The activity of carbonyl cluster derived Co-Ru/SiO$_2$ and Co-Rh/SiO$_2$ catalysts in CO hydrogenation

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Abstract

We studied systematically the use of tetranuclear cobalt, cobalt–ruthenium, cobalt–rhodium and rhodium carbonyl clusters as catalyst precursors. The catalytic activities and the product distributions of the hydrogenation of carbon monoxide over Co$_{4-n}$Ru$_n$/SiO$_2$ and Co$_{4-n}$Rh$_n$/SiO$_2$ catalysts (where $n = 0$–4) and (Co$_4$ + Ru$_4$)/SiO$_2$ and(Co$_4$ + Rh$_4$)/SiO$_2$ catalysts derived from the transition-metal carbonyl clusters were compared. Activities were highest for the catalysts derived from homometallic clusters, and lowest for catalysts with 1:1 ratio of Co/Ru or Co/Rh. Interestingly enough, the highly active homometallic cobalt catalyst was the most resistant to deactivation. On Co$_{4-n}$Rh$_n$/SiO$_2$ catalysts the deactivation was stronger on bimetallic sites and on the Co$_{4-n}$Ru$_n$/SiO$_2$ catalysts the deactivation was closely related to the presence of ruthenium. The selectivities for oxygenated compounds were clearly promoted by the bimetallic sites of Co–Rh catalysts. This result is very plausible since the probability to find dual active sites responsible for the formation of oxygenates is greater in bimetallic than in homometallic catalysts.

Keywords: Carbon monoxide; Hydrogenation; Cluster; Silica support; Synthesis gas

1. Introduction

Transition-metal clusters have been under intensive investigation in view of their potential both as models for the catalytic metal surface and as catalysts in their own right. The application of multimetallic catalysts has also attracted much interest because their catalytic activity and selectivity has often differed significantly from that of the homometallic systems of the constituent metals [1]. Mixed-transition-metal clusters should find important application in heterogeneous catalysts since a suitable combination of different metals in the mixed metal clusters should permit more efficient interaction with substrates than obtained with mononuclear metal complexes or homometallic clusters [2]. With mixed-transition-metal clusters as precursors highly dispersed metal particles and a uniform metal composition as well as a specific structure of the two metal components manageable at the molecular level can be achieved in the oxide supported catalysts [3,4].

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Synthesis gas conversion has been one of the most intriguing topics in the field of heterogeneous catalysis by transition metals. In the synthesis gas reaction the selectivity to hydrocarbons and alcohols has been limited by the Schulz–Flory distribution of the products, and tremendous efforts have been directed towards finding more selective catalysts particularly for the production of oxygenated compounds [5–11]. A number of reports have suggested that the size of metal particles in the catalysts might have a significant effect on the product distribution [9,11,12]. Metal clusters have been used as precursors to obtain high metal dispersion with particles smaller than 10 Å [9,11]. Metal–carbonyl clusters have provided zero valent metal particles at lower reduction temperatures than have conventional precursors [13]. Also, catalysts prepared from metal carbonyl clusters are free from contamination by residual materials such as Cl^- and NO_3^-. In particular, the residual Cl^- is often strongly bound with the basic sites of oxide supports, thereby inhibiting the activation of CO by metals [5].

The main purpose of our work was to study, systematically, the use of tetranuclear cobalt, cobalt–ruthenium, cobalt–rhodium and rhodium carbonyl clusters as catalyst precursors. The influence of the metal composition on the activity and selectivity of silica-supported catalysts was determined in the synthesis gas reaction. To determine the benefits of the mixed metal preparations, the catalysts prepared from mixed metal clusters were also compared with catalysts prepared from homometallic clusters of the same metals and metal contents.

2. Experimental

2.1. Preparation of catalysts

Commercially available $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ were obtained from Strem Chemicals, Inc. The other metal carbonyl clusters were prepared by published methods and were as follows: $H_4Ru_4(CO)_{12}$ [14], $CoRu_3H_3(CO)_{12}$ [15], $Co_2Ru_2H_2(CO)_{12}$ [16], $Co_2Ru_2(CO)_{13}$ [17], $Co_3RuH(CO)_{12}$ [2], $Co_2Rh_2(CO)_{12}$ and $Co_3Rh(CO)_{12}$ [18].

Grace 432 silica support was dried under vacuum at 600°C/2 h to dehydroxylate the surface [13,19]. The homo- or heterometallic carbonyl cluster catalysts were prepared by impregnation from nitrogenated dichloromethane solution under deoxygenated atmosphere. The metal loading of all preparations was 0.9 mmol/1 g SiO_2 and the catalysts were dried slowly under vacuum at room temperature. The final metal loading was between 5 wt.-% ($Co_4(CO)_{12}$) and 8.5 wt.-% ($Rh_4(CO)_{12}$). Every step in the preparation of the catalyst was carried out under inert atmosphere using a glove box and nitrogen vacuum line.

2.2. Reaction tests

Hydrogenation of carbon monoxide was carried out in a modified SOTELEM LCT-570 continuous flow fixed bed tubular reactor equipped with an on-line GC system consisting of two HP-5890 series II gas chromatographs. Because the product mixture is complex, six columns, 3 FIDs and 1 TCD were necessary for the analysis. Light hydrocarbons were separated on an Al_2O_3–KCl column, HP-1 was used for heavy hydrocarbons, TCEP together with HP-1 was chosen for oxygenates, and a combination of the Porapak-Q and a packed column with squalane on activated carbon was utilized for permanent gases and water. The response factors were determined by measurements of the standard samples.

The catalyst was loaded into the reactor in a glove box under deoxygenated (< 1 ppm) and dried argon atmosphere. The amount of catalyst used in reaction tests was 1.0 g (2.75 ml). The reactor was connected to the reactor system without contact with air. Just prior to use the catalyst was reduced in situ under flowing hydrogen at 300°C/2 h ($r = 2$°C/min). After reduction, the catalyst was slowly cooled to 190°C

Table 1

Effect of the precursor of $Co_{4-n}Ru_n/SiO_2$ catalysts on the catalyst activity and product distribution in the hydrogenation of carbon monoxide

Catalyst	GHSV (h^{-1})	C_1 (C-%)	C_2–C_4 (C-%)	C_5–C_8 (C-%)	$> C_8$ (C-%)	Oxygenates (C-%)	CO_2 (C-%)	Aromatics (C-%)
Co_4/SiO_2	12700	12.9	22.3	29.5	28.2	4.2	2.8	0.2
Co_3Ru/SiO_2	9400	20.1	23.6	23.6	25.2	7.5	0	0
$Co_2Ru_2(I)/SiO_2$	8800	15.3	19.0	29.2	32.4	4.1	0	0.1
$CoRu_3/SiO_2$	11600	12.5	18.8	33.2	32.1	3.5	0	0
Ru_4/SiO_2	14500	6.3	6.2	11.3	75.7	0.4	0	0.2
$Co_2Ru_2(II)/SiO_2$	12700	17.7	19.0	26.7	28.6	5.9	2.0	0
$(Co_4 + Ru_4)/SiO_2$	4000	22.0	24.5	28.1	16.9	8.6	0	0

Reaction conditions: $CO/H_2/Ar$ = 3:6:1, pressure 2.1 MPa, T = 233°C and conversion = 3%.

under H_2 flow. The reaction was initiated by changing the gas flow to synthesis gas and by increasing the pressure of the reactant gas to the desired reaction pressure.

The composition of the synthesis gas was $CO/H_2/Ar$ = 3/6/1, and argon was used as an internal standard for the analysis. The product selectivities were determined as carbon efficiencies (C-%) based on the amount of CO reacted. The reaction pressure was kept constant at 2.1 MPa and the typical reaction temperature was 233°C. However, the temperature dependence of the conversion and the selectivities was studied by varying the temperature within 190–290°C. The conversion was adjusted to 3% by changing the flow rate of the synthesis gas (2–40 l/h) while temperature (233°C) and pressure (2.1 MPa) were kept constant.

In the remainder of this paper the following abbreviations indicate the precursor in the names of the catalysts: $Co_4 = Co_4(CO)_{12}$, $Ru_4 = Ru_4H_4(CO)_{12}$, $Co_3Ru = Co_3RuH(CO)_{12}$, $Co_2Ru_2(I) = Co_2Ru_2H_2(CO)_{12}$, $Co_2Ru_2(II)$ $= Co_2Ru_2(CO)_{13}$, $CoRu_3 = CoRu_3H_3(CO)_{12}$, $Rh_4 = Rh_4(CO)_{12}$, $Co_3Rh = Co_3Rh(CO)_{12}$ and $Co_2Rh_2 = Co_2Rh_2(CO)_{12}$.

3. Results and discussion

The catalytic activities and the product distributions of the hydrogenation of carbon monoxide over $Co_{4-n}Ru_n/SiO_2$ and $Co_{4-n}Rh_n/SiO_2$ catalysts (where n = 0–4) and $(Co_4 + Ru_4)/SiO_2$ and $(Co_4 + Rh_4)/SiO_2$ catalysts derived from the transition-metal carbonyl clusters are given in Tables 1 and 2.

3.1. Co–Ru catalysts

The activity of the $Co_{4-n}Ru_n/SiO_2$ and $(Co_4 + Ru_4)/SiO_2$ catalysts decreased in the precursor order $Ru_4 > Co_4 = Co_2Ru_2(II) > CoRu_3 > Co_3Ru > Co_2Ru_2(I) > (Co_4 + Ru_4)$. The catalyst prepared from the two homometallic clusters was least active, while the catalyst pre-

Table 2

Effect of the precursor of $Co_{4-n}Rh_n/SiO_2$ catalysts on the catalyst activity and product distribution in the hydrogenation of carbon monoxide

Catalyst	GHSV (h^{-1})	C_1 (C-%)	C_2–C_4 (C-%)	C_5–C_8 (C-%)	$> C_8$ (C-%)	Oxygenates (C-%)	CO_2 (C-%)	Aromatics (C-%)
Co_4/SiO_2	12700	12.9	22.3	29.5	28.2	4.2	2.8	0.2
Co_3Rh/SiO_2	5300	28.8	27.6	17.4	8.1	18.2	0	0
Co_2Rh_2/SiO_2	1700	55.2	15.3	7.0	0.8	21.6	0	0.1
Rh_4/SiO_2	2200	39.4	36.8	8.0	1.2	14.4	0	0.3
$(Co_4 + Rh_4)/SiO_2$	1600	56.5	9.7	4.0	0.9	28.8	0	0

Reaction conditions: $CO/H_2/Ar$ = 3:6:1, pressure = 2.1 MPa, T = 233°C and conversion = 3%.

pared from the $Co_2Ru_2(I)$ and $Co_2Ru_2(II)$ bimetallic clusters with equal metal ratio exhibited much higher activity.

The Ru_4/SiO_2 and Co_4/SiO_2 catalysts exhibited a very high activity for CO conversion, and both formed mainly hydrocarbons, in particular the high hydrocarbons. The bimetallic catalysts exhibited lower activity than the homometallic catalysts except for $Co_2Ru_2(II)/SiO_2$ which exhibited equal activity with the Co_4/SiO_2 catalyst. Our results are in disagreement with those of Xiao et al. [3]. In their experiments the activity of the bimetallic catalysts increased with the increasing molar ratio of Co/Ru, and the homometallic cobalt and ruthenium carbonyl catalysts were the least active. The most important reason for these differences is the pretreatment of the catalysts. Namely, Xiao et al. [3] calcined their catalysts under O_2 flow at 300°C before in situ reduction, whereas we handled our catalysts in inert atmosphere.

Except for the $Co_2Ru_2(II)/SiO_2$ catalyst, as the molar ratio of Co/Ru in the $Co_{4-n}Ru_n/SiO_2$ catalysts increased, the activity first decreased, reaching a minimum when the ratio was 1:1, and then increased. The $Co_2Ru_2(II)/SiO_2$ catalyst exhibited equal activity with Co_4/SiO_2 and much higher activity than $Co_2Ru_2(I)/SiO_2$. This extraordinary behaviour may be related to the composition of the precursor: all other $Co_{4-n}Ru_n$ precursors had equal amounts of hydrogen and ruthenium in their molecular structure, but in $Co_2Ru_2(II)$, two hydrogens were replaced by a carbonyl making the number of carbonyl groups 13 instead of 12. Dobos et al. [20] and Schay et al. [21] have studied the interaction between FeRu bimetallic carbonyl cluster and silica support. Dobos et al. [20] observed that $H_2FeRu_3(CO)_{13}$ reacts with hydrogen to produce $H_4FeRu_3(CO)_{12}$ and CO. Analogously $Co_2Ru_2(II)$ may have reacted with hydrogen to produce $Co_2Ru_2(I)$ and CO, and the CO may have reacted with the metal species already present on the surface to form metal–carbon

species. Such metal–carbon species have been observed to enhance the dispersion in Fe–Ru catalysts [21]. Our results [22], too, indicate that the catalysts are more dispersed in the presence of CO.

In the case of $Co_{4-n}Ru_n/SiO_2$ and $(Co_4 + Ru_4)/SiO_2$ catalysts, there was a clear product orientation towards hydrocarbons. In all cases the selectivity to hydrocarbons was more than 90 C-%. The tendency to produce an abundance of C_5–C_{13} hydrocarbons (45–65 C-%) and little methane (< 20 C-%) was also clear, except for Ru_4/SiO_2 which much preferred $C_8 +$ hydrocarbons (> 75 C-%). The chain growth probability α was within 0.72–0.82 for all $Co_{4-n}Ru_n/SiO_2$ catalysts except Ru_4/SiO_2, for which α was 0.91. The Schulz–Flory equation, with the conclusion that the maximum mass selectivity to the C_5–C_{11} cut is 48% [23], holds fairly well for the $Co_{4-n}Ru_n/SiO_2$ catalysts.

Precursors influenced the hydrocarbon distribution even with equal Co/Ru ratio, as shown in Fig. 1. The plot of ln (W_n/n) vs. carbon number was a similar straight line for the $Co_2Ru_2(I)/SiO_2$ and $Co_2Ru_2(II)/SiO_2$ catalysts but differed for the $(Co_4 + Ru_4)/SiO_2$ catalyst, which produced more C_1–C_4 hydrocarbons, the same amount of C_5–C_8 and less
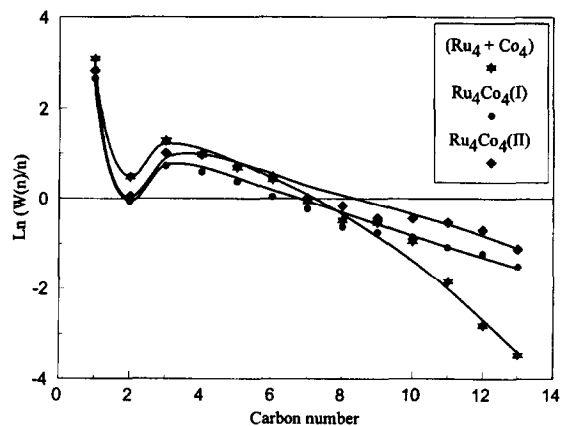

Fig. 1. The influence of the precursors on the hydrocarbon distribution with equal Co/Ru ratio. ($T = 233$°C, $p = 2.1$ MPa, $CO/H_2/Ar = 3:6:1$).

C_9–C_{13} hydrocarbons relative to the other two catalysts.

The $Co_{4-n}Ru_n/SiO_2$ catalysts formed only small amounts of oxygenates. For instance, the selectivity of Co_4/SiO_2, Co_3Ru/SiO_2, $Co_2Ru_2(I)/SiO_2$, $CoRu_3/SiO_2$ and Ru_4/SiO_2 for oxygenates was only 4.2, 7.5, 4.1, 3.5 and 0.4 C-% respectively. The selectivity to oxygenates was highest when the Co/Ru ratio was 3 and lowest when the catalyst contained only ruthenium. However, the $(Co_4 + Ru_4)/SiO_2$ catalyst prepared from the two homometallic clusters had the highest selectivity to oxygenates (8.6 C-%). The selectivity was noticeably higher than with $Co_2Ru_2(I)/SiO_2$ and $Co_2Ru_2(II)/SiO_2$, even though the Co/Ru ratio was the same. The differing selectivities for oxygenates indicate that both the nature of the precursor and the ratio of the metals influence the reactivity of the catalysts.

3.2. Co–Rh catalysts

The activity of the $Co_{4-n}Rh_n/SiO_2$ and $(Co_4 + Rh_4)/SiO_2$ catalysts decreased with respect to the precursor in the following order: $Co_4 > Co_3Rh > Rh_4 > Co_2Rh_2 > (Co_4 + Rh_4)$. The catalysts were least active when the Co/Rh ratio was 1:1. The catalyst prepared from the two homometallic cluster precursors $(Co_4 + Rh_4)$ exhibited somewhat weaker activity than the catalyst prepared from the corresponding bimetallic cluster. The activities of the bimetallic $Co_{4-n}Rh_n/SiO_2$ catalysts did not lie between those of the homometallic Co_4/SiO_2 and Rh_4/SiO_2, and the Co_2Rh_2/SiO_2 catalyst

was less active than the pure rhodium catalyst. Our findings are opposite to those of Ceriotti et al. [24], who found Co_2Rh_2/Al_2O_3 to be significantly more active than Rh_4/Al_2O_3 catalyst. The disagreement in the results may be due to the different metal loading and support as well as to the much lower reaction pressure used in their experiments. The difference might also be related to the pretreatment of the catalysts: high temperature reduction at 500°C has resulted in cobalt enrichment at the surface of bimetallic Co–Rh particles [25].

All $Co_{4-n}Rh_n/SiO_2$ catalysts, except Co_4/SiO_2, exhibited fairly weak activity for CO conversion and had strong tendency to produce methane as well as light hydrocarbons. The chain growth probability decreased in the order $Co_4 > Co_3Rh > (Co_4 + Rh_4) > Co_2Rh_2 > Rh_4$, i.e. it correlated well with the number of cobalt atoms in the precursor. The selectivities for oxygenates for Co_4/SiO_2, Co_3Rh/SiO_2, Co_2Rh_2/SiO_2, $(Co_4 + Rh_4)/SiO_2$ and Rh_4/SiO_2 were 4.2, 18.2, 21.6, 28.8 and 14.4 C-%, respectively. This result shows, in agreement with the findings of Huang et al. [26], that the catalysts prepared from the bimetallic clusters produced a greater quantity of oxygenates than did the catalysts prepared from the homometallic clusters. The result is plausible since the active sites for the formation of oxygenates are dual sites where CO is both dissociatively (site 1) and nondissociatively adsorbed (site 2) [27]. The probability of finding these dual active sites is higher in bimetallic than in homometallic catalysts. However, it should be noted that when the selectivities for

Table 3
The selectivities for oxygenates on $Co_{4-n}Rh_n/SiO_2$ catalyst

Catalyst	MeOH (C-%)	EtOH (C-%)	PrOH (C-%)	BuOH (C-%)	> C_5OH (C-%)	AcH (C-%)	MeOAc (C-%)	EtOAc (C-%)	AcOH (C-%)
Co_4/SiO_2	0.4	1.5	1.0	0.0	0.3	0.5	0.0	0.0	0.5
Co_3Rh/SiO_2	2.8	5.0	2.5	4.1	2.3	0.5	0.4	0.1	0.5
Co_2Rh_2/SiO_2	3.2	11.1	1.3	0.4	0.0	0.8	3.5	1.3	0.0
$(Co_4 + Rh_4)/SiO_2$	5.8	14.8	1.8	1.5	0.3	0.7	2.6	1.0	0.3
Rh_4/SiO_2	0.3	5.2	2.2	0.1	0.0	0.6	0.9	2.3	2.8

Reaction conditions: $CO/H_2/Ar = 3:6:1$, $p = 2.1$ MPa, $T = 233$°C and conversion = 3%.

oxygenates increased, the activity of the catalysts decreased at the same time.

The product distributions of oxygenates at the constant conversion level of 3% were sensitive to the Co/Rh ratio in the catalyst (Table 3). The only product present in significant amount in all runs was ethanol, and its selectivity changed drastically with the amount of rhodium in the $Co_{4-n}Rh_n$ precursor. The maximum selectivity to ethanol was obtained with the 1:1 ratio of Co/Rh; it was 11.1 C-% for Co_2Rh_2/SiO_2 and 14.8 C-% for $(Co_4 + Rh_4)/SiO_2$. Methanol formation was higher on the bimetallic catalysts than the homometallic catalysts. The homometallic Rh_4/SiO_2 catalyst produced a lot of oxygenates such as acetic acid and ethyl acetate, whereas the other catalysts produced them in much smaller amount or not at all. In addition, the Co_2Rh_2/SiO_2 and $(Co_4 + Rh_4)/SiO_2$ catalysts produced surprisingly much methyl acetate, while the amount of acetic

acid was small or undetectable. This may indicate that, on the bimetallic catalyst with Co/Rh ratio 1:1, acetic acid reacted with methanol to form methyl acetate. The Co_2Rh_2/SiO_2 and $(Co_4 + Rh_4)/SiO_2$ catalysts behave similarly but not the same; the $(Co_4 + Rh_4)/SiO_2$ catalyst produced a slightly greater proportion of higher alcohols than the Co_2Rh_2/SiO_2 catalyst did. Perhaps the preparation of the $(Co_4 + Rh_4)/SiO_2$ catalyst did not ensure the formation of the alloy phase with constant overall composition. In fact, this catalyst had a higher chain growth probability than the Co_2Rh_2/SiO_2 catalyst, probably because it had some pure Co_4 ensembles on the surface.

3.3. Influence of reaction temperature

The influence of the reaction temperature on the activities and selectivities was determined at 190 to 290°C at constant pressure (2.1 MPa)
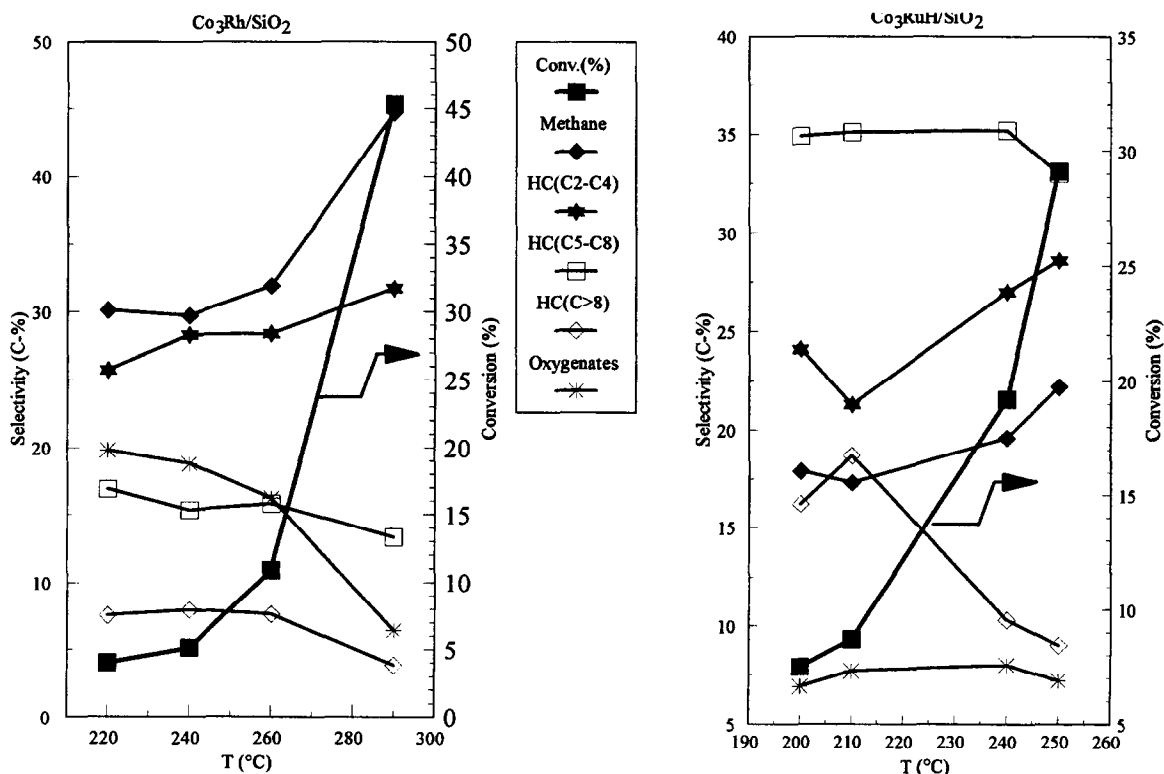

Fig. 2. The influence of the reaction temperature on the activity and selectivities of the Co_3Rh/SiO_2 and Co_3Ru/SiO_2 catalysts in the hydrogenation of carbon monoxide.

and flow rate of synthesis gas (6 1/h). The activity of all our catalysts increased dramatically with increasing reaction temperature, as shown by the examples in Fig. 2. Nevertheless, the influence of temperature was fairly small for $Co_{4-n}Rh_n/SiO_2$ catalysts until 250°C, but greater for the more active $Co_{4-n}Ru_n/SiO_2$ catalysts under the same conditions. Selectivities for methane and C_2–C_4 hydrocarbons increased, and the selectivity to C_{8+} hydrocarbons decreased on all catalysts with increasing temperature. At the same time the selectivity to C_5–C_8 hydrocarbons decreased moderately on the $Co_{4-n}Rh_n/SiO_2$ catalysts and remained almost constant on the $Co_{4-n}Ru_n/SiO_2$ catalysts.

$Co_{4-n}Ru_n/SiO_2$ catalysts did not produce a lot of oxygenates at any conditions and the selectivity to oxygenates was low regardless of temperature. For the $Co_{4-n}Rh_n/SiO_2$ catalysts, which are efficient in the formation of oxygenates, the selectivity to oxygenates depended strongly on temperature: the amount of oxygenates decreased sharply above 260°C. Most influenced by the reaction temperature was ethanol formation, the selectivity to ethanol on the Co_3Rh/SiO_2 catalyst, for instance, decreased from 7.5 to 1.6 C-% when the temperature increased from 210 to 290°C. Benitez et al. [27] have proposed that the competition between the insertion step and the complete hydrogenation to methane controls the selectivity to ethanol. With increasing temperature, the sharp increase in the selectivity to methane and the simultaneous decrease in the selectivity to ethanol, agree well with the proposed competition between the insertion step and the complete hydrogenation. The amount of other oxygenates also decreased with increasing temperature, but the influence of temperature was much less important than for ethanol. The reaction mechanism for the other oxygenates must therefore be entirely different, or at least another parallel route that is less temperature sensitive must be operative. One possibility is the combination of alkyl species with the adsorbed surface OH group as proposed by Wojciechowski [28].

Likewise Orita et al. [29] and Jackson et al. [30] have claimed that the formation of ethanol and acetaldehyde on rhodium catalysts takes place differently: the reaction of molecular CO with H^* results in an alcohol, whereas the reaction with CH_2^* results in an aldehyde.

3.4. Catalyst deactivation

A clean catalyst surface begins to deactivate as soon as it encounters reactant molecules. Usually, this initial state is too fast to be detected by conventional reactor systems such as ours. The steady state is achieved after the deactivation of initially very active sites that play no further role in the catalysis [11]. In our experiments the steady state was achieved after five hours of reaction time and thereafter the conversion was measured periodically during the following 75 h. All catalysts were deactivated as indicated by the decay of the relative activity (Fig. 3). The relative activity is determined as C_t/C_i where C_i is the initial conversion at 5 h reaction time and C_t is the conversion at time t.

The order of relative activity of $Co_{4-n}Rh_n/SiO_2$ catalysts after 75 h reaction time was the following: $Co_4 = Rh_4 > (Co_4 + Rh_4) > Co_2Rh_2 > Co_3Rh$. The results show that the homometallic catalysts were the most resistant to deactivation. The bimetallic catalysts deactivated rapidly and after 75 h their relative activity was very low. For instance, the activity of the Co_3Rh/SiO_2 catalyst was only 0.43. These results indicate that the nature of the precursor affected the deactivation process considerably, because all other parameters were kept constant.

The deactivation was probably caused by coking, i.e. layers of coke deposit decreased the accessible surface area and the active metals became encapsulated by carbon. The combined site of cobalt and rhodium appeared to play an important role in the deactivation of bimetallic $Co_{4-n}Rh_n/SiO_2$ catalysts, although the exact mechanism remains unknown.
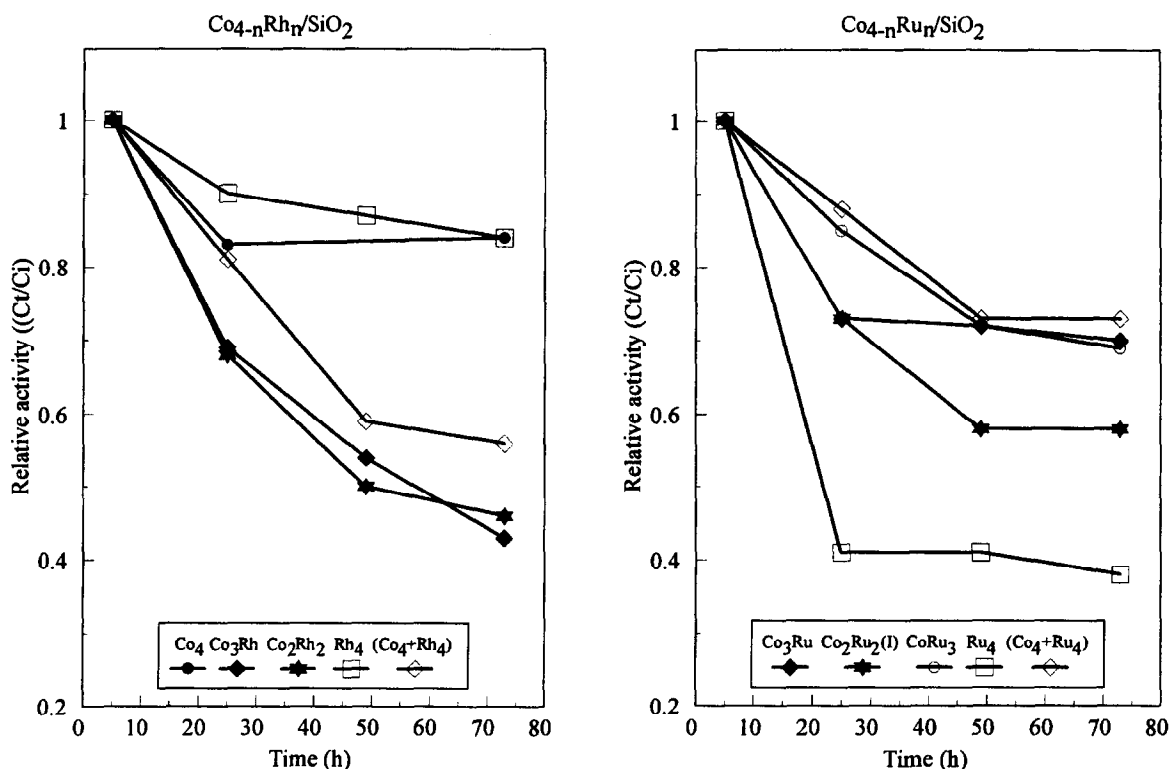
Fig. 3. Catalyst deactivation at 233°C and 2.1 MPa in the hydrogenation of carbon monoxide.

The order of relative activity of $Co_{4-n}Ru_n/SiO_2$ catalysts after 75 h reaction time was the following: $Co_4 > (Co_4 + Ru_4) \approx Co_3Ru \approx CoRu_3 > Co_2Ru_2(I) > Ru_4$. In every case, the initial deactivation was rapid, but the further deactivation, within 25 and 50 h of reaction was moderate. The activity of the homometallic Ru_4/SiO_2 catalyst declined most dramatically and after 25 h of reaction time was only about 40% of the initial activity. Probably the high hydrocarbons, such as waxes, plugged the small pores and blocked the active metal surfaces inside the pores. In fact, the probability of chain growth was exceptionally high for Ru_4/SiO_2. However, Krishna and Bell [31] have estimated that only 3–7% of the exposed Ru sites on Ru/TiO_2 could have been covered by wax after the reaction. They concluded that the immediate initial deactivation was mainly due to the accumulation of carbidic carbon species.

The homometallic Co_4/SiO_2 and Ru_4/SiO_2 catalysts were the most and the least resistant to deactivation, respectively. All bimetallic cobalt–ruthenium catalysts fell in between the homometallic catalysts in terms of deactivation. This clearly demonstrates that the deactivation of the $Co_{4-n}Ru_n/SiO_2$ catalysts is closely related to the presence of ruthenium.

4. Conclusions

We studied systematically the tetranuclear cobalt, cobalt–ruthenium, cobalt–rhodium and rhodium carbonyl clusters as catalyst precursors in the synthesis gas reaction. Activities were highest for the catalysts derived from homometallic clusters, and lowest for catalysts with 1:1 ratio of Co/Ru or Co/Rh. The unexpectedly low activities might have been due to the relatively low reduction temperature (300°C) used for our catalysts, which could have caused incomplete alloying.

Interestingly enough, the highly active homometallic cobalt catalyst was also the most resistant to deactivation. After 75 h reaction time, the homometallic cobalt and rhodium catalysts were the most active ones, whereas the ruthenium catalyst had lost most of its activity. The deactivation was stronger on bimetallic sites. On the $Co_{4-n}Ru_n/SiO_2$ catalysts the deactivation was closely related to the presence of ruthenium, which is known to strongly promote the formation of high molecular weight hydrocarbons.

The selectivities for oxygenated compounds were clearly promoted by the bimetallic sites of Co–Rh catalysts. This result is very plausible since the probability to find dual active sites responsible for the formation of oxygenates is greater in bimetallic than in homometallic catalysts. Our results also provide evidence for a reaction mechanism with two separate pathways for oxygenate formation: one for ethanol and the other for aldehydes.

Acknowledgements

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