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Cobalt and ruthenium-cobalt catalysts in CO hydrogenation and hydroformylation

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Abstract

Cobalt and ruthenium-cobalt catalysts prepared from various precursors were studied in the activation of CO using CO hydrogenation and vapour phase hydroformylation as test reactions. The characteristics and activity were related to the precursor, composition, promoters and the method of preparation.

Catalysts prepared from carbonyls exhibited the highest activity in CO hydrogenation. In addition to hydrocarbons, $Co_2(CO)_8/SiO_2$ had a high (20%) selectivity for oxygenates such as alcohols and esters. Likewise, the $Co_2(CO)_8/SiO_2$ catalyst was active in the hydroformylation of ethene, whereas the conventional cobalt catalysts prepared from inorganic salts were virtually inactive in this reaction.

Promotion by alkali or alkaline earth cations affected the performance of the $Co_2(CO)_8/SiO_2$ catalyst significantly: the activity decreased in both CO hydrogenation and ethene hydroformylation, but at the same time the selectivity for oxygenates and oxo-products, respectively, was tremendously increased. An exceptionally high selectivity for propanoic acid (47%) was observed on an alkaline earth oxide promoted $Co_2(CO)_8/SiO_2$.

The results for ruthenium containing catalysts indicated that the precursor and/or the combination of metals significantly influenced the interaction of the catalytic species with the support. The method of preparation also had a profound effect on the attachment of catalytic species to the support and their reducibility. In addition, the pretreatment exerted a significant influence on the catalyst, since the surface was restructured during the pretreatment resulting in changes in/losses of the active sites. As a result of the sensitivity to preparation, the performance of the catalysts differed significantly in CO hydrogenation, both in terms of activity and selectivity. Interestingly, the Co-Ru/SiO_2 catalyst

prepared by ionic adsorption exhibited unique selectivity in the Fischer-Tropsch synthesis, pronounced formation of methanol, compared with similar catalyst compositions prepared by impregnation or reflux methods.

In all, the work clearly demonstrated the strong interrelation of catalyst preparation and performance. It also indicated that catalysts with very unusual performance could be prepared, particularly from $Co_2(CO)_8$ precursor. The commercial applicability of all the carbonyl based catalysts is, however, limited by their air sensitive nature and by the losses occurring during the catalyst pretreatment. Thus, the catalysts with a less sensitive preparation method but nevertheless unique characteristics, such as Co-Ru/SiO_2 prepared by ionic adsorption, appear more interesting in the light of further development work.

Preface

This research was carried out at VTT Chemical Technology during the years 1990–1998. I wish to thank VTT Chemical Technology for the excellent working facilities. Part of the experimental work was carried out at the National Chemical Laboratory for Industry in Tsukuba, Japan. I am very grateful to the Agency of Industrial Science and Technology (AIST) and Professor Veikko Komppa for the opportunity to work in Japan, which started a new fruitful and enjoyable era in my life.

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I wish to thank my brother, father and grandmother for all their love and support. I also believe that my late mother and grandfathers knew how extremely important they were to me. Finally, to my wife Päivi I wish to express my deepest gratitude for her understanding, patience and love during these years.

Espoo, May 1998

Matti Reinikainen

List of publications

The thesis is based on the following publications which are referred to by their Roman numerals:

I Takeuchi, K., Hanaoka, T., Matsuzaki, T., Reinikainen, M. and Sugi, Y., Selective vapor phase hydroformylation of ethylene over cluster-derived cobalt catalyst. Catal. Lett., 8 (1991), pp. 253–261.

II Matsuzaki, T., Hanaoka, T., Takeuchi, K., Sugi, Y. and Reinikainen, M., Effects of modification of highly dispersed cobalt catalysts with alkali cations on the hydrogenation of carbon monoxide. Catal. Lett., 10 (1991), pp. 193–199.

III Takeuchi, K., Hanaoka, T., Matsuzaki, T., Sugi, Y. and Reinikainen, M., Promoting effects of alkaline earth oxides on the vapor-phase carbonylation of ethylene over cluster-derived cobalt catalysts. Appl. Catal., 73 (1991), pp. 281–287.

IV Kiviaho, J., Reinikainen, M., Niemelä, M., 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), pp. 187–195.

V Niemelä, M., Krause, O., Vaara, T., Kiviaho, J. and Reinikainen, M., The effect of the precursor on the characteristics of Co/SiO_2 catalysts. Appl. Catal., A: General, 147 (1996), pp. 325–345.

VI Reinikainen, M**.,** Kiviaho, J., Kröger, M., Niemelä, M. and Jääskeläinen, S., CO hydrogenation activity of carbonyl cluster derived Co-Ru/SiO_2 catalysts prepared by reflux method. J. Mol. Catal. A: Chemical., 118 (1997), pp. 137–144.

VII Matsuzaki, T., Hanaoka, T., Takeuchi, K., Arakawa, H., Sugi, Y., Wei, K., Dong, T. and Reinikainen, M., Oxygenates from syngas over highly dispersed cobalt catalysts, Catal. Today, 36 (1997), pp. 311–324.

VIII Reinikainen, M., Niemelä, M., Kakuta, N. and Suhonen, S., Characterisation and activity evaluation of silica supported cobalt and ruthenium catalysts, Accepted for publishing in Appl. Catal.

The thesis is supplemented by the following articles, posters, and congress abstracts which are referred to as additional publications (A1 for example):

Articles:

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A2. Matsuzaki, T., Takeuchi, K., Hanaoka, T., Arakawa, H., Sugi, Y., Wei, K., Dong, T., and Reinikainen, M., Preparation and modification of highly dispersed cobalt catalysts for CO hydrogenation, J. Nat. Inst. of Mat. and Chem. Res., 3 (1996), pp. 1–18.

A3. Kiviaho, J., Niemelä, M., Reinikainen, M. and Pakkanen, T., TPR and FT-IR studies on carbonyl cluster derived Co-Ru/SiO_2 catalysts. Appl. Catal., A: General, 149 (1997), pp. 353–372.

A4. Kiviaho, J., Niemelä, M., Reinikainen, M., Vaara, T. and Pakkanen, T., The effect of decomposition atmosphere on the activity and selectivity of the carbonyl cluster derived Co/SiO_2 and Rh/SiO_2 catalysts. J. Mol. Catal. A: Chemical, 121 (1997), pp. 1–8.

A5. Niemelä, M., Reinikainen, M. and Kiviaho, J., The interrelation of the preparation method and activity of the Co-Ru/SiO_2 catalysts, Accepted for publishing in: Preparation of Catalysts VII. Proceedings of the 7th International Symposium on Scientific Bases for the Preparation of Heterogeneous Catalysts, Louvain-la-Neuve, Belgium, 1–4 Sept., 1998.

A6. Niemelä, M. and Reinikainen, M., Reactions of synthesis gas on CoIr/SiO_2 and CoRu/SiO_2 catalysts, Accepted for publishing in: Proceedings of the 5th Natural Gas Conversion Symposium, Taormina, Italy, 20–25 Sept., 1998; edited by Parmaliana et al.

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A7. Reinikainen, M., Matsuzaki, T., Takeuchi, K., Hanaoka, T. and Sugi, Y., Hydrogenation of carbon monoxide over cobalt catalysts derived from $Co_2(CO)_8$, Poster, 3rd Nordic Symposium on Catalysis, 27–28 Sept., 1990, Espoo, Finland.

A8. Takeuchi, K., Hanaoka, T., Matsuzaki, T., Reinikainen, M. and Sugi, Y., Vapor phase hydroformylation of ethylene using cobalt catalysts prepared from $Co_2(CO)_8$, Poster, 3rd Nordic Symposium on Catalysis, 27–28 Sept., 1990, Espoo.

A9. Matsuzaki, T., Takeuchi, K., Hanaoka, T., Arakawa, H., Sugi, Y. and Reinikainen, M., Promoting effect of basic additives on cobalt catalysts for CO hydrogenation, Oral presentation, Annual meeting of Catalysis Society of Japan, Oct. 1990, Hiroshima, Japan (in Japanese).

A10. Matsuzaki, T.,Takeuchi, K., Hanaoka, T., Sugi, Y. and Reinikainen, M., Formation of oxygenated compounds from synthesis gas over highly dispersed cobalt catalysts. The effect of additives and support, Oral presentation, Meeting of Japanese Petroleum Society, Nov. 1990, Naha, Japan (in Japanese).

A11. Reinikainen, M., Takeuchi, K., Matsuzaki, T., Fischer-Tropsch synthesis over $Co_2(CO)_8$ catalysts supported on zeolites, Poster and abstract, 4th Nordic Symposium on Catalysis, 3–4 Oct., 1991, Trondheim, Norway.

A12. Matsuzaki, T., Takeuchi, K., Hanaoka, T., Reinikainen, M. and Sugi, Y., Promoting effect of transition metals and basic additives for the synthesis of ethanol in the hydrogenation of carbon monoxide over Co/SiO_2 catalyst, Poster, 4th Nordic Symposium on Catalysis, 3–4 Oct., 1991, Trondheim, Norway.

A13. Takeuchi, K., Hanaoka, T., Matsuzaki, T., Sugi, Y., Reinikainen, M. and Huuska, M., Selective vapor phase hydroformylation of olefins over cluster-derived cobalt catalysts promoted by alkaline earth oxides, Poster, 10th International Congress on Catalysis, 19–24 July 1992, Budapest, Hungary.

A14. Reinikainen, M., Matsuzaki, T. and Huuska, M., CO hydrogenation over promoted $Co_2(CO)_8$/zeolite catalysts, Oral presentation, 5th Nordic Symposium on Catalysis, 22–23 Oct., 1992, Lund, Sweden.

A15. Reinikainen, M., Iwasaki, T., Kataja, K., Kiviaho J., and Komppa, V., CO hydrogenation over cobalt catalysts supported on silicate crystallite mesoporous materials, Poster, 6th Nordic Symposium on Catalysis, 1–3 June, 1994, Hornbaek, Denmark.

A16. Iwasaki, T. and Reinikainen, M., CO hydrogenation over silicate crystallite porous material supported cobalt catalyst, Poster, 38th ClayScience Forum, 28–30 Sept., 1994, Morioka, Japan.

A17. Iwasaki, T., Reinikainen, M., Onodera, Y. and Torii, K., Synthesis of silicate crystallite porous materials and its application for CO hydrogenation, Oral presentation, 1994 Ceramics Society of Japan, Tohoku Hokkaido Branch Meeting, 1–2 Dec., 1994, Kohriyama, Japan.

A18. Morioka, Y., Kiviaho, J., Kataja, K. and Reinikainen, M., Studies on the thermal decomposition process of metal-carbonyl complexes supported on silica by an *in situ* drift technique, Poster, 10th Int. Conf. on Fourier Transform Spectroscopy, 28 Aug.–1 Sep., 1995, Budapest, Hungary.

A19. Kataja, K., Kiviaho, J., Reinikainen, M. and Mattinen, M., The utilization of FT-IR *in situ* technique in the studies of carbon monoxide adsorption on Co-Rh/SiO_2 catalysts, Poster, 10th Int. Conf. on Fourier Transform Spectroscopy, 28 Aug.–1 Sep., 1995, Budapest, Hungary.

A20. Yoshida, A., Reinikainen, M. and Maijanen, A., Hydrogenation of carbon monoxide by Co/dealuminated Y zeolite catalysts, Oral presentation, Zeolite Conference of Japan, 8–11 Nov., 1995, Ehime, Japan.

A21. Yoshida, A., Reinikainen, M. and Maijanen, A., Effects of dealumination on the CO hydrogenation activity of Co/Y-zeolite catalysts, Poster, 1995 International Chemical Congress of Pacific Basin Societies (PACIFICHEM-95), 17–22 Dec., 1995, Honolulu, Hawaii, USA.

A22. Kataja, K., Kiviaho, J. and Reinikainen, M., FTIR spectroscopic studies of carbon monoxide adsorption on Co-Rh/SiO_2 catalysts, Poster, 7th Nordic Symposium on Catalysis, 2–4 June, 1996, Turku, Finland.

A23. Reinikainen, M., Kiviaho, J., Niemelä, M., Kataja, K. and Jääskeläinen S., The activity of carbonyl cluster derived Co-Ru/SiO_2 and Co-Rh/SiO_2 catalysts in CO hydrogenation, Poster, 11th Int. Congr. Catal, 30 June – 5 July, 1996, Baltimore, MD, USA.

The author's contribution

The author has had an active role at all stages of the work reported in this thesis. He designed the on-line analysis system used in the reaction tests in papers IV, VI and VIII, and designed and constructed the equipment used for TPD/TPR in papers V and VIII.

The author participated in the planning and performing or supervising of the work in all papers. He contributed to the interpretation of the results in a major way in papers VI and VIII and to a significant extent in papers I–V and VII. The author wrote most of papers VI and VIII, contributed significantly to the writing of paper IV and significantly to the preparation of paper V.

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Abbreviations

Catalysts:

Precursor/Silica, a general form of presenting the catalysts, in which

Co(N)	$Co(NO_3)_2$
Co(A)	$Co(CH_3COO)_2$
Co(Cl)	$CoCl_2$
Co(AM)	$Co(NH_3)_6Cl_3$
Co(CO)	$Co_2(CO)_8$ or $Co_4(CO)_{12}$
Ir(Cl)	$IrCl_4$
Pd(Cl)	$PdCl_2$
Ru(Cl)	$RuCl_3$
Rh(Cl)	$RhCl_3$

Methods:

AAS	Atomic absorption spectroscopy
EXAFS	Extended X-ray Absorption Fine Structure
FT-IR	Fourier Transform Infrared Spectroscopy
TEM	Transmission electron microscopy
TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

Other:

X	Conversion, %
GHSV	Gas hourly space velocity, h^{-1}
α	Probability of chain growth
C-%	Selectivity expressed as carbon efficiency
FID	Flame Ionisation Detector
TCD	Temperature Conductivity Detector
C_6-O	Oxygenates containing six carbon atoms

1. Introduction

The chemistry of synthesis gas ($CO + H_2$) has gained a lot of attention since it is a very versatile starting material in the production of fuels and chemicals, as described in a number of excellent reviews [1–6] and illustrated in Figure 1 [2]. Quite a number of these production routes are very well proven commercially. For example, the Monsanto acetic acid process, Sasol Fischer-Tropsch (FT) process, Lurgi and ICI processes for methanol production, and the OXO process for hydroformylation are operating at the moment.

In terms of the production of fuels, the FT synthesis has been envisaged as an alternative or supplement for oil refining; it produces middle distillates free of sulphur, nitrogen and aromatics, which are desirable properties for environmentally friendly fuels [3]. In addition to FT technology (Sasol in South Africa and Shell in Malaysia), synfuels are produced, for example, by the Mobil Methanol To Gasoline (MTG) process, which started up in 1985 in New Zealand. Some other processes have also been developed, but not yet commercialised; for example the IFP process for the production of higher alcohols. Other areas, such as the oxidative coupling of methane, still require further research to demonstrate their feasibility [6]. Research efforts are still required, since the major problem with the synfuels processes is the need for improved catalysts to enhance product specificity.

One of the key problems for research is that there is no agreement on what will constitute the environmentally preferred motor fuel of the future. Methanol might be useful, either alone, or as a mixture with isoparaffins. Other clean fuels such as compressed natural gas, LPG and reformulated gasoline (added oxygenates and alkylates) may be preferred. In terms of reformulated gasoline, MTBE is very important, together with mixed alcohols produced from synthesis gas. Also, mixed ethers produced from these mixed alcohols may be possible gasoline blending components [5]. It should also be noted that the increasing demand for MTBE increases the demand for methanol (which reacts with isobutylene to form MTBE), and methanol may further be converted to gasoline (Mobil MTG process). High quality distillates may also be formed by FT synthesis or by the oligomerization of light olefins [1, 3, 5, 6]. Thus, whatever the ultimate choice for an environmentally preferred fuel – hydrogen, methanol, ethanol, other alcohols, ethers, hydrocarbons – it may be, at least in part, produced via synthesis gas.

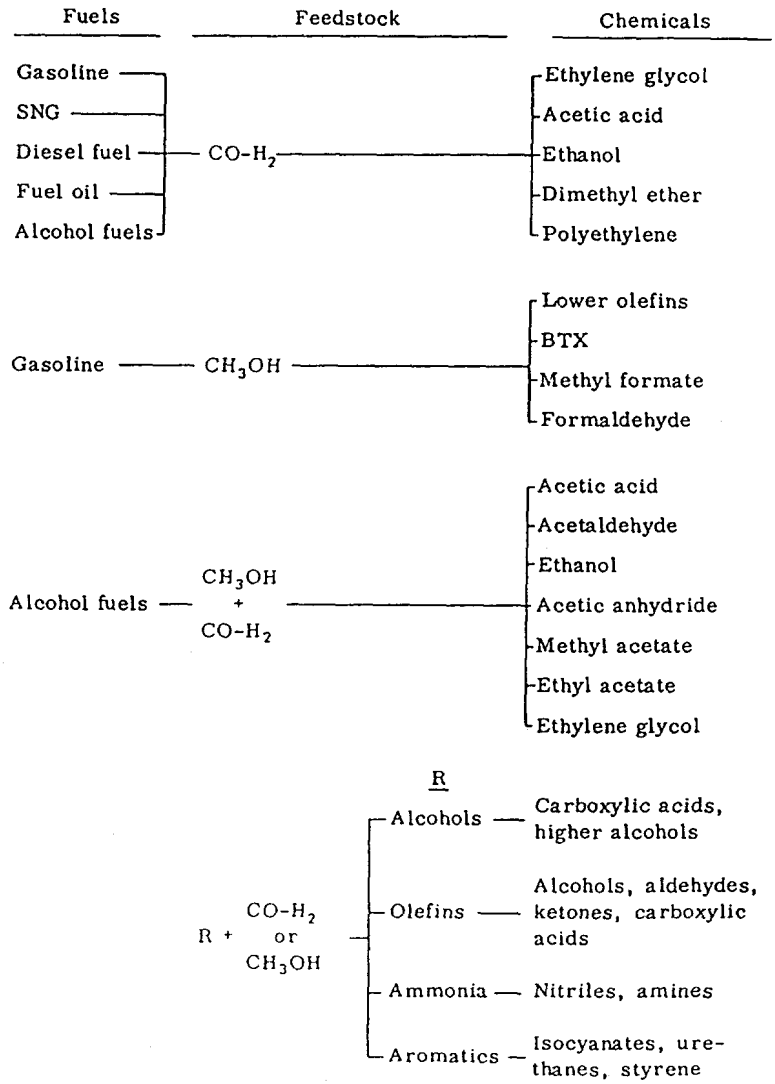

Figure 1. Building blocks in C1 chemistry [2].

2. Test reactions for catalyst performance

The reactions of the synthesis gas are influenced by the mode of activation of CO; it may react in its dissociated or molecular form. In this work, FT synthesis was chosen to study the ability of the catalysts to activate CO dissociatively, and hydroformylation was chosen to mimic the activity of the catalysts in the molecular reaction of CO. In addition, hydroformylation has been used to investigate the CO insertion step of the FT reaction mechanism.

2.1 FT synthesis

The synthesis gas reaction or FT synthesis is a very complex polymerization reaction, as shown schematically in Figure 2 [6]. Accordingly, the reaction produces straight chained hydrocarbons, branched products and various oxygen containing compounds. The progress of this polymerization reaction is described by the Schulz-Flory polymerization law, and the particular carbon number distribution of the products, in other words, the length of the chains formed, is determined by the probability of chain growth, alpha, as illustrated in Figure 3 [7]. Consequently, the limited selectivity for premium products (light olefins, gasoline or diesel fuel) is one of the main problems of this technology. However, the selectivity may, in part, be influenced by the process conditions, as Schulz has described in detail [8], but any marked increases in selectivity have been envisaged to proceed via catalyst development.

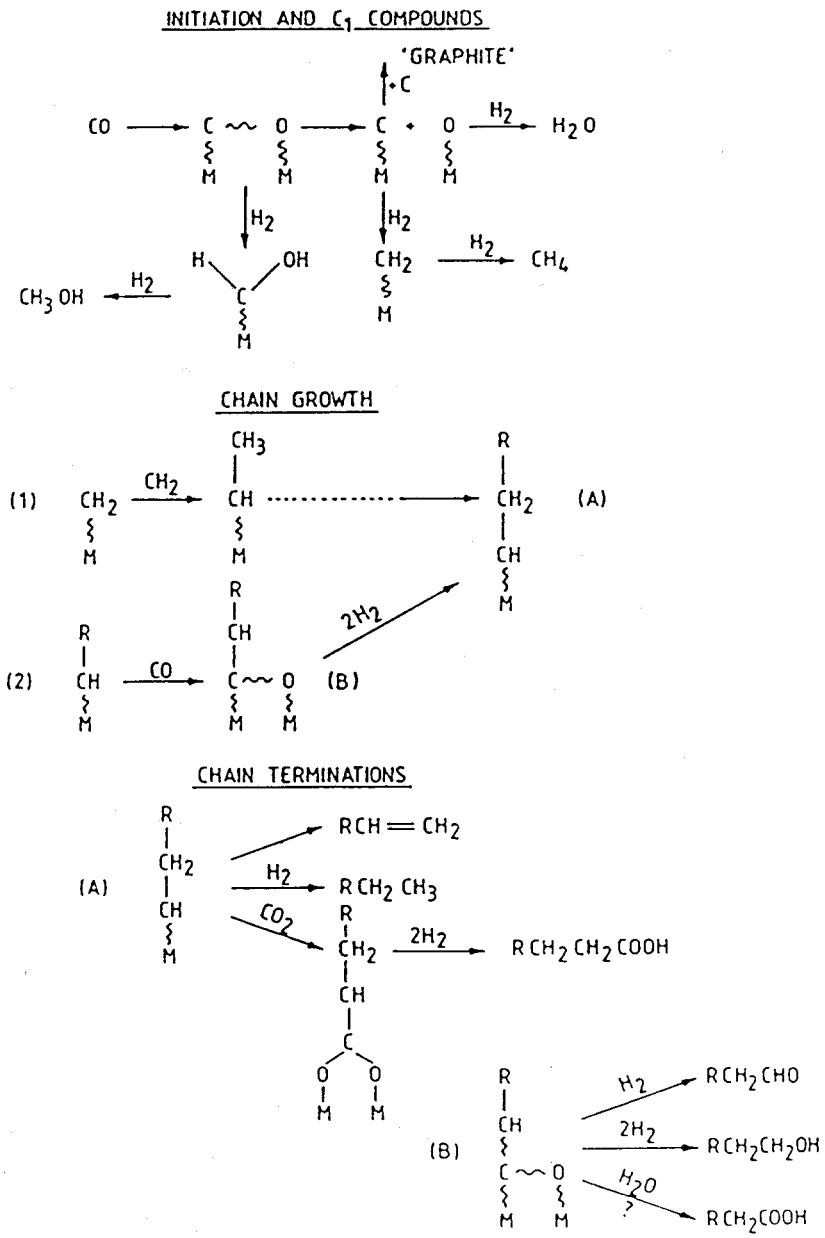

Figure 2. The reaction mechanism of the FT synthesis reaction [6].

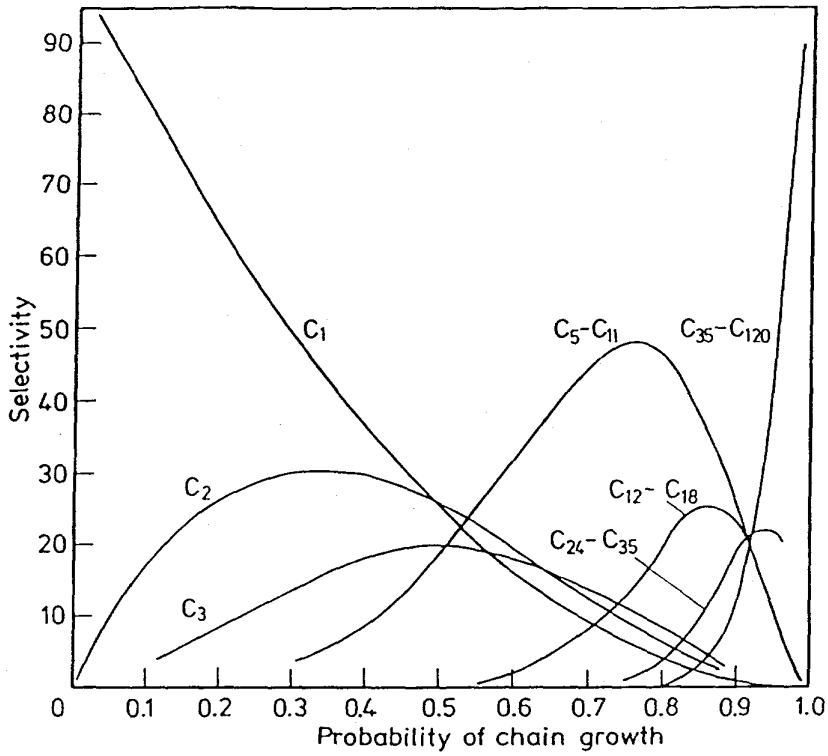

Figure 3. The effect of the Schulz-Flory distribution on the selectivity of FT synthesis [7].

2.2 Hydroformylation

Hydroformylation is an industrial process for the manufacture of aldehydes from olefins, carbon monoxide and hydrogen. These aldehydes are important reaction intermediates for the production of alcohols, carboxylic acids and products formed by aldol condensation. At the present time, the important final OXO-products are propanoic acid, n-butanol and 2-ethylhexanol. Current industrial processes use only homogeneous rhodium and cobalt catalysts [1, 2, 4, 9]. Nevertheless, heterogenisation of the active catalysts has gained a lot of attention, and several methods for heterogenisation have been suggested [9]. Homogeneous and heterogeneous modes of operation are compared in Table 1 [10]

Table 1. Advantages and disadvantages of homogeneous and heterogeneous systems [10].

	Homogeneous system	Heterogeneous system
Activity (relative to metal content)	high	variable
Selectivity	high	variable
Reaction conditions	mild	harsh
Service life of catalyst	low	high
Sensitivity toward catalyst poisons	low	high
Diffusion problems	none	may be important
Catalyst recycling	expensive	not necessary
Variability of steric and electronic properties of catalysts	possible	not possible
Mechanistic understanding	plausible under random conditions	more or less impossible (except for model systems)

Despite the drawbacks (Table 1), heterogeneous hydroformylation in the vapour phase is a promising alternative to the present homogeneous processes because of the following advantages: (1) it is a solvent-free process, (2) it is easy to separate and recover the catalyst from the products and (3) it is possible to reduce the reaction pressure [9, 11]. Success in developing an efficient process for vapour phase hydroformylation would thus lead to great economic benefits.

The majority of the studies on vapour phase hydroformylation have been carried out with rhodium catalysts, and only a few reports on the use of other metals have been published. Heterogeneous cobalt and other non-rhodium catalysts have usually shown a poor performance in this reaction, the main reason being their high activity for olefin hydrogenation [9, 12–16].

The studies on heterogeneous hydroformylation also provide important information on the reaction mechanisms of the CO hydrogenation reaction. In

this reaction the formation of oxygen containing products is envisaged to take place between the CH_x surface species and molecularly adsorbed CO, see also Figure 2. The insertion of CO in the surface-alkyl bonds has therefore received considerable attention [14, 17].

2.3 Scope of the work

In this work, an obvious choice for the catalytic metal was cobalt, since it is active in both CO hydrogenation and hydroformylation, and is accordingly used in both of these reactions on an industrial scale. Therefore, the first part of the work concentrates on the use of $Co_2(CO)_8$ as a catalyst precursor, in combination with various promoters, to enhance the selectivity of the catalyst both in CO hydrogenation and in the hydroformylation reaction. In view of this, my study aimed at elucidating the interrelation of characteristics and performance by comparing the $Co_2(CO)_8$ based catalyst to cobalt catalysts prepared from salt precursors.

As already described, the FT synthesis has suffered from limitations in selectivity (see also Figures 2 and 3). One approach used to benefit from the product distribution is to operate at high values of α, and accordingly to develop catalysts that facilitate such operation under mild reaction conditions. Since it is well known that the characteristic feature of ruthenium is to produce very high molecular weight hydrocarbons and waxes in FT synthesis [18], it seemed appropriate to study ruthenium containing catalysts in detail. Thus, in the second part of the work, the performance of the Ru/SiO_2 or bimetallic Co-Ru/SiO_2 catalysts is described in an attempt to determine the relation to precursor and preparation method.

3. Experimental

3.1 Catalyst preparation

Silica is widely used as a catalyst support due to low metal-support interaction. Nevertheless, it may influence the catalytic performance of the active metal. Some studies have clearly shown [19–21] that changes in selectivity are introduced by impurities incorporated into the support matrix (the unintentional promotion effect).

In this work, Davison 57 silica was used in papers I–III, VII and VIII and Grace 432 silica (B) in papers IV, V and VI. The purities of the silicas have been determined elsewhere [21, 22], and the matrix of both types was found to contain sodium, iron, magnesium and potassium. In particular the traces of sodium and iron might induce a promoting effect on the catalysts in the form of enhanced alcohol formation [19].

The methods used for the preparation of the catalysts, with references to the relevant papers, are summarised in Tables 2 and 3. It should be noted that in the case of alkali- and alkaline earth promoters, the promoter was first added to the support from its acetate solution, and thereafter the promoted support was impregnated with the active metal (papers II, V and VII). It is also important to emphasise that, in the case of carbonyl precursors, special care was taken to prevent the catalysts from contact with air at all steps of preparation and handling. The preparation methods have been described in more detail in the appended publications.

Table 2. Catalysts in CO hydrogenation.

Precursor	Support	Promoters	Preparation method	Solvent	Activation	Ref.
$Co_4(CO)_{12}$	SiO_2	-	Reflux, 5 h	n-hexane	H_2, 573K, 2h	VI
$Co_3RuH(CO)_{12}$	SiO_2	-	Reflux, 5 h	n-hexane	H_2, 573K, 2h	VI
$Co_2Ru_2H_2(CO)_{12}$	SiO_2	-	Reflux, 5 h	n-hexane	H_2, 573K, 2h	VI
$Co_2Ru_2(CO)_{13}$	SiO_2	-	Reflux, 5 h	n-hexane	H_2, 573K, 2h	VI
$CoRu_3H_3(CO)_{12}$	SiO_2	-	Reflux, 5 h	n-hexane	H_2, 573K, 2h	VI
$Ru_4H_4(CO)_{12}$	SiO_2	-	Reflux, 5 h	n-hexane	H_2, 573K, 2h	VI
$Co_2Ru_2H_2(CO)_{12}$	SiO_2	-	Impregnation/wash	n-hexane	H_2, 573K, 2h	VI
$Co_2Ru_2(CO)_{13}$	SiO_2	-	Impregnation/wash	n-hexane	H_2, 573K, 2h	VI
$Co_4(CO)_{12}$ + $Ru_4H_4(CO)_{12}$	SiO_2	-	Reflux, 5 h	n-hexane	H_2, 573K, 2h	VI
$Co_4(CO)_{12}$	SiO_2	-	Impregnation	dichloromethane	H_2, 573K, 2h	IV, V
$Co_3RuH(CO)_{12}$	SiO_2	-	Impregnation	dichloromethane	H_2, 573K, 2h	IV
$Co_2Ru_2H_2(CO)_{12}$	SiO_2	-	Impregnation	dichloromethane	H_2, 573K, 2h	IV
$Co_2Ru_2(CO)_{13}$	SiO_2	-	Impregnation	dichloromethane	H_2, 573K, 2h	IV
$CoRu_3H_3(CO)_{12}$	SiO_2	-	Impregnation	dichloromethane	H_2, 573K, 2h	IV
$Ru_4H_4(CO)_{12}$	SiO_2	-	Impregnation	dichloromethane	H_2, 573K, 2h	IV
$Co_4(CO)_{12}$ + $Ru_4H_4(CO)_{12}$	SiO_2	-	Impregnation	dichloromethane	H_2, 573K, 2h	IV
$Co_3Rh(CO)_{12}$	SiO_2	-	Impregnation	dichloromethane	H_2, 573K, 2h	IV
$Co_2Rh_2(CO)_{12}$	SiO_2	-	Impregnation	dichloromethane	H_2, 573K, 2h	IV
$Rh_4(CO)_{12}$	SiO_2	-	Impregnation	dichloromethane	H_2, 573K, 2h	IV

(Table 2, continued)

Precursor	Support	Promoters	Preparation method	Solvent	Activation	Ref.
$Co_2(CO)_8$	SiO_2	-, Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba	Impregnation	n-hexane	H_2, 723K, 2h	II, V, VII
$Co_2(CO)_8$	Al_2O_3, ZnO, TiO_2, ZrO_2, MgO, La_2O_3	-, Sr	Impregnation	n-hexane	H_2, 723K, 2h	VII
$Co_2(CO)_8 + Ru_3(CO)_{12}$	SiO_2	-, Sr, Ba	Impregnation	n-hexane	H_2, 723K, 2h	VII
$Co_2(CO)_8 + Ir_4(CO)_{12}$	SiO_2	-, Sr	Impregnation	n-hexane	H_2, 723K, 2h	VII
$Ru_3(CO)_{12}$	SiO_2	-	Impregnation	n-hexane	H_2, 723K, 2h	VII
$Co(NH_3)_6Cl_3$	SiO_2	-	Ion-exchange	NH_3/water	H_2, 723K, 2h	VIII
$RuCl_3$	SiO_2	-	Ion-exchange	NH_3/water	H_2, 723K, 2h	VIII
$Co(NH_3)_6Cl_3 + RuCl_3$	SiO_2	-	Ion-exchange	NH_3/water	H_2, 723K, 2h	VIII
$CoCl_2$	SiO_2	-	Impregnation	Water	H_2, 723K, 2h	VII
$Co(NO_3)_2$	SiO_2	-	Impregnation	Water	H_2, 723K, 2h	VII
$Co(NO_3)_2$	SiO_2	-	Impregnation	Water	air, 573K, 12h + H_2, 673K, 7h	V
$Co(CH_3COO)_2$	SiO_2	-	Impregnation	Water	H_2, 723K, 2h	VII

Table 3. Catalysts in hydroformylation.

Precursor	Support	Promoters	Preparation method	Solvent	Activation	Ref.
$Co_2(CO)_8$	SiO_2	-, Mg, Ca, Sr, Ba	Impregnation	n-hexane	H_2, 723 K, 2h	I, III
$CoCl_2$	SiO_2	-, Ba	Impregnation	water	H_2, 723 K, 2h	I, III
$Co(NO_3)_2$	SiO_2	-, Ba	Impregnation	water	H_2, 723 K, 2h	I, III
$Co(CH_3COO)_2$	SiO_2	-, Ba	Impregnation	water	H_2, 723 K, 2h	I, III
$RhCl_3$	SiO_2	-	Impregnation	water	H_2, 723 K, 2h	I
$PdCl_2$	SiO_2	-	Impregnation	water	H_2, 723 K, 2h	I
$IrCl_4$	SiO_2	-	Impregnation	water	H_2, 723 K, 2h	I

3.2 Catalyst characterisation

The catalysts have been characterised using several techniques. Metal analyses were generally performed by XRF but occasionally AAS was also used (papers V and VIII). The extents of reduction were determined by XPS in papers V and VIII, and by oxygen titration in paper VIII. In papers I and VII the EXAFS method was used to study the transformations of cobalt species on the silica support during impregnation and hydrogenation.

All the temperature programmed studies, *i.e.* TPR, TPD, and pulse mode reaction experiments, were carried out using an in-house built, down flow tubular quartz microreactor, connected to a Balzers GAM-415 quadrupole mass spectrometer. TPR was used in paper V, the hydrogen and CO uptake measurements were performed by TPD in paper V, and the pulse mode reaction studies were performed in papers V and VIII. In paper VII FT-IR was used to study the state of adsorbed CO on the catalyst surface under the reaction conditions. In addition, some TPR and FT-IR data from the supplementary publications [A1, A7, A12, A22] are included in this work.

3.3 Reaction tests

All the reaction tests were carried out with two continuous flow reactors equipped with on-line GC analysis; one for CO hydrogenation and the other for vapour phase hydroformylation. Both of the reactor systems employed stainless steel tubular reactors. The temperature measurement was carried out by calibrated K-type thermocouples, which could be moved inside the thermocouple pocket for axial temperature profile measurement.

In the vapour phase hydroformylation, sufficient separation of the reaction product could be achieved with four packed columns (PEG-6000, PEG-1500, VZ-10 and squalane on activated carbon). In CO hydrogenation, the reaction product mixture is very complex; the hydrocarbon fraction ranges from methane to heavy waxes. In addition, water and many organic oxygen-containing products are also present in the stream. Some on-line analysis systems for the FT reaction have been described in the literature [23–26] but none of them appeared appropriate: the analysis times were long, water could not be analysed,

the separation of oxygen-containing products was inadequate, the use of a coolant was necessary, or the data handling and report generation were tedious. Thus, a tailored analytical system was developed, and this merits a more detailed description than is given in the appended publications.

The analysis system consisted of two HP-5890 gas chromatographs, one for the analysis of heavy hydrocarbons (>C_7) and permanent gases and the other for the analysis of light hydrocarbons (C_1-C_7) and oxygenates. The gas chromatographs were equipped with three FID:s, one TCD, five pneumatic valves and six wide-bore capillary or packed columns. Detector responses were corrected using response factors published by Dietz [27]. When data for a compound was not available in the literature, it was estimated or measured by injecting standard samples. Methane, which could be detected by all the four detectors, was used for the calibration of the sensitivities of the detectors. Data storage and handling were performed using HP-Chemstation and Custom Report Generator software. The data from the resulting four report files (one for each detector) were collected by a command macro on the final report template, where the calculation of CO conversion, selectivities and the generation of figures took place. The operation of the analysis system is shown schematically in Figures 4 and 5.

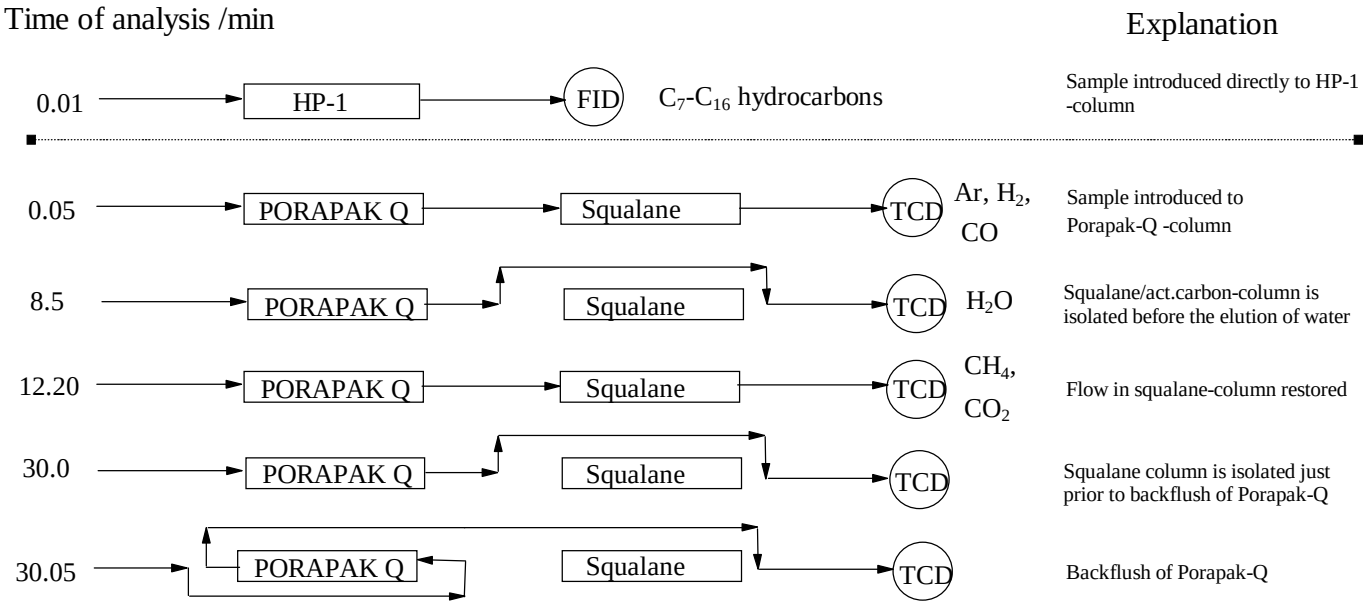

Figure 4. The analysis of heavy hydrocarbons and permanent gases.

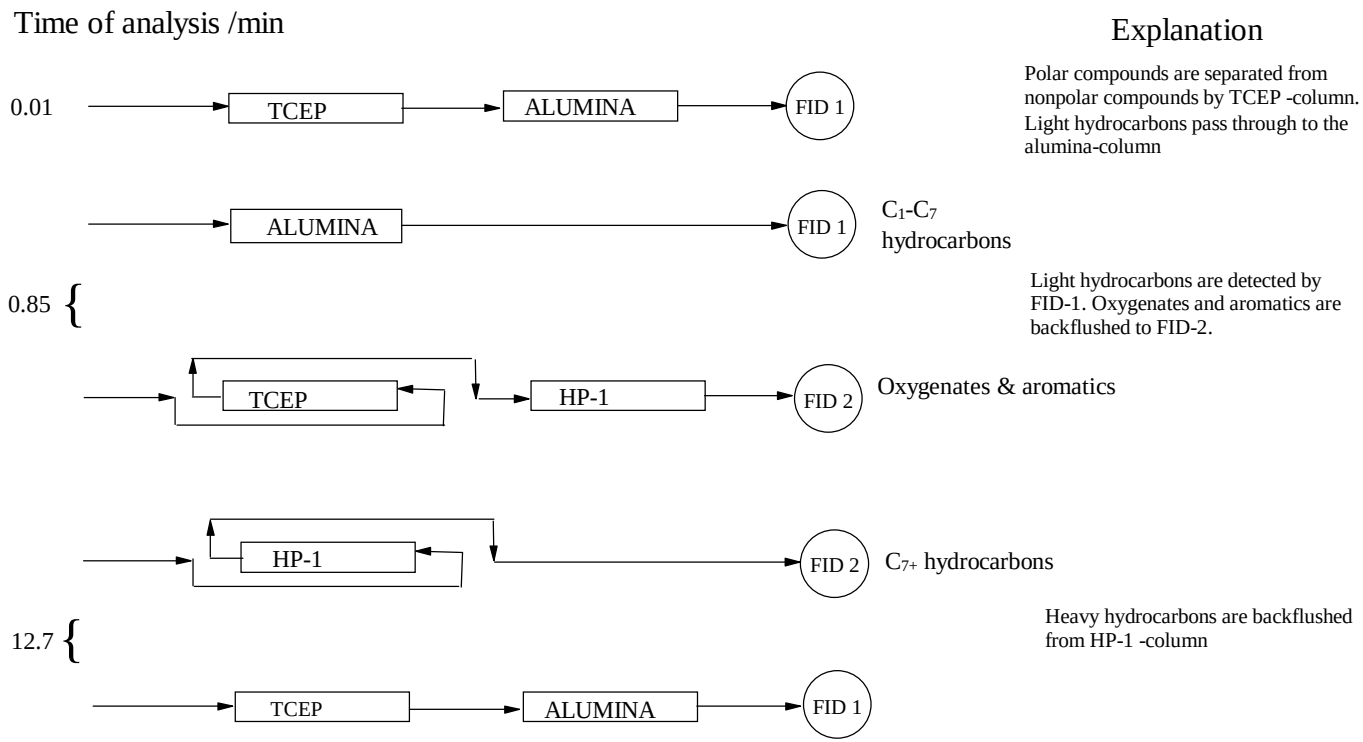

Figure 5. The analysis of light hydrocarbons (C_1-C_7) and oxygenates.

4. Cobalt catalysts

The cobalt catalysts are cheap, easily modifiable and some of the most active in the reactions of synthesis gas, both in CO hydrogenation and hydroformylation. Thus, they provided a natural starting point for this work.

4.1 CO hydrogenation

4.1.1 Co/SiO_2

The effect of the precursor and preparation method on the cobalt catalysts was studied by supporting $Co_2(CO)_8$, cobalt nitrate, -chloride and -acetate on silica as described in detail in papers II and VII, and in brief in Table 2. For comparison, the catalysts prepared from $Co_4(CO)_{12}$ (paper IV) and $Co(NH_3)_6Cl_3$ (paper VIII) were also studied. The activities and selectivities of these catalysts in CO hydrogenation are summarised in Figure 6.

The results indicate that the catalysts prepared from cobalt carbonyls were considerably more active than those prepared from inorganic salts. For catalysts of carbonyl origin, the method of preparation and the precursor used also played a role in the catalyst activity; the cobalt catalyst prepared from the tetranuclear carbonyl appeared significantly more active than that prepared from $Co_2(CO)_8$, although $Co_2(CO)_8$ decomposes to $Co_4(CO)_{12}$ upon contact with silica [V, VII, 28]. In addition, the detailed comparative study presented in paper V indicated that the catalysts prepared from the two cobalt precursors were different. Nevertheless, the superiority of either of the precursors in connection with impregnation could not be unambiguously determined. Very clearly, however, for cobalt precursors, the reflux method was inferior to impregnation, see in detail paper VI, because no cobalt was attached to the support during reflux.

A remarkable difference in the product distributions of the different Co/SiO_2 catalysts was also observed; oxygenates such as alcohols and esters were formed in selectivities of more than 20% on $Co_2(CO)_8/SiO_2$, whereas the other catalysts, including $Co_4(CO)_{12}/SiO_2$, were much less active with respect to the formation of oxygenates. The readily commercially available $Co_2(CO)_8$ catalyst precursor was chosen for further studies, although it was clearly observed that these catalysts are highly sensitive to air. For example, the high activity and

selectivity for oxygenates was not restored after a new hydrogenation treatment following exposure to air, as shown in Figure 6.

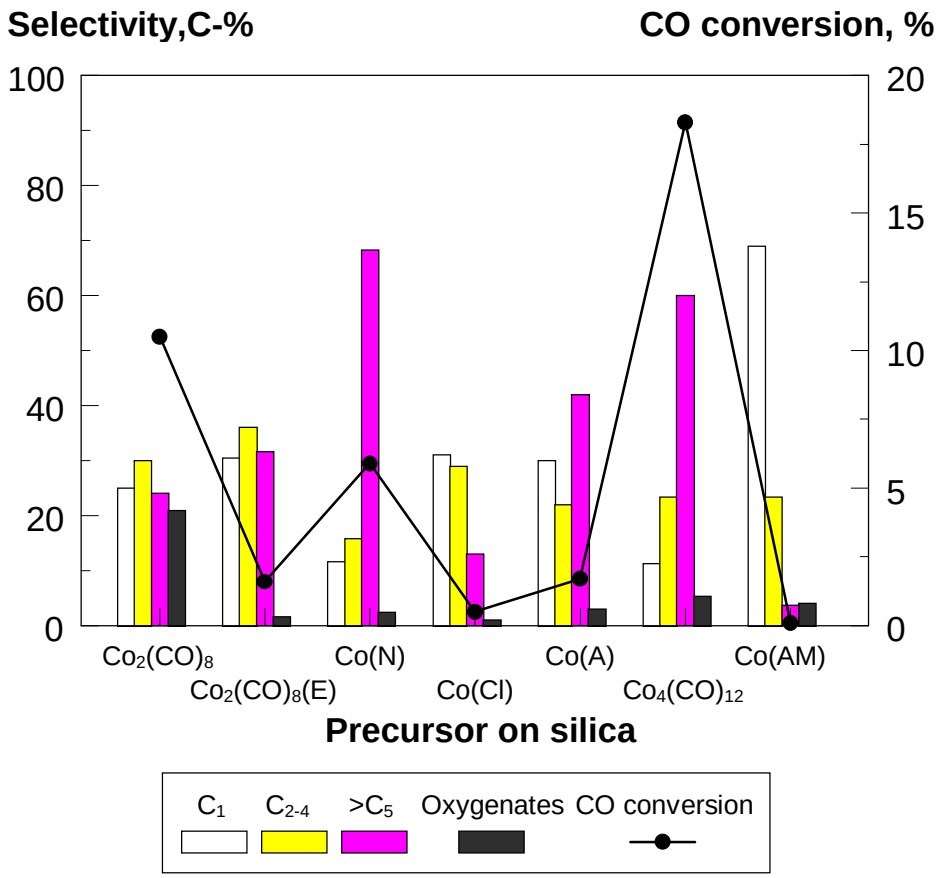

Figure 6. CO hydrogenation over cobalt catalysts. T=493 K, P=2.1 MPa, GHSV=2000 h^{-1}, CO:H_2:Ar=3:6:1. $Co_2(CO)_8$(E) exposed to air and rereduced. The metal loading was 5 wt.-% with the exception of 3 wt.-% for Co(AM)/SiO_2.

4.1.2 The effect of promotion

Already, in the early stages of work on the FT synthesis, alkaline earth promoters such as Mg have been used as structural promoters to the catalysts [4]. The effect of Mg, Ca, Sr and Ba on Co/SiO_2 has also been investigated during the course of this work, as reported in paper VII and as illustrated in

Figure 7. The results indicate that Mg was virtually ineffective as a promoter. Instead, the addition of Ca, and especially Sr or Ba, remarkably enhanced the formation of oxygenated compounds, with selectivities as high as 45%. The addition of alkaline earth promoters mainly enhanced the formation of ethanol, although in the case of Ba a remarkable amount of acetic acid was also formed.

Alkali metal additives, such as potassium, are known to affect the kinetics and energetics of the adsorption of H_2 and CO on the surface of the catalysts. Relative surface coverages are thereby changed, leading to a lower H/C ratio, and thus to a more olefinic product [4]. In addition, alkali additives have been found to enhance the formation of oxygenated compounds on iron catalysts [29, 30]. Likewise, in this work, all alkali additives clearly improved the selectivity of the $Co_2(CO)_8/SiO_2$ for oxygenated compounds, and at the same time CO conversion decreased - a result in general terms similar to the effect of alkaline earth promoters. However, a striking difference in the product distributions was observed: the alkali promoted catalysts produced mainly acetaldehyde and acetic acid, whereas alkali earth promoted catalysts yielded mainly ethanol, see Figures 6 and 7. It should also be noted that the ratio of acetaldehyde to acetic acid depended on the reaction temperature; the increase in temperature decreased the ratio (increased the share of acetic acid). Contrastingly, the selectivities of the other oxygenated compounds and hydrocarbons were not so strongly affected by the reaction temperature.

The results may be discussed from yet another viewpoint, since alkanes and ethanol are hydrogenation products of olefins and acetaldehyde, respectively. Thus, the ratios of acetaldehyde to ethanol and olefins to total hydrocarbons are measures of the hydrogenation activity of the catalyst. In this respect, the results indicate that in the presence of alkali cations the share of olefins in the hydrocarbon fraction was significantly increased, and much more so than in the presence of alkaline earth cations. Thus, the alkali cations effectively decreased the hydrogenation activity of $Co_2(CO)_8/SiO_2$ catalysts.

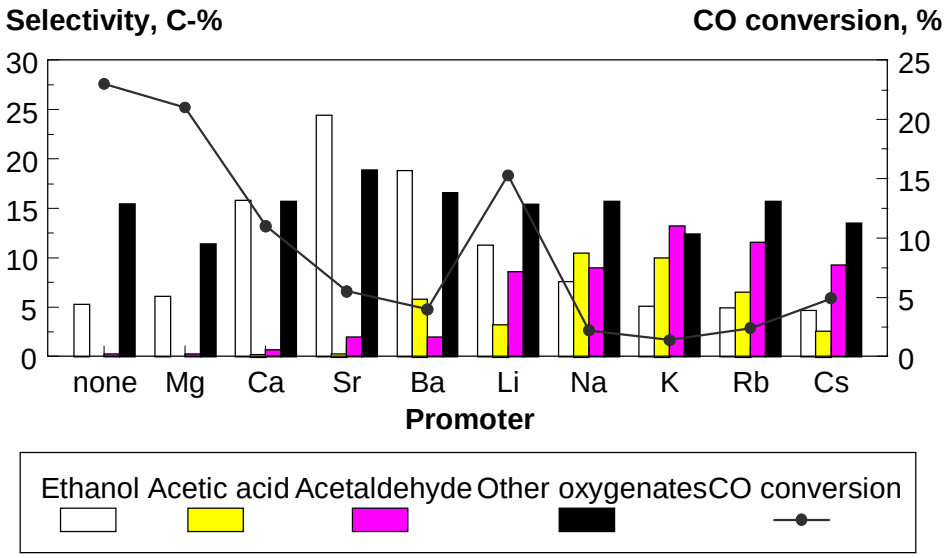

Figure 7. The composition of the oxygenates fraction in CO hydrogenation on promoted $Co_2(CO)_8/SiO_2$. T=523 K, P=2.1 MPa, GHSV=2000 h^{-1}, $CO:H_2:Ar=3:6:1$. The loading of the promoters was 25 mmol/100g with the exception of 43 mmol/100g for Li and 200 mmol/100g for Sr.

The modifying effect of additives has generally been attributed to different processes such as coverage of the surface of the active phase by the additive, the presence of partially reduced sites or electronic effects. In this work, the effect of an alkali promoter was found to be closely related to its basicity. The selectivity of the C_2-oxygenates increased and CO conversion decreased in the order of none<Li<Na<K, *i.e.* in order of increasing basicity. A similar effect was observed with alkaline earth additives: the selectivity for oxygenates increased in the order none<Mg<Ca<Sr<Ba. These results indicate that the role of these promoters is electronic.

In sum, the addition of alkali promoters led to the following changes in the catalytic performance of $Co_2(CO)_8/SiO_2$: 1) the catalytic activity decreased 2) the formation of methane decreased 3) the mole fraction of olefins increased 4) the formation of oxygenates was enhanced and 5) the primary oxygenated product shifted from ethanol to acetaldehyde and acetic acid. Pronounced formation of acetaldehyde and acetic acid has typically been obtained with rhodium [31] and iron catalysts [29, 32] promoted by potassium.

4.1.3 The effect of support

In addition to silica, several other oxides were used as supports for $Co_2(CO)_8$, since the support in known to significantly influence the performance of the active metal. Figure 8. summarises the results over these catalysts in CO hydrogenation [VII, A7].

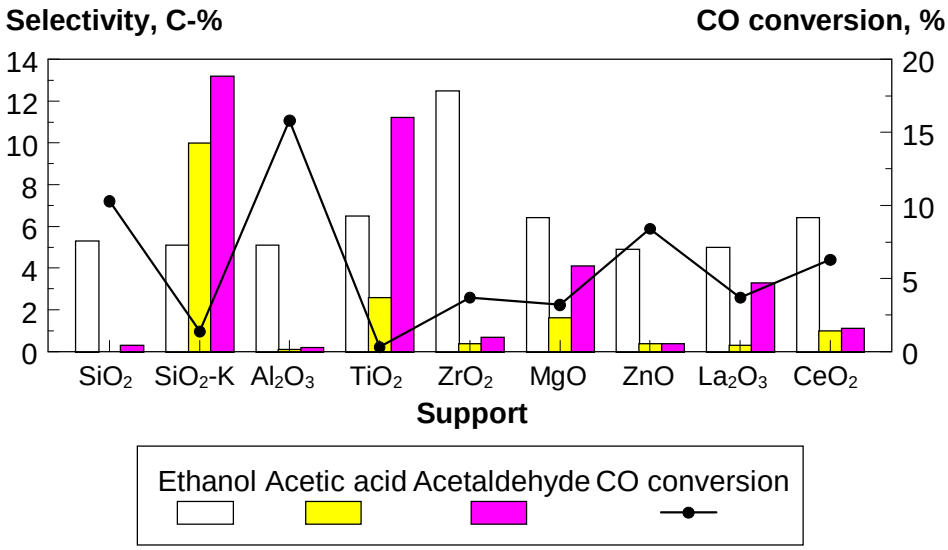

Figure 8. The effect of support on the CO hydrogenation activity of $Co_2(CO)_8$ based catalysts with metal loading of 5 wt.-%. T=523 K (493 K for Al_2O_3 and ZnO), P=2.1 MPa, GHSV=2000 h^{-1}, CO:H_2:Ar=3:6:1.

$Co_2(CO)_8$ supported on SiO_2, Al_2O_3 and ZnO exhibited similar activities and product distributions. In the case of TiO_2 and ZrO_2, the selectivities for oxygenates were high, even without the addition of a promoter. It was also noteworthy that $Co_2(CO)_8/TiO_2$ produced more acetaldehyde and acetic acid than ethanol, in the same way as silica-supported catalysts promoted by alkali metal cations. This type of product distribution is more typical of rhodium catalysts [31, 33], and these results are among the very few examples of cobalt catalysts capable of producing significantly larger amounts of acetaldehyde and acetic acid than ethanol.

4.2 Hydroformylation

4.2.1 Co/SiO_2

The results for CO hydrogenation indicated that CO insertion took place on the $Co_2(CO)_8/SiO_2$ catalyst, and therefore it may be envisaged to exhibit activity in the vapour phase hydroformylation of light olefins, a reaction which also proceeds through CO insertion. Accordingly, the activity of these catalysts was determined in the hydroformylation of ethene at 423–503 K. For comparison, conventional cobalt catalysts prepared from cobalt nitrate, chloride and acetate as well as rhodium, iridium and palladium catalysts were also studied.

The main reaction products in the vapour phase hydroformylation of ethene were ethane, propanal, n-propanol, propanoic acid, 2-methyl-2-pentenal, 2-methyl pentanal and 2-methyl-1-pentanol, *i.e.*, typical primary hydroformylation products together with secondary C_6-oxygenates formed by aldol condensation and subsequent dehydration and hydrogenation. It should be noted that only minor amounts of CO hydrogenation products, such as methane, methanol or ethanol were formed under the reaction conditions on any of the studied catalysts. Figure 9 summarises the activities and selectivities of the main products in ethene hydroformylation on the studied catalysts.

The results indicate that the catalyst prepared from $Co_2(CO)_8$ exhibited high activity for ethene conversion and it gave hydroformylated products at a selectivity of about 36%. At 463 K, the ethene conversion and the total oxo-selectivity on $Rh(Cl)/SiO_2$ were almost identical to those of $Co_2(CO)_8/SiO_2$, but the composition of the oxo-products was very different; large amounts of n-propanol were formed on $Co_2(CO)_8/SiO_2$, whereas on $Rh(Cl)/SiO_2$ the formation of propanal predominated.

Since n-propanol is formed from propanal by hydrogenation, the ratio of n-propanol to propanal can be used as a measure of the hydrogenation activity of the catalysts. Thus, $Co_2(CO)_8/SiO_2$ exhibited much higher activity for the hydrogenation of aldehydes to alcohols than did $Rh(Cl)/SiO_2$. Yet, the hydrogenation of ethene to ethane took place on $Rh(Cl)/SiO_2$ even more readily than on $Co_2(CO)_8/SiO_2$. Therefore, the hydrogenation activity can be divided into two independent reactions: 1) the hydrogenation of olefins to alkanes and 2) the hydrogenation of aldehydes to alcohols.

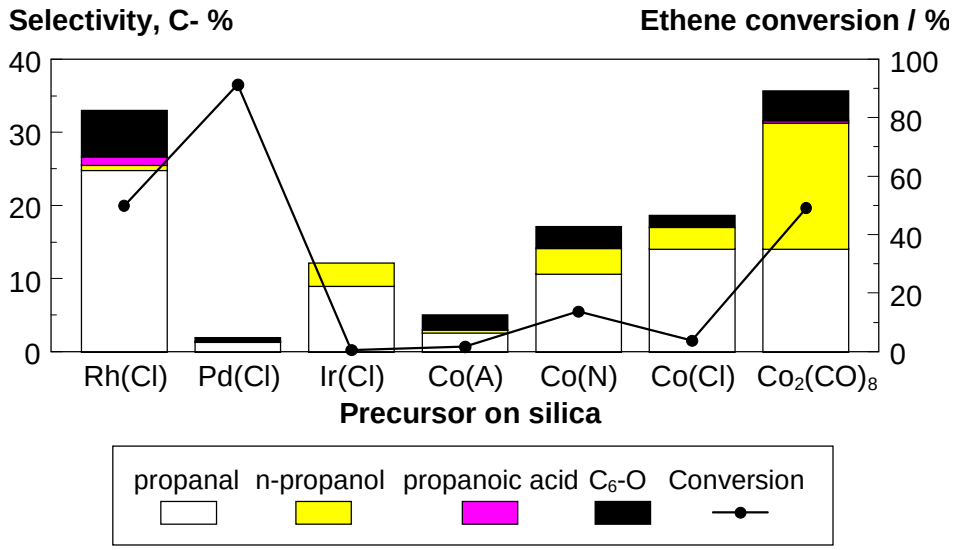

Figure 9. Vapour phase hydroformylation of ethene on M/SiO_2. Metal loading 5 wt.-%, T=463 K P=1.1 MPa, GHSV=600 h^{-1}, Ar:CO:C_2H_4:H_2=1:3:3:3.

Conventional cobalt catalysts prepared from cobalt nitrate, chloride and acetate were clearly less active in ethene hydroformylation than was $Co_2(CO)_8/SiO_2$, see Figure 9. Thus, the results indicate that CO insertion to the surface alkyl species also took place to some extent on the conventional cobalt catalysts, but the high hydrogenation activity of ethene to ethane kept the oxo-selectivities low. As a result, the yield for hydroformylated products decreased in the order Co(CO)>> Co(N)> Co(Cl).

The reactivity of propene was much lower than that of ethene [A1]. For example, at 463 K the conversion of propene on $Co_2(CO)_8/SiO_2$ was only 2.1%, whereas a conversion of 49.1% was obtained with ethene under similar conditions (Ar:CO:olefin:H_2=1:3:3:3, P=1.1 MPa, GHSV=600 h^{-1}). The main reaction products in the hydroformylation of propene were n-butanal, butanoic acid, n-butanol, isobutanal and isobutanol. In addition, several branched C_8-oxygenates formed by aldol condensation of butanals could be identified by mass spectroscopy [A1].

4.2.2 The effect of promotion

The performance of $Co_2(CO)_8/SiO_2$ was studied further in connection with promotion, since the promoters exerted a beneficial increase in the selectivity of oxygenates in CO hydrogenation, *i.e.* enhanced the CO insertion which determines the rate in hydroformylation.

As expected, the oxo-selectivity on $Co_2(CO)_8/SiO_2$ was significantly improved by modifying the catalyst with alkaline earth oxides; the formation of propanoic acid was strongly enhanced and, at best, selectivities as high as 47% were achieved. Such a high selectivity for propanoic acid on $Co_2(CO)_8/SiO_2$ was the first published example of the pronounced formation of a carboxylic acid in a single step in hydroformylation (paper III). In addition to propanoic acid, large amounts of C_6-oxygenates, such as 2-methyl-2-pentenal, 2-methyl-pentanal and 2-methyl-1-pentanol, were formed.

The interesting product distribution merits some further remarks in regard to the type of active sites responsible for the observed product distribution. The reaction conditions in vapour phase hydroformylation are reductive rather than oxidative, and thus propanoic acid was probably formed by the addition of a hydroxyl group to the surface acyl-species. On the other hand, the pronounced formation of aldol condensation products of propanal seemed to be due to the presence of the basic alkaline earth cation. The hydroxyl-groups generated by the dehydration of the aldol condensate may then be consumed in the formation of propanoic acid.

It should also be noted that the effect of alkaline earth oxides on the hydroformylation of propene was less profound than in the case of ethene [A1]. Only calcium and strontium were found to improve the oxo-selectivity. However, all the studied alkaline earth additives clearly promoted the formation of branched C_8-oxygenates, such as 2-ethylhexenal, via aldol condensation.

4.3 Characterisations

In order to obtain a better understanding of the origin of the superior performance of $Co_2(CO)_8/SiO_2$ compared to conventional catalysts, as well as to

elucidate the effect of promoters, some characterisation results [V, VII, A1, A7, A12, A22] will now be presented.

4.3.1 Studies by temperature programmed techniques

TPD (Temperature-Programmed-Desorption) studies were carried out in order to study the strength of interaction of adsorbed CO on cobalt, as described in brief in section 3.2 and in detail in paper V. The temperature of the catalyst surface saturated with pulses of CO was elevated under an inert gas, and the desorption of CO, CO_2, hydrogen and water were monitored by a mass spectrometer. In the case of the conventional $Co(N)/SiO_2$ catalyst and the $Co_4(CO)_{12}/SiO_2$ catalyst, the desorption of CO was accompanied by desorption of CO_2 and water, whereas in the case of the $Co_2(CO)_8/SiO_2$ catalyst CO desorption was accompanied by CO_2 and methane desorption, *i.e.* the surfaces of the carbonyl based catalysts appeared to be different, although $Co_2(CO)_8$ decomposes to $Co_4(CO)_{12}$ upon contact with silica [VII]. Furthermore, the differencies in the desorption of CO were significant, as the results shown in Figure 10 (paper V) indicate. The CO uptake was significantly higher for both $Co_2(CO)_8/SiO_2$ and $Co_4(CO)_{12}/SiO_2$ than for their conventional counterpart, and the desorption occurred at a higher temperature. Thus, CO was adsorbed more strongly on $Co_2(CO)_8/SiO_2$ than on its conventional counterpart, and the CO insertion to alkyl species should be correspondingly higher – a result in agreement with the activity data [I].

In another experiment, the $Co_2(CO)_8/SiO_2$ catalyst surface was saturated with CO, and the temperature was elevated by 15 K/min under H_2 flow. The desorption of CO and the formation of CH_4, H_2O and CO_2 were detected with a mass spectrometer [A1]. The species chosen for comparative purposes were CO and methane, and the effect of alkaline earth promoters on the desorption temperatures of these species is shown in Figure 11. The results indicate that in the presence of alkaline earth promoters, the peak for the maximum rate of CO desorption shifted to a significantly higher temperature, whereas the maximum for the methane formation remained practically constant. The increase in CO desorption temperature clearly indicates that alkaline earth oxides strengthen the interaction between CO and cobalt, which is considered to promote CO insertion to alkyl species. In support of this view, the CO desorption temperature seemed to correlate with the oxo-selectivity, as well as with the catalyst activity, see Figure 12.

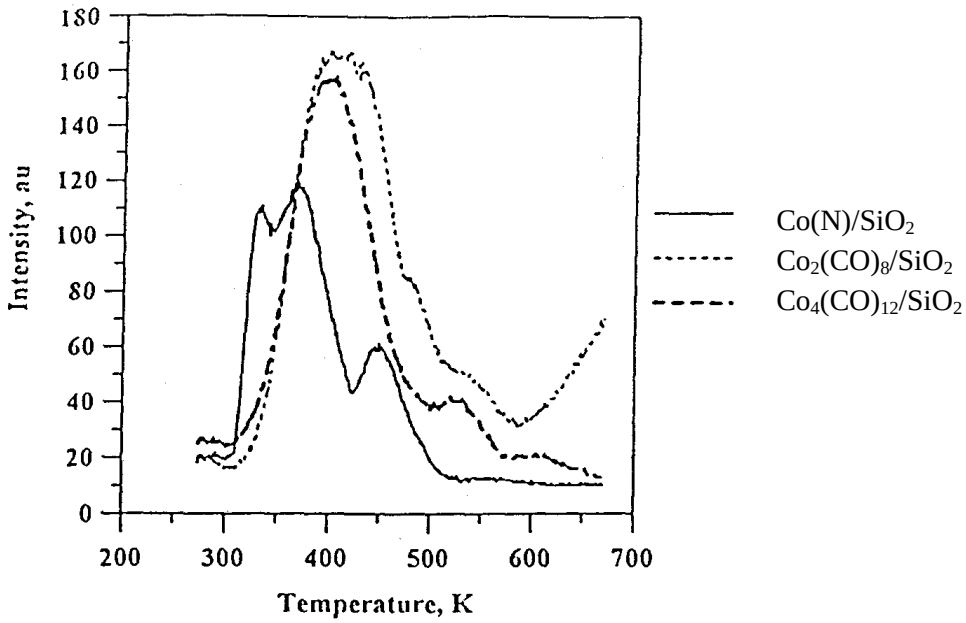

Figure 10. CO desorption during the TPD subsequent to CO pulsing [V].

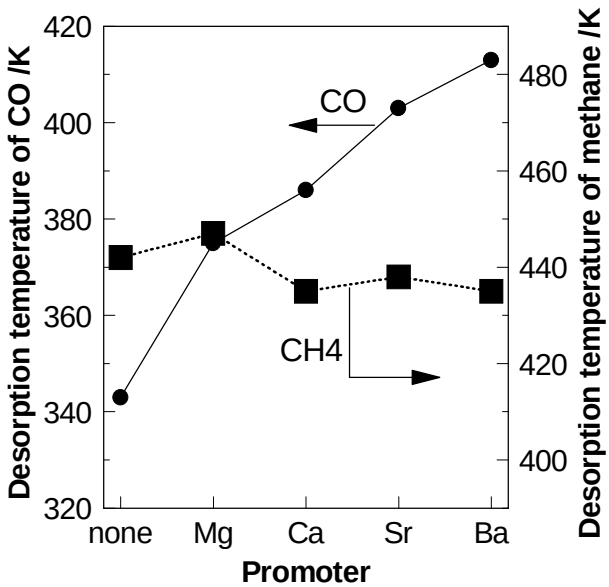

Figure 11. The effect of alkaline earth oxides on CO and CH_4 desorption temperatures [A1].

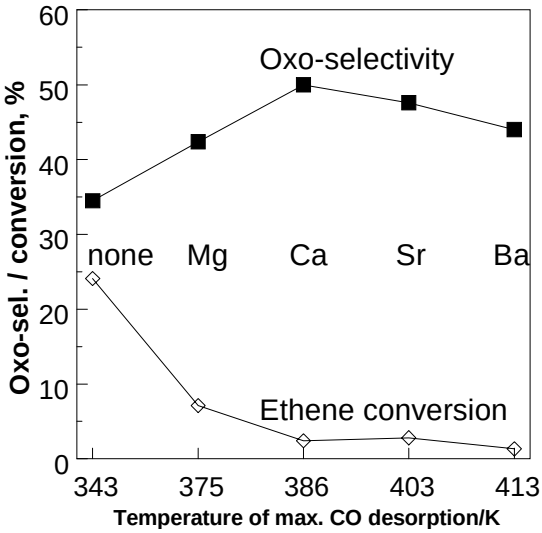

Figure 12. Oxo-selectivity and catalyst activity vs. CO desorption temperature. Selectivities and conversion were obtained at the following conditions: T=443 K, P=1.1 MPa, GHSV=600 h^{-1}, Ar:CO:C_2H_4:H_2=1:3:3:3 [A1].

4.3.2 *In-situ* FT-IR measurements

In situ FT-IR spectroscopic experiments were performed to investigate, in more detail, the adsorption state of CO on $Co_2(CO)_8/SiO_2$ catalysts and its role in the formation of oxygenates [VII, A7, A12, 34].

Figure 13 depicts the FT-IR spectra of adsorbed CO on the $Co_2(CO)_8/SiO_2$ catalysts under typical reaction conditions. Linear-CO (2075 cm^{-1}) species predominated on the $Co_2(CO)_8/SiO_2$ catalyst, and it shifted to a lower wave number (2056 cm^{-1}) on the $Co_2(CO)_8$-Ba/SiO_2 catalyst. In addition to linear CO, clear bands of bridged-CO (1946 and 1815 cm^{-1}) were observed for $Co_2(CO)_8$-Ba/SiO_2. The results seem to suggest that it is the presence of bridged-CO that led to the drastic increase in the formation of oxygenates, together with a decrease in CO conversion in the case of $Co_2(CO)_8$-Ba/SiO_2, see also section 4.1.2. However, the absence of bridged-CO does not indicate that the catalyst is inactive in the formation of ethanol and other oxygenates, see unpromoted $Co_2(CO)_8/SiO_2$ in section 4.1.1.

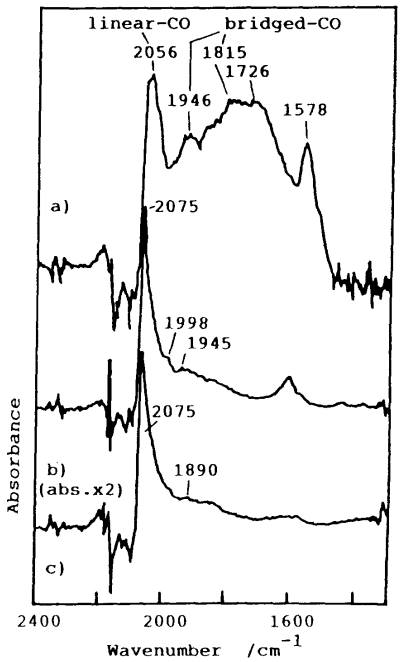

Figure 13. High-pressure in situ FT-IR spectra of cobalt catalysts. a) $Co_2(CO)_8$ -Ba, b) $Co_2(CO)_8$-Mg and c) $Co_2(CO)_8$ on SiO_2. CO:H_2=1:2, P= 2.1 MPa, T= 494 K.

Slightly different results were observed with $Co_2(CO)_8/SiO_2$ catalysts promoted by potassium [A7, A12]; the addition of potassium did shift the band of linear CO to a lower wave number (2058 cm^{-1}), but the band of bridged CO remained negligible on the catalysts promoted by potassium. Nevertheless, potassium greatly enhanced the formation of oxygenates, especially acetaldehyde and acetic acid, as reported in section 4.1.2.

Thus, it seems likely that linear-CO adsorbed on isolated metal sites plays a major role in the CO insertion step and the formation of oxygenates. This result is in agreement with the recent data on cobalt catalysts [16, 35]. In accordance, in the case of Rh-catalysts promoted by basic additives, such as Zn, the CO insertion is favoured on isolated metal atoms, and Zn-ions effectively block the large Rh-ensembles responsible for the dissociation of CO and H_2 [17].

Consequently, the presence of bridged-CO on the alkali earth promoted $Co_2(CO)_8/SiO_2$ catalysts may be a sign of non-uniform cobalt dispersion, larger clusters of cobalt atoms present on the surface together with very fine isolated Co-particles. The large clusters might be responsible for the high activity for hydrogenation of acetaldehyde to ethanol - a reaction observed on these catalysts. The non-uniform cobalt dispersion might be due to the very high amount of alkaline earth additive (typically 15 wt.-%) [VII, 34]; for alkali metals (only 1 wt.-%) the bridged-CO species were not observed, but nevertheless the amount was sufficient to give a full promoter effect [II].

4.3.3 Extents of reduction by oxygen titration and XPS

Since one explanation for the promoter effect has been oxidation state, the extents of reduction were estimated based on XPS [V, VIII, 50] and oxygen titration [VIII]. The results shown in Table 4 suggest that the extent of reduction was approx. 4–42% for cobalt catalysts. Relative to the previously reported data: 75% for 3 wt.-% Co/SiO_2 [36], and 89% for 15.8 wt.-% Co/SiO_2 [37], the values obtained for the conventional catalyst (42%) and for $Co_4(CO)_{12}/SiO_2$ (41%) were low. Indeed, another study revealed that the values should have been multiplied by a factor of 2 [38], and after multiplication, the extents of reduction for $Co(N)/SiO_2$ and $Co_4(CO)_{12}/SiO_2$ were appropriate, whereas those of $Co_2(CO)_8/SiO_2$, $Co(AM)/SiO_2$ and $Co(A)/SiO_2$ were certainly extremely low.

Table 4. Characteristics of the Co/SiO_2 catalysts after reduction with hydrogen [V, VIII, 22].

Precursor	H_2 uptake µmol/g_{cat}	Extent of reduction XPS, %	Dispersion %	Size[1] nm	Size[2] nm
Co(A)[3]		0			
Co(AM)[4]	3.6	4 / 8 [6]	42 / 21 [6]		2.3 / 4.6 [6]
Co(N)[3]	12.5	42 / 84 [6]	7.1 / 3.6 [6]	14	13 / 27 [6]
$Co_2(CO)_8$ [5]	46.2	15 / 30 [6]	80 / 40 [6]	2.3 [7]	1.2 / 2.4 [6]
$Co_4(CO)_{12}$ [5]	52.2	41 / 82 [6]	32 / 16 [6]	3.4 [7]	3.0 / 6.0 [6]

[1] XRD, [2] Chemisorption, [3] Reduced at 673 K, [4] Reduced at 723 K, [5] Reduced at 573 K, [6] The value based on the extent of reduction corrected by using the multiplication factor of 2, see [38] for details, and [7] Upper limit estimate only, since the sample was oxidized at 573 K prior to measurement

In the case of $Co_2(CO)_8/SiO_2$ the small particles might have interacted strongly with the support, thereby being made more difficult to reduce [V]. The dispersion effect does not, however, explain the low results for the other two catalysts, $Co(AM)/SiO_2$ and $Co(A)/SiO_2$. For $Co(A)/SiO_2$, the detailed characterisations have indicated that cobalt acetate forms a very stable cobalt oxide surface species, Co^{2+}-$(O\text{-}Si)_2$, which is resistant to reductive treatment [I,VII, 39, 40]. In the case of $Co(AM)/SiO_2$, the low extent of reduction may be discussed in terms of the migration of silica as well as the formation of cobalt silicates [VIII].

Migration of silica has been observed for materials with very small pores, and thus the limited transfer of water out of the pores during reduction, as discussed in paper VIII. Thus, migration of silica is not likely to be substantial on the present catalysts. Nevertheless, migration of silica cannot be entirely excluded in the case of $Co(AM)/SiO_2$, since the pH of the impregnating solution was high enough to facilitate partial dissolution of the silica. On the other hand, the formation of nonreducible cobalt silicates is also likely to proceed during ion exchange, since high surface area silicas have been shown to react with cobalt species under alkaline conditions to form cobalt silicates. Thus, the low extent of reduction for $Co(AM)/SiO_2$ was mainly due to the presence of cobalt silicates, as discussed in detail in paper VIII. It should, however, be noted that any formation of cobalt silicates on $Co(N)/SiO_2$ and carbonyl based catalysts during the reduction of the catalysts is less likely, since no silicates have been observed in closely related studies [38].

Thus, the results indicate that $Co(A)/SiO_2$ and $Co(AM)/SiO_2$ exhibited predominantly Co^{2+} sites, whereas $Co(N)/SiO_2$ and $Co_4(CO)_{12}/SiO_2$ exhibited predominantly metallic sites. $Co_2(CO)_8/SiO_2$ had both metallic sites and partially reduced sites. In addition, the particle size of the $Co(CO)/SiO_2$ catalysts was significantly lower than for the conventional catalysts, and the dispersion was highest for $Co_2(CO)_8/SiO_2$.

4.4 The interrelations of activity and characteristics

The results allow the suggestion that the following interrelations existed between the characteristics and performance of the catalysts: 1) the high activity of the $Co_2(CO)_8/SiO_2$ in CO hydrogenation was due to the presence of a large

amount of well dispersed metal sites 2) the high oxygenate selectivity in CO hydrogenation and the high activity in hydroformylation were related to the presence of linear-CO species adsorbed on isolated metallic or, most likely, on partially oxidised sites, and 3) the alkaline earth metal and alkali metals decreased the activity of the catalysts in both CO hydrogenation and hydroformylation, but at the same time they enhanced the formation of oxygenated compounds through an electronic effect.

5. Ruthenium catalysts

Cobalt and ruthenium catalysts have been studied extensively [4, 21, 41, 42] due to their high activity in FT synthesis. The characteristics and the performance of the catalysts have depended on the precursor [4, 21], the method of preparation [36, 41–44] and the pretreatment procedures [38, A4]. For example, carbonyl compounds have gained a lot of attention as precursors; it has been suggested that the tailored active sites improve the selectivity of the Fischer-Tropsch synthesis [45]. Accordingly, this work describes the work carried out on ruthenium containing carbonyls as well as conventional precursors, in an attempt to determine the effect of catalyst preparation method on its performance in the synthesis gas reaction.

5.1 Ru/SiO_2 in CO hydrogenation

The ruthenium catalysts were prepared on the silica support using different techniques. First, catalysts were supported on partially dehydroxylated silica (pretreated at 873 K in vacuum) from tetranuclear carbonyl precursors under air-free conditions by impregnation [IV] and reflux methods [VI]. For comparative purposes, catalysts were prepared from $Ru_3(CO)_{12}$ on silica support by air-free impregnation [VII, A7, A12] or from salt precursors by ionic adsorption [VIII]. The recipes and pretreatment procedures of the bimetallic catalysts are summarised in Table 6, page 52. None of the catalysts were calcined to avoid oxidation and/or agglomeration of the active sites.

The activities of the ruthenium catalysts were determined in CO hydrogenation, and the results are shown in Figure 14. In the case of ruthenium carbonyls, the results indicate that the method of preparation did not effect the catalyst activity, since both of the carbonyl based ruthenium catalysts were highly active, and clearly more active than the catalyst prepared by ionic adsorption. Characteristic of ruthenium, the catalysts prepared from carbonyls produced mainly heavy hydrocarbons, whereas an exceptionally large amount of light C_1–C_8 hydrocarbons was formed on the catalyst prepared by ionic adsorption. It is also important to mention that the ruthenium precursors are not as air sensitive as cobalt carbonyls, and thus the catalyst preparation from ruthenium carbonyls would also be straightforward on a larger scale.

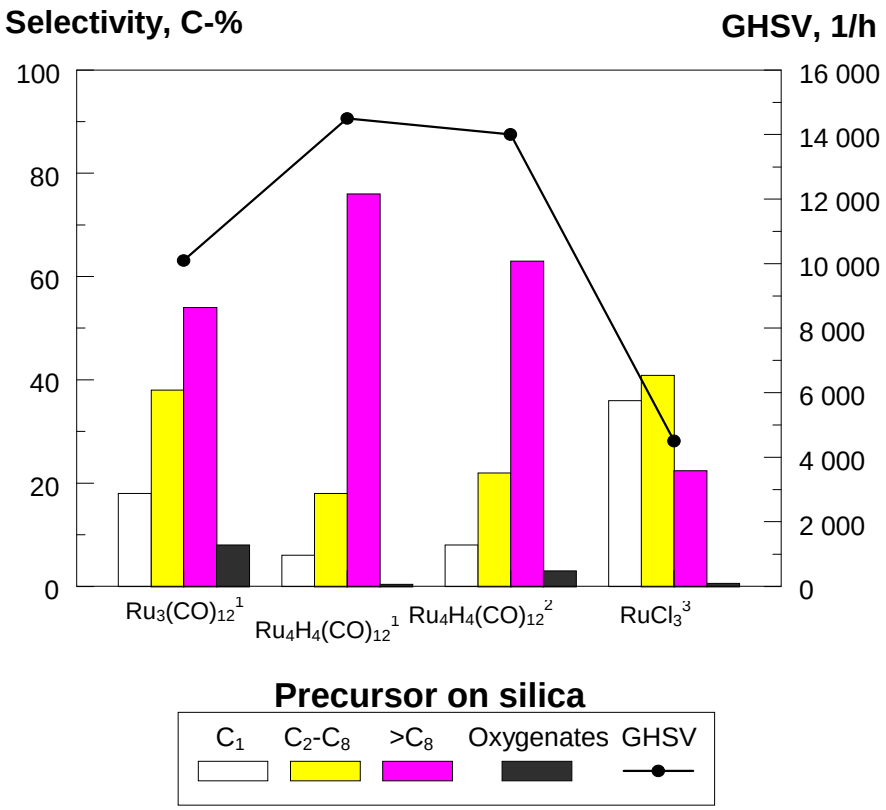

Figure 14. CO hydrogenation over Ru/SiO_2 catalysts. T=506 K, P=2.1 MPa, CO conversion = 3%, CO:H_2:Ar=3:6:1. [1]Prepared by impregnation, [2]Prepared by reflux method, [3]Prepared by ionic adsorption.

5.2 Co-Ru/SiO_2 in CO hydrogenation

In FT synthesis, the selectivity of the catalysts is, however, even more important than the activity. In connection with Co-Ru catalysts, some previous studies had suggested that higher selectivities for heavier (>C_5) hydrocarbons could be achieved by adding ruthenium to cobalt catalysts [41, 42]. Others claim that the catalysts derived from bimetallic clusters containing ruthenium and cobalt exhibited higher selectivities for the higher oxygenates than did the catalysts prepared by mixing the monometallic clusters or metal chloride precursors [46–48]. Thus, in this work the bimetallic catalysts containing ruthenium and cobalt were studied in detail to elucidate the interrelation of catalyst preparation and performance.

The bimetallic cobalt-ruthenium catalysts were prepared on a silica support in the same way as the monometallic ones: from tetranuclear carbonyl precursors under air-free conditions by impregnation [IV] and reflux methods [VI], from $Ru_3(CO)_{12}$ and $Co_2(CO)_8$ by air-free impregnation [A7, A12] and by ionic adsorption from salt precursors [VIII], see Table 6, page 52.

In regard to the performance in CO hydrogenation, the results depicted in Figure 15 indicate that the activities of the bimetallic catalysts were no better then those of the monometallic ones. In addition, the bimetallic catalysts prepared from the tetranuclear clusters did not exhibit a higher selectivity for oxygenates than the monometallic ones, or those prepared by mixing the monometallic clusters. In the same way, the data for the catalysts prepared by the reflux method indicated no improvement in activity nor enhancement in the formation of oxygenates, see Figure 16. The results further indicated that the catalysts prepared from $Ru_3(CO)_{12}$ and $Co_2(CO)_8$ by impregnation performed well in comparison with the ones prepared from tetranuclear clusters, see Figure 15. For example, the oxygenate yield (particularly methyl acetate) was significantly higher for the catalysts prepared from $Ru_3(CO)_{12}$ and $Co_2(CO)_8$.

Very interestingly, in regard to the selectivities, all the bimetallic catalysts were clearly more cobalt-like than ruthenium-like, see Figures 15 and 16. Thus, the reactivity results suggest that ruthenium was bonded to silica and cobalt was located on top of the ruthenium, as reported previously [49, 50]. In other words, the working surfaces of all bimetallic catalysts appear to be cobalt rich.

In regard to bimetallic synergy, however, a very intriguing finding was made in the case of the catalysts prepared by ionic adsorption. The Co(AM)-Ru(Cl)/SiO_2 catalyst was much more selective in the formation of oxygenates (particularly methanol) than either of the monometallic or any of the carbonyl based catalysts, see Table 5. This extraordinary selectivity was a novel finding, and it indicated very clearly that the two metals interacted during catalyst preparation to form active sites with unique characteristics. Perhaps, a positively charged mixed ensemble was formed to account for the observed synergistic enhancement in the formation of methanol.

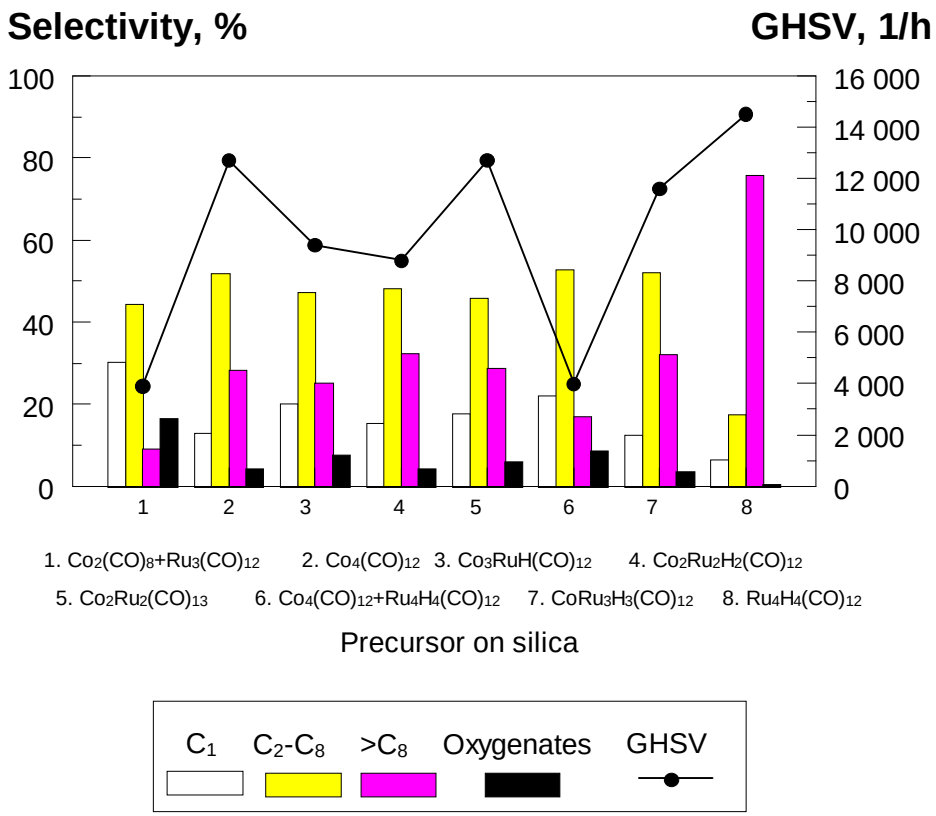

Figure 15. The results in FT synthesis: catalysts prepared by impregnation. T=506 K, P=2.1 MPa, CO conversion = 3%, CO:H_2:Ar 3:6:1 [10].

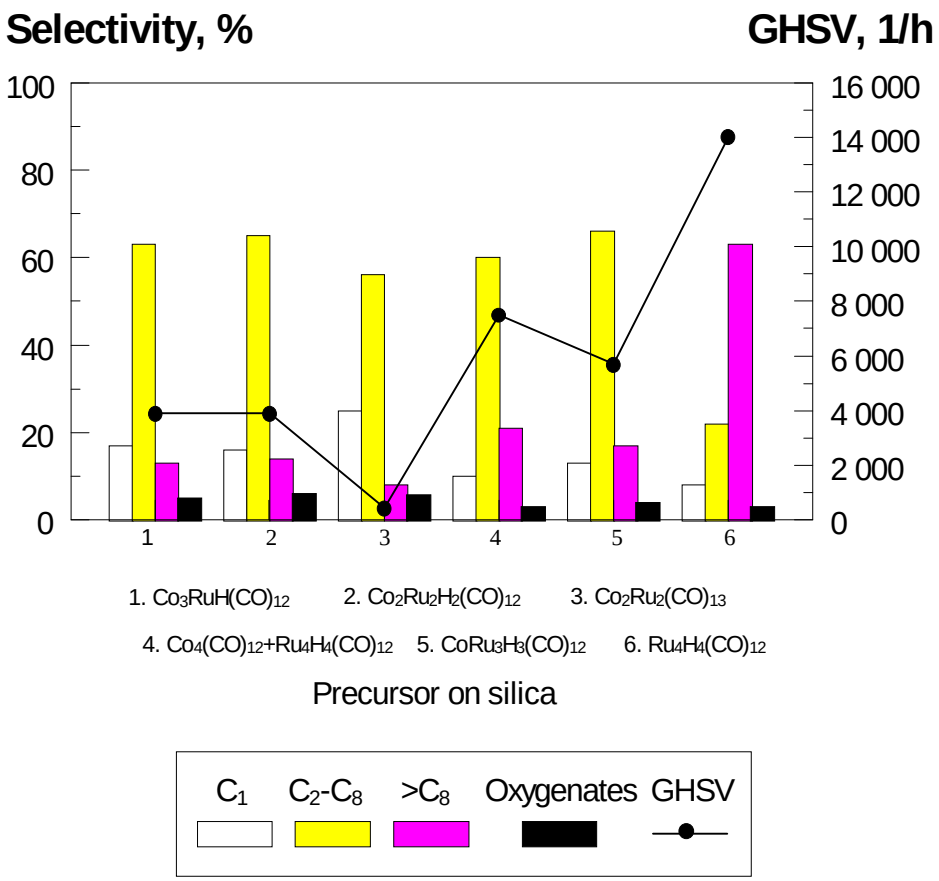

Figure 16. The results in FT synthesis. Catalysts prepared by the reflux method. T=506 K, P=2.1 MPa, CO conversion = 3%, CO:H_2:Ar 3:6:1

Table 5. The results obtained for CO hydrogenation at 523K, P=2.1 MPa, GHSV = 2000 h^{-1}, $CO:H_2:Ar=3:6:1$.

Precursor	Co[2] w%	Ru[2] w%	X %	CH_4 (%)	C_{2-8} (%)	C_{8+} (%)	MeOH (%)	EtOH (%)	PrOH (%)	CO_2 (%)
Co(AM)[1]	2.5		2.1	71.4	22.3	2.3	3.8	0.1	-	-
Co(AM)+ Ru(Cl)[3]	2.0	1.7	9.6	36.1	38.2	5.5	15.7	1	3.47	-
Co(AM) and Ru(Cl)[4]	1.3[5]	0.6[5]	4.5	50.2	41.3	4.2	4.0	0.22	-	-
Ru(Cl)		1.1	18.7	36	40.9	22.4	0.5	0.1	-	-

[1] *The reaction carried out at 573 K*
[2] *Metal contents of the used catalysts, analysed by AAS.*
[3] *Simultaneous ion exchange*
[4] *Physical mixture of the catalysts prepared by ion exchange*
[5] *Estimate based on the analysis of the respective monometallic catalysts*

In all, the activity and selectivity results indicate that the catalyst performance may be significantly influenced not only by the choice of the right combination of metals but also by the preparation method. Consequently, the Co-Ru/SiO_2 catalyst prepared by ionic adsorption exhibited unique selectivity in the FT synthesis compared to similar catalyst compositions prepared by impregnation or the reflux method.

5.3 Catalyst characterisation

5.3.1 The metal contents of the fresh and used catalysts

The metal contents of the fresh and used catalysts were determined by XRF, because ruthenium is known to form volatile oxides, and carbonyl precursors may form volatile species during pretreatment and/or reaction. The results, shown in Table 6, page 52, indicated that the metal contents of the fresh Ru/SiO_2 prepared by reflux were lower than those loaded on catalysts prepared by impregnation [VI]. Yet, the amount of tightly bound ruthenium was higher in conjunction with reflux at an elevated temperature than with adsorption at room

temperature, see paper VI. It thus seems likely that at room temperature, during impregnation, the tetranuclear carbonyls are not chemisorbed on the silica surface to a high degree – a conclusion supported by the literature data [45]. Nevertheless, all of the loaded ruthenium was strongly attached to the support for $Ru(Cl)/SiO_2$ prepared by ionic adsorption, but in this case, the precursor chosen for preparation was known to interact strongly with the support under alkaline conditions [VIII].

The metal analyses also revealed that $Co_4(CO)_{12}$ was not attached to the silica during reflux, but some cobalt was attached to the support if a mixture of ($Co_4(CO)_{12}$ + $Ru_4H_4(CO)_{12}$) or a bimetallic carbonyl was used. Thus, the presence of ruthenium was essential for the adsorption of cobalt [VI, A5]. In other words, the interaction of the ruthenium species with the support was stronger than that of the cobalt species, and it was ruthenium that was attached to the support with cobalt attached on top. Furthermore, in the presence of ruthenium, some cobalt was also adsorbed on the catalyst at room temperature, although cobalt alone has not previously been found to adsorb on silica to a significant degree [45, 51]. This observation allows for the suggestion that in the impregnation method the interaction of the metals proceeds in the same way.

Yet, the metal contents of the fresh catalysts are only the first implication of the success of the catalyst preparation, since the catalyst surface is significantly altered during the pretreatment, as discussed in more detail elsewhere [A5]. Indeed, during the reduction of the present catalysts, the formation of metallic mirrors was observed as a result of sublimation of the carbonyls. Accordingly, the analyses in Table V indicate that the metal content of the reduced/used catalyst was much lower than the loading implies – a significant drawback in the use of carbonyl compounds as catalyst precursors. It is, however, not possible to dictate how much of the losses might have occurred through room temperature decomposition of RuO_4 [52].

The metal contents of the tetranuclear bimetallic catalysts merit a further remark, since the results indicate, very interestingly, that the two tetranuclear carbonyl compounds, $Co_2Ru_2H_2(CO)_{12}$ and $Co_2Ru_2(CO)_{13}$, behaved very differently, *i.e.*, significantly more of $Co_2Ru_2H_2(CO)_{12}$ was adsorbed on silica, both under reflux and at room temperature, see Table 6. Since the difference is evident at both temperatures, it cannot be entirely related to the different thermal stability of the clusters. Perhaps, the $Co_2Ru_2H_2(CO)_{12}$ cluster was more

susceptible to structural change upon contact with partially dehydroxylated silica than was $Co_2Ru_2(CO)_{13}$; the hydrides in the hydrido cluster are mobile [53, 54], whereas the structure of $Co_2Ru_2(CO)_{13}$ might be more stable, even at elevated temperatures [55]. Consequently, it seems that the restructured $Co_2Ru_2H_2(CO)_{12}$ cluster was at least in part chemisorbed on the surface, whereas the adsorption of $Co_2Ru_2(CO)_{13}$ was dominated by physisorption.

Table 6. Summary of the Co-Ru/SiO_2 catalyst preparation methods.

Precursor	Method	Solvent	Co wt.-% fresh	Co wt.-% used [1]	Ru wt.-% fresh	Ru wt.-% used [1]	Reduction in H_2
$Co_4(CO)_{12}$	impregnation	dichloromethane, rt[2]	5.0[3]	n.a[4]			573 K, 2 h
$Co_3RuH(CO)_{12}$	impregnation	dichloromethane, rt	4.4[3]	n.a	1.3[3]	n.a	573 K, 2 h
$Co_2Ru_2H_2(CO)_{12}$	impregnation	dichloromethane, rt	2.6[3]	n.a.	4.5[3]	n.a.	573 K, 2h
$Co_2Ru_2(CO)_{13}$	impregnation	dichloromethane, rt.	2.6[3]	2.0	4.5[3]	2.0	573 K, 2h
$CoRu_3H_3(CO)_{12}$	impregnation	dichloromethane, rt	6.8[3]	n.a	1.3[3]	n.a	573 K, 2 h
$Co_4(CO)_{12}$+$Ru_4H_4(CO)_{12}$	impregnation	dichloromethane, rt.	2.6[3]	1.8	4.5[3]	0.7	573 K, 2h
$Ru_4H_4(CO)_{12}$	impregnation	dichloromethane, rt.			8.9[3]	1.4	573 K, 2h
$Co_2(CO)_8$+$Ru_3(CO)_{12}$	impregnation	n-hexane, rt	5	4.1	2.7	2.2	723 K, 2h
$Ru_3(CO)_{12}$	impregnation	n-hexane, rt			3.1	2.7	573 K, 2h
$Co_4(CO)_{12}$	reflux	n-hexane, 5h bp[5]	0.1	0.05			573 K, 2 h
$Co_3RuH(CO)_{12}$	reflux	n-hexane, 5h bp	1.4	n.a	1.4	n.a	573 K, 2h
$Co_2Ru_2H_2(CO)_{12}$	reflux	n-hexane, 5h bp.	1.6	1.8	1.8	2.6	573 K, 2h
$Co_2Ru_2(CO)_{13}$	reflux	n-hexane, 5h bp.	0.6	0.6	0.6	0.6	573 K, 2h
$CoRu_3H_3(CO)_{12}$	reflux	n-hexane, 5h bp	0.5	n.a	2.6	n.a	573 K, 2h

(Table 6, continued)

Precursor	Method	Solvent	Co wt.-% fresh	Co wt.-% used [1]	Ru wt.-% fresh	Ru wt.-% used [1]	Reduction in H_2
$Co_4(CO)_{12}$+$Ru_4H_4(CO)_{12}$	reflux	n-hexane, 5h bp.	0.4	0.3	2.6	2.7	573 K, 2h
$Ru_4H_4(CO)_{12}$	reflux	n-hexane, 5h bp			3.5	n.a	573 K, 2h
$Co_2Ru_2H_2(CO)_{12}$	ads.	n-hexane, 5h rt.	0.8	n.a.	1.2	n.a.	n.a.
$Co_2Ru_2(CO)_{13}$	ads.	n-hexane, 5h rt.	0.2	n.a.	0.2	n.a.	n.a.
$Co(NH_3)_6Cl_3$	ionic ads.	8% NH_3	3	2.5			723 K, 3h
$Co(NH_3)_6Cl_3$+ $RuCl_3$	ionic ads.	8% NH_3	3	2.0	3	1.7	723 K, 3h
$Co(NH_3)_6Cl_3$ and $RuCl_3$[6]	ionic ads.	8% NH_3	1.5	1.5	1.3[7]	0.6[7]	723 K, 3h
$RuCl_3$	ionic ads.	8% NH_3			3	1.1	723 K, 3h

[1] *used = after reduction or after reaction*
[2] *rt = room temperature*
[3] *loading*
[4] *n.a. = not available*
[5] *bp = boiling point*
[6] *physical mixture of the catalysts*
[7] *Estimate based on the analysis of the respective monometallic catalysts*

5.3.2 FT-IR, TPR and XPS

The decomposition of the tetranuclear clusters on silica has been studied under a hydrogen atmosphere by *in situ* FT-IR and TPR [A3]. The results are summarised in Table 7. It should be noted that the supported clusters with a 1:1 ratio of Co:Ru decomposed smoothly and slowly without showing any distinct temperature of decomposition, and that the decomposition of the silica supported $CoRu_3H_3(CO)_{12}$ and $Ru_4H_4(CO)_{12}$ clusters seemed to proceed via the formation of oxidic ruthenium species.

After decarbonylation (573 K, 2 h), the XP spectra [56] have been recorded. The data analysis for the ruthenium $3d_{5/2}$ and $3d_{3/2}$ lines was carried out by assuming that ruthenium was present only in its fully reduced state. In the case of cobalt, the $Co2p_{3/2}$ line fitting was performed by applying Shirley background correction, which yields a higher value than the linear correction, as discussed in paper V [38]. In the case of the catalysts prepared by ion exchange, the XPS data was measured after reduction (673 K, 2 h), and the results were analysed using a Gaussian peak fit using a Shirley (for ruthenium) or linear (for cobalt) background correction, as presented in detail in paper VIII. The ratio of Co:Ru on the catalyst surface was also calculated from the XPS data, which also is summarised in Table 7.

Table 7. The decomposition of precursors on silica.

Precursor	Decomposition, K		Extent of reduction, %		Co:Ru molar ratio	
	FT-IR	TPR	Co	Ru.	Theor.	Meas.
$Co_4(CO)_{12}$	393	410	24[1], 41[2]			
$Co_3RuH(CO)_{12}$	413	421	21[1]	100[3]	3	4.6
$Co_2Ru_2H_2(CO)_{12}$	not evident	417	21[1]	100[3]	1	3.0
$Co_2Ru_2(CO)_{13}$	not evident	406	29[1]	100[3]	1	5.9
$(Co_4(CO)_{12}+Ru_4H_4(CO)_{12})$	not evident	396	18[1]	100[3]	1	11
$CoRu_3H_3(CO)_{12}$	413	400	26[1]	100[3]	0.3	1.7
$Ru_4H_4(CO)_{12}$	423	458		100[3]		
$Ru_3(CO)_{12}+Co_2(CO)_8$		400				
$Ru_3(CO)_{12}$		446				
$Co(NH_3)_6Cl_3$ + $RuCl_3$ [6]			30-40[4]	90-100[4]	2.0	0.01
$RuCl_3$ [6]				0-10[4], 17[5]		

[1] *according to XPS [56] with Shirley background correction for cobalt*
[2] *according to XPS [V] with linear background correction for cobalt*
[3] *according to XPS [56] with ruthenium assumed fully reduced*
[4] *according to XPS [VIII] with Shirley background correction for ruthenium and linear background for cobalt*
[5] *oxygen titration [VIII]*
[6] *prepared by ionic adsorption*
[7] *based on the analysed metal contents of used catalyst*

The results indicate that the extent of reduction for cobalt in the bimetallic catalysts was unexpectedly low. A significantly higher extent of reduction has been observed for cobalt alone, and the presence of ruthenium has, in some previous studies, been shown to promote the reduction of cobalt [57, 58, 59], as discussed in papers and VIII.

In the case of the catalyst prepared from tetranuclear clusters, the XPS analysis was carried out assuming that all of ruthenium was fully reduced, since ruthenium is usually well reducible (the binding energies for $Ru3d_{5/2}$ were 279.4 and 279.8 eV). For example, Iglesia et al. [60] report that the ruthenium species were predominantly zero-valent for an impregnated Ru/SiO_2 catalyst after reduction at 723 K, passivation by oxygen and rereduction at 673 K. In addition, Gonzales and Miura [61] have reported that direct reduction of silica supported ruthenium catalysts prepared using $[Ru(NH_3)_6]^{3+}$ has resulted in very high ruthenium dispersions approaching 80%, thereby providing further evidence for the high degree of reduction. Yet, this assumption may not have been appropriate since later results indicated that for the Ru/SiO_2 catalyst prepared by ion exchange, the extent of reduction for Ru was very low, only 17% [VIII]. However, the preparation method was significantly different since the pH was alkaline, *i.e.* some ruthenium sites might be encapsulated by silica, which partially dissolved during the ion exchange under alkaline conditions and then precipitated on top of the exchanged surface during filtering/washing. Thus, the low extent of reduction observed for Ru/SiO_2 prepared by ionic adsorption is an exception.

Very importantly, the XPS measurements revealed that for all bimetallic carbonyl based catalysts, the Co:Ru ratios were much higher than could be expected from the composition of the clusters. Hence, the XPS measurements confirmed that ruthenium was attached to the support, and cobalt was located on top of ruthenium. This positioning is plausible, since zero valent ruthenium and cobalt are of limited solubility [18]. In addition, the measured Co:Ru ratios were very different for the catalysts with 1:1 ratio of metals in the original clusters or mixtures, and thus this difference may explain the different performance of the catalysts. However, in the case of the $Co\text{-}Ru/SiO_2$ catalyst prepared by simultaneous ion exchange, the ratio of Co:Ru on the surface was only 0.01, *i.e.* much less than expected based on the amount of metals loaded. Thus, the surface of the ion exchanged catalyst appeared ruthenium rich – a finding which perhaps explains the unique selectivity of this bimetallic catalyst.

5.4 The interrelations of activity and characteristics

The results for ruthenium containing catalysts indicate that: (1) the precursor and/or the combination of metals significantly influences the interaction of the catalytic species with the support, (2) the method of preparation has a profound effect on the attachment and reducibility of the catalytic species on the support, (3) the catalyst surface is restructured during the pretreatment and, as a result, cobalt is enriched on the surface in the case of tetranuclear carbonyl precursors, (4) the performance of the catalysts in CO hydrogenation is significantly influenced by all of these factors.

6. Concluding remarks

The characteristics, activity and product formation of the cobalt catalysts prepared from catalysts prepared from inorganic salts such as nitrate, chloride or acetate, as well as from cobalt carbonyls, were related to both the precursor and to the method of preparation. As a result, the carbonyl catalysts exhibited the highest activity in CO hydrogenation, and $Co_2(CO)_8/SiO_2$ exhibited a high (20%) selectivity for oxygenates such as alcohols and esters. Likewise, the $Co_2(CO)_8/SiO_2$ catalyst was active in the hydroformylation of ethene, wherein the yield decreased in the order Co(CO)>> Co(N)> Co(Cl), *i.e* in order of increasing cobalt particle size.

The promotion affected the performance of the $Co_2(CO)_8/SiO_2$ catalyst significantly; the activity was decreased both in CO hydrogenation and in ethene hydroformylation, but at the same time the selectivity to oxygenates and oxo-products, respectively, was tremendously increased. As a result, an exceptionally high selectivity for propanoic acid (47%) was observed on an alkaline earth oxide promoted $Co_2(CO)_8/SiO_2$. Most likely, the hydroxyl group bound to the alkali earth compound reacted with the surface acyl-species to form propanoic acid.

The results for ruthenium containing catalysts indicated that the precursor and/or the combination of metals significantly influenced the interaction of the catalytic species with the support, and the method of preparation also had a profound effect on the attachment and reducibility. In addition, the pretreatment of the catalyst was important, since the surface was restructured during the pretreatment, resulting in changes/losses of the active sites. As a result of the sensitivity to preparation, the performance of the catalysts differed significantly in CO hydrogenation, both in terms of activity and selectivity. Very interestingly, the Co-Ru/SiO_2 catalyst prepared by ionic adsorption exhibited unique selectivity, pronounced formation of methanol, in the FT synthesis compared to similar catalyst compositions prepared by impregnation or the reflux method.

In all, the work clearly demonstrated the strong interrelation of catalyst preparation and performance. It also indicated that catalysts with very unusual performance could be prepared from $Co_2(CO)_8$ precursor. The commercial

applicability of all the carbonyl based catalysts is, however, limited by their air sensitive nature and by the losses occurring during the catalyst pretreatment. Thus, the catalysts with a less sensitive preparation method but nevertheless unique characteristics, such as Co-Ru/SiO_2 prepared by simultaneous ionic adsorption, appear more interesting in the light of further development work.

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