Reactions of synthesis gas on silica supported transition metal catalysts

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Abstract

The effect of catalyst precursor and composition on the activation of CO was investigated using CO hydrogenation as a test reaction. The interrelations of preparation, pretreatment, characteristics and activity were clarified.

For Co/SiO_2 catalyst, MgO promotion increased the CO adsorption capacity and the hydrogen uptake, although the extent of reduction for cobalt remained the same or decreased. The conversion per active metallic cobalt site consequently increased in conjunction with MgO promotion, while the effect on overall performance per 1 g of catalyst remained moderate.

The precursor affected the performance of Co/SiO_2 considerably. CO was more strongly adsorbed on catalysts of carbonyl origin than on those derived from cobalt nitrate, the activity thus being higher. Although the nitrate derived Co/SiO_2 appeared both to retain its activity and to regain its adsorption capacity better than the catalysts of carbonyl origin, the performance of the latter was superior with time on stream.

For tetranuclear cluster based Co-Ru and Co-Rh catalysts, rhodium or ruthenium was in contact with the support and cobalt was enriched on top. On $Co-Ru/SiO_2$, ruthenium enhanced deactivation, and no benefits in activity or oxygenate selectivity were achieved relative to the monometallic catalysts of cluster origin. The $Co-Rh/SiO_2$ catalysts were also less active than those derived from monometallic clusters, but they exhibited higher selectivities to oxygenated compounds due to the presence of active sites on the perimeter of the cobalt particles located on rhodium. The highest selectivity to oxygenates was achieved by changing the decomposition atmosphere of $Rh_4(CO)_{12}/SiO_2$ from hydrogen to carbon monoxide. The results also showed two types of active sites to be operative in the formation of oxygenates - one for ethanol and another for aldehydes.

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My greatest debt of gratitude lies with the members of my family, who have filled my life with daily joys and sorrows making the frustrations of an extended research effort easier to handle. And vice versa, it is surely the members of my family who are most grateful that this work is finally at an end.

Espoo, February 1997

Marita Niemelä

List of publications

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

I   Niemelä, M.K., Krause, A.O.I., Vaara, T. and Lahtinen, J., Preparation and characterization of Co/SiO2, Co-Mg/SiO2 and Mg-Co/SiO2 catalysts and their activity in CO hydrogenation. Topics Catal., 2 (1995), pp. 45 - 57

II   Niemelä, M.K. and Krause, A.O.I, Characterization of magnesium promoted Co/SiO2 catalysts. Catal. Lett., 34 (1995), pp. 75 - 84

III   Niemelä, M.K., Krause, A.O.I., Vaara, T., Kiviaho, J.J. and Reinikainen, M.K.O., The effect of the precursor on the characteristics of Co/SiO2 catalysts. Appl. Catal. A General, 147 (1996), pp. 325 - 345

IV   Niemelä, M.K. and Krause, A.O.I., The long term performance of Co/SiO2 catalysts in CO hydrogenation. Catal. Lett., 42 (1996), pp. 161 - 166

V   Niemelä, M.K., Backman, L., Krause, A.O.I. and Vaara, T., The activity of the Co/SiO2 catalyst in relation to pretreatment, accepted for publication in Appl. Catal.

VI   Kiviaho, J., Reinikainen, M., Niemelä, M.K., Kataja, K. and Jääskeläinen, S., The activity of carbonyl cluster derived Co-Ru/SiO2 and Co-Rh/SiO2 catalysts in CO hydrogenation. J. Mol. Catal. A: Chemical, 106 (1996), pp. 187-195

VII 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/SiO2 and Rh/SiO2 catalysts, accepted for publication in J. Mol. Catal. A: Chemical

The author's contribution

The author has had an active role in all stages of the work reported in this thesis. She participated in the planning and carrying out of the experiments reported in publications I - V and VII. She analysed and interpreted the results of papers II and IV, and contributed in a major way to studies I, III and V. The author also contributed substantially to the evaluation of the results reported in publications VI and VII. She wrote papers II and IV, the major part of papers I, III and V, and contributed significantly to the writing of publications VI - VII.

Contents

Abbreviations

Catalysts:

Precursor/Silica   a general form of presenting the catalysts, in which
      Co(N)   cobalt nitrate
      Co(A)   cobalt acetate
      Co(CO) $Co_2(CO)_8$ or $Co_4(CO)_{12}$

½-Mg-Co/SiO_2 silica impregnated with cobalt nitrate and then with magnesium nitrate, Mg:Co molar ratio **½**

2-Mg-Co/SiO_2 silica impregnated with cobalt nitrate and then with magnesium nitrate, Mg:Co molar ratio 2

2-Co-Mg/SiO_2 silica impregnated with magnesium nitrate and then with cobalt nitrate, Mg:Co molar ratio 2

Methods:

TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
AAS	Atomic absorption spectroscopy
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
SIMS	Secondary ion mass spectrometry
TGA	Thermogravimetric analysis
TEM	Tunnelling electron microscopy

Other:

X	Conversion, %
GHSV	Gas hourly space velocity, h^{-1}
α	Probability of chain growth
C-%	Selectivity expressed as carbon efficiency

1. Foreword

The C1-chemistry project forms part of the national Synthesis Technology Programme that was administered and funded by the Technology Development Centre of Finland between April 1992 and March 1997. The project was aimed at developing new means for the activation of CO, with use of homogeneous and heterogeneous catalysts. The vision of the project was to find novel catalyst compositions that the industrial partners would be willing to develop to a commercial stage.

The C1-chemistry project comprised four collaborating parties: at the Helsinki University of Technology Laboratories of Physics and of Industrial Chemistry, the University of Joensuu and VTT Chemical Technology. Development of novel catalyst precursors and reactivity studies on homogeneous catalysis were undertaken at the University of Joensuu, surface science and model catalyst studies were carried out in the Laboratory of Physics, and catalyst preparation, characterization and testing were performed in the Laboratory of Industrial Chemistry and at VTT Chemical Technology.

The task of the Laboratory of Industrial Chemistry was to elucidate the effect of the catalyst precursor and composition on the activation of CO, by using test reactions such as CO hydrogenation, methanol (hydro)carbonylation and olefin hydroformylation. Thus, the focus of the research was the dissociative and molecular activation of CO by heterogeneous catalysts. The work included construction of the experimental facilities, preparation and characterization of catalytic materials and testing of the activity and selectivity of the catalysts. This thesis summarizes the results of the studies on silica supported transition metal catalysts in CO hydrogenation [I - VII]. The supplementary presentations or publications by the author of this thesis are provided as references 1 - 14.

2. General

2.1 Synthesis gas and catalysis

Since the early part of the century catalytical synthesis gas ($CO+H_2$) chemistry has been an interesting subject of development and research, because it offers many routes to fuels and chemicals through hydrogenation of carbon monoxide to alkanes, alkenes and oxygen containing products [15 - 17]. CO hydrogenation is best known as the Fischer-Tropsch (FT) synthesis, which involves a stepwise hydrocarbon chain growth described by the Schulz-Flory polymerization law [15, 18]. The chain-growth probability, α, is a fundamental property of any FT catalyst, and together with the process operating conditions determines the product distribution [18]. At present, FT technology is utilized at Sasol in South Africa in the production of a wide array of products and by Shell in Malaysia in the manufacture of middle distillates [17, 19, 20].

The exothermic, but slow, reaction of CO with H_2 is catalysed by metals of Group VIII with specific activities decreasing in the order ruthenium > iron > nickel > cobalt > rhodium > palladium > platinum and iridium [21]. In commercial applications, methanation catalysts are mainly in the form of nickel on a support [22], Fischer-Tropsch synthesis is carried out with iron based catalysts [16, 23], and the process recently developed by Shell for middle distillates utilizes a modified cobalt catalyst [20]. In terms of researched compositions, the voluminous collection of different metal/support combinations renders a comprehensive summary impossible. In relation to the present work, interesting development work has been summarized in recent reviews [23 - 25].

The present FT catalyst technology suffers from limitations in catalyst selectivity and deactivation [23]. Wide product distribution with relatively low yields for any product other than C1, is a natural outcome of the stepwise growth of the hydrocarbon chain growth [15, 24]. While novel catalytic compositions and tailored process conditions may offer a way to improved selectivity [23], there are still other demands to be met, such as the ability of the catalyst to withstand the long term adverse effects of sulphur, carbon lay down and water vapour [22, 26].

2.2 Reaction mechanism

Both methanation and CO hydrogenation involve the formation of metal-carbon bonds, but carbon-carbon bond formation is unique to FT synthesis. The reaction network of growing chains on the surface of FT-catalysts has been described, among others by Sachtler and Ichikawa [27], who suggest a unifying general scheme for the formation of hydrocarbons and oxygenates in CO hydrogenation on metal catalysts. However intriguing this idea of a general scheme of elementary steps may be, the more recent reviews of Ponec [23 Chapter 4, 28] and Hindermann et al. [24] clearly demonstrate that each of the three global pathways leading from the synthesis gas to methanol, hydrocarbons or higher alcohols (or other C_{2+} oxygenates) warrants a separate discussion. In connection with catalysts of Co, Ru or Rh on silica, nevertheless, only the pathways leading to the latter two products need to be addressed [28].

It is commonly explained that the synthesis of hydrocarbons commences with dissociation of adsorbed CO to form CH_x followed by polymerization [23, 24, 27, 28]. This reaction requires an ensemble of several active metal atoms [23, 27, 28], and the propensity to dissociate CO is different for individual metals [23, 28]. The most active metals for CO dissociation are Fe, Co, Ni, Ru and Os. However, the propensity to dissociate CO is enhanced by alkali metal compounds [23, 28], and on Rh the dissociation rate has been enhanced by oxophilic metal ions [27] or transition metal oxides [28].

Much detailed information also is available on the formation of higher alcohols and other C_{2+} oxygen containing products [23, 24, 28, 29]. The most likely pathway from synthesis gas to these products comprises the reaction of the formed CH_x species with CO, *i.e.*, insertion of CO in the surface-alkyl bonds [27, 28, 30]. Sachtler and Ichikawa [27] and Ponec [28, 30] are of the opinion that higher alcohols and aldehydes are formed via the same route, but Orita et al. [31], using isotopic labelling, found that ethanol is not produced via direct hydrogenation of acetaldehyde. Jackson et al. [32] have shown in addition that ethanol and ethanal are produced independently with no common intermediate. More precisely, they [32] suggest that the first step in the reaction of molecularly adsorbed carbon monoxide is decisive: a reaction with adsorbed hydrogen results in an alcohol, while a reaction with CH_2 results in an aldehyde. Hindermann et al. [24] are of the opinion, however, that the stability of an acyl intermediate may correlate

with the selectivity for alcohol synthesis, although the experimental evidence they refer to indicates that different surface intermediates are stabilized by different catalysts.

In terms of the active site, the results are also contradictory: some results suggest that the formation of oxygenates is favoured on isolated metal atoms, *e.g.*, Rh [24, 27], whereas others [24, 25, 28 - 30] suggest that the formation of oxygenates is possible only in conjunction with promotion by metal oxide. In fact, it appears highly likely that the reported particle size effects may rather be related to unintentional promotion effects [24, 28]. Thus, the formation of alcohols appears to require a promotor, whereas the formation of hydrocarbons and aldehydes may proceed without one.

Against the background of recent excellent reviews [23 - 25, 28] it is clear that the detailed mechanism for the different catalyst system remains unresolved and more experimentation needs to be carried out. The present brief summary is meant only to illustrate the complexity of the mechanism of the catalytic reaction of synthesis gas and to provide a framework for the analysis of the reactivity data.

2.3 Scope of the work

The metal compositions that were studied were dictated in part by the cooperation with other C1-chemistry parties: the surface science group was dealing with magnesium promoted cobalt surfaces [33], and the group doing synthesis and experimental studies on catalyst precursors was working with mono and mixed metal carbonyl clusters composed of Co, Rh and Ru [34 - 36]. In view of this, my study was aimed at elucidating the applicability of the surface science studies to the heterogeneous catalytic system and comparing the characteristics of the homogeneous carbonyl clusters and the corresponding heterogeneous catalysts.

The conventional cobalt catalyst, being cheap, easily modifiable and one of the most active in the reactions of synthesis gas, provided an appropriate starting point for the studies. Ruthenium and rhodium were obvious choices as modifiers. The addition of small amounts of ruthenium to Co/SiO_2 both increases catalyst activity and enhances the production of high molecular weight waxes of commercial value [37, 38]. Indeed, it is well known in the art that ruthenium catalysts produce of very high molecular weight

paraffinic hydrocarbons [39]. It should be noted, however, that the selectivity of the Co and Ru catalysts has recently been strongly linked to the transport-limited reactant arrival and product removal processes, in addition to intrinsic chain growth kinetics [40 - 43].

In terms of directing the selectivity of cobalt to oxygenates, rhodium seemed a suitable choice since it is unique in being capable of catalysing the formation of both hydrocarbons and oxygenated compounds [23, 24, 25]. Rhodium thus offered a challenge: reproduce its excellent performance in activation of CO with modified compositions less rich in this very expensive metal.

3. Pretreatment and characteristics of Co(N)/SiO$_2$

Cobalt catalyst prepared by impregnation of cobalt nitrate on a silica support provided the reference in this study. The catalyst composition is cheap, easily modifiable and, as described in detail in paper I, does not require any specific equipment for preparation. Although silica is widely used as an inert catalyst support (low metal-support interaction), it may influence the catalytic behaviour of cobalt by changing the selectivity. Namely, impurities incorporated into the support matrix have been associated with unintentional promotion effects [44, 45]. To investigate such effects, the purity of the silica support was determined in study I. The traces of sodium and iron that were found have been shown to have a promoting effect on the catalysts in the enhancement of alcohol formation [44] - a result relevant to the interpretation of the reactivity data.

The characteristics of the impregnated Co(N)/SiO$_2$ were determined after drying, calcination and reduction [I, III, IV]. The SIMS measurements indicated that, after vacuum drying, cobalt species were evenly distributed on the silica, whereas after calcination at 300°C the cobalt was concentrated on the outer surface of the silica grains. Thus, the partial decomposition of the nitrate species probably produced mobile Co species which migrated out of the pores [I]. The XPS measurements indicated further that the cobalt species on the calcined Co(N)/SiO$_2$ catalysts were Co$_3$O$_4$, and the XRD results suggested that the crystal size was 12 ± 4 nm [I]. As discussed in paper I, the results were in good agreement with the literature data.

The effect of calcination temperature on the hydrogen uptake of the Co(N)/SiO$_2$ catalyst was studied by first calcining the catalyst at 300°C or 500°C and then reducing it at 400°C [V]. Since the hydrogen uptake was lower after high temperature calcination, 300°C was chosen for subsequent catalyst preparations. In the following, therefore, calcination refers to thermal treatment in air at 300°C.

The reducibility of the calcined Co(N)/SiO$_2$ catalyst was studied at 200 - 500°C by XPS and TGA [I, III, V]. The TGA data gave systematically slightly higher degrees of reduction than XPS, which has access to the outermost surface only [I]. XPS was, nevertheless, employed in all subsequent analyses because the spectra are also useful in determining the

ratio of elements on the surface and in estimating the particle size [III]. In sections that follow, the extent of reduction refers to the near surface values determined by XPS.

The rather complex method of determining the extent of reduction from the XPS data was discussed recently [46]; the improvements to the method of analysis made in the course of this study are merely summarized here. The data analysis in papers I - VII differed in terms of both peak fitting and background correction. Namely, the satellite structures were ignored in the first determinations [I], but were accounted for in later studies II, III, V and VII. In regard to the background, either Shirley background correction [I, II, III] or linear background subtraction [III, IV, V, VII] was used. At first, the values obtained by Shirley background correction appeared more appropriate
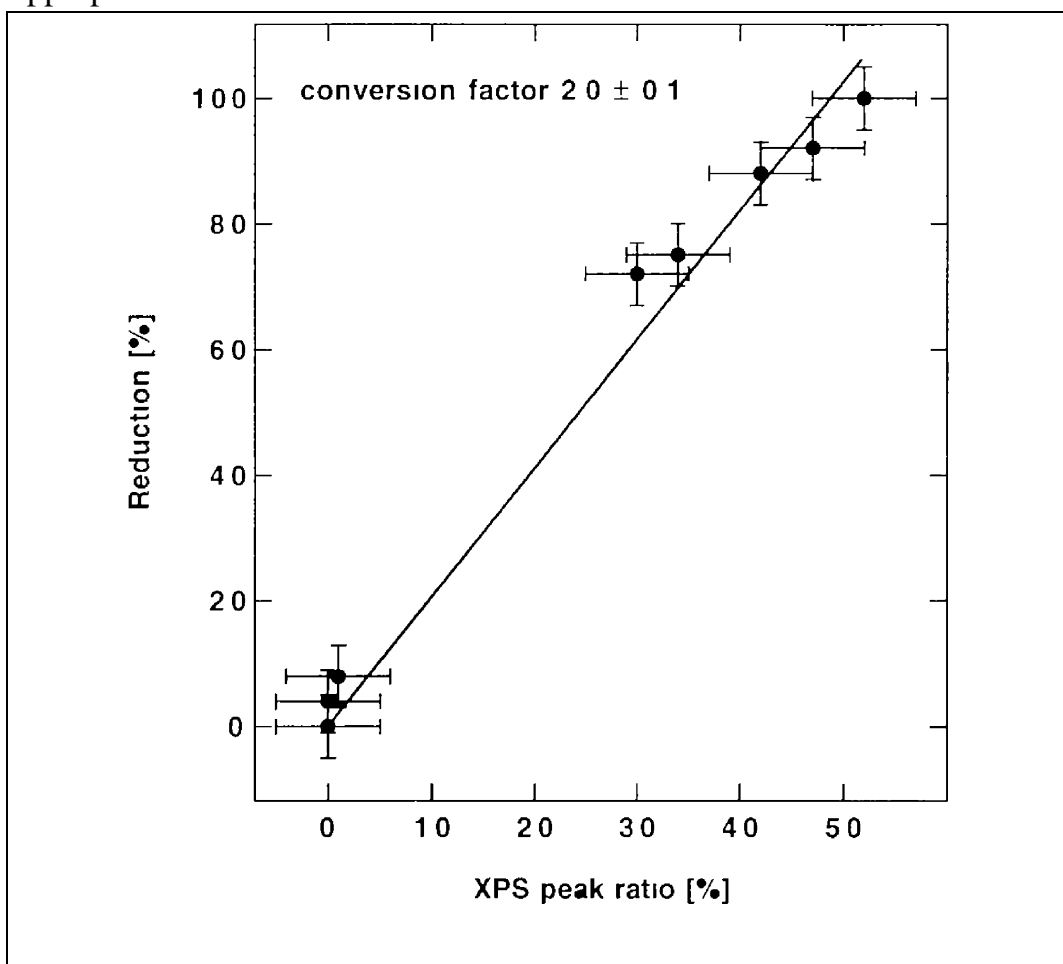

Figure 1.   *The extent of reduction is correlated with the ratio of the metallic component of the XPS $Co2p_{3/2}$ line (Co^0) to the total $Co2p_{3/2}$ peak area, i.e., XPS peak ratio refers to $Co^0/Co2p_{3/2}$ peak ratio.*

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since they were more similar to the values presented in the literature. However, closer study [III] showed the linear correction to describe the background better. Thus, the values obtained for the extent of reduction were somewhat low relative to published values [III], but the proportion of different components was not distorted.

Yet another improvement was achieved by applying external reference points. In this method, the reference values for completely oxidized (calcined $Co(N)/SiO_2$) to fully reduced samples (cobalt foil) [V] were plotted as a function of the respective XPS $Co^0/Co2p_{3/2}$ peak ratios (linear background correction) (Figure 1). Since the data points correlate linearly, correct values for the extent of reduction may be obtained by multiplying the $Co^0/Co2p_{3/2}$ peak ratios by a factor of 2 [V]. This method was applied in this thesis to data published in papers III - VII as shown in section 5 onwards.
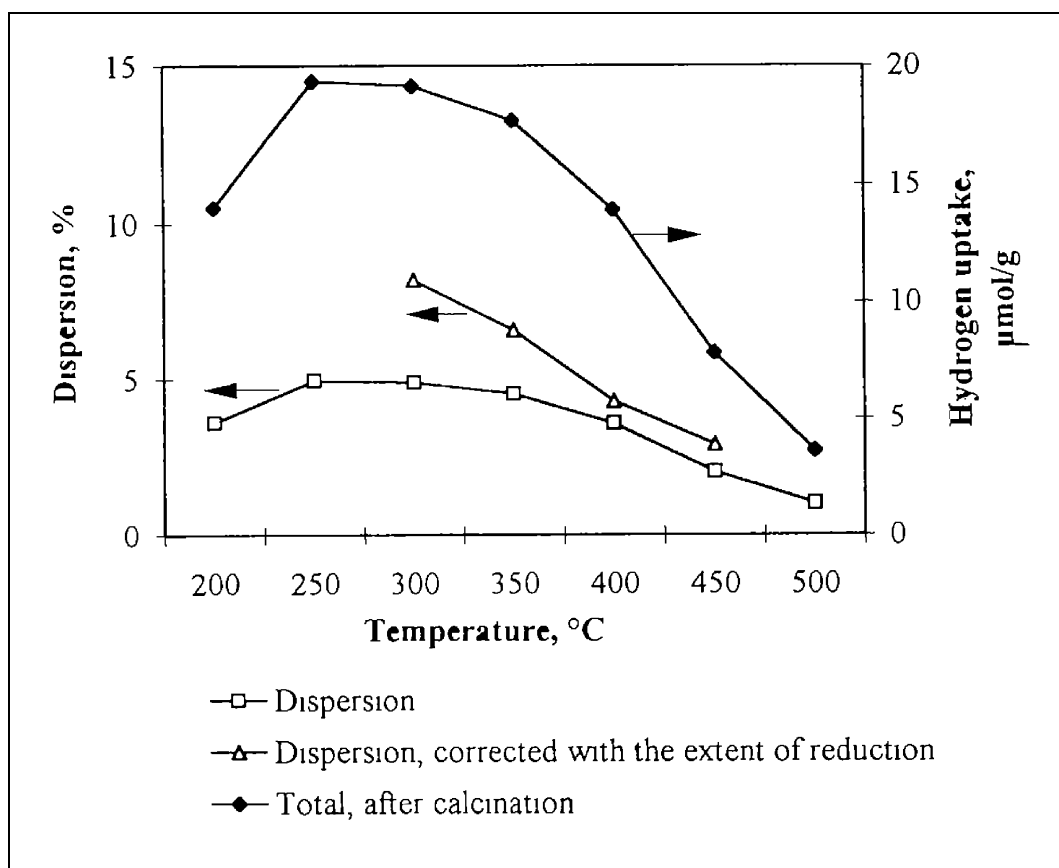
Figure 2. *Effect of reduction temperature on the extent of reduction, hydrogen uptake and dispersion for Co(N)/SiO₂.*

According to XPS, the extent of reduction of $Co(N)/SiO_2$ was maximum

84% [V] after reduction at 400°C. However, the hydrogen uptake passed through a maximum at a reduction temperature of approx. 300°C, whereas carbon monoxide uptake remained essentially constant at 200 - 400°C and decreased thereafter [V]. Consequently, the dispersion calculated from the hydrogen uptake and corrected with the extent of reduction decreased with increasing temperature of reduction (Figure 2). The results obtained were plausible in the light of previous reports as discussed in papers I, III and V, and confirmed the suitability of $Co(N)/SiO_2$ as reference case for further studies.

4. Effect of magnesium promotion on Co(N)/SiO$_2$

During the early years of the FT-synthesis, magnesium oxide was used to stabilise Co/ThO$_2$/KG (KG stands for kieselguhr) [47]. More recently, magnesium promoted heterogeneous catalysts have been found to produce more oxygenated compounds than have their unpromoted counterparts [48, 49]. Furthermore, work carried out on cobalt foil model catalysts [I] indicates that magnesium promotion enhances chain growth - yet another characteristic feature. Keeping these different results in mind, the attempt was made to specify the effect of magnesium promotion on heterogeneous catalysts. At the same time, the relation between the foil model catalysts and the supported catalysts was investigated.

4.1 Catalyst characteristics

The characteristics of the promoted catalysts were determined by XPS and hydrogen chemisorption as described in papers I and II. The XPS analysis indicated that the surface Mg:Co ratio depends on the order of impregnation, *i.e.,* magnesium covered cobalt when it was impregnated last, and vice versa [I]. Although the extent of reduction was lower with magnesium promotion [I], the hydrogen uptakes of 2-Mg-Co/SiO$_2$ and 2-Co-Mg/SiO$_2$ in the static chemisorption were higher than the hydrogen uptake of Co(N)/SiO$_2$ [II]. The dispersions, corrected for the extent of reduction, were similar for Co(N)/SiO$_2$ and ½-Mg-Co/SiO$_2$, and twice those for 2-Mg-Co/SiO$_2$ and 2-Co-Mg/SiO$_2$ [II]. The values for particle sizes obtained by chemisorption correlated well with the XRD determinations [I], *i.e.*, provided further evidence that MgO promotion at a Mg:Co molar ratio of 2 decreased the particle size of cobalt or, in other words, increased the dispersion (see Table 1, page 21).

4.2 Pulse-mode studies

The pulsing technique was used to elucidate the CO adsorption and desorption characteristics, and to study the initial reactivity of the catalysts. The experimental setup is described in papers II and III.

To determine the interaction of CO with the catalyst, the samples reduced at 400°C were saturated with CO pulses at 25°C. During a pulse of 0.5 cm^3, hydrogen, methane, CO, and CO_2 were detected with a mass spectrometer. It is noteworthy that the size of the methane peak was about the same for all catalysts, whereas the CO_2 formation decreased with increasing amount of MgO [II].

The species adsorbed during the pulsing were removed by subsequent heating under helium flow. As the temperature increased, CO, CO_2, and water were desorbed from the surface. An interesting observation was made: the CO adsorption capacity increased in the presence of MgO, and the increase was considerable for a Mg:Co atomic ratio of ½ and slight for an atomic ratio of 2 [II]. Likewise, the hydrogen uptake increased with MgO promotion. Probably, the amount of adsorption was related to the number of sites at the interphase of MgO and cobalt, which were greatest at a Mg:Co atomic ratio of ½. Further evidence for this interpretation is the observation of Vaari et al. [50] that, as the coverage of Mg on the cobalt model surface increased above 0.4, the neighbouring islands began to merge.

At the same time, MgO promotion was associated with decreased extent of reduction (see Table 1, page 21). One may speculate that, in this partially reduced environment, some of the CO adsorption on the edge sites resulted in the formation of $Co(CO)_4^-$ and CO_3^{2-} species as have been observed on Co/MgO catalyst [51]. Thus, the presence of MgO appeared to create new types of active sites, most likely at the perimeter of the cobalt particles [II].

In accordance with the altered nature of the active sites, the desorption of CO_2 differed noticeably in the presence of MgO. The total amount of CO_2 desorbed decreased in the order ½-Mg-Co/SiO$_2$ > Co(N)/SiO$_2$ > 2-Co-Mg/SiO$_2$ and 2-Mg-Co/SiO$_2$. Some of the desorption may be attributed to the decomposition and desorption of the $Co(CO)_4^-$ and CO_3^{2-} species [52].

Further evidence for the different kind of active sites was obtained when the catalyst samples were treated with hydrogen (from 25 to 400°C) after TPD in order to remove any carbonaceous residues. During this treatment Co(N)/SiO$_2$ released water, whereas the MgO promoted catalysts released water, CO and CO_2. Apparently, some of the surface species generated by the interaction of cobalt and MgO were stable under inert gas, but decomposed under hydrogen atmosphere [II].

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The initial reactivity was studied by commencing CO pulses in the presence of hydrogen at 25 or 250°C. At room temperature, methane and ethane were detected, whereas at 250°C the surface reactions also produced water and CO_2 - reaction products typical for CO hydrogenation. Interestingly, the water evolution decreased with increasing amount of magnesium promotion: $Co(N)/SiO_2$ > ½-Mg-Co/SiO_2 > 2-Mg-Co/SiO_2, 2-Co-Mg/SiO_2. However, the decreasing amount of water was not accompanied by increased formation of CO_2 but rather the reverse. It is also noteworthy that the CH_3O^+ species was observed for ½-Mg-Co/SiO_2 and 2-Mg-Co/SiO_2, but not for $Co(N)/SiO_2$. Unfortunately CH_3O^+ was not investigated for 2-Co-Mg/SiO_2.

4.3 Catalyst activity

The steady-state results showed the order of impregnation to influence the conversion of CO (to hydrocarbons and CO_2) with the magnesium promoted $Co(N)/SiO_2$ catalysts (Figure 3). The catalysts with more accessible cobalt, *i.e.*, 2-Co-Mg/SiO_2 and $Co(N)/SiO_2$, appeared to be more active [I, II], and the differences in activity were more pronounced at the higher reaction temperatures of 260°C and 290°C. It should be noted that the probabilities of chain growth were slightly lower for the catalysts with Mg:Co molar ratio of 2, *i.e.*, for catalysts with lower extent of reduction, smaller particle size (XRD) and higher dispersion. The result is in agreement with the observation of Reuel and Bartholomew [53] that the molecular weight of hydrocarbon products decreases with increasing dispersion and with decreasing extent of reduction.

The $Co(N)/SiO_2$ catalysts promoted with magnesium were better able than their unpromoted counterparts to withstand high reduction temperatures, *i.e.*, their activity in terms of conversion was maintained [I, II]. Thus, in reduction at 450°C, the conversion per active cobalt site [II] was clearly enhanced in the presence of magnesium (see Table 1). The highest activity was observed with ½-Mg-Co/SiO_2, though the activity of both 2-Mg-Co/SiO_2 and 2-Co-Mg/SiO_2 increased as well [I, II]. Thus, magnesium oxide supplied a stable surface area for the catalysts [47].
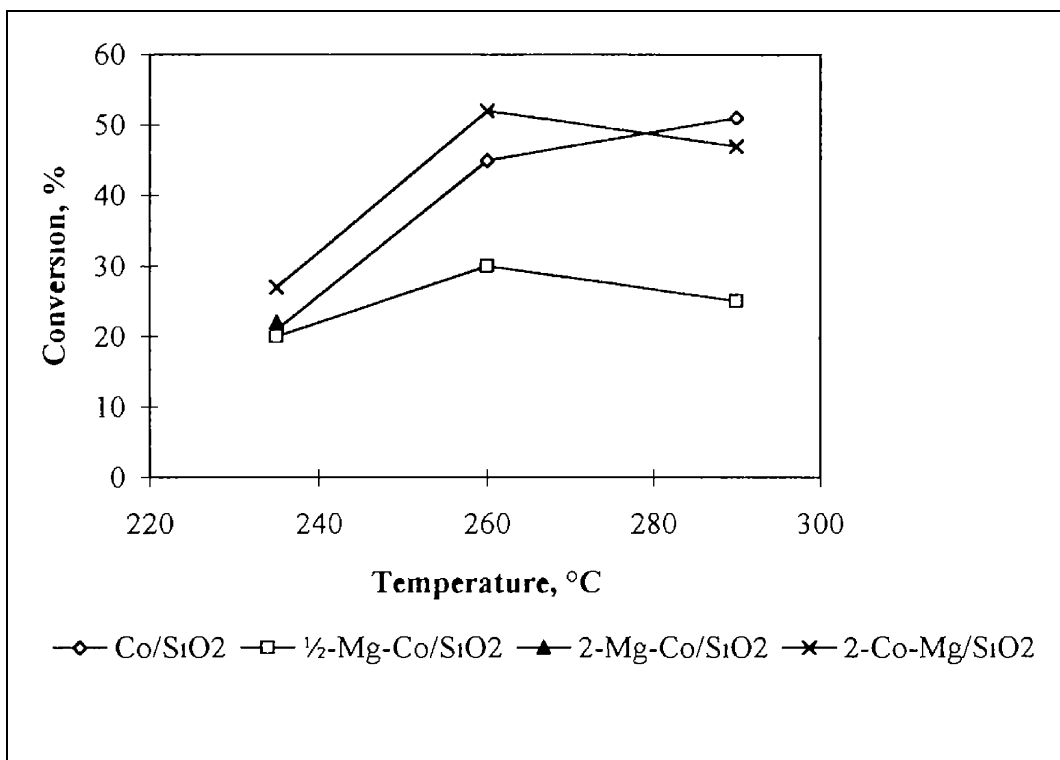
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Figure 3. *Activity of magnesium promoted Co(N)/SiO$_2$ catalysts after reduction at 400°C at 0.5 MPa, GHSV = 2600 h^{-1}, CO:H$_2$:Ar=1:3:3 and 1 g catalyst.*

Table 1. *Results obtained at 0.5 MPa and 235°C with GHSV = 2600 h^{-1} and 1 g catalyst. Reproduced from paper [II].*

Catalyst on SiO$_2$	X_{CO} [1] %	X_{CO} [2] %	Dispersion %	Co mg	Reduction %	X_{CO} [3] %/mg$_{met}$	CO_2 [2] mol-%
Co(N)	21	11	5.5	51	54	7	2.2
½-Mg-Co	20	20	5.1	47	55	15	0
2-Mg-Co	22	22	12	44	35	12	0
2-Co-Mg	27	23	9.7	45	41	13	0

[1] Reduction at 400°C

[2] Reduction at 450°C

[3] X(%):[Co(mg)·(D(%)/100)·(R(%)/100)]

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A distinct effect of the magnesium promotion was the disappearance of CO_2 from the product stream [I, II]. This is also in accordance with the TPD results, although low extents of reduction of Co/MgO have previously been found to result in high yields of CO_2 at 300°C [53]. More recent studies [54] have related the amount of CO_2 formation to the chemical nature of the support rather than to the extent of reduction. Thus, the effects of magnesium were most likely due to modification of the active sites [I, II], to the presence of formate species, for example [49, 55]. In support of this interpretation, traces of methanol were observed in the presence of magnesium during the pulse experiments.

Although interesting observations were made on magnesium promoted Co(N)/SiO$_2$ catalysts in studies I and II, the results could not be reproduced when cobalt acetate was used as a precursor. Irrespective of the impregnation order, the only effect of magnesium promotion on Co(A)/SiO$_2$ was loss of activity and CO_2 selectivity. Indeed, all Co(A)/SiO$_2$ catalysts exhibited very low extents of reduction, if any, and much lower activity than the respective catalysts prepared from nitrate-salts. The results clearly indicate that the precursor has a greater effect on the overall activity than magnesium promotion, and the attention was accordingly directed towards the effect of the precursor.

5. Effect of precursor on Co/SiO$_2$

The classical precursors for Co/SiO$_2$ catalysts are cobalt chloride, acetate and nitrate. Of these, the chlorides have attracted little attention because chloride residues have a disadvantageous effect on the adsorption of CO on metal surfaces [23, Section 2.5]. The acetate precursors have also been found undesirable due to low activity of the respective catalysts [I]. In contrast, the nitrate derived catalyst has been widely studied and characterized over the past decades. More recently, interest has turned to the activity and selectivity of cobalt carbonyl derived catalysts. The activity of cobalt catalysts of carbonyl origin has often been reported to be significantly higher than that of Co(N)/SiO$_2$, and the selectivity to oxygenates has at times been exceptional. Thus, carbonyl based catalysts merited attention, to clarify the source and nature of their performance.

5.1 Catalyst characteristics

Catalysts prepared from nitrate and carbonyl precursors were characterized by XRD, XPS and chemisorption. The results are collected in Table 2. Relative to the conventional catalyst with 84% extent of reduction, the value obtained for Co$_4$(CO)$_{12}$/SiO$_2$ (82%) was not exceptional; the value (30%) obtained for Co$_2$(CO)$_8$/SiO$_2$, in turn, was quite unexpected. Co$_2$(CO)$_8$ would be expected to decompose readily to Co$_4$(CO)$_{12}$ [56 - 58], and the TPR results suggested that the formation of products during the thermal treatment essentially ceased below 300°C for both carbonyl precursors [III]. The low extent of reduction for Co$_2$(CO)$_8$/SiO$_2$ was probably due to the high dispersion (40%), since small particles interact strongly with the support and are more difficult to reduce [III]. The dispersion of Co$_4$(CO)$_{12}$/SiO$_2$ was considerably low (16%) and the dispersion of Co(N)/SiO$_2$ was much lower still (3.6%).

Table 2.   Characteristics of the Co/SiO₂ catalysts after reduction with hydrogen. Reproduced from paper [III].

Precursor	H₂ uptake µmol/g$_{cat}$	Reduction % XPS	Dispersion %	Size[1] nm	Size[2] nm
Co(N)[3]	12.5	84	3.6	14	27
Co₂(CO)₈ [4]	46.2	30	40	2.3[5]	2.4
Co₄(CO)₁₂ [4]	52.2	82	16	3.4[5]	5.7

[1] XRD

[2] Chemisorption

[3] Reduced at 400°C

[4] Reduced at 300°C

[5] Upper limit estimate; the sample was oxidized at 300°C before measurement

5.2 Pulse-mode studies

The CO adsorption characteristics and the initial reactivity of the catalysts were determined in a micro reactor system as described in detail in papers II and III. The adsorption characteristics were studied by saturating the reduced catalyst samples with 10 pulses of CO at 25°C, and by removing the adsorbed species by elevating the temperature under inert gas flow (TPD).

The amount of CO desorption during TPD decreased in the order $Co_2(CO)_8/SiO_2 > Co_4(CO)_{12}/SiO_2 > Co(N)/SiO_2$. In contrast, the hydrogen uptake of $Co_2(CO)_8/SiO_2$ was similar to that of $Co_4(CO)_{12}/SiO_2$ (46.2 vs. 52.2 µmol/g$_{cat}$) while the dispersion was more than two fold (40% vs. 16%) (Table 2). Evidently, owing to the higher dispersion, more CO molecules are able to adsorb per surface cobalt atom on $Co_2(CO)_8/SiO_2$ than on $Co_4(CO)_{12}/SiO_2$. This is also in accordance with the finding of Reuel and Bartholomew [59] that the subcarbonyl adsorption forms are prevalent on well-dispersed cobalt catalysts.

The temperature at which the CO desorption took place increased in the order $Co(N)/SiO_2 < Co_4(CO)_{12}/SiO_2 < Co_2(CO)_8/SiO_2$. The shift of desorption to higher temperatures suggests that CO is adsorbed more strongly on the $Co(CO)/SiO_2$ catalysts than on their conventional

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counterpart, and higher activities would be expected [III]. It is further noteworthy that the number of peaks for good fitting to the overall desorption curve was four for the $Co(CO)/SiO_2$ catalysts and three for $Co(N)/SiO_2$. Evidently, the adsorption sites of $Co(CO)/SiO_2$ differ from those of the conventional catalyst [III].

During TPD, hydrogen along with water, CO and CO_2 desorbed from the well-reduced $Co(N)/SiO_2$ and $Co_4(CO)_{12}/SiO_2$ catalysts. However, hydrogen, CO, CO_2 and methane, but not water desorbed from the $Co_2(CO)_8/SiO_2$ catalyst, which was characterized by highest dispersion [III]. Similarly, upon reaction at 250°C with simultaneous pulses of carbon monoxide and hydrogen, the $Co(N)/SiO_2$ and $Co_4(CO)_{12}/SiO_2$ catalysts produced methane, ethane, CO_2 and a small amount of water, and the consumption of hydrogen was of the same order for both catalysts. In contrast, the $Co_2(CO)_8/SiO_2$ catalyst produced no water and much less ethane while consuming more hydrogen.

These results mean that the oxygen containing species on the surface of $Co_2(CO)_8/SiO_2$ did not react to form water, and must have formed other oxygen containing products instead. The formation of C_{2+} oxygenates has been related to highly dispersed active sites in the literature [27, 49, 60], and indeed it was the $Co_2(CO)_8/SiO_2$ catalyst that exhibited the highest dispersion out of the catalysts under study. Furthermore, Ponec [23, Chapter 4] has attributed the formation of oxygenated compounds to the presence of positively charged sites, and it was the $Co_2(CO)_8/SiO_2$ catalyst that exhibited the lowest extent of reduction. The low ethane formation of $Co_2(CO)_8/SiO_2$ was probably due to the high dispersion of the catalyst and the resultant lack of adjacent sites large enough to accommodate CH_x species.

5.3 Catalyst activity

The CO hydrogenation activity of the carbonyl based preparations was too high for the experimental setup: the temperature of the catalyst bed oscillated at high reaction temperatures, limiting the testing [IV]. At 235°C, the activities of all catalysts were of the same order of magnitude, but the catalysts of carbonyl origin nevertheless appeared more active [I, IV]. Hence, the steady-state activity correlated fairly well with the hydrogen uptakes and strong CO adsorption [III]. However, the conventional preparation appeared to maintain its activity better in the long run [IV].

All the catalysts produced small amounts of oxygenated compounds probably due to impurities in the silica matrix (see Table 3). The yields were slightly higher for $Co_2(CO)_8/SiO_2$ although the formation of oxygenated compounds is not favoured by the low reaction pressure [18]. Thus, and as expected, the catalyst with highest dispersion appeared to produce more oxygenates. Takeuchi et al. [49] found clearly higher yields of oxygenated compounds with carbonyl preparations used at higher pressures (see Table 4) [49]. Also, catalysts of carbonyl origin have exhibited hydroformylation activity [61 - 63] - a further proof of their CO insertion capacity.

The nature of the precursor also affected the hydrocarbon product distribution. The probability of chain growth (α) after 20 - 30 h reaction time was higher for the conventional catalyst than the carbonyl derived one [I]. However, the values of α remained constant or decreased slightly for the $Co(N)/SiO_2$ catalyst, whereas those for $Co_2(CO)_8/SiO_2$ and $Co_4(CO)_{12}/SiO_2$ increased towards 120 h reaction time. Consequently, at reaction temperature of 235°C the probability of chain growth was highest for $Co_2(CO)_8/SiO_2$ at reaction times above 100 h. The increase was probably due to agglomeration of the highly dispersed sites as well as to blockage of the active sites by high molecular weight products. In the case of $Co(N)/SiO_2$ the cobalt species on are located mainly on the outer surface of the silica particle [I], and are there more accessible to the reacting gas and less susceptible to site blockage.

The activities of the catalysts of carbonyl origin remained high throughout the reaction although they suffered from accumulation of carbonaceous species (see Table 3). After oxidation by air, during sample transfer, the $Co(CO)/SiO_2$ catalysts required high temperatures for rereduction, and only 36% of their initial hydrogen uptake could be reproduced after rereduction at 400°C, *i.e.*, at 100°C higher than the initial temperature of reduction. Although the rereduction of $Co(N)/SiO_2$ produced 60% of the initial hydrogen uptake, the value was much lower than those for the catalysts of carbonyl origin.

Thus, the $Co(N)/SiO_2$ catalyst appeared both to retain its activity and to restore its adsorption capacity better than $Co(CO)/SiO_2$, but the performance of the $Co(CO)/SiO_2$ catalysts nevertheless remained superior in terms of both activity and selectivity. In particular, the tetranuclear carbonyl clusters may be considered potential candidates for the production of highly reduced, highly dispersed contaminant-free supported metals - an important area of study within FT catalysis.

Table 3. *Experimental conditions and characteristics of the catalysts after CO hydrogenation reaction at 0.5 MPa [IV].*

Precursor	Temp. °C	GHSV h^{-1}	X_{2h} %	α_{2h}	C_xO^1 mol-%	BET, m^2/g	Carbon wt.-%
$Co(N)^2$	235	5200	15.0	0.81	6.5	239	2.7
$Co(N)^2$	260	5200	21.1	0.70	3.6	224	2.2
$Co(N)^2$	290	6500	37.3	0.54	2.6	247	0.4
$Co_2(CO)_8$ [3]	235	5200	12.2	0.74	7.3	53	16
$Co_2(CO)_8$ [3]	245	6500	20.7	0.72	7.0	216	1.4
$Co_4(CO)_{12}$ [3]	235	6500	11.2	0.70	6.4	203	3.3
$Co_4(CO)_{12}$ [3]	245	7800	20.0	0.73	5.8	275	1.6

[1] After 95 h of reaction time
[2] Reduced at 400°C
[3] Reduced at 300°C

Table 4. *Product distribution in CO hydrogenation on Co(N)/SiO$_2$ and 2-Co(CO)/SiO$_2$ at 2.1 MPa and 220°C with GHSV of 2000 l/h and CO:H$_2$:Ar ratio of 3:6:1 [49].*

Catalyst	X_{CO} %	CO_2^1 C-%	HC^1 C-%	$C\text{-}O^1$ C-%	$C_2\text{-}O^1$ C-%
$Co(N)/SiO_2$	5.9	2	96	2	2
$Co_2(CO)_8/SiO_2$	10.0	2	78	20	5

[1] Selectivity as carbon efficiency: HC = sum of C_1-C_8 hydrocarbons, C-O = sum of C_1-C_8 oxygenated compounds, C_2-O = sum of C_2 oxygenated compounds

6. Carbonyl clusters as precursors

Among the monometallic catalyst preparations the carbonyl derived catalysts were proved active and more selective to valuable oxygenated compounds than was their conventional counterpart. Further studies were then made to find out whether mixed-transition-metal clusters might provide even higher activities and selectivities. The results obtained for tetranuclear Co-Ru and Co-Rh carbonyl cluster derived catalysts are evaluated in the following [VI, VII].

6.1 Co-Ru catalysts

Higher activities and C_{5+} selectivities can be achieved by adding small amounts of ruthenium to conventional cobalt catalysts [37]. The bimetallic interactions occurring upon the formation of mixed Co-Ru oxides during oxidation at high temperatures [37] facilitated ruthenium promoted cleaning of the cobalt surface ensembles during Fischer-Tropsch synthesis [37, 38] thereby inhibiting deactivation. This bimetallic synergy requires intimate contact between Co and Ru components [38].

The interaction of cobalt and ruthenium is definitely intimate in clusters, and yet the results differ markedly from those described for catalysts prepared by conventional techniques [37, 38]. Namely, the catalysts derived from bimetallic Co-Ru clusters exhibit higher activity and selectivity for the higher oxygenates than do catalysts prepared by mixing the monometallic clusters or metal chloride precursors [64 - 66]. The catalysts derived from the mixed metal clusters thus differ strikingly from the catalysts with similar metal loading but other precursor source [65].

In this work, Co-Ru/SiO$_2$ catalysts prepared from $Co_4(CO)_{12}$, $Co_3RuH(CO)_{12}$, $Co_2Ru_2H_2(CO)_{12}$, $Co_2Ru_2(CO)_{13}$, $CoRu_3H_3(CO)_{12}$, $Ru_4H_4(CO)_{12}$ were studied to elucidate the effect of precursor on the characteristics and performance of the catalyst. The cluster derived bimetallic catalysts with 1:1 ratio of Co:Ru were also compared with the catalyst prepared by mixing the respective amounts of $Co_4(CO)_{12}$ and $Ru_4H_4(CO)_{12}$. *In situ* diffuse reflectance FT-IR [12, 67], temperature programmed reduction (TPR) [12, 67], XPS [68], and reactivity testing [VI, VII] were used in these studies.

6.1.1 Characteristics

Although the interaction of the carbonyl cluster species with the dehydroxylated silica support is known to be weak [12], some ruthenium is chemisorbed on the silica surface under reflux conditions [13]. In the case of bimetallic clusters, the presence of ruthenium also enhances the chemisorption of cobalt, which is washed off from the support if used alone [13]. Since the chemisorption of cobalt on silica is insignificant, it is logical to presume that, in the case of bimetallic carbonyls, ruthenium is attached on the support and cobalt is bound to ruthenium [12, 13].

According to *in situ* FT-IR, the $Co_4(CO)_{12}$ and $Co_3RuH(CO)_{12}$ clusters adsorbed on silica decomposed readily under hydrogen atmosphere at approx. 120°C and 140°C, respectively, whereas the supported $Co_2Ru_2H_2(CO)_{12}$, $Co_2Ru_2(CO)_{13}$ and $(Co_4(CO)_{12}+Ru_4H_4(CO)_{12})$ with 1:1 ratio of Co:Ru decomposed smoothly and slowly without showing any distinct temperature of decomposition. Interestingly, the decomposition of the $CoRu_3H_3(CO)_{12}$ and $Ru_4H_4(CO)_{12}$ clusters on silica has been considered to proceed via the formation of oxidic ruthenium species [12, 67], and the clusters appear to be essentially decomposed at about 140°C and 150°C, respectively. Nevertheless, according to the TPR (under hydrogen atmosphere), the CO desorption maxima for the clusters supported on silica are as follows: 123°C for $(Co_4(CO)_{12}+Ru_4H_4(CO)_{12})$, 127°C for $CoRu_3H_3(CO)_{12}$, 133°C for $Co_2Ru_2(CO)_{13}$, 137°C for $Co_4(CO)_{12}$, 144°C for $Co_2Ru_2H_2(CO)_{12}$, 148°C for $Co_3RuH(CO)_{12}$ and 185°C for $Ru_4H_4(CO)_{12}$ [12, 67]. Although the results obtained by the two techniques are somewhat contradictory [12, 67], they nevertheless suggest that the catalysts with 1:1 ratio of Co:Ru are not identical.

Before recording of the XP spectra [68], the catalysts were decarbonylated under hydrogen flow at 300°C for 2 h - a treatment sufficient to decompose the precursors [III, 12, 67]. 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, the values for the extent of reduction therefore being erroneous (see Section 3). Nevertheless, the extent of reduction for cobalt increased in the precursor order $(Co_4(CO)_{12} + Ru_4H_4(CO)_{12}) < Co_3RuH(CO)_{12} < Co_4(CO)_{12} \sim CoRu_3H_3(CO)_{12} < Co_2Ru_2H_2(CO)_{12} \sim Co_2Ru_2(CO)_{13}$, *i.e.*, the presence of

ruthenium did not increase the reduction of cobalt. The differences were small, however: within 10%.

More importantly, the XPS measurements revealed that the Co:Ru ratios were much higher for all bimetallic catalysts than could be expected from the composition of the clusters. Hence, the XPS measurements support the hypothesis that ruthenium is attached to the support, and cobalt covers ruthenium. This positioning is plausible, since zero valent ruthenium and cobalt are of limited solubility [39]. A more careful interpretation of the XPS results also provided evidence for different working surfaces of the catalysts with 1:1 theoretical ratio of Co:Ru. Namely, the measured Co:Ru ratio decreased in the order $(Co_4(CO)_{12} + Ru_4H_4(CO)_{12}) > Co_2Ru_2(CO)_{13} > Co_2Ru_2H_2(CO)_{12}$.

6.1.2 Activity

The activities of the catalysts in CO hydrogenation are reported in paper VI. Expressed as GHSV required for 3% conversion, the activities indicated no synergistic effect of activity enhancement. Namely, the activity of the monometallic $Ru_4H_4(CO)_{12}/SiO_2$ catalyst was the highest, followed by $Co_4(CO)_{12}/SiO_2$ and $Co_2Ru_2(CO)_{13}/SiO_2$ (see Figure 4). However, the monometallic $Co_4(CO)_{12}/SiO_2$ was superior with time on stream, being the most resistant to deactivation. The initially highly active $Ru_4H_4(CO)_{12}/SiO_2$ catalyst in turn was the least resistant to deactivation, and all bimetallic cobalt-ruthenium catalysts fell in between the monometallic catalysts in terms of long-term performance. Hence, the deactivation was closely related to the presence of ruthenium, and probably due to the formation of heavy hydrocarbons, which plugged the small pores and blocked the active metal surfaces, as well as to accumulation of carbidic species [VI].

At all events, the selectivity to hydrocarbons was more than 90 C-%; and the chain growth probability was 0.72 - 0.82 for cobalt containing catalysts, whereas for the $Ru_4H_4(CO)_{12}/SiO_2$ catalyst it was as high as 0.91. Furthermore, the bimetallic catalysts did not necessarily form more oxygenates than did the monometallic catalysts - an observation unexpected in the light of earlier findings [64 - 66]. At most, the amount of oxygenates was 8.6 C-% for the catalyst prepared from the two monometallic clusters, whereas it was 4.2 C-% for $Co_4(CO)_4/SiO_2$ (see Figure 4). The selectivities to oxygenates could not, however, be related to the ratio of the metals in the

precursor since the performance of the bimetallic catalysts with 1:1 ratio of Co:Ru differed.
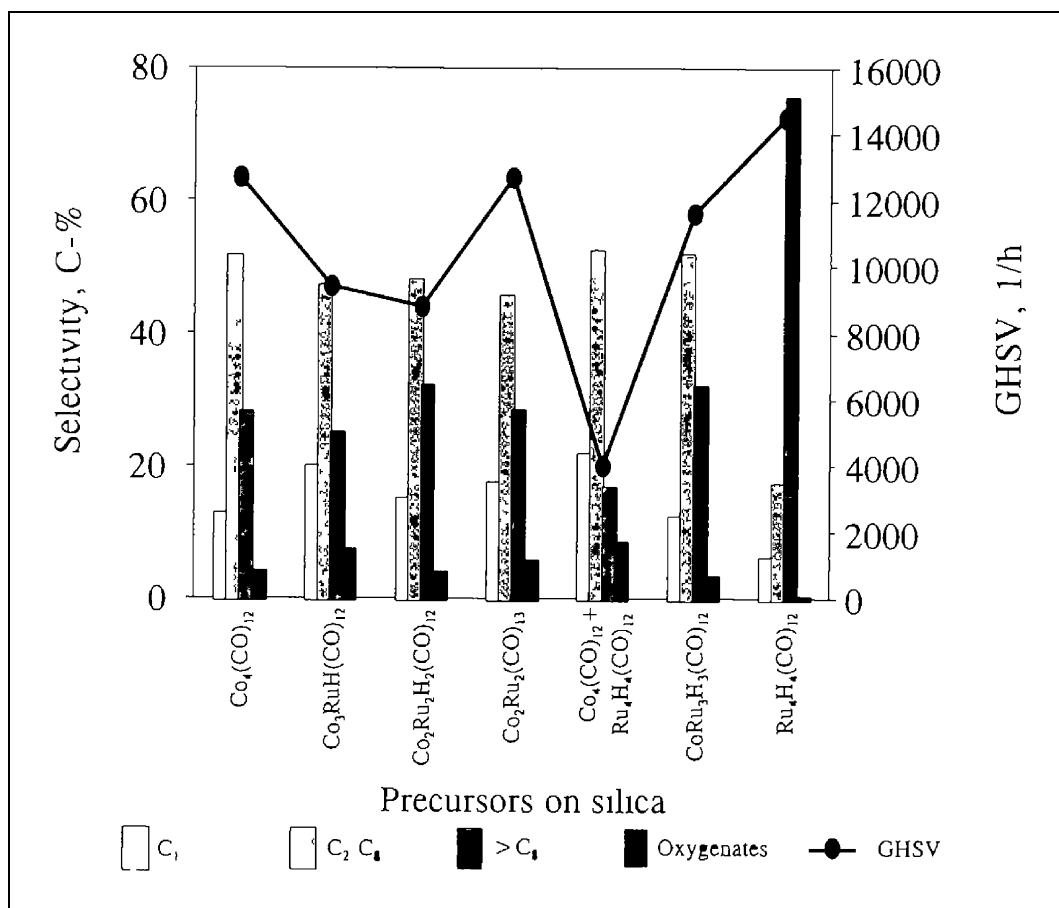

Figure 4.   The GHSV and selectivity of the catalysts at 2.1 MPa, 233°C, conversion 3%, $CO:H_2:Ar$ 3:6:1.

The differing characteristics of the catalysts with similar metal loading may in part be explained by the TPR [12] and XPS results [68]. Namely, the decarbonylation maxima of $Co_2Ru_2(CO)_{13}/SiO_2$ and $(Co_4(CO)_{12} + Ru_4H_4(CO)_{12})/SiO_2$ were as low as 133 and 123°C, whereas the maximum for $Co_2Ru_2H_2(CO)_{12}/SiO_2$ was 144°C. Considering the value of 137°C for $Co_4(CO)_{12}/SiO_2$, and 185°C for $Ru_4H_4(CO)_{12}/SiO_2$, one may speculate that the Co:Ru ratio on the surface of the $Co_2Ru_2(CO)_{13}/SiO_2$ and $(Co_4(CO)_{12} + Ru_4H_4(CO)_{12})/SiO_2$ catalysts may have been higher than the ratio on $Co_2Ru_2H_2(CO)_{12}/SiO_2$ - a speculation supported by the XPS data. Further

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specification of the nature of the catalyst surfaces would require more sophisticated techniques.

The bimetallic catalysts of cluster origin, with intimate contact of the metals, did therefore not provide either the synergistic effect of activity enhancement or the inhibition of deactivation observed for conventional catalysts promoted with ruthenium [37, 38]. Furthermore, no significant benefits in the production of oxygenates were observed in contrast to reports for other bimetallic catalysts [64 - 66]. Probably, the discrepancy in the results was due to the different pretreatment and different testing conditions. The characteristics of the catalysts of carbonyl cluster origin are sensitive not only to the composition of the cluster but to the method of preparation, since catalysts with the same ratio of Co and Ru exhibited different characteristics. In future, more attention needs to be paid to the method of preparation to ensure repeatable attachment of the active component on the support [13].

6.2 Co-Rh catalysts

In terms of directing the selectivity of cobalt to oxygenates, rhodium would be expected to be more effective than ruthenium since it is known in the art for its ability to catalyse the formation of alcohols, particularly ethanol [23 - 25]. The results for Co-Ru catalysts already indicated, however, that in addition to the right choice of metals and their ratio, the performance of the catalysts is also very sensitive to the nature of the precursor and the method of preparation [VI, 12].

Catalysts have been calcined during the preparation even though calcination is known to be undesirable in terms of dispersion and preservation of the original clusters. More often, the decomposition of the carbonyl clusters has been carried out under inert atmosphere or hydrogen, and at times the thermal treatment has been performed in the presence of CO, which stabilizes the carbonyl precursor [10]. Since the decomposition atmosphere may have a significant influence on the characteristics of the catalysts, studies VI and VII investigated the behaviour of $Co_{4-n}Rh_n(CO)_{12}/SiO_2$ (n=0-4) and $(Co_4(CO)_{12} + Rh_4(CO)_{12})/SiO_2$ decomposed in hydrogen and in CO. The temperature programmed reduction (TPR) and *in-situ* diffuse reflectance FT-IR techniques [10, 67] used to provide information relevant to the interpretation of the results are also briefly described below.

6.2.1 Characteristics

The TPR results for Co-Rh/SiO$_2$ indicated a pattern similar to Co-Ru/SiO$_2$ catalysts: probably there was an interaction between the rhodium species and the support, and cobalt was bound to rhodium [10]. In support of this, the decarbonylation maximum of the bimetallic catalysts (123 - 135°C) was fairly similar to that of Co$_4$(CO)$_{12}$/SiO$_2$ (137°C), whereas that of Rh$_4$(CO)$_{12}$/SiO$_2$ (178°C) was significantly higher [10].

The decomposition of the catalysts was also carried out in an *in situ* FT-IR cell in the presence of hydrogen at 30 - 250°C [10]. The FT-IR spectra suggested that the decomposition of the clusters began with the formation of hexanuclear clusters. The bands due to the presence of Co$_4$(CO)$_{12}$ on the silica surface disappeared at approx. 110 - 120°C, *i.e.*, at slightly lower temperature than in TPR. The decomposition of other precursors occurred similarly, and above about 120°C only weak bands were observed for Co$_3$Rh(CO)$_{12}$/SiO$_2$, Co$_2$Rh$_2$(CO)$_{12}$ and (Co$_4$(CO)$_{12}$ + Rh$_4$(CO)$_{12}$)SiO$_2$. The supported Rh$_4$(CO)$_{12}$ was transformed quickly to Rh$_6$(CO)$_{16}$, which decomposed by about 150°C. At the end, at 250°C, there were broad bands at 2037 and 1750 cm^{-1} for the Rh$_4$(CO)$_{12}$/SiO$_2$ catalyst, which were assigned to terminal and bridged type CO on metallic Rh, respectively [10]. To be more precise, the band at 1750 cm^{-1} was assigned to face-bridged adsorption of CO, *i.e.*, one CO is bound to three metal atoms, as discussed in paper VII. Thus, one may assume that the propensity for the face-bridged adsorption is higher on large ensembles of metal than on very highly dispersed particles [VII].

The decomposition of Co$_4$(CO)$_{12}$/SiO$_2$ and Rh$_4$(CO)$_{12}$/SiO$_2$ in an *in situ* FT-IR cell was also carried out under CO atmosphere. Most noticeably, the stability of the clusters on silica was clearly enhanced in the presence of CO atmosphere, *i.e.*, sharp bands were observed for both catalysts at 250°C. In particular, the original FT-IR spectrum of the Rh$_4$(CO)$_{12}$/SiO$_2$ catalyst, where the cluster appears in its hexanuclear form, was well retained and the face-bridged adsorption form was absent. Thus, it may be that the metal particles remained more highly dispersed under CO atmosphere than under hydrogen atmosphere [VII].

In contrast, the uptake of hydrogen was considerably lower for the CO than the hydrogen treated catalysts [VII]. The chemisorption capacity of the

catalysts was most likely suppressed by the carbonaceous residues since the XP spectra showed that more carbon was retained on the catalysts decomposed under CO than on those decomposed under hydrogen. The difference was much smaller for $Rh_4(CO)_{12}/SiO_2$ than for $Co_4(CO)_{12}/SiO_2$, however, evidently because the partial carbon coverage facilitated the formation of small particles on $Rh_4(CO)_{12}/SiO_2$, whereas most of the active sites on $Co_4(CO)_{12}/SiO_2$ were blocked [VII]. In accordance with this interpretation, the TEM results indicated that the metal particle size distribution was wider for the $Rh_4(CO)_{12}/SiO_2$ catalyst decomposed under CO than that decomposed under hydrogen. The weighted average particle size was similar, however: in both cases 4 nm.

It is also noteworthy that for the $Rh_4(CO)_{12}/SiO_2$ and $Co_4(CO)_{12}/SiO_2$ catalysts the extent of reduction determined by XPS was not influenced by the decomposition atmosphere: $Rh_4(CO)_{12}/SiO_2$ was totally reduced in both CO and hydrogen, and the extent of reduction for $Co_4(CO)_{12}/SiO_2$ ranged between 26 and 36%. The low value of 26% for the $Co_4(CO)_{12}/SiO_2$ catalyst was unexpected in view of earlier results (82%, paper III) for a catalyst of the same formulation, since the hydrogen uptake was similar (52.2 µmol/g_{cat} in paper III and 56.8 µmol/g_{cat} in paper VII).

6.2.2 Activity

Paper VI discusses the catalytic performance of a systematic series of clusters on the silica support ($Co_{4-n}Rh_n(CO)_{12}/SiO_2$, n = 0-4) in conjunction with hydrogen pretreatment. The activity of the $Co_{4-n}Rh_n(CO)_{12}/SiO_2$ catalysts, expressed as the GHSV required for 3% conversion, was found to decrease in the following order of the precursor: $Co_4(CO)_{12}$ > $Co_3Rh(CO)_{12}$ > $Rh_4(CO)_{12}$> $Co_2Rh_2(CO)_{12}$ > ($Co_4(CO)_{12}$ + $Rh_4(CO)_{12}$) (see also Figure 5). Hence, in contrast to the results for Co_2Rh_2/Al_2O_3 [69], the catalysts were least active when the ratio of Co:Rh was 1:1. This low activity of the present bimetallic catalysts is reasonable in the light of the characterizations, however: the TPR results suggested that, on bimetallic catalysts, rhodium was probably covered with cobalt, which reduced the total number of active sites on the surface [10].
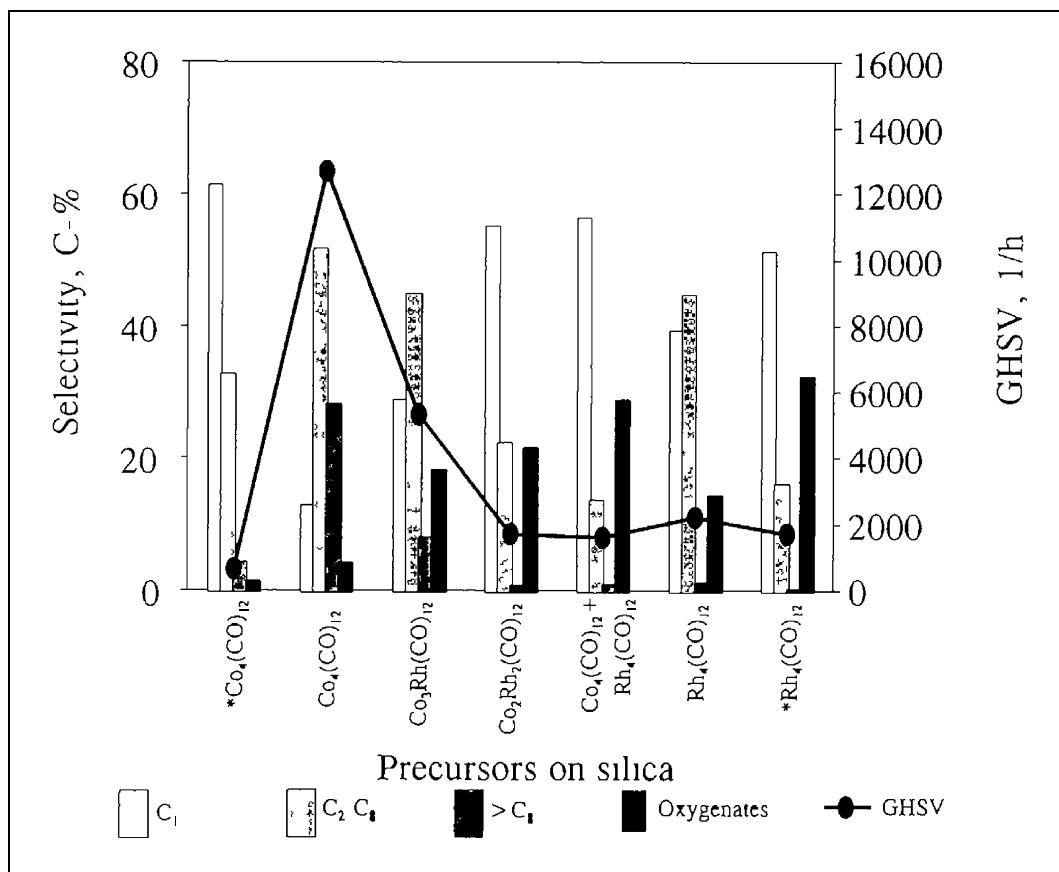
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Figure 5. The GHSV and selectivity of the catalysts at 2.1 MPa, 233°C, conversion 3%, $CO:H_2:Ar$ 3:6:1. The precursors have been decomposed under hydrogen except for those marked by *.

The combined site of cobalt and rhodium appeared to play an important role in the deactivation of the catalysts, since the order of relative activity after 75 hours reaction time decreased in the precursor order $Co_4(CO)_{12}$ = $Rh_4(CO)_{12}$ > $(Co_4(CO)_{12}+Rh_4(CO)_{12})$ > $Co_2Rh_2(CO)_{12}$ > $Co_3Rh(CO)_{12}$, that is, the monometallic catalysts were the most resistant to deactivation. The deactivation was most likely caused by coking, *i.e.,* layers of coke deposit decreased the accessible surface area and the active metals became encapsulated by carbon [VI].

The relevance of carbon coverage to activity became clear in study VII, where the activity of the $Co_4(CO)_{12}/SiO_2$ and $Rh_4(CO)_{12}/SiO_2$ catalysts decomposed under CO atmosphere was investigated. The results depicted in Figure 5 indicate that for $Co_4(CO)_{12}/SiO_2$ the activity decreased significantly when hydrogen was replaced by carbon monoxide in pretreatment. The surface of the catalyst was apparently poisoned by

carbonaceous residues, and the active sites were permanently blocked. Instead, the activity of the $Rh_4(CO)_{12}/SiO_2$ catalyst decomposed under carbon monoxide was only slightly lower than the activity of the catalyst decomposed under hydrogen, although the decrease in hydrogen uptake was considerable. Thus, CO pretreatment induced only partial coverage of the active surface by carbonaceous residues in the case of $Rh_4(CO)_{12}/SiO_2$.

In regard to the selectivity of the catalysts after hydrogen reduction, it is noteworthy that the chain growth probability decreased with decreasing ratio of Co:Rh in the catalysts, a result in accordance with the characteristic reactivity of cobalt towards higher paraffins [39]. Furthermore, the catalysts prepared from the bimetallic clusters produced more oxygenates than did the monometallic catalysts (see Figure 5). A maximum selectivity to ethanol was observed with 1:1 ratio of Co:Rh: 11.1 C-% for $Co_2Rh_2(CO)_{12}/SiO_2$ and 14.8 C-% for $(Co_4(CO)_{12} + Rh_4(CO)_{12})/SiO_2$. Also, the same two catalysts, $Co_2Rh_2(CO)_{12}/SiO_2$ and $(Co_4(CO)_{12} + Rh_4(CO)_{12})/SiO_2$, produced more methyl and ethyl acetate than the other cobalt-containing catalysts. Nevertheless, the selectivity of the $(Co_4(CO)_{12} + Rh_4(CO)_{12})/SiO_2$ catalyst also differed from that of $Co_2Rh_2(CO)_{12}/SiO_2$, *i.e.*, it produced slightly more of the higher alcohols. Probably, the method of preparing the $(Co_4(CO)_{12} + Rh_4(CO)_{12})/SiO_2$ catalyst did not ensure uniform distribution of the metals [13]. The selectivities indicate that the bimetallic catalysts are more likely to accommodate active sites, essential for the formation of oxygenates, than are the monometallic catalysts [VI]. These active sites were probably located at the edge of the cobalt particles lying on top of the rhodium particles [10].

For $Rh_4(CO)_{12}/SiO_2$ the selectivities to oxygenated compounds, and in particular to ethanol and ethyl acetate, increased noticeably when the catalyst was pretreated with carbon monoxide instead of hydrogen. Since the selectivity to oxygenates has been related to the presence of isolated active sites capable of insertion of CO [27], the particle size on the carbon monoxide treated $Rh_4(CO)_{12}/SiO_2$ catalyst could have been smaller owing to partial carbon coverage, than on the corresponding hydrogen treated catalyst. This speculation is supported by TEM. Yet it is impossible to conclusively determine the nature of the active sites for the formation of oxygenates since the unintentional promotion by the impurities in the silica matrix can not be excluded.

7. Concluding remarks

The characteristics, activity and product formation of the magnesium oxide promoted $Co(N)/SiO_2$ catalyst were related both to the impregnation order and to the molar ratio of Mg:Co in the bulk. Although MgO promotion was effective in enhancing the activity per metallic cobalt site, conversion per 1 g of catalyst was decreased due to the lower extent of reduction and thus fewer active sites. Magnesium promotion had no significant effect on the hydrocarbon product distributions, in contrast to findings for both cobalt foil model catalysts and supported catalysts. The difference probably is attributable to the different oxidation states.

The precursor exhibited a significant effect on the performance of the Co/SiO_2 catalyst. Carbon monoxide was more strongly adsorbed on catalysts of carbonyl origin than on $Co(N)/SiO_2$, and the activity in CO hydrogenation was higher accordingly. Although $Co(N)/SiO_2$ appeared both to retain its activity and to restore its adsorption capacity better than $Co(CO)/SiO_2$, the performance of the $Co(CO)/SiO_2$ remained superior with time on stream, in terms of both activity and selectivity to oxygenates.

In the bimetallic catalysts of carbonyl cluster origin, rhodium or ruthenium was in contact with the support and cobalt at least partially covered it. The monometallic catalysts, with larger number of accessible active sites, were most active, therefore. In the case of Co-Ru catalysts, the presence of ruthenium appeared to enhance deactivation, and no significant benefits were attained in selectivity relative to the monometallic catalysts. In contrast, the Co-Rh catalysts, with their active sites on the perimeter of the cobalt particles located on rhodium, exhibited higher selectivities to oxygenated compounds than did the monometallic catalysts. Yet another improvement in the oxygenate selectivities was provided when the pretreatment atmosphere of $Rh_4(CO)_{12}/SiO_2$ was changed from hydrogen to carbon monoxide. The results also suggested that two pathways were operating for the formation of oxygenates - one for ethanol and the other for aldehydes.

In all, the work clearly demonstrated the advantage of carbonyl preparations in CO hydrogenation: high activity and enhanced selectivity towards oxygenated compounds together with good performance with time on stream. Commercial applicability is not yet feasible, however, due to the

considerable difficulties in preparation: air-free impregnation or reflux-techniques needing to be combined with a particular decomposition method. Moreover, any formation of volatile carbonyls would induce losses of the active species - a problem that might be avoided by entrapping the carbonyls in the pores of zeolite supports. And this is yet another complication for catalyst preparation.

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