

CO hydrogenation activity of carbonyl cluster derived Co–Ru/SiO₂ catalysts prepared by reflux method

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Abstract

The applicability of a reflux method for the preparation of cluster-derived Co–Ru catalysts supported on silica was studied. The properties of the resulting catalysts were compared with those of the corresponding catalysts prepared by impregnation. The presence of ruthenium either as a component of a bimetallic cluster or in a physical mixture of the two metals was essential for the adsorption of cobalt on silica. The activity and selectivity of these catalysts in CO hydrogenation were different from those obtained with catalysts prepared by impregnation.

Keywords: Carbonyl cluster; Preparation method; CO hydrogenation

1. Introduction

With mixed-metal-clusters it is possible to prepare heterogeneous catalysts which possess a contaminant-free, uniform and highly dispersed metal phase under well controlled conditions [1]. Several methods such as sublimation, dry-mixing, impregnation or adsorption have been used to deposit carbonyl clusters on the support [2–4]. Since the majority of the metal carbonyl clusters of interest are sensitive to oxygen, bimetallic catalysts have been prepared most often by impregnation from various organic solvents under inert atmosphere [5,6] and after

impregnation the solvent is removed and the carbonyl is thermally decomposed. Partially dehydroxylated silica is known to interact weakly with impregnated carbonyl clusters [7] and, for example, ruthenium has practically been removed from silica by repeated washing with pentane [8]. Compared with impregnation, by a preparation method based on extraction and refluxing, higher metal loading and dispersion could be obtained with catalysts supported on alumina [4,9]. These effects were explained by the improved solubility of the clusters in the boiling solvent, the slow adsorption and the elimination of the crystallization of clusters on the support [4,9].

When hydrido mixed-metal clusters interact

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with inorganic oxides such as SiO_2 , Al_2O_3 and MgO , ionic bond forms between the negatively charged cluster and a surface metal cation. This bond occurs via a carbonyl ligand [10]. Silica has been found not to be basic enough to give remarkable deprotonation of hydrido mixed-metal cluster although slight deprotonation accompanied by other kind of cluster-support interaction, which involve the loss of coordinated CO may occur [11]. Nevertheless, hydrido ligand may thus have effect on the bonding between mixed-metal cluster and SiO_2 .

In this work, we studied the applicability of a reflux method for the preparation of bimetallic Co–Ru catalysts supported on silica. The catalysts were prepared by refluxing $\text{Co}_{4-n}\text{Ru}_n\text{H}_n(\text{CO})_{12}$ ($n = 0-4$) or $\text{Co}_2\text{Ru}_2(\text{CO})_{13}$ carbonyl clusters and silica in an organic solvent, and thereafter washing the loosely bound metal species from the support. In addition, the effect of the hydrido ligand of $\text{Co}_{4-n}\text{Ru}_n\text{H}_n(\text{CO})_{12}$ cluster on the interaction of cluster and silica-support was also of our interest. The activity of these catalysts was studied in CO hydrogenation. The results were compared with those obtained with catalysts prepared by impregnation [12].

2. Experimental

Commercial Grace 432 silica was used as the support for the catalysts. Prior to use the support was ground and sieved to 0.5–1.0 mm, and heated under vacuum at 600°C for 3 h. This treatment brings about partial dehydroxylation and leaves the silica with a small amount of weakly acidic OH-groups [13] which may act as adsorption sites for the precursors [7]. Tetranuclear carbonyl clusters were used as precursors for the catalysts. Commercially available $\text{Co}_4(\text{CO})_{12}$ carbonyl was obtained from Strem Chemicals. The other metal carbonyl clusters were synthesized according to published methods and were as follows: $\text{Ru}_4\text{H}_4(\text{CO})_{12}$ [14],

$\text{CoRu}_3\text{H}_3(\text{CO})_{12}$ [15], $\text{Co}_2\text{Ru}_2\text{H}_2(\text{CO})_{12}$ [16], $\text{Co}_2\text{Ru}_2(\text{CO})_{13}$ [17], $\text{Co}_3\text{RuH}(\text{CO})_{12}$ [18].

2.1. Preparation of refluxed catalysts

The catalyst precursor and silica were weighed in a flask in an inert gas glove-box ($\text{O}_2 < 1$ ppm). The amount of precursor was calculated to give a total amount of metal of 0.9 mmol/1 g in a ready catalyst in accordance with the metal contents of the catalysts prepared by impregnation [12]. Dried, oxygen-free n-hexane (15 ml/1 g SiO_2) was added, and the mixture was stirred and refluxed under nitrogen atmosphere for 5 h. After cooling to room temperature excess solvent was removed, and the catalyst was washed 5–10 times with n-hexane by means of a filter cannula until the solvent remained clear. The metal content of the catalysts were determined by XRF.

In order to study the effect of the preparation temperature and the possible thermal degradation of the clusters, two additional reference catalysts were prepared from $\text{Co}_2\text{Ru}_2\text{H}_2(\text{CO})_{12}$ and $\text{Co}_2\text{Ru}_2(\text{CO})_{13}$ at room temperature. The preparation was carried out by stirring the mixture for 5 h at room temperature instead of refluxing the solvent.

2.2. Preparation of impregnated catalysts

The catalysts used for comparison were prepared by impregnation from nitrogenated dichloromethane solution under a deoxygenated atmosphere [12]. After impregnation the catalysts were dried slowly under vacuum at room temperature. The metal contents of all the impregnated catalysts were about 0.9 mmol/1 g of catalyst.

2.3. Reaction tests

The catalytic activity of the catalysts in CO hydrogenation was tested by a continuous flow fixed bed tubular reactor equipped with an on-

line GC system consisting of two HP-5890 chromatographs with six columns, 3 FIDs and 1 TCD. 1.0 g of the catalyst was loaded in the reactor tube in a glove-box. The reactor tube was connected to the system without contact with air. Just prior to use the catalyst was activated in situ under flowing hydrogen at 300°C for 2 h. After cooling down the reactor to 190°C the reaction was initiated by replacing hydrogen flow with synthesis gas (CO:H₂:Ar = 3:6:1) and increasing the pressure to the normal reaction condition at 2.1 MPa. The product selectivities were determined as carbon efficiencies based on the amount of CO reacted. Typical reaction temperature was 233°C and reactant flow rate was varied in order to change CO conversion. Selectivities were interpolated to 3% CO conversion level. The length of the reaction test with each catalyst was 5 days making it possible to study also the deactivation rate of the catalysts.

In the remainder of this paper the following abbreviations will be used to denote the precursor used for the preparation of the catalysts: Co₄ = Co₄(CO)₁₂, Ru₄ = Ru₄H₄(CO)₁₂, CoRu₃ = CoRu₃H₃(CO)₁₂, Co₂Ru₂(I) = Co₂Ru₂H₂(CO)₁₂, Co₂Ru₂(II) = Co₂Ru₂(CO)₁₃ and Co₃Ru = Co₃RuH(CO)₁₂. The reference catalysts prepared at room temperature were marked with an additional symbol (rt), i.e., Co₂Ru₂(I)(rt) and Co₂Ru₂(II)(rt).

3. Results and discussion

3.1. Characterization

The metal contents of the different catalyst preparations were determined by XRF, and compared with the calculated amounts based on the loading of precursors. The results shown in Table 1 indicate that the cobalt content of the Co₄/SiO₂ was very low, although a high loading of tightly bound cobalt has been deposited on alumina by refluxing the same cluster in cyclohexane [9]. The result can be explained by the very low interaction of the cluster with silica [7]. Consequently, most of the metal was easily washed off the surface by an excess amount of the solvent. Also, with all the other clusters the final metal contents were significantly lower than those expected by the amount of precursors.

It is noteworthy that the metal content of Co₂Ru₂(II)/SiO₂ was only about one third of the metal content of the Co₂Ru₂(I)/SiO₂ catalyst. Thus, the behaviour of the two equimolar clusters Co₂Ru₂(I) and Co₂Ru₂(II) was very different from each other. The structure of the Co₂Ru₂(II) cluster was unique among the studied bimetallic clusters since all the other precursors were hydridocarbonyls, whereas the protons had been replaced by a carbonyl group in the Co₂Ru₂(II). Also with the reference cata-

Table 1

The measured and calculated metal contents of the refluxed Co_{4-n}Ru_n/SiO₂ and (Co₄ + Ru₄)/SiO₂ catalysts ^a

| Catalyst | Measured metal contents/1 g catalyst (mmol) | | Calculated metal contents/1 g catalyst (mmol) | |
|--|---|------|---|------|
| | Co | Ru | Co | Ru |
| Co ₄ /SiO ₂ | 0.02 | 0 | 0.89 | 0 |
| Co ₃ Ru/SiO ₂ | 0.24 | 0.14 | 0.67 | 0.22 |
| Co ₂ Ru ₂ (I)/SiO ₂ | 0.27 | 0.18 | 0.45 | 0.45 |
| CoRu ₃ /SiO ₂ | 0.09 | 0.26 | 0.22 | 0.67 |
| Ru ₄ /SiO ₂ | 0 | 0.35 | 0 | 0.89 |
| Co ₂ Ru ₂ (II)/SiO ₂ | 0.10 | 0.06 | 0.45 | 0.45 |
| (Ru ₄ + Co ₄)/SiO ₂ | 0.07 | 0.26 | 0.45 | 0.45 |
| Co ₂ Ru ₂ (I)/SiO ₂ ^b | 0.13 | 0.12 | 0.45 | 0.45 |
| Co ₂ Ru ₂ (II)/SiO ₂ ^b | 0.04 | 0.02 | 0.45 | 0.45 |

^a The total metal contents of all impregnated catalyst with no wash were about 0.9 mmol/1 g catalyst.

^b Catalysts were impregnated in n-hexane and washed with excess of n-hexane.

lysts prepared at room temperature the metal content of the $\text{Co}_2\text{Ru}_2(\text{II})(\text{rt})/\text{SiO}_2$ after washing was significantly lower than that of the catalyst prepared from the corresponding hydridocarbonyl, $\text{Co}_2\text{Ru}_2(\text{I})(\text{rt})/\text{SiO}_2$. Thus, the different metal loading of $\text{Co}_2\text{Ru}_2(\text{I})/\text{SiO}_2$ and $\text{Co}_2\text{Ru}_2(\text{II})/\text{SiO}_2$ could not be explained by the different thermal stabilities and possible degradation of the clusters at elevated temperature during refluxing. The protons of the hydridocarbonyl seemed to play an important role in the adsorption mechanism of the metal species on the support, but the detailed interaction mechanism still remains unsolved. Nevertheless, in the absence of protons the interaction of metals with the support seemed weak resulting in a low metal content after washing the catalyst with an excess amount of the solvent. The metal loading of both of the catalysts prepared at room temperature were lower than those of their refluxed counterparts. This result indicated that by the reflux method it is possible to increase the amount of tightly bound metal on the support in accordance with results with alumina supported carbonyl catalysts [4,9].

Also, when a physical mixture of $(\text{Co}_4 + \text{Ru}_4)$ was used as a precursor, the cobalt content of the catalyst was significantly higher than with Co_4 alone, see Table 1. We presume that the Ru_4 cluster might have interacted with the silica support, whereas cobalt was bound to ruthenium

already attached on the surface. Thus, the presence of ruthenium either as a component of a bimetallic cluster or in a physical mixture of the two metals was essential for the adsorption of cobalt on silica.

However, a single factor such as the ratio of the two metals in the precursor did not determine the strength of interaction of the cluster or the final contents of the cluster components on silica alone. In fact, the original metal ratio of the cluster was retained during the reflux process only in the case of $\text{CoRu}_3/\text{SiO}_2$. With $\text{Co}_3\text{Ru}/\text{SiO}_2$ and $(\text{Co}_4 + \text{Ru}_4)/\text{SiO}_2$ catalysts the Co/Ru-ratio of the original cluster, or the mixture of the monometallic clusters, decreased significantly upon adsorption on the support, whereas with $\text{Co}_2\text{Ru}_2(\text{I})/\text{SiO}_2$ and $\text{Co}_2\text{Ru}_2(\text{II})/\text{SiO}_2$ it increased.

3.2. Reactivity

Table 2 summarizes the activities and product selectivities in the hydrogenation of carbon monoxide at 233°C and 2.1 MPa over $\text{Co}_{4-n}\text{Ru}_n/\text{SiO}_2$ catalysts prepared by refluxing. The activities are given as gas hourly space velocities (GHSV) needed to obtain 3% CO conversion, and the selectivities are given at this conversion level. Since the metal content of the refluxed catalysts varied greatly with the precursor and differed significantly from the metal

Table 2

The effect of the precursor of the refluxed $\text{Co}_{4-n}\text{Ru}_n/\text{SiO}_2$ and $(\text{Co}_4 + \text{Ru}_4)/\text{SiO}_2$ catalysts on the activity and product distribution in the hydrogenation of carbon monoxide ^a

| Catalyst | GHSV (h^{-1}) | GHSV/metal ($\text{h}^{-1} \text{mmol}^{-1}$) | CH_4 (C%) | $\text{C}_2\text{--C}_4$ (C%) | $\text{C}_5\text{--C}_8$ (C%) | $> \text{C}_8$ (C%) | Oxygenates (C%) | CO_2 (C%) |
|--|--------------------------|---|--------------------|-------------------------------|-------------------------------|---------------------|------------------|--------------------|
| Co_4SiO_2 | ^b (12 700) | ^b (14 100) | ^b (13) | ^b (22) | ^b (30) | ^b (28) | ^b (4) | ^b (3) |
| $\text{Co}_3\text{Ru}/\text{SiO}_2$ | 3800 (9400) | 10000 (10 400) | 17 (20) | 22 (24) | 41 (24) | 13 (25) | 5 (8) | 3 (0) |
| $\text{Co}_2\text{Ru}_2(\text{I})\text{SiO}_2$ | 3900 (8800) | 8700 (9800) | 16 (15) | 28 (19) | 37 (29) | 14 (32) | 6 (4) | 0.2 (0) |
| $\text{CoRu}_3/\text{SiO}_2$ | 5700 (11 600) | 16 200 (12 900) | 13 (13) | 20 (19) | 46 (33) | 17 (32) | 4 (4) | 0.2 (0) |
| Ru_4/SiO_2 | 14 000 (14 500) | 40 000 (16 100) | 8 (6) | 10 (6) | 12 (11) | 63 (76) | 3 (0.4) | 4 (0) |
| $\text{Co}_2\text{Ru}_2(\text{II})/\text{SiO}_2$ | 440 (12 700) | 2800 (14 100) | 25 (18) | 27 (19) | 29 (27) | 8 (29) | 7 (6) | 5 (2) |
| $(\text{Co}_4 + \text{Ru}_4)\text{SiO}_2$ | 7500 (4000) | 22 700 (4400) | 10 (22) | 15 (25) | 45 (28) | 21 (17) | 3 (9) | 3 (0) |

Reaction conditions: $\text{CO}/\text{H}_2/\text{Ar} = 3:6:1$, pressure = 2.1 MPa, $T = 233^\circ\text{C}$ and CO conversion = 3%.

^a Results obtained with catalysts prepared by impregnation are shown for comparison (in parentheses) [13].

^b Virtually inactive.

contents of the impregnated catalysts, the activities were given also proportional to the actual metal content (GHSV/mmol of metal) to make comparison of activities easier. For comparison, data obtained with catalysts prepared by impregnation [12] were also included in Table 2.

The Co_4/SiO_2 showed only negligible activity for CO hydrogenation and the low activity was most likely related to the very low metal loading. Also $\text{Co}_2\text{Ru}_2(\text{II})/\text{SiO}_2$ was only slightly active which may originate from the unique structure of the cluster and its different interaction with silica support compared with the other studied clusters. From the rest of the catalysts, Ru_4 exhibited superior activity, and its catalytic performance was very similar to its counterpart prepared by impregnation. In all, the catalyst activity (GHSV/metal loading) decreased in the order: $\text{Ru}_4/\text{SiO}_2 \gg (\text{Co}_4 + \text{Ru}_4)/\text{SiO}_2 > \text{CoRu}_3/\text{SiO}_2 > \text{Co}_3\text{Ru}/\text{SiO}_2 > \text{Co}_2\text{Ru}_2(\text{I})/\text{SiO}_2 > \text{Co}_2\text{Ru}_2(\text{II})/\text{SiO}_2 \gg \text{Co}_4/\text{SiO}_2$. This order was significantly different from that reported earlier for the catalysts

prepared by impregnation of the same clusters on silica [12].

Especially, the low activity of $\text{Co}_2\text{Ru}_2(\text{II})$ was unexpected, even in the light of the low metal content, since in the case of impregnated catalysts $\text{Co}_2\text{Ru}_2(\text{II})/\text{SiO}_2$ showed very high activity being clearly more active than the catalyst prepared from the corresponding hydrido-carbonyl $\text{Co}_2\text{Ru}_2(\text{I})$. It is also notable that the catalyst prepared from the mixture of the two homometallic clusters ($\text{Co}_4 + \text{Ru}_4$) was the least active among the catalysts prepared by impregnation [12], whereas now it was second only to the monometallic Ru_4/SiO_2 . Thus, the activity of the refluxed $(\text{Co}_4 + \text{Ru}_4)/\text{SiO}_2$ was much higher than that of its impregnated counterpart.

In order to study the effect of Co/Ru-ratio of the precursor the activities of the refluxed and impregnated catalysts corrected by the actual metal content were plotted in Fig. 1. Refluxed catalysts showed generally higher activity per metal atom compared with the corresponding impregnated catalysts indicating a difference in

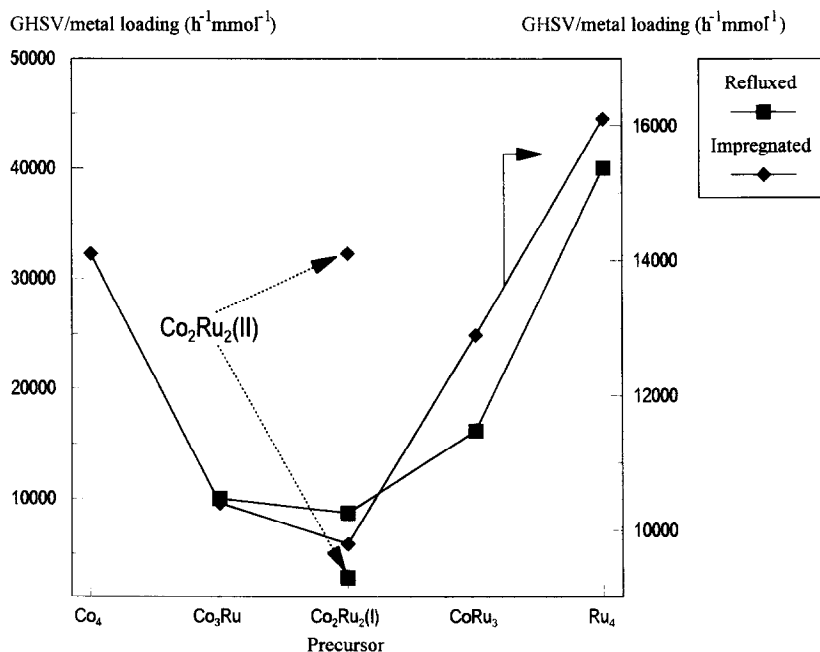


Fig. 1. The effect of precursor on the activity of the catalysts.

the state of the metal atoms on silica on these catalysts. However, since the metal contents of the refluxed catalysts were significantly lower than those of the impregnated ones, the observed overall reaction rates over refluxed catalysts were also lower. The correlation between the ratio of the two metals in the cluster and the catalyst activity was very similar with both types of catalysts. The activity of the refluxed and impregnated catalysts reached a minimum with a molar Co/Ru-ratio of 1:1. The behaviour of $\text{Co}_2\text{Ru}_2(\text{II})/\text{SiO}_2$ catalyst was again exceptional: In the case of impregnated catalysts $\text{Co}_2\text{Ru}_2(\text{II})/\text{SiO}_2$ exhibited much higher activity than $\text{Co}_2\text{Ru}_2(\text{I})/\text{SiO}_2$, whereas, the opposite was observed with their refluxed counterparts. In contrast to our results, Xiao et al. [19] found the activity of the bimetallic catalysts to increase with increasing Co/Ru molar ratio. In their experiments, however, the catalysts were calcined in oxygen prior to the reaction tests. These contradictory results indicate that not only the structure and composition of the cluster but also the method of deposition of the precursor on the support as well as details of the preparation process are of crucial importance to the properties of the resulting catalysts. In addition to calcination, factors such as the rate of drying [20], and the atmosphere of decomposition [1,21,22] have been found to significantly influence the catalysts performance.

The main products of the reaction were straight chained hydrocarbons (> 90 C%). The distribution of hydrocarbons followed fairly well the Anderson–Schulz–Flory rule. Generally, the products over refluxed catalysts were not as heavy as over impregnated catalysts, and the share of C_5 – C_8 hydrocarbons increased with respect to the heaviest C_{8+} products. All the studied catalysts showed remarkably low activity for hydrogenation of olefins to paraffins, and among the C_3 – C_7 hydrocarbons the 1-olefins predominated over the corresponding n-alkanes. The fraction of heavy hydrocarbons increased with the increasing share of ruthenium, and the probability of chain growth (α) reached 0.88

with the Ru_4/SiO_2 catalyst. In addition to aliphatic hydrocarbons, only small amounts of aromatic products (benzene, toluene) were formed on any of the refluxed catalysts.

In addition to hydrocarbons, oxygen-containing compounds were formed in selectivities of 3%–7%. It is noteworthy that the share of carbonyl compounds (acetaldehyde, acetic acid, esters) was remarkably high, and in many cases they constituted the main part of the oxygenates instead of alcohols. For instance, none of the impregnated catalysts produced methylacetate whereas refluxed $\text{Co}_3\text{Ru}/\text{SiO}_2$, $\text{Co}_2\text{Ru}_2(\text{I})/\text{SiO}_2$, $\text{CoRu}_3/\text{SiO}_2$, Ru_4/SiO_2 , $\text{Co}_2\text{Ru}_2(\text{II})/\text{SiO}_2$ and $(\text{Co}_4 + \text{Ru}_4)/\text{SiO}_2$ catalysts produced methylacetate with selectivities 0.9%, 0.8%, 0.5%, 0.1% and 1.2%, respectively. This kind of product distribution has been observed with rhodium catalysts [23] and some highly dispersed cobalt catalysts promoted by alkali metal cations [24]. The results suggested that the insertion of molecular carbon monoxide to surface alkyl species [25] took place on these catalysts, and these catalysts may thus be potential for the hydroformylation of olefins in the vapour phase. In addition, the low activity for the hydrogenation of olefins observed with these catalysts is beneficial for the vapour phase hydroformylation since the main problem of this reaction has been the high rate of direct hydrogenation of the olefin used as the starting material of the reaction [26].

A notable difference in the catalytic activity of the refluxed and impregnated catalysts was also observed in the formation of carbon dioxide. The formation of remarkable amounts of carbon dioxide with all of the refluxed catalysts indicated that the water–gas shift reaction took place on these catalysts whereas with catalysts prepared by impregnation the formation of CO_2 was substantial only for $\text{Co}_2\text{Ru}_2(\text{II})$ [12].

3.3. Deactivation

All the catalysts deactivated during the reaction test as indicated by the decay of the relative

activity, see Fig. 2. For comparison, results with impregnated catalysts [12] were added to Fig. 2. The relative activity was determined as C_t/C_i where C_i is the initial CO conversion about 5 h after the start of the reaction and C_t is the conversion at time t . By XRF it was verified that the metal content of the catalysts did not decrease in the course of the reaction and the deactivation was probably caused by coking. The decrease of activity was smooth and in contrast to impregnated catalysts, a state of practically constant activity was not obtained during the test. The order of relative activity of $\text{Co}_{4-n}\text{Ru}_n/\text{SiO}_2$ catalysts after 75 h of reaction was as follows: $\text{CoRu}_3 > (\text{Co}_4 + \text{Ru}_4) > \text{Co}_2\text{Ru}_2(\text{I}) \approx \text{Co}_3\text{Ru} > \text{Ru}_4 \gg \text{Co}_2\text{Ru}_2(\text{II})$. The highly active monometallic Ru_4/SiO_2 catalyst deactivated fairly quickly probably by the plugging of active sites by the heavy, waxy hydrocarbons formed in large quantities with this catalyst. The $\text{Co}_2\text{Ru}_2(\text{II})/\text{SiO}_2$ was again exceptional since the already originally low activity was almost completely lost within 50 h-on-stream.

4. Conclusions

The presence of ruthenium either as a component of a bimetallic cluster or in a physical mixture of the two metals seemed to be essential for the adsorption of cobalt on silica. However, a single factor such as the ratio of cobalt and ruthenium in the precursor did not alone determine the strength of interaction of the cluster with silica. The protons of the hydridocarbonyl appeared to have an important effect on the adsorption mechanism of the cluster on silica and further to the catalytic properties of the resulting catalyst. By a reflux method it was possible to increase the amount of tightly bound metal on silica which was not removed by washing with an excess of solvent. Refluxed catalysts showed generally higher activity per metal atom compared with the corresponding impregnated catalysts. The correlation between the ratio of the two metals in the cluster and the catalyst activity was very similar with both types of catalysts; over both types of catalysts minimum activity was reached with a Co/Ru-

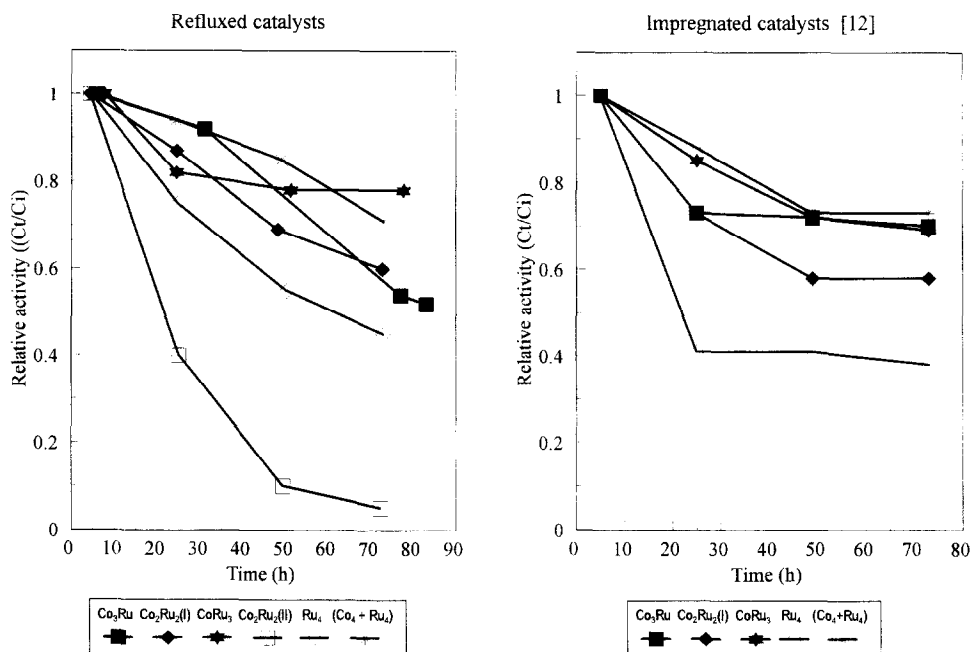


Fig. 2. Catalyst deactivation at 233°C and 2.1 MPa in the hydrogenation of carbon monoxide.

ratio 1:1. However, some differences in the selectivities of olefins, oxygenates and carbon dioxide could be observed.

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