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The effect of decomposition atmosphere on the activity and selectivity of the carbonyl cluster derived Co/SiO₂ and Rh/SiO₂ catalysts

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Abstract

The effect of pretreatment atmosphere, hydrogen or carbon monoxide, on the activity and selectivity of the Rh₄(CO)₁₂/SiO₂ and Co₄(CO)₁₂/SiO₂ catalysts in CO hydrogenation was determined. The catalysts pretreated under hydrogen exhibited a higher degree of decomposition of the original cluster, higher hydrogen uptake and lower carbon content than those decomposed under CO. Therefore, some of the active sites of the catalysts were encapsulated by carbon, and in the case of Co₄(CO)₁₂ poorly reducible cobalt silicates were probably also formed. The activity of the hydrogen-treated Rh₄(CO)₁₂/SiO₂ was fairly similar to that of the CO-treated catalyst, but significantly fewer oxygenates were formed. Thus, the carbon monoxide treatment appeared to facilitate the formation of oxygenates. Probably the original structure of rhodium carbonyl was better retained, and thereby some of the rhodium particles remained more dispersed under CO than under hydrogen. In the case of Co₄(CO)₁₂/SiO₂ catalysts, however, no benefit was observed in conjunction with CO pretreatment either in activity or selectivity. Most likely the CO treatment resulted in the formation of unreactive carbonaceous species which permanently blocked most of the active sites.

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

1. Introduction

Molecular metal clusters and metal carbonyls are increasingly being used as precursors for supported catalysts because they produce highly dispersed and well reduced catalysts [1–4]. The carbonyl precursors may be fixed to the dehy-

droxylated support by dry-mixing, impregnation or adsorption. Since most of the metal carbonyl clusters are oxygen sensitive, catalysts have often been prepared by impregnation from various organic solvents [5,6] under an inert atmosphere. After impregnation, the solvent is evaporated, and the cluster is decomposed under vacuum [7], oxygen [5], inert gas [6,8], hydrogen [7–9], CO [7] or synthesis gas [10] at elevated temperatures. The decomposition atmosphere has been found to significantly influ-

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ence the stability of the carbonyl cluster on the silica support [7], as well as the dispersion and activity of the catalysts [5,8,10–13].

Results pertaining to the decomposition of metal carbonyls on silica are somewhat contradictory in terms of the characterization of the catalysts. Some claim [14] that calcination is to be avoided if highly dispersed reducible clusters are required, whereas others [5] report that the hydrogen uptake of the oxygen-treated $\text{Co}_2\text{Rh}_2(\text{CO})_{12}/\text{SiO}_2$ catalyst was higher than that of its nitrogen-treated counterpart. On the other hand, inert gas treatment has been found to be beneficial [8,11]; the dispersion of Fe–Ru carbonyl catalysts was improved by decomposing the precursor under helium instead of hydrogen. Guczi et al. [8] assumed that, under helium flow, about 20–40% of the carbon evolved during the decomposition remained on the catalyst and stabilized the dispersion [8]. In general, the studies agree that the decomposition of the clusters proceeds readily in inert gas, oxygen or hydrogen, whereas in the presence of carbon monoxide the carbonyl precursor is stabilized and its decomposition is delayed [7]. Also, Koerts et al. [15] have discovered that the additional treatment of the reduced Ru/SiO₂ catalyst with carbon monoxide or CO/H₂ at 250°C significantly increased the carbon monoxide chemisorption capacity of the catalyst. Thus, the previous results suggest that the commonly used hydrogen treatment is not necessarily the best in terms of chemisorption capacity and dispersion.

The activity of the catalysts has been found to vary after different pretreatments. For example, Xiao et al. [12] calcined the $\text{Co}_4(\text{CO})_{12}$ derived catalyst before reduction, and found the catalyst fairly inactive for CO hydrogenation, whereas we obtained high activity for the same catalyst in the absence of calcination [13]. Guczi et al. [8,11] have observed that the activity of the Fe–Ru carbonyl catalysts was better when the catalysts were decomposed under helium than when they were decomposed under hydrogen [8]. However, in case of $\text{Co}_2(\text{CO})_8$ supported on zirconium-promoted alumina, Withers

et al. [10] have observed that activation with hydrogen significantly improved both activity and liquid fuel selectivity relative to activation with synthesis gas (CO/H₂ = 1) in a slurry test. The increased activity was tentatively attributed to a higher degree of cobalt reduction, but the enhanced selectivity could not be explained. For the conventional ruthenium catalyst preparations, Koerts et al. [15] found that the carbon monoxide treatment resulted in a catalyst that possessed a higher activity for carbon monoxide dissociation, because it was more easily reducible and had larger metal ensembles. In terms of the extent of reduction, however, Rosynek and Polanski [16] have stated that the activities and selectivities of the various Co/SiO₂ catalysts were comparable, because the presence of the H₂/CO/H₂O system during the reaction appeared to produce a similar working surface in all cases. Thus, the activity is affected both by dispersion and extent of reduction, although some recent studies suggest that the activity of the well reduced catalysts is independent of dispersion [17,18].

The present study deals with the activity and selectivity of the $\text{Co}_4(\text{CO})_{12}/\text{SiO}_2$ and $\text{Rh}_4(\text{CO})_{12}/\text{SiO}_2$ catalysts, with an emphasis on the effect of decomposition atmosphere on the properties of the catalysts. The results are also discussed in terms of previous in situ FT-IR studies concerning the decomposition of the clusters under a hydrogen or carbon monoxide atmosphere [19].

2. Experimental

2.1. Preparation and characterization of the catalysts

The preparation of the $\text{Co}_4(\text{CO})_{12}/\text{SiO}_2$ and $\text{Rh}_4(\text{CO})_{12}/\text{SiO}_2$ catalysts is described in detail in our previous publication [13]. Commercially available $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$ were obtained from Strem Chemicals. Grace 432 silica support was dried under vacuum at 600°C/2

h to dehydroxylate the surface [2,20]. The support was impregnated with a nitrogenated dichloromethane solution with 0.9 mmol of metal for 1 g SiO₂ under a deoxygenated atmosphere, and the catalysts were dried slowly under vacuum at room temperature. In the remainder of this paper, Co₄ refers to Co₄(CO)₁₂ and Rh₄ to Rh₄(CO)₁₂.

The prereduced catalyst samples were analyzed by X-ray photoelectron spectroscopy (XPS) to determine the extent of reduction and to estimate the particle size. The XPS apparatus was a Perkin-Elmer model 3057 PC-controlled ESCA lab system, with a dual-anode X-ray source operating under UHV (ultra high vacuum). AlK α X-rays and a hemispherical analyzer operating at the constant pass energy reference of 50 eV were used. The Si 2p binding energy of 103.7 eV was used as an energy reference to account for the charging of the insulating SiO₂ samples [21]. The peak area of the metallic component of the Co 2p_{3/2} photoelectron peak was determined from a Gauss–Lorentzian peak fit in combination with linear background correction, the calculation method being described in more detail in a previous publication [22]. In the case of a Rh 3d photoelectron peak, a Doniach–Sunjic–Gaussian peak fit [23] was used together with a Shirley-type background correction algorithm [24]. This method provides a lower limit for the extent of reduction, since only the outermost layers are analyzed by XPS, and the energy losses cannot be resolved from the real chemical shifts.

The hydrogen uptakes of the reduced catalysts were determined by static hydrogen chemisorption measurements, using an Omnisorp 100CX instrument. Prior to the measurements, the catalysts were decarbonylated and transferred to the measuring vessel in oxygen-free conditions. The decarbonylation was ensured by an additional decarbonylation in situ for 0.5 h (either H₂ or CO atmosphere). The standard experimental procedure [25,26] was utilized, and the results are given for total hydrogen uptake and irreversible uptake at 30°C.

The metal particle size was studied with transmission electron microscopy (TEM) using a Jeol JEM-2010F and Philips CM200 FEG. The particle size was determined from several images and the weighed average was calculated.

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. This system was described in more detail in our previous publication [13]. The catalyst (1 g, 2.75 ml) was treated with hydrogen or carbon monoxide in situ at 300°C for 2 h prior to the reaction.

3. Results and discussion

3.1. Characterization

In our previous paper [19], we studied the decarbonylation of Co₄/SiO₂ and Rh₄/SiO₂ catalysts using TPR and in situ FT-IR. Under a hydrogen atmosphere, Co₄/SiO₂ decomposed at approx. 120°C–137°C, and thereafter the IR-bands were too weak to be detected, see Fig. 1a [19]. The Rh₄ cluster was transformed to Rh₆(CO)₁₆ by contact with SiO₂, decomposed at approx. 150°C, and at 250°C we detected only two broad bands (2037 and 1750 cm⁻¹) assigned to terminal and bridged CO on metallic Rh, see Fig. 2a [19].

In more detail, we now suggest that the band at 1750 cm⁻¹ was in fact due to the face-bridged adsorption of CO, which has also been observed for NaY zeolite entrapped Rh₆(CO)₁₆ by Ichikawa et al. [27] at 200°C. In the face-bridged adsorption form, one CO molecule is bound to three metal atoms. Therefore, the propensity for the face-bridged adsorption appears higher on large ensembles of metal than on isolated sites. In other words, we presume that, under a hydro-

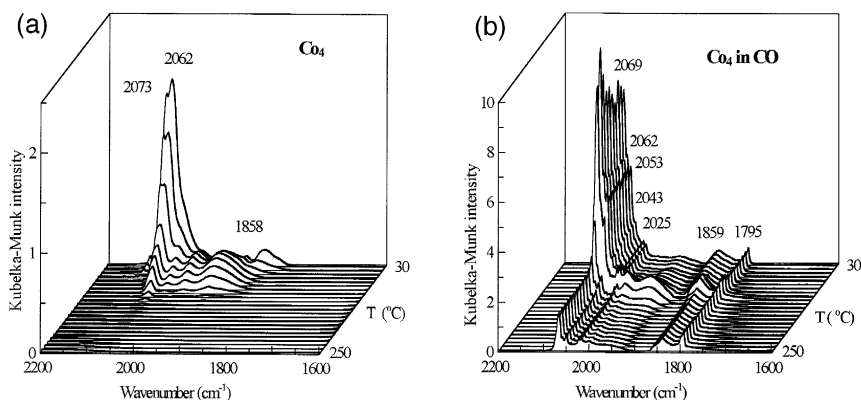


Fig. 1. (a) In situ DRIFT FT-IR spectra of the thermal decomposition of the Co_4/SiO_2 catalyst under H_2 atmosphere [19]. (b) In situ DRIFT FT-IR spectra of the thermal decomposition of the Co_4/SiO_2 catalyst under CO atmosphere [19].

gen atmosphere at elevated temperature, metal was slightly agglomerated. In support of our view, Solymosi and Raskó [28] have observed agglomeration of Ru^0 particles on raising the temperature in the presence of hydrogen.

Since carbonaceous residues have been found to enhance dispersion [8,11], we also decomposed the catalysts under carbon monoxide. As expected [7], the original FT-IR spectra for Co_4/SiO_2 and Rh_4/SiO_2 was much better retained under a CO atmosphere than under hydrogen, see Fig. 1b and Fig. 2b [19]. At the end of decomposition at 250°C sharp bands were still observed for Co_4/SiO_2 at 2069 cm^{-1} , 2043 cm^{-1} and 1795 cm^{-1} , together with a broad band at 1842 cm^{-1} , Fig. 1b. Similarly, at

250°C , we still observed bands for Rh_4/SiO_2 at 2069 cm^{-1} , 2053 cm^{-1} , 2043 cm^{-1} and 1794 cm^{-1} , together with a broad band at 1856 cm^{-1} , Fig. 2b. Thus, the cluster structures could have been partially retained under a CO atmosphere [19].

The FT-IR spectra may, however, also be interpreted in terms of particle size. Both Theolier et al. [29] and Bilou et al. [30] have reported that the close similarities between the shapes and intensities of the bands for the metallic particles, and for $\text{Rh}_6(\text{CO})_{16}$, indicate that the size of the particles is very small. In our case, the band intensities are lower than the initial ones, but the shape of the spectrum is well retained, indeed much more so than for the

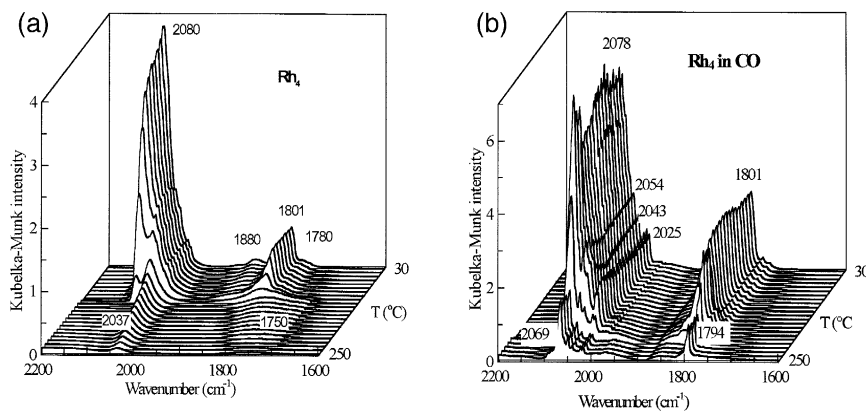


Fig. 2. (a) In situ DRIFT FT-IR spectra of the thermal decomposition of the Rh_4/SiO_2 catalyst under H_2 atmosphere [19]. (b) In situ DRIFT FT-IR spectra of the thermal decomposition of the Rh_4/SiO_2 catalyst under CO atmosphere [19].

catalysts decomposed under a hydrogen atmosphere. Since the spectra were better retained in respect to the initial spectra, we presume the metal remained in part more highly dispersed under a CO atmosphere than under a hydrogen atmosphere. In support of our assumption, Gucci et al. [8,11] have obtained higher dispersion for Fe–Ru carbonyl catalysts decomposed under He than for the same catalysts decomposed under H₂. They explained [8] that more carbon remained on the catalyst under inert gas than under hydrogen, and this stabilized the dispersion. In the same way, carbon formed by the dissociation of CO may stabilize the dispersion under a CO atmosphere.

To determine in more detail the effect of decomposition atmosphere on the catalysts, the XP spectra were determined, see Figs. 3 and 4 as well as Table 1. The extent of reduction for Co₄/SiO₂ was 18% and 13% under CO and hydrogen, respectively, whereas Rh₄/SiO₂ was totally reduced in both cases. The low values obtained for Co₄/SiO₂ can be explained by the formation of cobalt silicates resistant to reduction [31]. The lack of sensitivity towards pre-treatment atmosphere in terms of the extent of reduction was unexpected in the light of the literature data [10,15].

In conjunction with carbon deposition, the XPS results (Table 1) showed that more carbon was deposited on the catalysts decomposed under a CO atmosphere than on the ones decomposed under hydrogen. The XPS analysis suggested that the additional carbon was in carbidic form. Hence, under a CO atmosphere, some of the active metal sites probably became encapsulated by carbon, and the available surface area

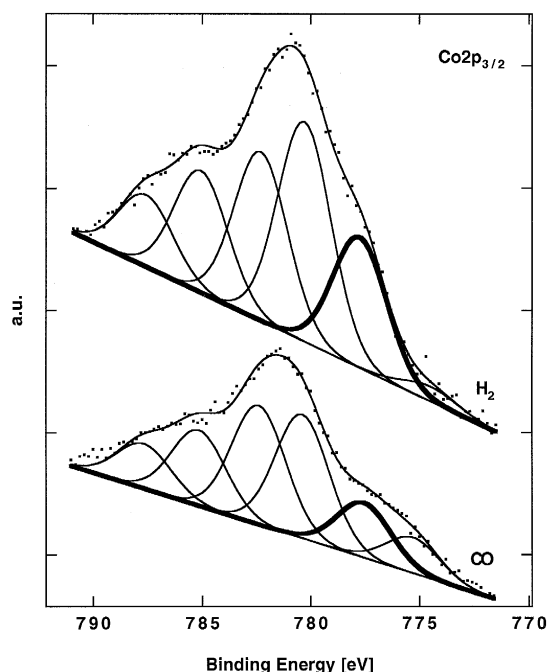


Fig. 3. XP spectra of the Co₄/SiO₂ catalysts decomposed under H₂ and CO atmosphere. Bold line = metallic cobalt.

of the metal was decreased. In accordance, the hydrogen uptakes were lower for the catalysts decomposed under CO than for those decomposed under hydrogen (see Table 1). The decrease in the hydrogen uptake may, in fact, be directly related to carbon coverage, since the extent of catalyst reduction remained the same or even increased on changing the pretreatment atmosphere from hydrogen to carbon monoxide.

In the light of the XPS and chemisorption results, we suggest that most of the active sites were blocked on Co₄/SiO₂, although some characteristic bands were observed at 250°C by

Table 1
The characteristics of the Co₄/SiO₂ and Rh₄/SiO₂ catalysts

Catalyst	Decomposition atmosphere	H ₂ uptake, total (μmol/g)	H ₂ uptake, irreversible (μmol/g)	XPS, reduction (%)	XPS, carbon (mol%)	TEM, particle size (nm)
Co ₄ /SiO ₂	H ₂	56.8	23.2	13	11	n.a.
Co ₄ /SiO ₂	CO	1.7	1.9	18	16	n.a.
Rh ₄ /SiO ₂	H ₂	145.7	43.4	100	8	4
Rh ₄ /SiO ₂	CO	48.6	27.2	100	10	4

n.a. = not available.

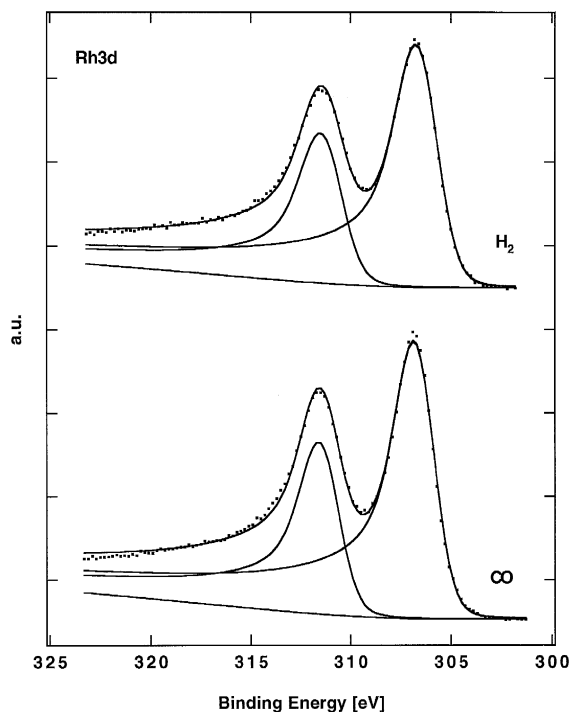


Fig. 4. XP spectra of the Rh_4/SiO_2 catalysts decomposed under H_2 and CO atmosphere.

in situ FT-IR. For Rh_4/SiO_2 , the in situ FT-IR, XPS and chemisorption results allowed us to assume that the partially retained structure of the carbonyl probably facilitated the formation of smaller metal particles. In accordance, the metal particle size distribution was wider for the Rh_4/SiO_2 catalyst decomposed under CO than under H_2 , although the weighed average particle size was approx. 4 nm in both cases, see Table 1. However, Koerts et al. [15] have reported, for a silica supported ruthenium catalyst,

that the carbon monoxide treatment resulted in a catalyst that exhibited only slightly larger metal ensembles than the one treated under hydrogen.

3.2. Activity

In support of our findings, we determined the activity and selectivity of the catalysts in CO hydrogenation after pretreatment in hydrogen [13] and carbon monoxide. The results depicted in Table 2 indicate that, for Co_4/SiO_2 , we observed significantly decreased activity when hydrogen was replaced by carbon monoxide in thermal pretreatment. The activity collapsed, and the selectivity was shifted towards methane. The surface of the catalyst was apparently poisoned by carbonaceous residues, as shown by the XPS results. In accordance, Nakamura et al. [32] have reported that when the disproportionation of CO was performed on $\text{Co}/\text{Al}_2\text{O}_3$ catalyst at 230°C, the predominant species was carbidic carbon. By raising the temperature, carbidic carbon was transformed rather rapidly to graphitic carbon, which is inactive towards hydrogen up to 430°C [32]. Thus, the inactive carbonaceous residues permanently blocked the active sites, and the performance of the catalyst deteriorated drastically.

In the case of Rh_4/SiO_2 , the activity of the catalyst decomposed under carbon monoxide was slightly lower than that of the catalyst decomposed under hydrogen. Thus, the reactivity results confirmed that carbonaceous residues had blocked some of the active sites. However,

Table 2

The effect of decomposition atmosphere on the function of catalysts

Catalyst	GHSV (h^{-1})	C_1 (C%)	$\text{C}_2\text{--}\text{C}_4$ (C%)	$\text{C}_5\text{--}\text{C}_8$ (C%)	$> \text{C}_8$ (C%)	Oxygenates (C%)	CO_2 (C%)	Aromatics (C%)
$\text{Co}_4/\text{SiO}_2^a$	12700	12.9	22.3	29.5	28.2	4.2	2.8	0.2
$\text{Co}_4/\text{SiO}_2^b$	650	61.4	19.9	12.8	4.4	1.5	0	0
$\text{Rh}_4/\text{SiO}_2^a$	2200	39.4	36.8	8.0	1.2	14.4	0	0.3
$\text{Rh}_4/\text{SiO}_2^b$	1700	51.3	8.9	7.2	0.2	32.3	0	0.1

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

^a = The clusters were decomposed under a hydrogen atmosphere [13].

^b = The clusters were decomposed under a CO atmosphere.

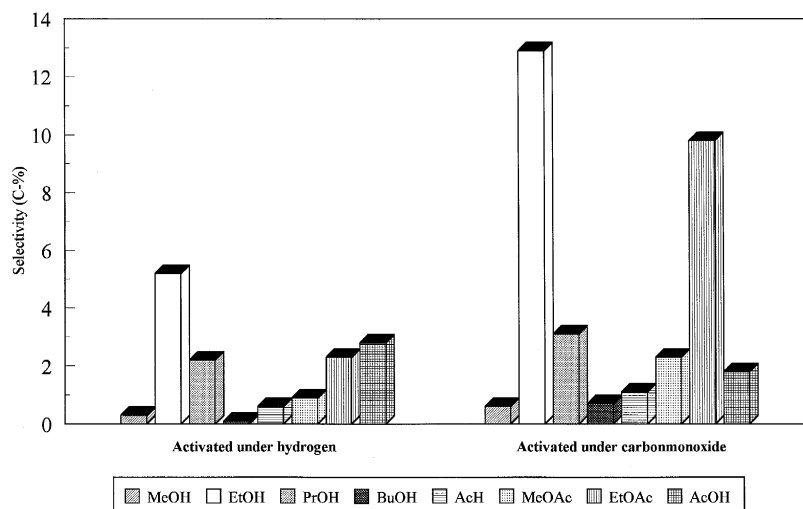


Fig. 5. Effect of decomposition atmosphere on the selectivity of the Rh_4/SiO_2 catalyst.

at the same level of conversion (3%), the selectivities differed considerably, see Fig. 5. The selectivities towards oxygenated compounds, and in particular towards ethanol and ethyl acetate, increased remarkably when the catalyst was treated with carbon monoxide instead of hydrogen. Since the selectivity towards oxygenates has been related to the presence of isolated active sites capable of CO insertion [33], the carbon monoxide-treated Rh_4/SiO_2 catalyst more plausibly exhibited more small particles than the hydrogen-treated counterpart. Thus, the reactivity of the Rh_4/SiO_2 catalyst provided further support for the speculations based on the characterizations.

4. Summary

Under a CO atmosphere, the structures initially present on the silica surface for Co_4/SiO_2 and Rh_4/SiO_2 were much more stable, and the decomposition of the clusters occurred at a significantly higher temperature than under a hydrogen atmosphere. The FT-IR spectra were better retained in respect to the initial spectra in the presence of CO than H_2 . Thus, we presumed that some part of metal particles re-

mained more highly dispersed under a CO than under a hydrogen atmosphere. To support our view, we determined the effect of pretreatment atmosphere, hydrogen or carbon monoxide, on the XP spectra, the hydrogen chemisorption capacity, and the activity and selectivity of the Co_4/SiO_2 and Rh_4/SiO_2 catalysts in CO hydrogenation.

The XPS results showed that more carbon was deposited on the catalysts decomposed under a CO atmosphere than on the ones decomposed under hydrogen. The carbonaceous residues encapsulated some of the active metal sites and thereby decreased the available surface area of the metal. Thus, the hydrogen uptakes of the CO treated catalysts were lower than those of the hydrogen treated ones. Nevertheless, we suggest that this partial carbon coverage, or the partially retained cluster, facilitated the formation of small particles on Rh_4/SiO_2 , whereas most of the active sites were blocked on Co_4/SiO_2 . The decomposition atmosphere had a minor effect on the extent of reduction: in both cases Rh_4/SiO_2 was totally reduced, whereas the extent of reduction for Co_4/SiO_2 was 18% and 13% under CO and hydrogen, respectively. The low values obtained for Co_4/SiO_2 can be explained by the formation of cobalt silicates resistant to reduction.

The activity of the Rh₄/SiO₂ catalyst decomposed under carbon monoxide was similar to that for the catalyst decomposed under hydrogen but the selectivity towards oxygenates was clearly higher. By contrast, the activity of the Co₄/SiO₂ catalyst collapsed when the cluster was decomposed under carbon monoxide instead of hydrogen, but the selectivities remained unaffected. Thus, cobalt carbide formation initiated blockage of the active sites. In summary, we suggest that the decomposition of metal carbonyls under CO atmosphere facilitates the preparation of metal catalysts selective to oxygenates in case of metals which do not favor the formation of non-reactive metal carbides.

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