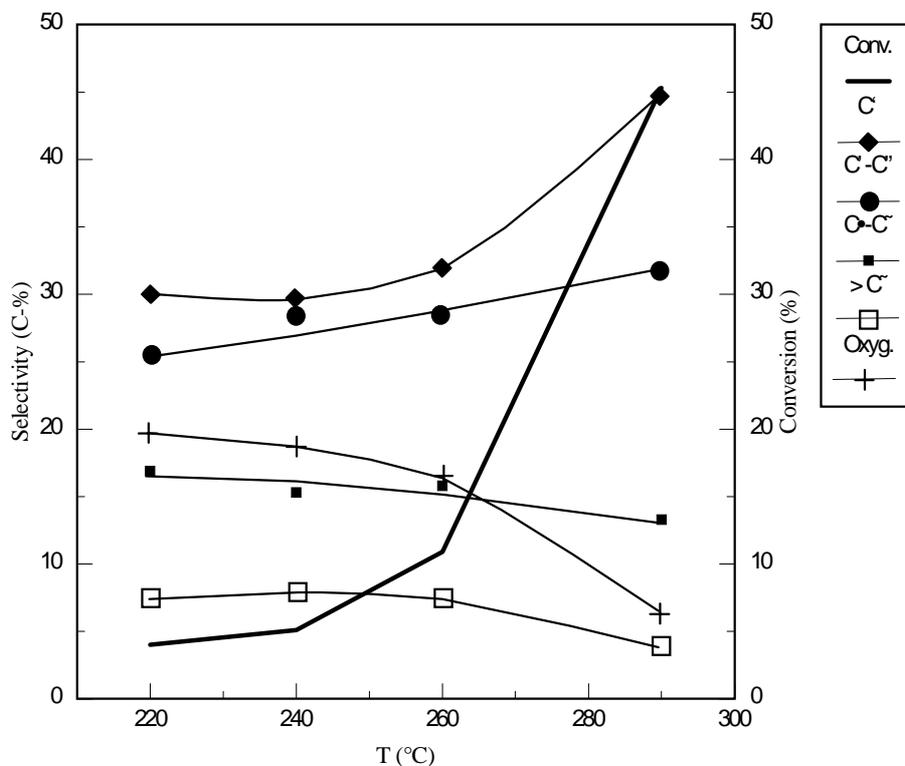

Figure 9. Effect of reaction temperature on the activity and selectivity of the Co_3Rh/SiO_2 catalyst [I].

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The oxygenate most affected was ethanol, in agreement with the findings of Ceriotti et al. [29]; although the selectivity for other oxygenates also decreased with increasing temperature, the temperature dependence was much less important than for ethanol. This may indicate that the formation of other oxygenates than ethanol follows a different or at least parallel route which is less temperature sensitive.

The activity of $Co_{4-n}Ru_nH_n(CO)_{12}$ and $Co_2Ru_2(CO)_{13}$ clusters impregnated on silica increased dramatically with temperature even below 250 °C. Selectivities for methane and C_2-C_4 hydrocarbon increased, while selectivities for C_5-C_8 hydrocarbons remained constant and those for C_{8+} hydrocarbons decreased moderately. These catalysts did not produce a lot of oxygenates under any conditions, and selectivity for oxygenates remained almost constant at every temperature. Contrary to this, Xiao et al. [18] have found that, on $CoRu_3/SiO_2$ catalyst, selectivity for oxygenates decreases considerably with increasing temperature. This difference in the results may be due to the lower metal loading, different pretreatment of the catalyst and lower reaction pressure used in their experiments. It is notable that, even though in our experiments the selectivity for oxygenates remained almost constant with increasing temperature, the yield of oxygenates increased markedly because of the higher conversion.

3.5. EFFECT OF PRETREATMENT ATMOSPHERE [V]

The pretreatment atmosphere has been found significantly to influence the stability of carbonyl clusters on silica, as well as the dispersion and activity of the catalysts. Carbonyl clusters decompose easily when the pretreatment atmosphere is inert gas, oxygen or hydrogen, whereas they stabilize and their decomposition is delayed in the presence of carbon monoxide [18, 42, 46, 51-53, III]. In the present studies the effect of pretreatment atmosphere on the Co_4/SiO_2 and Rh_4/SiO_2 catalysts was determined with hydrogen or carbon monoxide.

The extent of reduction for Co_4/SiO_2 was 18% and 13% under CO and hydrogen, respectively, whereas Rh_4/SiO_2 was totally in metallic form in both cases. Thus, the extent of reduction was not sensitive to the pretreatment atmosphere where this was CO or hydrogen. However, the hydrogen uptake was less for the catalysts decomposed under CO than for those decomposed under hydrogen. The lower uptake is related to the carbon coverage, and some of the active metal sites became encapsulated with carbidic carbon when the cluster on silica were decomposed under CO (Table 1).

Table 1. Characteristics of the Co_4/SiO_2 and Rh_4/SiO_2 catalysts after pretreatment in H_2 and CO atmospheres [V].

Catalyst	Pre-treatment atmosphere	H_2 uptake (μmol/g)	Reduction (%)	GHSV (h^{-1})	Oxygen-ates (C-%)	Particle size (nm)
Co_4/SiO_2	H_2	56.8	13	12700	4.2	n.a.
Co_4/SiO_2	CO	1.7	18	650	1.5	n.a.
Rh_4/SiO_2	H_2	145.7	100	2200	14.4	4
Rh_4/SiO_2	CO	48.6	100	1700	32.3	4

n.a. = not available

In our studies the original FT-IR spectra for Co_4/SiO_2 and Rh_4/SiO_2 were much better preserved when thermal treatment was under CO rather than hydrogen; band intensities were lower than initial ones, but the shape of the spectrum was well retained. Evidently, the partially retained structure of the carbonyl clusters under CO facilitates the formation of small metal particles. In agreement with this, Theolier et al. [44] and Bilhou et al. [54] suggest that since the shapes and intensities of the bands for the metallic rhodium particles and $Rh_6(CO)_{16}$ are closely similar, the size of the particles must be very small. Furthermore, in the present work the metal particle size distribution was broader when Rh_4/SiO_2 was decomposed under CO than when it was decomposed under hydrogen, although the weighted average particle size was approximately 4 nm in both cases.

The activity of Co_4/SiO_2 collapsed and selectivity was shifted towards methane when hydrogen was replaced by carbon monoxide in pretreatment. The inactive carbonaceous residues permanently blocked the active sites, causing the performance of the catalyst to deteriorate drastically. This is in agreement with the report of Nakamura et al. [55] that, when the disproportionation of CO is performed on Co/Al_2O_3 catalyst at 230 °C, the predominant species is carbidic carbon. With increasing temperature, the carbidic carbon is transformed to graphitic carbon, which is not reactive below 400 °C.

In the case of Rh_4/SiO_2, the activity of the catalyst was slightly lower when it was decomposed under carbon monoxide than when it was decomposed under hydrogen. This result confirms that carbonaceous residues had blocked some of the active sites. However, the selectivity for oxygenates, and particularly for ethanol and ethylacetate, was significantly higher when the pretreatment atmosphere was CO rather than hydrogen. This provides further support for the speculation that the catalyst treated under CO has

more small metal particles than its hydrogen treated counterpart, because highly dispersed Rh-based catalysts are known to be effective for the formation of oxygenates, and especially ethanol [56].

3.6 EFFECT OF METHOD OF PREPARING THE CATALYST [II]

The final part of the work was a study on the applicability of a reflux method for the anchoring of $Co_{4-n}Ru_nH_n(CO)_{12}$ and $Co_2Ru_2(CO)_{13}$ clusters on silica. Loosely bound metal species were washed off the support with excess of solvent.

The final metal contents of the refluxed catalysts were significantly lower than expected from the amounts of cluster used. The result can be explained by the poor interaction of the cluster with silica [57], so that most of the metal was easily washed off the surface. Nevertheless, the metal loading of the refluxed catalysts was higher than that of the corresponding impregnated catalysts after those were washed. In accordance with results of alumina-supported carbonyl catalysts [58], this indicates that the amount of tightly bound metal can be increased by the reflux method. In both the impregnated and refluxed catalysts, the presence of ruthenium is essential for the adsorption of cobalt on silica because the cobalt evidently is bound to ruthenium already attached on the surface and not to the silica surface itself.

The protons in hydridocarbonyls ($Co_{4-n}Ru_nH_n(CO)_{12}$) appear to have a role in the adsorption of the metal species on the support; for in the absence of proton the interaction of the metals and silica seems to be weaker. The hydridocarbonyl cluster $Co_2Ru_2(I)$ interacts more strongly with silica than does its counterpart $Co_2Ru_2(II)$ cluster, and the final metal contents on the catalysts are 0.45 and 0.16 mmol/1g SiO_2, respectively.

Compared with the corresponding impregnated catalysts, the refluxed catalysts generally showed higher activity in CO hydrogenation per metal atom, indicating a difference in the state of the metal atoms on silica. However, since the metal content of the refluxed catalysts was significantly lower than that of the impregnated ones, the overall reaction rates over refluxed catalysts were also lower. The activity was minimum when the Co/Ru ratio in the cluster was 1:1.

The main product of the refluxed $Co_{4-n}Ru_nH_n(CO)_{12}/SiO_2$ and $Co_2Ru_2(CO)_{13}/SiO_2$ catalysts was hydrocarbon (> 90 C-%) and the product distribution more or less faithfully followed the Schulz-Flory equation. In general, the product produced over the refluxed catalysts was lighter than

that produced over the impregnated catalysts, and the proportion of the C_5-C_8 hydrocarbons was increased with respect to the C_{8+} hydrocarbons. The selectivity for oxygenates was between 3 and 7 C-%; the proportion of oxygenates such as acetaldehyde, acetic acid and esters was relatively high and in many cases they instead of alcohols, constituted the main part of the oxygenates. A similar distribution of oxygenates has been observed with rhodium catalysts [28] and with highly dispersed cobalt catalysts promoted with alkali metal cations [59].

4 CONCLUSIONS

Monometallic Co_4/SiO_2 and Ru_4/SiO_2 catalysts were the most active in Fischer-Tropsch synthesis, and all catalysts produced mainly hydrocarbons, when $Co_{4-n}Ru_nH_n(CO)_{12}$ clusters were used as catalyst precursors. The lowest activity was found for bimetallic catalysts with 1:1 ratio of Co/Ru, excepting $Co_2Ru_2(CO)_{13}/SiO_2$ catalyst, which was equal in activity to $Co_4(CO)_{12}/SiO_2$. Deactivation of the catalysts was associated with the presence of ruthenium, and the least resistant to deactivation was monometallic $Ru_4(CO)_{12}/SiO_2$, while the most resistant was $Co_4(CO)_{12}/SiO_2$.

All rhodium-containing $Co_{4-n}Rh_n(CO)_{12}$ clusters on silica exhibited fairly weak activity in Fischer-Tropsch synthesis, and the least active catalysts were those with Co/Rh ratio 1:1. All catalysts produced mainly hydrocarbons but also significant amounts of oxygenates. It should be noted, however, that when the selectivity for oxygenates increased, the activity of the catalysts decreased. Monometallic $Rh_4(CO)_{12}/SiO_2$ catalyst was the most resistant against deactivation, and it seems that the deactivation process is related to the presence of bimetallic sites.

The effect of temperature on the catalysts followed a well known trend: when the temperature increased, product selectivity shifted to lighter molecular mass compounds and selectivity for oxygenates mainly decreased.

When $Co_4(CO)_{12}/SiO_2$ was pretreated under carbon monoxide and the active sites of the catalyst became encapsulated with carbidic carbon, the catalyst was almost inactive. After the same treatment of the $Rh_4(CO)_{12}/SiO_2$ catalyst, the activity remained virtually unchanged and the selectivity for oxygenates increased. In addition, treatment with carbon monoxide facilitated the formation of small rhodium particles on the $Rh_4(CO)_{12}/SiO_2$ catalyst.

Compared with the corresponding impregnated catalysts, refluxed catalysts generally showed higher activity in Fischer-Tropsch synthesis per metal atom. Since the metal content was significantly lower in the refluxed catalysts, however, the overall reaction rates over refluxed catalysts were lower.

In the bimetallic catalysts, the interaction probably occurred between the rhodium species and silica, and between ruthenium species and silica, not

between cobalt and silica. In other words, rhodium and ruthenium interact more strongly with silica than cobalt does.

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