ELSEVIER

Catalysis Today 43 (1998) 11–19

CATALYSIS TODAY

A novel Co/SiO$_2$ catalyst for hydrogenation

L.B. Backman[a,*], A. Rautiainen[b], A.O.I. Krause[a], M. Lindblad[b]

[a] *Helsinki University of Technology, Laboratory of Industrial Chemistry, P.O. Box 6100, FIN-02015 HUT, Finland*
[b] *Microchemistry Ltd., P.O. Box 45, FIN-02151 Espoo, Finland*

Abstract

The effect of preparation and calcination on reducibility, dispersion and catalyst activity of Co/SiO$_2$ catalysts was studied. The Co/SiO$_2$ catalysts were prepared by a gas-phase deposition technique, atomic layer epitaxy (ALE), using Co(acac)$_3$ as precursor and by impregnation from Co(NO$_3$)$_2$. The cobalt content of the catalysts varied from 5 to 20 wt.%. The cobalt loading of the ALE catalysts was increased by repeating Co(acac)$_3$ and air reaction sequences. Air calcination of ALE catalysts ('calcined' catalysts) produced cobalt species at least partly in the form of silicates that were hard to reduce. The reducibility was enhanced when the calcination step after the last Co(acac)$_3$ reaction step was omitted ('uncalcined' catalysts). This could be explained by a more easily reducible layer on the surface of the catalysts containing ligand residues from the precursor. High reduction temperatures were still needed compared to the impregnated catalysts. However, the cobalt dispersion on the uncalcined ALE catalysts was in the same range as on the calcined catalysts and clearly higher than on the impregnated catalysts. The uncalcined ALE catalysts showed significantly improved activities in toluene hydrogenation compared to the calcined ALE and the impregnated catalyst. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Cobalt catalysts have been extensively used for hydrogen transfer reactions. The most common application is the Fischer–Tropsch reaction, in which cobalt based catalysts are used in industrial scale [1,2]. The wide applicability of supported cobalt catalysts makes it important to understand the interaction between catalytically active cobalt species and the support. In the Fischer–Tropsch reaction, as generally in hydrogenation reactions, the active phase is metallic cobalt. The metal surface areas can be increased by dispersing the cobalt precursor on high surface area supports. For the supported catalysts the strength of interaction between cobalt and the support surface (metal-support interaction) has a significant influence on the reduction behaviour. The reducibility of the cobalt catalysts has been shown to be affected by the support [3–7], the precursor [8,9], the preparation method [6,10], the metal loading [4–7], the treatments [8,11–13], and the ions added (modifiers) [14–19].

The degree of reduction of cobalt is generally higher on SiO$_2$ than on Al$_2$O$_3$, especially at low cobalt concentrations [5,7]. Cobalt is known to form aluminates by migrating into the lattice sites of alumina [3]. The species formed are resistant to reduction. Silica is considered to be more inert than alumina [20,21]. However, the formation of cobalt silicates or hydrosilicates has recently been reported [12,22,23]. The formation of silicates on Co/SiO$_2$ catalyst has been shown to increase with increasing surface area of the support [22]. Silicates decrease the reducibility of the

---

*Corresponding author. Tel.: +358 9 451 2627; fax: +358 9 451 2622; e-mail: backman@polte.hut.fi

0920-5861/98/$32.00 © 1998 Elsevier Science B.V. All rights reserved.
PII S0920-5861(98)00132-1

catalyst thus lowering the surface area of the active metallic phase.

The choice of the precursor also influences the reducibility properties strongly. Supported cobalt catalysts prepared from different cobalt salts but otherwise treated similarly (e.g. calcination) exhibited considerable differences in the degree of reduction [8]. A calcined $CoCl_2$ based catalyst reduced fully while a corresponding $Co(NO_3)_2$ based catalyst reduced only to an extent of 73%. Catalysts prepared from Co-acetate have been shown to be extremely difficult to reduce [8,24].

Direct reduction of supported cobalt precursors in hydrogen using low heating rates has been found to improve the dispersion [6,11]. However, reduction without calcination has also been found to result in decreased reducibility [8]. The reduction of nitrate based catalysts was more difficult due to CoO_x–SiO_2 surface species formed in the reductive decomposition of $Co(NO_3)_2$. The calcination temperature has been found to affect the dispersion and the degree of reduction [3,13]. Cobalt dispersion decreased with increasing calcination temperature. Vacuum treatment at 200–400°C prior to calcination or reduction has been found to increase cobalt dispersion [12,13].

The reduction behaviour of cobalt catalysts is also affected by loading. In general, the reducibility of cobalt catalysts increases with increasing metal loading [4,5,7]. Addition of modifiers (e.g. La, Pt, Th, Zr) has been used to increase the reducibility of Co/SiO_2 catalysts [14,16,25]. A hydrogen spillover effect has been proposed as a possible explanation for the improvement. However, the mechanism for the increased reducibility is not yet fully understood. Modifiers (Mg, Th) have also been found to decrease the reducibility, probably due to the formation of a solid solution between CoO and MgO or ThO_2 [19].

Smeds et al. [26] have reported higher Ni dispersion on the gas phase deposited Ni/Al_2O_3 catalyst than on a commercial Ni catalyst. This was explained to be caused by the catalyst preparation method, atomic layer epitaxy (ALE) [27], giving an optimal dispersion of Ni. Backman et al. [28,29] have shown that cobalt dispersion in ALE-prepared Co/SiO_2 catalysts is also high. However, this high dispersion of cobalt on silica was shown to lead to decreased reducibility of the catalysts. Hence, a low activity in toluene hydrogenation was observed. In this paper, the reducibility and the effect of different treatments thereon of the impregnated and ALE-prepared Co/SiO_2 catalysts were studied.

2. Experimental

2.1. Preparation of Co/SiO_2 catalysts via the gas phase

The support used for all catalysts was Grace 432 silica with a particle size of 0.5–1.0 mm, surface area of 320 m^2/g and a pore volume of 1.2 cm^3/g. The purity of the support has been reported earlier [30]. The Co/SiO_2 catalysts were prepared via the gas phase using ALE technique [28]. The precursor used for the depositions was cobalt(III)acetylacetonate, $Co(acac)_3$ (Merck, >98%). The catalyst preparation by ALE consisted of the following separate steps: (a) preheating of the support, (b) chemisorption of the gaseous cobalt precursor up to surface saturation, and (c) removal of the remaining ligands by calcination in synthetic air. To increase the cobalt content of the catalysts several ALE cycles were repeated by alternating the steps (b) and (c), Fig. 1.

The silica support was first preheated in air in a muffle furnace for 16 h at 600°C, and further inside the ALE reactor at 450°C for 3 hours under a nitrogen (AGA) atmosphere at a reduced pressure (6–10 kPa). $Co(acac)_3$ was evaporated at 180°C and was passed through the silica bed at 180°C with nitrogen carrier gas. A nitrogen purge at the same temperature followed the reaction. The acac-ligands were removed with synthetic air (AGA) at 450°C for 4 h. To increase the cobalt concentration, the $Co(acac)_3$, N_2, synthetic air, N_2 phases (ALE cycles) were repeated up to five

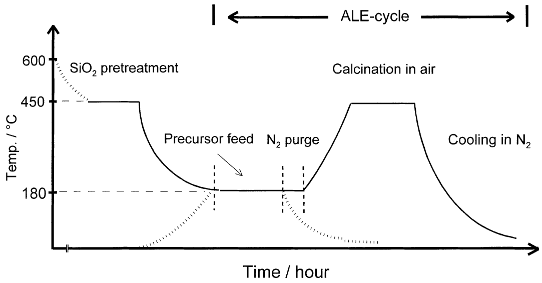

Fig. 1. Preparation of the catalysts using ALE cycles.

times. Two sets of Co/SiO$_2$ catalysts were prepared: so-called ‘calcined’ and ‘uncalcined’ catalysts. The ‘calcined’ catalysts were prepared using a calcination step after each precursor deposition step. When preparing the ‘uncalcined’ catalysts the very last calcination step was omitted and the acac-ligand residues were still present on the surface.

2.2. *Preparation of Co/SiO$_2$ catalysts via impregnation*

Reference Co/SiO$_2$ samples were prepared by impregnation using Co(NO$_3$)$_2$ as precursor [31]. The support (Grace 432 silica) was pretreated with a volumetric 1:1 ethanol–water solution to equalise the OH group distribution and dried (120°C/16 h, in air and 200°C/2 h, 1–4 mbar). The precursor, Co(NO$_3$)$_2$·6 H$_2$O (Merck, p.a.), was dissolved in the pore volume amount of deionised water and added to the support. The catalyst was then dried (65°C/2 h, 1–4 mbar) and calcined in synthetic air (AGA) at 300°C for 12 h.

2.3. *Characterisation of the catalysts*

The cobalt concentration of the catalysts was determined with instrumental neutron activation analysis (INAA, 250 kW Triga Mk II research reactor at VTT Chemical Technology) or atomic absorption spectrometry (AAS, Varian SpectrAA-600). Samples for AAS measurements were prepared by dissolving the catalysts in a mixture of hydrochloric, nitric and hydrofluoric acid. Carbon was determined using a LECO CR 12 carbon analyser. The interaction of Co(acac)$_x$ species with silica (ALE samples) was studied using diffuse reflectance IR Fourier transform spectroscopy (DRIFTS). The spectra were recorded at the wave number range of 4000 to 600 cm^{-1} with a spectral resolution of 2 cm^{-1}. The details of the study are presented in Ref. [28].

Static volumetric hydrogen chemisorption was performed with a Coulter OMNISORP 100CX on catalysts reduced in situ in flowing hydrogen at 200–600°C for 7 h. The samples were purged with helium at 150°C for 30 min. Thereafter, the temperature was elevated to the reduction temperature in vacuum and the reduction was performed. The samples were outgassed for 40 min at the reduction temperature before allowing them to cool down to the chemisorption temperature (30°C). The procedure is described in detail in Ref. [31]. The estimate for the average particle size was calculated assuming spherical geometry of the cobalt particles. These calculations were based on the total hydrogen uptakes [6,15]. The values obtained for dispersion and particle size were corrected for the degree of reduction.

The degree of reduction of calcined ALE catalysts was estimated using X-ray photoelectron spectroscopy (XPS) [29]. The samples were reduced and transferred under inert atmosphere to the XPS measurement chamber. For uncalcined ALE catalysts and impregnated catalysts oxygen titration was used. Determinations were made by performing static volumetric chemisorption measurements at 400°C using a 20 vol% O$_2$/He gas mixture. Metallic cobalt was assumed to fully oxidise to Co$_3$O$_4$ at these conditions.

Temperature programmed reduction (TPR) measurements were performed with an Altamira Instruments AMI-100 catalyst characterisation system. The catalyst samples (50 mg) were flushed with argon at 150°C for 30 min and cooled down to 30°C. After that the samples were heated from 30 to 880°C at a rate of 10°C/min while flowing a 10 vol% H$_2$/Ar mixture (30 cm^3/min) through the sample. The consumption of hydrogen was monitored by a thermal conductivity detector (TCD). In some of the measurements the gas stream was also analysed at the outlet by a Balzers MSC-200 Thermocube mass spectrometer (MS).

The transmission electron microscopy (TEM) micrographs were obtained with a JEOL JEM-1200EX II apparatus operated at an accelerating voltage of 100 keV. The samples were finely ground using an agate mortar, and were collected on a carbonised copper-grid. Two sets of every sample were ground separately. The samples were studied visually by different magnifications to confirm the homogeneity of the samples. The actual micrographs were obtained using a magnification of 100 000 times. The lower limit for measuring crystallite diameters with this apparatus was about 2 nm.

A number of the catalysts were tested for toluene hydrogenation in a tubular reactor. The activity runs were made at atmospheric pressure with a total molar flow of 0.8 mol/h and a molar ratio of hydrogen to toluene of 7 to 1. The reaction temperature was 170°C. The amount of catalyst used was 50–500 mg. The impregnated catalysts were reduced in situ at 300°C for 7 h and the gas phase deposited catalysts were reduced at 550°C for 7 h in flowing hydrogen.

3. Results

The cobalt concentration on the SiO_2-supported catalysts varied from 5 to 20 wt.%, see Table 1. The metal content obtained after one ALE cycle was about 5 wt.% Co. By using additional cycles the cobalt concentration increased almost linearly at a rate of approx. 3.5 wt.% per cycle. The impregnated catalysts were prepared using the desired amount of cobalt precursor in one impregnation step.

The hydrogen uptake on the 4.6 wt.% nitrate based reference catalyst was measured as a function of the reduction temperature (Fig. 2) [31–33]. A maximum uptake (0.43 cm^3/g_{cat}) was obtained after reduction at 300°C for 7 h. The use of reduction temperatures in excess of 400°C significantly decreased the hydrogen uptake. The uptake per gram of catalyst increased with increasing cobalt content while the uptake per gram of cobalt remained almost constant (Fig. 3).

The effect of the reduction temperature on the hydrogen uptake on the calcined ALE catalysts was tested by reducing the catalysts at 500, 550 and 600°C for 7 h. At lower reduction temperatures the hydrogen uptake was negligible [29]. A maximum uptake was obtained after reduction at 550°C for all cobalt loadings. On the 5.9 wt.% Co sample the maximum uptake was 0.20 cm^3/g_{cat} (Fig. 2). The hydrogen uptake increased slightly with increasing cobalt concentration. The amount per gram of cobalt decreased with increasing metal loading (Fig. 3). The hydrogen uptake increased significantly on the uncalcined ALE catalysts (last calcination step omitted) compared to the calcined ones. The maximum hydrogen uptake was obtained by reduction at 550°C when cobalt concentrations were below 10 wt.% (Fig. 2). The optimum reduction temperature was found to be 500°C at cobalt concentrations over 10 wt.%. Nevertheless, the uptakes shown in Fig. 3 are for catalysts reduced at 550°C in order to be comparable with the uptakes obtained for the calcined catalysts. The high loading catalysts suffered from this high reduction temperature. Hence, the hydrogen uptake per gram of

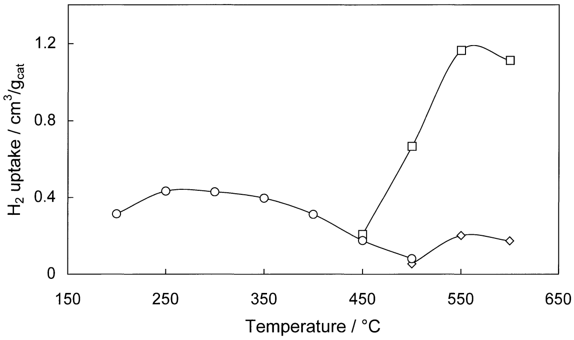

Fig. 2. Hydrogen chemisorption as a function of reduction temperature (○ impregnated; ◇ ALE calcined; □ ALE uncalcined, all samples containing around 5 wt.% Co).

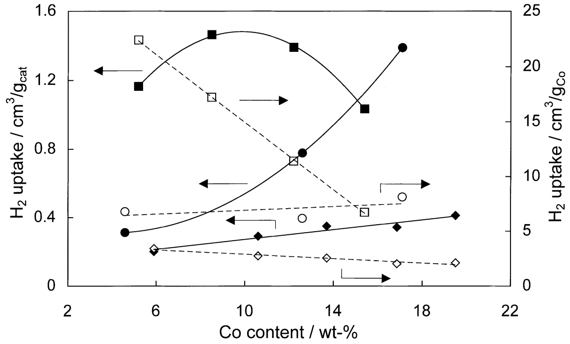

Fig. 3. Hydrogen chemisorption as a function of metal concentration, impregnated catalysts reduced at 400°C and ALE catalysts reduced at 550°C. Open symbols represent hydrogen uptake per gram of Co and filled symbols uptake per gram of catalyst (○ impregnated; ◇ ALE calcined; □ ALE uncalcined).

Table 1
Cobalt and carbon concentrations of the catalysts prepared

Catalyst	Co/wt.%	C/wt.%	Notice
1	4.6	n.d.	Impregnated
2	13	n.d.	Impregnated
3	17	n.d.	Impregnated
4; 4′	5.9; 5.7	<0.1; <0.1	ALE, calcined
5	11	<0.1	ALE, calcined
6; 6′	14; 13	<0.1; <0.1	ALE, calcined
7	17	<0.1	ALE, calcined
8; 8′	20; 19	<0.1; <0.1	ALE, calcined
9; 9′	5.2; 5.0	7.5; 7.0	ALE, uncalcined
10; 10′	8.5; 8.4	6.4; 6.2	ALE, uncalcined
11	12	6.6	ALE, uncalcined
12; 12′	15; 16	6.4; 6.5	ALE, uncalcined
13	17	5.5	ALE, uncalcined

n.d. = not determined.

Table 2
Degree of reduction (f), dispersion (D) and crystallite size (d) on Co/SiO_2. Dispersion and crystallite sizes were corrected for the degree of reduction. The reduction temperature for impregnated catalysts (1–2) was 400°C, and for ALE catalysts (4–12) 550°C. Catalysts labelling, see Table 1.

Catalyst	*f* (%)	*D* (%)	*d* (nm)
1	84	4.2	23
2	87	3.7	26
4	4	24	4.1
6	23	3.5	27
8	28	3.4	28
9	52	23	4.2
10	63	14	6.7
11	54	11	8.7
12	63	5.6	17

catalyst reached a maximum at about 10 wt.% (Fig. 3).

Dispersions and crystallite sizes calculated from the hydrogen chemisorption measurements corrected for the degree of reduction are shown in Table 2. The degree of reduction of the impregnated and uncalcined catalysts was measured by oxygen titration. The reducibility of the calcined catalysts was estimated by XPS. The reducibility of the impregnated catalysts (85–90%) was high compared to that of the ALE catalysts (calcined: max 30%, uncalcined: 50–60%). The difference in reducibility between calcined and uncalcined catalysts was most profound for the samples with the lowest cobalt content (4% and 52%, respectively). The dispersion and crystallite size of impregnated catalysts were near 4% and 25 nm, respectively. For the ALE catalysts the dispersion decreased and the crystallite size increased with cobalt loading. At the lowest cobalt loading the dispersion and the crystallite size were the same (24% and 4 nm, respectively) for both calcined and uncalcined catalysts. The dispersion on the uncalcined samples was higher than on the calcined samples at increasing cobalt loading.

TPR measurements clearly showed the differences in reducibility of the Co/SiO_2 catalysts (Fig. 4). The impregnated catalyst showed hydrogen consumption at two temperatures, 300°C and 350°C. The calcined ALE catalysts consumed hydrogen mainly above 700°C. A very small peak was recorded at 330°C for the 20 wt.% Co sample. Three broad hydrogen consumption peaks were measured around 400°C, 600°C and 750°C for the uncalcined ALE catalysts. At the first two peaks the ligand residues were removed from the surface. Analysis of the outlet gas with a mass spectrometer showed evolution of acetone at 350–400°C and mainly methane and other light hydrocarbons above 500°C. Water was formed mainly at the first and third hydrogen consumption peaks (Fig. 5). The relative size of the high temperature peak increased with cobalt loading.

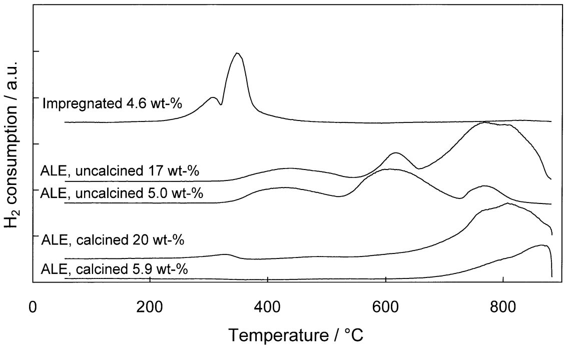

Fig. 4. TPR spectra of impregnated, calcined ALE and uncalcined ALE Co/SiO_2 catalysts.

The TEM micrographs showed round shaped cobalt particles of about 10 nm in size on both calcined and uncalcined catalysts for all metal loadings. Although, the crystallite size distribution was more even on the uncalcined samples. The micrographs of the calcined catalyst with more than 15 wt.% Co showed some larger agglomerates [32].

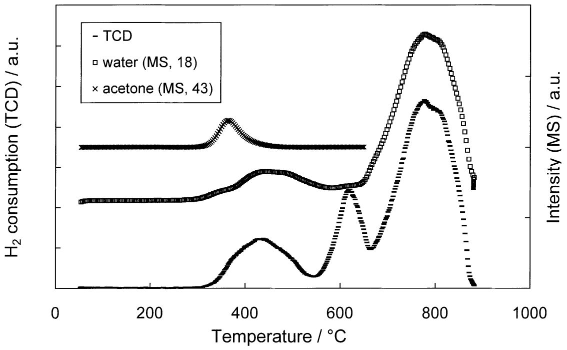

Fig. 5. TPR spectra of an uncalcined ALE catalyst (17 wt.% Co), analysed with TCD and MS (mass number 18 for water and 43 for acetone).

Table 3
Toluene hydrogenation activity of the Co/SiO_2 catalysts. Catalyst labelling, see Table 1

Catalyst	Co(wt.%)	T_{red}(°C)	Reaction rate[a]/10^{-5} mol/g s	TOF/s^{-1}
1	4.6	300	0.86	0.22
4′	5.7	550	0.30	0.33
6′	13	550	0.36	0.20
8′	19	550	0.73	0.24
9′	5.0	550	5.5	0.61
10′	8.4	550	6.4	0.49
12′	16	550	5.6	0.60

[a] Reaction conditions: 170°C, total molar flow 0.8 mol/h, H_2/toluene =7/1.

The catalysts were tested in gas-phase hydrogenation of toluene. The reaction rates are given in Table 3. With Co-nitrate based catalysts the activity reached a maximum with reduction at 300°C while reduction at 500°C resulted in almost inactive catalysts, probably due to sintering [31]. Reduction at 400°C was not sufficient to reduce the calcined ALE catalysts while reduction at 500°C gave slightly active catalysts. The activity of the uncalcined catalysts reduced at 550°C was significantly higher than that of the calcined ones. The observed activity was in line with the hydrogen uptakes (Fig. 2). However, the turnover frequency (TOF) per exposed Co atom calculated using the hydrogen uptake data was not equal for all samples. The TOFs for the uncalcined ALE catalysts were about two to three times higher compared to the other catalysts (Table 3).

4. Discussion

The chemisorption of hydrogen indicated significant differences in the dispersions and degrees of reduction on the catalysts studied. The hydrogen uptake on the impregnated catalyst (4.6 wt.%) reached a maximum after reduction at 300°C (Fig. 2). The same trend was also indicated for higher cobalt concentrations. Reduction at 450°C or higher probably induced agglomeration [12,31,34], resulting in a severe decrease in hydrogen chemisorption capacity (Fig. 2). The calcined ALE catalysts behaved in a remarkably different way. The maximum uptake was reached after reduction at 550°C (Fig. 2). Although the uptakes increased with increasing cobalt concentration (Fig. 3), they remained low compared to the impregnated catalysts, indicating either a low dispersion or a very low reducibility [29]. The latter seemed more probable considering the high reduction temperatures required. In fact, XRD detected very small crystallites even on the samples with 20 wt.% Co [29].

The chemisorption of hydrogen on supported Co catalysts is considered to be an activated process [6,29,31]. However, the values reported here are based on measurements obtained at 30°C. Hydrogen chemisorption performed at higher temperatures (100°C and 200°C) showed an increase in uptake by a factor of 1.1 for the nitrate based catalysts [31] and by a factor of around 1.3 for the calcined ALE catalysts [29]. The activation factors are relatively small compared to the differences in uptakes of the studied catalysts. Therefore, the uptakes measured at 30°C can be considered to give a good basis for comparing the amounts of exposed Co atoms on the samples.

When the calcination after the last deposition step was omitted (uncalcined catalysts) the uptakes reached a maximum after reduction at 500–550°C depending on cobalt loading. For the 5 wt.% Co catalyst the hydrogen chemisorption capacity increased up to six times (Fig. 2). The increase at higher cobalt concentrations was less profound but still significant. The maximum uptake for both calcined and uncalcined catalysts (ALE) was reached at a remarkably high reduction temperature compared to the impregnated ones. The high reduction temperatures required were possibly due to high dispersion leading to strong interaction between the cobalt species and the support.

TEM measurements showed that the cobalt particle size was in the same range on the calcined and uncalcined catalysts. This ruled out the possibility that the increase in the total hydrogen uptake was only due to differences in cobalt particle size. The explanation for the improvement was in the different degrees of reduction of these catalysts. The degree of reduction of the calcined catalysts reduced at 550°C was estimated by XPS, and was found to be less than 30% for all catalysts [29]. Oxygen titrations showed that the degree of reduction of the uncalcined catalysts after reduction at 550°C was between 50% and 60% independent of the cobalt loading (Table 2). For comparison, the degrees of reduction of the impregnated catalysts (400°C/7 h) were 85–90% (Table 2). These are typical values reported in the literature for impregnated Co/SiO_2 catalysts [6,12,15,31].

The TPR measurement of an impregnated catalyst (4.6 wt.% Co) showed a two-step reduction profile. The first peak at 300°C was about one third of the second peak observed at 350°C. This two-stage pattern has been explained in the literature as the reduction of Co_3O_4 via CoO to Co [21,35,36]. It could also be explained by a bimodal distribution of Co_3O_4 particles. Okamoto et al. [9] proposed that the TPR peak temperature increases with increasing particle size because of diffusional limitations. This would, in our opinion, lead to broadening of the peaks resulting in a decrease in resolution. In addition, the reducibility has been found to increase with particle size because of decreased interaction with the support [4,6,37]. In the TPR spectrum there was no hydrogen consumption above 500°C, thus indicating that the formation of silicates was negligible [14] or the species were in a non-reducible (880°C) state. The TPR measurements showed that after calcination the major part of the cobalt was present as Co_3O_4.

During the TPR measurements of the calcined ALE catalysts reduction started to occur at 700°C and increased as the temperature was raised (Fig. 4). This behaviour can be explained by the presence of cobalt silicates or hydrosilicates [9,22,23,36]. With a high cobalt loading catalyst (20 wt.%) a small amount of hydrogen was consumed at 330°C, showing that some Co_3O_4 had probably been formed.

The uncalcined ALE catalysts produced some acetone at 350–400°C (Fig. 5) and methane at higher temperatures during the TPR runs, indicating the presence of acetylacetonate-ligands on the cobalt species [38]. The presence of acac-ligands on the surface was shown by the DRIFTS study [28]. The intensity of the stretching vibration of the silica hydroxyl group decreased compared to pure silica. This indicated an exchange reaction between SiO_2 OH-groups and the acac-ligands of the precursor. After the calcination step the intensity of ν(Si-OH) increased, and the spectra resembled that of a naked support. The traces of the vibrations of cobalt hydroxide, oxide and silicate were seen as the number of ALE cycles increased. Considering the DRIFTS measurements and the C to Co ratio of the uncalcined samples the $Co(acac)_3$ precursor has been proposed to lose one acac-ligand and attach to the silica as Si–O–$Co(acac)_2$ [28]. The calcination of this group could easily form CoO_x–SiO_2 species (calcined catalyst) [29]. The effect of calcination has been shown to be of great importance in determining the reducibility [8]. Direct reduction (400°C/16 h) without calcination of a 6 wt.% Co/SiO_2 catalyst prepared from nitrate gave 9% reduction. Calcination increased the degree of reduction to 73%. An increase in reducibility was also observed for chloride and acetate based catalysts after calcination. Rosynek and Polansky [8] proposed that the decrease in reducibility for the nitrate based catalyst was due to reductive decomposition of the nitrate salt forming CoO_x–SiO_2 surface species that were difficult to reduce. Direct reduction using low heating rates has been found to increase the dispersion [11]. The effect on the reducibility was not described. In our case (calcined vs. uncalcined catalysts) the reducibility was improved by using direct reduction thus avoiding the extensive silicate formation during calcination. With the uncalcined 6 wt.% Co ALE sample the direct reduction gave some species that reduced at 750°C, indicating formation of some CoO_x–SiO_2 species. The relative amount of species reducing over 700°C on the uncalcined catalysts increased with increasing cobalt loading (Fig. 4). This is mainly due to calcination between the preparation steps. The samples were stored under air prior to the measurements and were possibly partially oxidised. Some of the water released during the TPR runs at 400–550°C was probably due to this. The rest originated from the oxygen in the precursor. The water formed above 700°C was due to the reduction of silicates (Fig. 5).

The well-defined Co_3O_4 phase formed during calcination of the nitrate based samples reduced easily, as shown by the high degree of reduction (Table 2). The highly dispersed CoO_x–SiO_2 species (silicates) on the calcined ALE catalysts were more difficult to reduce. The degree of reduction was significantly higher on the uncalcined ALE catalysts. The difference was most profound for low cobalt loading (Table 2). The difference in reducibility between the calcined and uncalcined catalysts could be due to easily reducible cobalt species on top of the silicate layer. The increase in reducibility of the silicates could be induced by hydrogen spillover from the reduced cobalt phase [22]. From the TPR profiles it can be seen that the high temperature reduction peaks slightly shifted towards lower temperatures on the uncalcined samples. Also from the increase in degree of reduction it can be seen that the reducible species enhances the reducibility of previous layers (Table 2). The degree of reduction of the one-cycle sample was only 4% while the uncalcined two-cycle catalyst reduced to an extent of 63%. A comparison of the increase in cobalt content with the increase in metallic cobalt shows that 39% of the first cycle had reduced on the two-cycle sample compared to only 4% on the calcined one-cycle sample.

Dispersions obtained by hydrogen chemisorption corrected for the degree of reduction were approximately the same for calcined and uncalcined ALE catalysts at low cobalt loading. With increasing cobalt loading the dispersions were higher on the uncalcined samples. However, the degree of reduction of the calcined samples was determined by XPS while for uncalcined catalysts it was determined by oxygen titration. This might distort the calculated dispersion values. The dispersion of the nitrate based samples was low in comparison to the uncalcined ALE catalysts (Table 2). High reduction temperatures induced agglomeration on the easily reducible impregnated catalysts, decreasing the dispersion. The thermal stability of the ALE catalysts improved due to a silicate layer under the reduced species, and the dispersions remained high even at high temperatures.

The ALE catalysts were prepared by using the reaction cycles. In contrast, the impregnated catalysts were made using enough precursor to achieve the desired amount of cobalt on the catalyst in one step. The repeated calcination between the deposition steps could have affected the ALE catalyst. Already after the first preparation cycle the calcined ALE catalysts were not reducible while the impregnated 5 wt.% catalyst reduced to 84%. The calcination temperature for the ALE catalysts was 450°C as compared to 300°C for the impregnated ones. However, the effect of the calcination temperature was earlier found to be moderate on the impregnated catalysts [31], where, e.g. the hydrogen uptake on catalysts calcined at 500°C decreased the hydrogen uptake by less than 30%.

Despite high dispersion the hydrogenation activity of the calcined ALE catalysts remained low for all cobalt loadings due to low reducibility [29]. The activity of the uncalcined catalysts was approx. 10 times higher than that of the calcined ones. The well-dispersed and reduced cobalt gave a high metal surface area available for the reaction. The activity of the uncalcined catalysts was about six times higher than that of the impregnated catalysts. The degree of reduction of the impregnated catalyst was higher than that of the uncalcined catalyst but the low dispersion resulted in a moderate cobalt surface area. The turnover frequencies per surface Co atom (TOF) for the calcined ALE catalysts and the nitrate based catalyst were roughly the same. The TOFs for the uncalcined ALE catalyst were about two to three times higher compared to the calcined catalysts (Table 3).

5. Conclusions

Novel catalysts were prepared with the ALE technique using $Co(acac)_3$ as precursor. The chemisorption of the precursor at OH sites on silica followed by calcination forms silicate type CoO_x–SiO_2 species that are hard to reduce. More silicates form during the calcination on the well-dispersed catalysts prepared from $Co(acac)_3$ than on the nitrate based impregnated catalysts. The relatively low dispersion on the impregnated catalysts is probably responsible for keeping the silicate formation at a low level. Well-dispersed reducible Co/SiO_2 catalysts were obtained by omitting the last calcination step during the preparation of the catalysts. A layer of reducible cobalt species is thus left on the surface of the catalyst. The presence of a more easily reducible cobalt species enhances the reduction of the silicate species, probably due to a hydrogen spillover effect. The catalysts are thermally stable, i.e. the catalysts do not sinter significantly at 550°C. The silicate species at the silica surface probably decrease the sintering of cobalt. The reduced well-dispersed cobalt on the uncalcined catalysts has a high metal surface area compared to that on the calcined ones. The toluene hydrogenation activity is therefore increased significantly. The high thermal stability of the catalysts could possibly result in catalysts with long lifetimes.

Acknowledgements

The Academy of Finland is acknowledged for the financial support. The authors thank Petri Laiho for

ALE processing of the Co/SiO_2 catalysts, Neste Oy, Analytical Research for TEM and carbon analyses and the Technical Research Centre of Finland (VTT) and the Centre for Chemical Analysis of the Helsinki University of Technology for the cobalt determinations.

References

[1] J.H. Gregor, Catal. Lett. 7 (1990) 317.
[2] A. Chauvel, B. Delmon, W.F. Hölderich, Appl. Catal. A 115 (1994) 173.
[3] R. Chin, D.M. Hercules, J. Phys. Chem. 86 (1982) 360.
[4] J.-G. Choi, Catal. Lett. 35 (1995) 291.
[5] R.C. Reuel, C.H. Bartholomew, J. Catal. 85 (1984) 78.
[6] R.C. Reuel, C.H. Bartholomew, J. Catal. 85 (1984) 63.
[7] C.H. Bartholomew, R.C. Reuel, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 56.
[8] M.P. Rosynek, C.A. Polansky, Appl. Catal. 73 (1991) 97.
[9] Y. Okamoto, K. Nagata, T. Adachi, T. Imanaka, K. Inamura, T. Takyu, J. Phys. Chem. 95 (1991) 310.
[10] R. Srinivasan, R.J. De Angelis, P.J. Reucroft, A.G. Dhere, J. Bentley, J. Catal. 116 (1989) 144.
[11] E. Iglesia, Appl. Catal. A 161 (1997) 59.
[12] K.E. Coulter, A.G. Sault, J. Catal. 154 (1995) 56.
[13] S.-W. Ho, M. Houalla, D.M. Hercules, J. Phys. Chem. 94 (1990) 6396.
[14] S. Ali, B. Chen, J.G. Goodwin Jr., J. Catal. 157 (1995) 35.
[15] G.J. Haddad, J.G. Goodwin Jr., J. Catal. 157 (1995) 25.
[16] D. Schanke, S. Vada, E.A. Blekkan, A.M. Hilmen, A. Hoff, A. Holmen, J. Catal. 156 (1995) 85.
[17] B. Moraweck, R. Fréty, G. Pecchi, M. Morales, P. Reyes, Catal. Lett. 43 (1997) 85.
[18] B. Viswanathan, R. Gopalakrishnan, J. Catal. 99 (1986) 342.
[19] B.A. Sexton, A.E. Hughes, T.W. Turney, J. Catal. 97 (1986) 390.
[20] D.G. Castner, D.S. Santilli, ACS Symp. Ser. 248 (1984) 39.
[21] A. Lapidus, A. Krylova, V. Kazanskii, V. Borovkov, A. Zaitsev, J. Rathousky, A. Zukal, M. Jancálková, Appl. Catal. 73 (1991) 65.
[22] I. Puskas, T.H. Fleisch, J.B. Hall, B.L. Meyers, R.T. Roginski, J. Catal. 134 (1992) 615.
[23] A. Kogelbauer, J.C. Weber, J.C. Goodwin Jr., Catal. Lett. 34 (1995) 259.
[24] T. Matsuzaki, K. Takeuchi, T. Hanaoka, H. Arakawa, Y. Sugi, Appl. Catal. A 105 (1993) 159.
[25] G.J. Haddad, B. Chen, J.G. Goodwin Jr., J. Catal. 160 (1996) 43.
[26] S. Smeds, T. Salmi, L.P. Lindfors, O. Krause, Appl. Catal. A 144 (1996) 177.
[27] M. Lindblad, L.P. Lindfors, T. Suntola, Catal. Lett. 27 (1994) 323.
[28] A. Rautiainen, M. Lindblad, L. Backman, in preparation.
[29] L.B. Backman, A. Rautiainen, M. Lindblad, A.O.I. Krause, in preparation.
[30] M.K. Niemelä, A.O.I. Krause, T. Vaara, J. Lahtinen, Top. Catal. 2 (1995) 45.
[31] M.K. Niemelä, L. Backman, A.O.I. Krause, T. Vaara, Appl. Catal. A 156 (1997) 319.
[32] L.B. Backman, A. Rautiainen, M. Lindblad, A.O.I. Krause, E.-L. Lakomaa, 11th Int. Congr. on Catalysis, 30 June–5 July 1996, Baltimore MD, USA.
[33] L.B. Backman, A. Rautiainen, A.O.I. Krause, M. Lindblad, 15th North American Catalysis Society Meeting, 18–23 May 1997, Chicago IL, USA.
[34] L. Fu, C.A. Bartholomew, J. Catal. 92 (1985) 376.
[35] E. van Steen, G.S. Sewell, R.A. Makhothe, C. Micklethwaite, H. Manstein, M. de Lange, C.T. O'Connor, J. Catal. 162 (1996) 220.
[36] H. Ming, B.G. Baker, Appl. Catal. A 123 (1995) 23.
[37] A.Yu. Khodakov, J. Lynch, D. Bazin, B. Rebours, N. Zanier, B. Moisson, P. Chaumette, J. Catal. 168 (1997) 16.
[38] J. von Hoene, R.G. Charles, W.H. Hickam, J. Phys. Chem. 62 (1958) 1098.