Cobalt(III) acetylacetonate chemisorbed on aluminum-nitride-modified silica: characteristics and hydroformylation activity

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$Co/AlN/SiO_2$ catalysts were prepared by the saturative chemisorption of cobalt(III) acetylacetonate ($Co(acac)_3$). The support was bare silica or silica that had been modified with aluminum nitride (AlN) by repeated separate, saturated chemisorptions of trimethylaluminum and ammonia two or six times. Chemisorption of $Co(acac)_3$ occurred on all the supports up to a saturation ligand density of 2.7 acac nm^{-2}; the amount of bonded cobalt decreased from 2.1 to 1.5 $at_{Co}\,nm^{-2}$ with increasing extent of AlN modification of the support. Ligand exchange reaction, releasing Hacac, occurred less on AlN-modified silica than on bare silica. This induced difference in the reduction behavior of the catalysts, and catalytic activity in gas-phase hydroformylation of ethene, was lower with $Co/AlN/SiO_2$ than with Co/SiO_2 catalyst.

KEY WORDS: cobalt(III)acetylacetonate; chemisorption; atomic layer deposition; ALD; ALE; heterogeneous catalysts; ethene hydroformylation.

1. Introduction

Nitride materials have been successfully used as supports for metal catalysts, for example, in dehydrogenation [1–3], hydrogenation [4], hydroformylation [5], isomerization [6] and oxidation [7] reactions. The number of publications dealing with nitride supports is limited, however, partly because of the difficulty of obtaining nitrides in porous high-surface-area forms. Recently, a method was introduced for modifying the surface of porous high-surface-area silica and alumina with aluminum nitride (AlN), to produce "AlN/oxide supports" [8–11]. The preparation was done according to the atomic layer deposition (ALD) technique, which relies on separate, saturating gas–solid reactions of gaseous reactants with a solid support [12,13]. AlN was prepared by repeating the saturating reactions of trimethylaluminum (TMA) and ammonia [8–11]. One reaction cycle of TMA and ammonia added about 2.4 Al and N atoms per nm^2 of support [10,11]; after six reaction cycles, the coverage of silica by AlN species was about 75% [11].

Hydroformylation is an important process for the conversion of alkenes with carbon monoxide and hydrogen into aldehydes and alcohols, which are used in the production of a variety of chemicals [14]. For high gas-phase hydroformylation selectivities, catalysts should feature good dispersion and small particle size of the active metal, because the CO insertion needed for aldehyde production is favored on isolated metal sites [15,16]. Good dispersion of the catalyst metal and high selectivity in gas-phase hydroformylation have been obtained for Co/SiO_2 catalysts prepared by ALD from cobalt(III)acetylacetonate ($Co(acac)_3$) [17,18]. Several reactions take place during the catalyst preparation at 180 °C. Before bonding to the support, $Co(acac)_3$ apparently is transformed to $Co(acac)_2$ (reaction (1)) [17]. The $Co(acac)_2$ adsorbs on silica through ligand exchange reaction with OH groups, releasing gaseous acetylacetonate (Hacac) (reaction (2)), and through association with surface oxygen (reaction (3)) [17]. Two other reactions may be relevant. Although $Co(acac)_2$ does not dissociate onto siloxane bridges of bare silica [17], dissociative reaction of other metal acetylacetonates on the coordinatively unsaturated Al–O pairs on alumina, reaction (4), has been reported [19–21]. Similarly, the Hacac released in reaction (2) does not adsorb on silica support [22,23], but it does adsorb, for example, on the coordinatively unsaturated Al–O pairs (reaction (5)) [19,22,24]:

$$\mathrm{Co(acac)_3} \rightarrow \mathrm{Co(acac)_2} + \text{“acac”} \tag{1}$$

$$\text{▨}\mathrm{-OH} + \mathrm{Co(acac)_2(g)} \rightarrow \text{▨}\mathrm{-O-Co-acac} + \mathrm{Hacac(g)} \tag{2}$$

$$\text{▨}\mathrm{=O} + \mathrm{Co(acac)_2(g)} \rightarrow \text{▨}\mathrm{=O} \cdots \mathrm{Co(acac)_2} \tag{3}$$

$$\text{▨}\mathrm{-O-Al=}\text{▨} + \mathrm{Co(acac)_2(g)} \rightarrow \text{▨}\mathrm{-O-Co-acac} + \text{▨}\mathrm{=Al-acac} \tag{4}$$

$$\text{▨}\mathrm{-O-Al=}\text{▨} + \mathrm{Hacac(g)} \rightarrow \text{▨}\mathrm{-OH} + \text{▨}\mathrm{=Al-acac}. \tag{5}$$

In equations (2)–(5), ▨ denotes the solid surface.

In this work we investigated whether the use of an AlN/SiO_2 support might be beneficial for the cobalt dispersion and hydroformylation activity of cobalt catalysts prepared from $Co(acac)_3$ [17]. Cobalt was deposited on an SiO_2

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support, and on AlN/SiO$_2$ supports with different degrees of AlN-modification, by the saturating reaction of Co(acac)$_3$. The catalyst preparation on the different supports was compared in investigations by chemical analysis and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The catalysts were further characterized by hydrogen chemisorption and their activity was measured in the hydroformylation of ethene.

2. Experimental

2.1. Preparation of samples

The samples were prepared in an ALD reactor (ASM Microchemistry, Finland) operating at 1–10 kPa. Porous Grace Davidson 432 silica (288 $m^2 g^{-1}$) was used as support. AlN/SiO$_2$ samples were prepared in the reactor in three steps: (i) precalcination of the silica in ambient air at 750 °C for 16 h and subsequently in the reaction chamber at 550 °C for 3 h (to produce 1.1 OH groups per nm^2 [8]), (ii) reaction of TMA with the support at 150 °C, and (iii) reaction of ammonia with the TMA-modified sample, starting at 150 °C and terminating at 550 °C. Steps (ii) and (iii) were repeated up to six times to increase the concentration of AlN. Nitrogen purges were used between the reactions of TMA and ammonia to avoid gas-phase reactions. In the sample code, "*n*·AlN/SiO$_2$," the *n* denotes how many times the step was repeated. The preparation of the AlN/SiO$_2$ supports has been investigated in detail earlier [11].

The AlN-modified samples were stored in a glove box until their transfer to the ALD reactor for chemisorption of Co(acac)$_3$. The samples were inevitably slightly exposed to air during the transfer, and, to regenerate the AlN-modified surface, the samples were treated with ammonia at 550 °C for 4 h before reacting them with Co(acac)$_3$. The effect of this pretreatment was studied for the 4·AlN/SiO$_2$ sample.

Silica preheated at 750 °C and the 2·AlN/SiO$_2$ and 6·AlN/SiO$_2$ samples were used as supports for the cobalt catalysts. Co(acac)$_3$ was vaporized at 170 °C and reacted with the supports at 180 °C. For the preparation of one batch of catalyst, typically 5 g each of support and Co(acac)$_3$ were used. After the reaction, the reactor was purged at the reaction temperature to remove the unreacted precursor and the gaseous reaction products and cooled down, and the catalysts were transferred inertly to a glove box.

2.2. Characterization of Co(acac)$_3$-modified samples

The homogeneity of the support bed after chemisorption was investigated by taking samples from the top and bottom parts of the bed. The cobalt contents were determined by dissolving a known amount of sample in an aqueous solution of HCl and H_2O_2; the solution that was obtained was analyzed by flame atomic absorption spectrometry (AAS). The carbon contents of the Co(acac)$_3$-modified silica samples were analyzed with a Ströhlein CS-5500 analyzer by burning the samples at 1350 °C with oxygen. The carbon and nitrogen contents of the Co(acac)$_3$-modified AlN/SiO$_2$ samples were measured with a LECO CHN-600 analyzer by burning at 950 °C in air; samples for this analysis were prepared inertly.

The chemisorbed species in the Co(acac)$_3$-modified samples were qualitatively characterized by DRIFT spectroscopy. Spectra of ground samples were measured at room temperature in nitrogen with a Nicolet Impact 400 D diffuse reflectance spectrometer as described in ref. [9]. To obtain adequate resolution in the range 1700–900 cm^{-1}, which is partially opaque due to SiO$_2$ lattice vibrations, samples were diluted with dried potassium bromide. Reference spectra were measured for undiluted and diluted samples of Co(acac)$_3$, Co(acac)$_2$ and Al(acac)$_3$.

2.3. Hydrogen chemisorption

The hydrogen uptake of the catalysts was measured at 30 °C by static volumetric chemisorption of hydrogen as described in detail elsewhere [25]. The catalysts were reduced and the acac ligands were removed *in situ* in flowing hydrogen at 550 °C over a period of 7 h. The reduction temperature of 550 °C was adopted on the basis of hydrogen chemisorption measurements performed on silica-supported Co(acac)$_3$ samples, where a maximum in the total hydrogen chemisorption capacity was found for reduction at 550 °C [26]. The reduction temperature of 550 °C was not necessarily optimal for the *n*·AlN/SiO$_2$-supported samples. After the hydrogen chemisorption experiments, some samples were transferred through air to carbon and cobalt determinations. For the Co/silica sample, the extent of reduction was measured after the hydrogen chemisorption experiment by oxygen titration. The oxygen consumption was determined at 400 °C by static volumetric measurements using a 20 vol% O_2/He gas mixture. Metallic cobalt was assumed to fully oxidize to Co_3O_4 at these conditions.

2.4. Hydroformylation activity

Ethene hydroformylation activities were measured in gas phase at 0.5 MPa and 175 °C using a 1:2:2:2 molar ratio of $Ar:CO:H_2:C_2H_4$, a total flow rate of 7 l/h and 1 g of catalyst, as described in ref. [17]. Catalysts were packed into the reactor under inert atmosphere to avoid air-contamination of the samples. Before the experiments, the catalysts were reduced *in situ* with hydrogen for 7 h at 550 °C (H_2:Ar molar ratio 1:2, total flow rate 9.9 l/h). The reaction time was 24 h. After the catalytic runs, some samples were transferred through air to carbon and cobalt determinations. The steady-state activity and selectivity were calculated at a time on stream (TOS) of 20–24 h as an average of three successive analyses. In the calculations, conversion (X), selectivity (S) and yield (Y) were based on the amount of ethene consumed.

3. Results

3.1. Characterization of $Co(acac)_3$-modified samples

3.1.1. Elemental analysis

The results of the cobalt and carbon determinations are summarized in table 1. The cobalt content was slightly higher in the top than at the bottom of the support bed, and it decreased with increasing AlN content of the support (in wt%). The acac/Co ratios were between one and two in all cases, closer to one on the SiO_2 support and higher on the n·AlN/SiO_2 supports. The acac ligand ($C_5H_7O_2^-$) contents were calculated per unit surface area of the support, using the surface area of the support (288, 275 and 223 $m^2 g^{-1}$ for SiO_2, 2·AlN/SiO_2 and 6·AlN/SiO_2, respectively [11]) and correcting for the mass of the chemisorbed species (assuming that all carbon was present in acac ligands). The cobalt contents were also calculated per unit surface area. The acac ligand content per nm^2 was similar in all samples and in accord with earlier results for the chemisorption of $Co(acac)_3$ on different silica samples [18].

To determine whether nitrogen was lost from the samples when the AlN/SiO_2 support was brought through air to the ALD reactor, nitrogen content was measured for the 4·AlN/SiO_2 sample (240 $m^2 g^{-1}$ [11]) after the pre-treatment with ammonia. The nitrogen contents before and after the pre-treatment were 4.1 [11] and 3.5 wt% N, respectively. Since the difference between these values corresponds to about 1 $at_N nm^{-2}$, we conclude that nitrogen was lost when the support was brought to the reactor, and the ammonia treatment did not fully regenerate the surface.

3.1.2 DRIFT spectroscopy

DRIFT spectra were recorded to investigate the nature of the surface species generated in the chemisorption of $Co(acac)_3$. Figure 1 shows the DRIFT spectra measured for the $Co(acac)_3$-modified SiO_2 and n·AlN/SiO_2 samples and the reference acac compounds. The C–H stretching region of the spectra was similar to that earlier reported for $Co(acac)_3$-modified silica [18] and is not shown. The spectrum of the $Co(acac)_3$-modified SiO_2 sample showed combined C=C and C=O vibrations centered at 1584 and 1522 cm^{-1}, which are typical for metal acac complexes [18,27–29], whereas the spectra of the $Co(acac)_3$-modified 2·AlN/SiO_2 and 6·AlN/SiO_2 samples showed peaks at 1589 and 1524 cm^{-1} and 1596 and 1529 cm^{-1}, respectively. The reference spectrum of $Co(acac)_3$ exhibited corresponding peaks at 1574 and 1520 cm^{-1}, that of $Co(acac)_2$ at 1589 and 1527 cm^{-1} and that of $Al(acac)_3$ at 1593 and 1534 cm^{-1}. The spectrum of the $Co(acac)_3$-modified SiO_2 sample thus resembled the spectrum of $Co(acac)_2$, the spectrum of $Co(acac)_3$-modified 6·AlN/SiO_2 resembled that of $Al(acac)_3$, and the spectrum of $Co(acac)_3$-modified 2·AlN/SiO_2 had intermediate features.

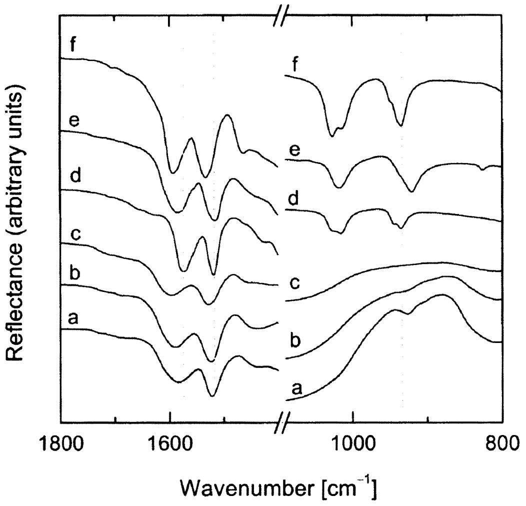

Figure 1. DRIFT spectra of (a) the $Co(acac)_3$-modified SiO_2 sample, (b) the $Co(acac)_3$-modified 2·AlN/SiO_2 sample, (c) the $Co(acac)_3$-modified 6·AlN/SiO_2 sample, (d) $Co(acac)_3$, (e) $Co(acac)_2$ and (f) $Al(acac)_3$. Samples were diluted with KBr. The dotted lines show the peak maxima for $Co(acac)_3$.

Although all the reference spectra presented a peak at 900–950 cm^{-1}, among the sample spectra only the spectrum of the $Co(acac)_3$-modified SiO_2 exhibited this peak (maximum at 926–927 cm^{-1} in accord with ref. [18]) (see figure 1). The peak was effectively absent in

Table 1
Results of elemental analysis for the $Co(acac)_3$-modified samples.

Support	Pretreatment (°C/h)		Co (wt%)		C (wt%)		Acac/Co (mol/mol)		Co (at_{Co} nm^{-2})	Acac ligands (nm^{-2})
	In air	In vacuum	Top	Bottom	Top	Bottom	Top	Bottom		
SiO_2	750/16	550/3	5.0	4.8	6.5	6.7	1.3	1.1	2.1	2.7
2·AlN/SiO_2	–	550/6[a]	5.0	4.6	6.1	6.1	1.3	1.3	2.0	2.6
6·AlN/SiO_2	–	550/6[a]	3.4	2.8	5.6	5.6	1.9	1.9	1.5	2.9

[a] In ammonia 4 h and in nitrogen 2 h.

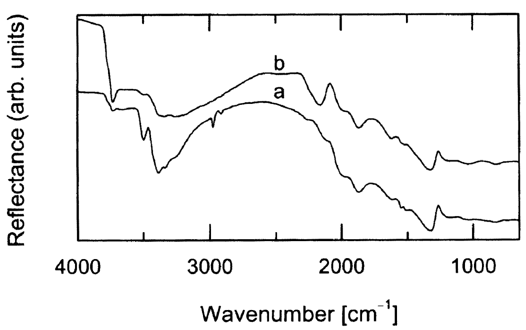

Figure 2. DRIFT spectra of the 4·AlN/SiO$_2$ sample measured (a) after preparation of the sample [11] and (b) after transfer of the sample back to the ALD reactor and treatment with ammonia at 550 °C.

the spectra of the 2·AlN/SiO$_2$ and 6·AlN/SiO$_2$ samples, because the absorbance of the AlN species filled the spectral windows of silica [11].

The DRIFT spectrum of the 4·AlN/SiO$_2$ sample measured after ammonia treatment is shown in figure 2. Compared with the spectrum of a freshly-prepared 4·AlN/SiO$_2$ sample [11] we see that the sharpness of the N–H stretching peaks (3500, 3389 and 3338 cm^{-1}) and N–H bending peaks (1548, 1504 cm^{-1}) of NH$_x$ [8,11] is lost, and some new OH groups absorb at 3734 cm^{-1} [30]. Some exchange of NH$_2$ groups with OH groups probably has taken place, and the ammonia treatment did not fully regenerate the amino surface. This result is in accordance with the nitrogen determinations.

3.2. Hydrogen chemisorption

As a means of estimating the surface area of metallic cobalt, the hydrogen chemisorption capacity of the samples was determined after reduction at 550 °C by measuring the amount of hydrogen adsorbed at 30 °C. The cobalt contents of the samples (3–5 wt% Co) were rather low, and support may have a complicating effect on the results [31]. The results of the hydrogen chemisorption tests are summarized in table 2. The total hydrogen uptake decreased and the fraction of reversible adsorption increased with the AlN content of the support.

When the samples were heated for the hydrogen treatment at 550 °C, a violet condensate (the colour of Co(acac)$_2$) was formed at the reactor outlet. To investigate whether cobalt was lost from the catalyst samples during the reduction, we measured cobalt contents of the Co/SiO$_2$ and Co/6·AlN/SiO$_2$ samples after the chemisorption experiment. The results are shown in table 2. In the case of the Co/SiO$_2$ sample, the cobalt concentration, expressed in wt%, increased during reduction. This increase was as expected and was caused by the decrease in sample mass during reduction as acac ligands were removed. For the Co(acac)$_3$/6·AlN/SiO$_2$ sample, in contrast, the cobalt concentration decreased during reduction. Evidently cobalt was lost from the Co/*n*·AlN/SiO$_2$ samples through vaporization as Co(acac)$_2$.

The dispersion and particle size of cobalt were calculated as described in ref. [25]. The calculation was done with respect to the original cobalt contents of the catalysts with no correction for the degree of reduction. The results are shown in table 2. The calculated particle size increased with increasing extent of AlN modification. No cobalt particles were seen in X-ray diffraction, however. For the Co/SiO$_2$ sample, the extent of reduction after hydrogen chemisorption was measured as 72% by oxygen titration. The dispersion and particle size corrected for the degree of reduction were 24% and 4.0 nm. For the Co/*n*·AlN/SiO$_2$ catalysts, the degree of reduction could not be measured because of the sensitivity of the *n*·AlN/SiO$_2$ supports to air.

3.3. Hydroformylation activity

The activities of the catalysts in ethene hydroformylation with time on stream is shown in figure 3. The main products were ethane, propanal and propanol. In addition, small amounts of condensation products of propanal—2-methyl-2-pentenal and 2-methyl-1-pentanal—were formed. During the first few hours of the run, the Co/*n*·AlN/SiO$_2$ samples deactivated strongly, whereas the Co/SiO$_2$ sample activated slightly. Steady-state conversion, reached after about 5 h for all the catalysts, decreased drastically with increasing AlN

Table 2
Characteristics of the Co/AlN/SiO$_2$ catalysts.

Catalyst	Total H$_2$ uptake at 30 °C (μmol/g$_{cat}$)	Fraction of reversible H$_2$ uptake	Dispersion (%)[a]	Particle size (nm)[a]	Co (wt%)			C (wt%)		
					Before reduction[b]	After reduction	After reaction	Before reduction[b]	After reduction	After reaction
Co/SiO$_2$	71	41%	17	6	4.9	5.4	5.3	6.6	–	5.6
Co/2·AlN/SiO$_2$	16	77%	4	25	4.8	–[c]	4.9	6.1	1.5	10.8
Co/6·AlN/SiO$_2$	8.8	83%	3	29	3.1	2.5	–	5.6	–	–

[a] Calculated from the total H$_2$ uptake and the cobalt contents before reduction without correcting for the extent of reduction.
[b] Average values.
[c] Not determined.

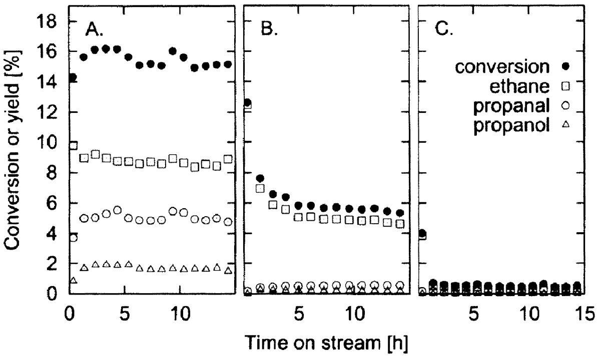

Figure 3. Activity of (A) the Co/SiO$_2$, (B) the Co/2·AlN/SiO$_2$, and (C) the Co/6·AlN/SiO$_2$ catalyst in ethene hydroformylation at 175 °C and 0.5 MPa.

content of the support. Moreover, the hydroformylation selectivity decreased and the hydrogenation selectivity increased with the AlN content of the support.

The cobalt and carbon contents were measured after the hydroformylation run and are shown in table 2. For the Co/2·AlN/SiO$_2$ sample, the cobalt content was about the same as in the fresh catalyst. This indicates minor loss of cobalt, if any, during the run. The carbon contents for the Co/SiO$_2$ and Co/2·AlN/SiO$_2$ catalysts were different: the Co/2·AlN/SiO$_2$ catalyst accumulated carbon during the reaction. The higher carbon content may be related to the initial deactivation of the Co/*n*·AlN/SiO$_2$ catalysts.

4. Discussion

4.1. Chemisorption of Co(acac)$_3$ on *n*·AlN/SiO$_2$

Our present findings for the Co(acac)$_3$ reaction on silica are in line with earlier results [18]: elemental analysis and DRIFT spectroscopy indicate that, after conversion of Co(acac)$_3$ to Co(acac)$_2$ (reaction (1)), mostly ligand exchange (reaction (2)) and some association (reaction (3)) occurred. With increasing AlN content of the support, the probability of reactions where the ratio of acac to Co remains two, as in the parent Co(acac)$_2$ molecule, increased. The reactions are association (3), dissociation (4) and a secondary reaction of Hacac (5). DRIFT indicated that the acac ligands on the SiO$_2$ support were bonded to cobalt, but some acac ligands on the 6·AlN/SiO$_2$ support seemed to be bonded to aluminum. The occurrence of dissociation (4) or secondary reaction of Hacac (5) on the AlN/SiO$_2$ supports thus seems probable. Association (3) through bonding between cobalt and surface nitrogen or oxygen may have occurred as well. Since there appeared to be less ligand exchange reaction with increasing AlN content of the support, it seems that hydrogen atoms in NH$_x$ groups are less prone to ligand exchange reaction than hydrogen atoms in OH groups.

Despite the differences in the bonding mode of the Co(acac)$_y$ species with increasing AlN content of the support, the controlling factor for the saturation of chemisorption remained unchanged. After the chemisorption of Co(acac)$_2$ formed from Co(acac)$_3$, the ligand density settled to the same value, about 2.7 acac nm^{-2}, on the three supports. This value agrees with the acac ligand density obtained in the chemisorption on silica with various OH group contents [18]. Thus, shortage of suitable bonding sites on the surface did not limit the extent of chemisorption of Co(acac)$_2$ on the *n*·AlN/SiO$_2$ supports.

The binding of Co(acac)$_2$ with an acac/Co ratio of almost two on the AlN/SiO$_2$ supports seems to be disadvantageous. When the samples were treated at high temperatures, desorption of Co(acac)$_2$ occurred for Co/*n*·AlN/SiO$_2$ but not for Co/SiO$_2$. Furthermore, the cobalt species remaining in the Co/*n*·AlN/SiO$_2$ samples may have been mobile on the surface during heating of the sample, leading to sintering and decreased dispersion for cobalt.

4.2. Catalytic properties

The total hydrogen chemisorption capacity decreased with increasing AlN content of the support (see table 2). The decreasing trend in the chemisorption capacity is partly related to the lower cobalt contents obtained for the *n*·AlN/SiO$_2$ supports and to the loss of cobalt through vaporization of Co(acac)$_2$ during pretreatment of the sample. However, the decrease in hydrogen chemisorption capacity was more drastic than what could be expected on the basis of the cobalt contents alone. The explanation seems to be the increase in cobalt particle size and the corresponding decrease in dispersion (table 2). Moreover, the fraction of the irreversible chemisorption capacity of the total chemisorption capacity decreased with increasing AlN content of the support, being negligible for the Co/6·AlN/SiO$_2$ sample. Niemelä *et al.* [25] observed very low fractions of irreversible hydrogen uptake for impregnated Co/SiO$_2$ samples when the optimum reduction temperature (300 °C) had been exceeded (500 °C) and particle size had grown drastically. The situation could be similar for our Co/*n*·AlN/SiO$_2$ samples: the reduction temperature of 550 °C was probably too high and allowed the cobalt species to form larger particles. The hydroformylation results are in accord with the hydrogen chemisorption results. The selectivity towards hydrogenation increased with increasing AlN content. Larger particle size and less dispersion typically improve the hydrogenation selectivity [15–17].

The activity of the Co/*n*·AlN/SiO$_2$ catalysts fell off rapidly at the start of the hydroformylation experiment. According to the carbon determinations, deactivation was accompanied by the formation of carbonaceous deposits on the surface. Perhaps some active sites were rapidly covered with carbon at the start of the experiment, causing the deactivation. However, the n·AlN/SiO$_2$ supports might also have accelerated the deactivation by inducing coke formation. How this could have occurred is not revealed by the present results.

5. Conclusions

Co/n·AlN/SiO$_2$ catalysts can be prepared by the saturating chemisorption of Co(acac)$_3$ on n·AlN/SiO$_2$ supports. The reaction mechanism of Co(acac)$_3$ is in general similar on SiO$_2$ and n·AlN/SiO$_2$ supports. However, the tendency for reactions that result in surface species with an acac/Co ratio of two is greater for n·AlN/SiO$_2$ supports than for SiO$_2$. Desorption of Co(acac)$_2$ during further processing of the catalysts becomes a problem, and this can lead to loss of cobalt from the samples and decreased dispersion for the remaining cobalt. Low dispersion was disadvantageous in hydroformylation.

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