Ethene hydroformylation on Co/SiO_2 catalysts

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The results from ethene hydroformylation at 173 °C showed that a $Co(acac)_3/SiO_2$ catalyst prepared from $Co(acac)_3$ precursor by gas-phase deposition was three times as active as a catalyst prepared by impregnation from cobalt nitrate, but oxo-selectivities were similar. The high propanal selectivities on the $Co(acac)_3/SiO_2$ seem to be related to the presence of highly dispersed active sites favouring CO insertion. As dispersion is decreased from 23 to 8% due to increasing metal content (from 5 to 16 wt%), oxo-selectivity decreased from 39 to 25%. The activity of $Co(acac)_3/SiO_2$ remained unchanged during 68 h on stream. The gas-phase deposition technique described here is a promising method for the preparation of active, selective and stable heterogeneous hydroformylation catalysts.

Keywords: ethene hydroformylation, heterogeneous catalysts, cobalt catalysts, gas-phase deposition, dispersion, stability

1. Introduction

Hydroformylation processes for the production of aldehydes from olefins, carbon monoxide and hydrogen are important steps in the manufacture of many oxygen-containing intermediates [1]. The majority of these oxo-products are manufactured employing unmodified cobalt catalysts, but phosphine-modified Rh catalysts find application particularly in the hydroformylation of propene [1]. The drawback of these homogeneous rhodium-based processes is the need for the recovery of rhodium at ppm level to ensure economical operation, due to the high cost of rhodium [2].

The problem of rhodium recovery has been approached by process modifications such as the two-phase process by Ruhrchemie/Rhône-Poulenc with a water-soluble Rh catalyst [3]. In another approach, heterogenised catalysts such as anchored metal complex catalysts [4–7], supported liquid-phase catalysts (SLPCs) [8,9] or, more recently, supported aqueous-phase catalysts (SAPCs) have been developed [10–13]. However, the commercial application of these catalysts in liquid-phase hydroformylation has been prohibited by leaching of the active component from the support or insufficient long-term stability [1,4,5,14–16] or by the need for operation within narrow water content limits (SAPCs) [1].

In gas-phase hydroformylation, the use of supported metal catalysts is more feasible, since the operating conditions are mild: the reaction can be carried out at low pressures below 423 K, where the competing Fischer–Tropsch reaction ceases. In mild environment, no volatile metal carbonyls are generated; and, thus, the active centres remain on the support surface. Accordingly, both rhodium- and cobalt-containing supported catalysts have gained attention in the hydroformylation of ethene [17–19]. The studies have revealed that gas-phase hydroformylation requires good dispersion, i.e., CO insertion is favoured on isolated metal sites [20,21].

With regard to highly dispersed catalysts, the carbonyl clusters have been a subject of extreme interest [22–25]. We have also obtained promising results with the $Co_2(CO)_8/SiO_2$ catalysts [26,27], but the results were difficult to reproduce; possibly, one reason was the air-sensitive nature of the precursor [28]. However, deposition of the metal compounds on the support via gas phase has also been shown to produce catalysts with very high dispersion [29]: cobalt catalysts prepared from cobalt(III) acetylacetonate possessed a remarkably high hydrogen uptake and, hence, a high dispersion and a small particle size of cobalt after high-temperature hydrogen pretreatment.

In this work, the highly dispersed $Co(acac)_3/SiO_2$ catalysts [29] were studied in the gas-phase hydroformylation of ethene in flow conditions. The catalyst, prepared by impregnation from cobalt nitrate, was used as a reference catalyst, and the stability of the catalysts with time on stream was evaluated.

2. Experimental

2.1. Catalyst preparation

Two different methods were used in the preparation of the Co/SiO_2 catalysts: gas-phase deposition and impregnation. 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 was used as the support for all catalysts.

Cobalt(III) acetylacetonate, $Co(acac)_3$ (Merck, $>98\%$) was used as the precursor in the gas-phase deposition described in more detail elsewhere [29]. It consisted

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Table 1
Characteristics of the Co/SiO$_2$ catalysts after hydrogen reduction.

Catalyst	Temp. of reduction (°C)	H_2 uptake[a] (cm^3/g(cat))	Ext. of reduction[b] (%)	Dispersion[c] (%)	Particle size[c] (nm)
4-Co(N)/SiO$_2$	400	0.55	84	8.5	11.3
5-Co(A)/SiO$_2$	550	1.2	52	23	4.3
11-Co(A)/SiO$_2$	550	1.9	54	17	5.6
16-Co(A)/SiO$_2$	550	1.5	63[d]	7.6	12.6

[a] Total hydrogen uptake.

[b] Determined by oxygen titration.

[c] Corrected by the extent of reduction.

[d] Estimated from the extent of reduction of Co(A)/SiO$_2$ catalyst containing 15 wt% cobalt.

of the following steps: (a) pretreatment of the support, (b) chemisorption of the gaseous precursor up to surface saturation, and (c) removal of the remaining ligands by calcination in synthetic air, except after the last deposition. Steps (b) and (c) were repeated to obtain higher cobalt contents. The catalyst after one, three or five preparation cycles yielded catalysts with cobalt contents of 5.2, 10.7 and 16.3 wt%, and the catalysts are denoted as 5-Co(A)/SiO$_2$, 11-Co(A)/SiO$_2$ and 16-Co(A)/SiO$_2$, respectively.

For the preparation of the reference catalyst, the silica support was pretreated with a water–ethanol solution, dried in air at 120 °C for 16 h, and further at 200 °C and 0.1–0.4 kPa for 2 h. Cobalt nitrate was impregnated on the pretreated support from aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (Merck, p.a.) and calcined under air flow at 300 °C for 12 h [30]. The resulting catalyst contained 4 wt% of cobalt, and it was thus denoted as 4-Co(N)/SiO$_2$.

2.2. Catalyst characterisation

The cobalt contents of the catalysts were determined by instrumental neutron activation analysis (INAA, 250 kV Triga Mk II research reactor at VTT Chemical Technology) or atomic absorption spectrometry (AAS, Varian SpectrAA-600 at Analysis Centre) according to the procedures described in more detail elsewhere [29]. The accuracy of the analyses was ±7%. The carbon contents of the catalysts were determined by a LECO CR 12 carbon analyser.

The hydrogen uptake of the reduced catalysts was measured at 30 °C with static volumetric chemisorption equipment, Coulter OMNISORP 100CX, as discussed in detail earlier [29] and here only in brief. Before the measurements, the catalysts were reduced *in situ* in flowing hydrogen for 7 h at 500 °C (Co(A)/SiO$_2$) or 400 °C (4-Co(N)/SiO$_2$). The estimate for the average particle size was calculated assuming spherical geometry of the cobalt particles. The values obtained for dispersion and particle size were corrected by the extent of reduction measured by oxygen titration. The properties of the catalysts are presented in table 1.

2.3. Reaction experiments

The ethene hydroformylation studies were carried out in an automated fixed-bed tubular reactor (i.d. = 12 mm; pocket for the thermocouples in the catalyst bed: o.d. = 6 mm) in gas phase at 0.5 MPa and 173 °C using 1 : 2 : 2 : 2 molar ratio of $Ar : CO : H_2 : C_2H_4$ and GHSV of $\sim$950 h^{-1} (0.5 MPa). The catalyst amount of 1 g ($\sim$2.4 cm^3) was diluted with glass beads in 1 : 1 volume ratio. In general, the isothermal conditions were maintained, i.e., the three control-point temperatures remained typically within ±0.5 °C with respect to the setpoint value. In addition, the vertical temperature gradient of the catalyst bed was within ±1 °C with respect to the setpoint value.

Before the experiments, the Co(N)/SiO$_2$ catalyst was reduced *in situ* under $H_2 : Ar$ flow (1 : 2 molar ratio, 9.9 l/h) for 7 h at 400 °C. The Co(A)/SiO$_2$ catalysts were, however, reduced under H_2 flow (5 l/h) for 7 h at 550 °C in a separate reactor without dilution with glass beads, which cannot withstand such high temperatures. After reduction, the Co(A)/SiO$_2$ were also diluted with glass beads and packed into the tubular reactor in a glove box.

The product analysis was carried out on-line by two HP 5890 gas chromatographs; one was equipped with a DB-1 of the J&W Scientific and PoraplotQ of Hewlett Packard, and the other one with a packed column, filled with activated carbon coated with 2% squalane. The response factors published by Dietz [31] were used in quantitative determinations.

The reaction time was usually 24 h, but in some cases longer times were used: 48 h for 11-Co(A)/SiO$_2$ and 68 h for 5-Co(A)/SiO$_2$ to see the long-term performance of the catalysts. The steady-state activity and selectivity were calculated at TOS = 20–24 h as an average of three subsequent analyses. In the calculations, conversion (X), selectivity (S) and yield (Y) were based on the amount of ethene consumed. The condensation products of propanal are denoted by C_6-O, and the oxo-selectivity (S_{oxo}) is defined as the sum of selectivities for propanal, propanol and C_6-O.

3. Results and discussion

3.1. Activity of the Co/SiO$_2$ catalysts

The activity of the Co(A)/SiO$_2$ and 4-Co(N)/SiO$_2$ catalysts in the hydroformylation of ethene was measured at 173 °C and 0.5 MPa, and the main products formed were

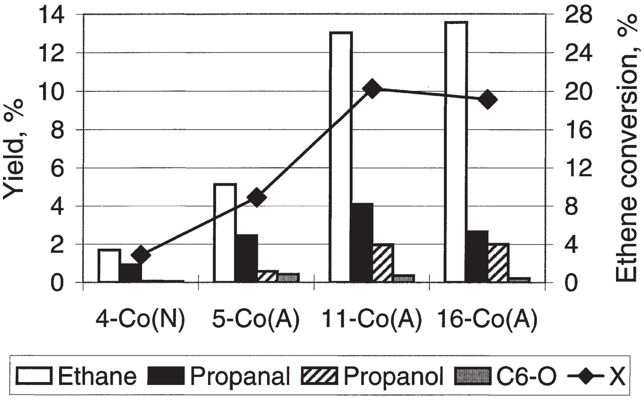

Figure 1. Ethene conversion (X) and product yields for Co/SiO$_2$ catalysts in ethene hydroformylation at 173 °C and 5 bar.

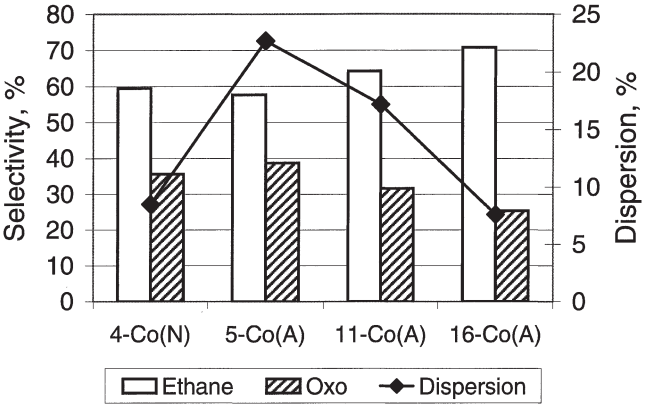

Figure 2. Selectivity for ethane and oxo products, and dispersion for Co/SiO$_2$ catalysts.

ethane and propanal. In addition, propanol, C_3–C_{11} hydrocarbons, methane and condensation products of propanal (C_6-O), i.e., 2-methyl-2-pentenal, 2-methyl-1-pentanal and 2-methyl-1-pentanol, were detected. Moreover, propanoic acid was formed on Co(A)/SiO$_2$ catalysts.

The ethene conversion and the yields of the main products in the steady state after 20 h on stream are presented in figure 1. The activity of the 5-Co(A)/SiO$_2$ ($X = 9\%$) was considerably higher than that of 4-Co(N)/SiO$_2$ ($X = 3\%$), even though the cobalt content was nearly the same. Accordingly, the total hydrogen uptake, i.e., the amount of metallic sites, was significantly higher for Co(A)/SiO$_2$ (see table 1). In regard to the activity, it is noteworthy that Takeuchi et al. [25] have observed higher conversion of ethene on cobalt-carbonyl-based catalyst than on respective nitrate-based catalyst. Thus, the results suggest that Co(acac)$_3$ and cobalt carbonyls as precursors might facilitate the formation of similar active sites effective in hydroformylation, whereas the nitrate precursor yields a less favourable composition.

The oxo-selectivity describing the CO insertion activity of the catalysts was fairly similar for 5-Co(A)/SiO$_2$ ($S_{\text{oxo}} = 39\%$) and for 4-Co(N)/SiO$_2$ ($S_{\text{oxo}} = 35\%$), but the selectivity for propanol and C_6-O was higher for 5-Co(A)/SiO$_2$ (6 and 5%, respectively) compared to those of 4-Co(N)/SiO$_2$ (2 and 1.4%). Thus, the 5-Co(A)/SiO$_2$ catalyst had greater ability to hydrogenate aldehydes to alcohols. However, the higher ability for the condensation and hydrogenation reaction might also be a consequence of the higher conversion level.

According to the characterisations, the two catalysts were very different: the extent of reduction was 84% for 4-Co(N)/SiO$_2$ and 52% for 5-Co(A)/SiO$_2$, and the average particle size of cobalt on the support was 11 and 4 nm, respectively. Thus, the 5-Co(A)/SiO$_2$ catalyst was clearly better dispersed than 4-Co(N)/SiO$_2$, but, nevertheless, the difference in oxo-selectivity was small.

The oxo-selectivity of 35% for our 4-Co(N)/SiO$_2$ is, in fact, quite exceptional, since Matsuzaki et al. [32] obtained an oxo-selectivity of 17% for a 5 wt% nitrate-based catalyst ($X = 14\%$) and 36% for a 5 wt% carbonyl-based catalyst ($X = 49\%$) at 463 K and 11 bar, i.e., at a higher pressure, which has been found to enhance the selectivity: the increase of pressure from 5 to 10 bar has increased the oxo-selectivity from 45 to 60% [33]. Thus, the oxo-selectivity of 39% for the 5-Co(A)/SiO$_2$ ($X = 9\%$) was very good considering the low reaction pressure used.

3.2. The effect of the varying metal content on the performance of Co(A)/SiO$_2$

The metal content of the Co(A)/SiO$_2$ catalysts was varied to study the effect of dispersion on the activity and selectivity of the catalysts. The highest ethene conversion was reached with the 11-Co(A)/SiO$_2$ catalyst ($X = 20\%$), which also exhibited the highest uptake of hydrogen (see table 1). Thus, it was this catalyst that had the highest amount of metallic sites available for the reaction. When the cobalt content was increased further to 16 wt%, the total activity diminished slightly (see 16-Co(A)/SiO$_2$ in figure 1). The total hydrogen uptake also decreased, suggesting that some larger aggregates were formed (see also table 1).

The interrelation between the product selectivity and the dispersion has been illustrated in figure 2, in which the ethane and oxo selectivities are plotted together with dispersion. For the Co(A)/SiO$_2$ catalysts, the oxo-selectivity correlated well with the dispersion: the higher the dispersion, the better the oxo-selectivity – a result in accordance with the suggestion that CO insertion proceeds on isolated metal sites [25]. On the other hand, the activity of the Co(A)/SiO$_2$ catalysts for ethene hydrogenation (figure 2) and also for propanol formation (changes from 6 to 10%) increases at higher metal loading. However, for the 4-Co(N)/SiO$_2$ catalyst the oxo-selectivity was high (35%), although the dispersion of the catalyst was low. The results may not, however, be directly comparable, since the conversion level of the catalysts in question varied; it was 9–20% for 5–16 wt% Co(A)/SiO$_2$ and only 3% for 4-Co(N)/SiO$_2$.

Therefore, the effect of conversion on the selectivity was elucidated on 4-Co(N)/SiO$_2$ by changing the reaction con-

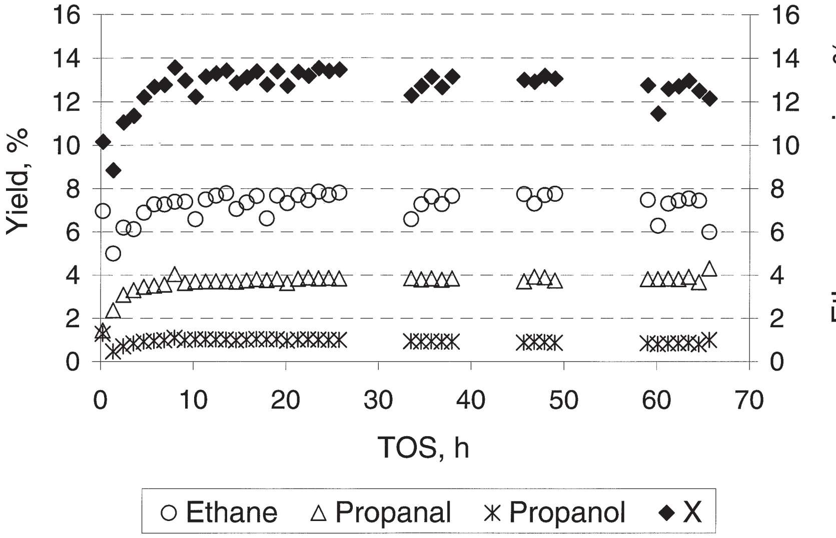

Figure 3. Ethene conversion (X) and product yields for the 5-Co(A)/SiO$_2$ catalyst as a function of reaction time.

Table 2
The metal and carbon contents of the Co/SiO$_2$ catalysts before and after the ethene hydroformylation reaction.

Catalyst	Reaction time (h)	Co (wt%)	Co (wt%) after reaction	C (wt%)	C (wt%) after reaction
4-Co(N)/SiO$_2$	72	4.0	4.0	0	7.9
5-Co(A)/SiO$_2$	24	5.2	5.2	7.5	2.5
5-Co(A)/SiO$_2$	72	4.7	4.8	4.2	3.2
11-Co(A)/SiO$_2$	48	10.6	10.3	5.2	4.6
16-Co(A)/SiO$_2$	24	16.3	15.7	3.5	5.9

ditions: 173 °C and GHSV of 950 h^{-1} gave S_{oxo} of 35% ($X = 3\%$), 173 °C and GHSV of 480 h^{-1} gave S_{oxo} of 35% ($X = 5\%$), 193 °C and GHSV of 950 h^{-1} yielded S_{oxo} of 34% ($X = 6\%$), and 193 °C and GHSV of 500 h^{-1} resulted in S_{oxo} of 28% ($X = 12\%$). Thus, the results show that the selectivities of the catalysts at different conversion levels cannot be directly compared. Takeuchi et al. [25], on the contrary, have suggested that the oxo-selectivity is unchanged at different conversion levels ($X = 6$–63%) for the 5 wt% cobalt-carbonyl-based Co/SiO$_2$ catalyst in the temperature range of 150–210 °C.

In conclusion, a clear correlation between the dispersion and the CO insertion selectivity for the Co(A)/SiO$_2$ is found: the higher the dispersion, the better the oxo-selectivity. However, due to the different conversion levels, the interrelation between the dispersion and the oxo-selectivity is not unambiguous.

3.3. Stability of the catalysts

The stability of the catalytic performance was evaluated for 68 h on the 5-Co(A)/SiO$_2$ catalyst (see the ethane conversion and the product yields in figure 3). The conversion increased from 10 to 13% during 10 h on stream and remained almost constant thereafter. The increase in conversion was also observed with the 11-Co(A)/SiO$_2$ catalyst (during 10 h on stream) but not with 16-Co(A)/SiO$_2$ or 4-Co(N)/SiO$_2$, which both maintained the same activity throughout the experiment. No time-dependent change in the activity on any of the Co(A)/SiO$_2$ catalysts was detected during 1 h on stream in toluene hydrogenation [29]. Thus, it seems appropriate to assume that hydrogen did not induce the change.

Although the activity of the 5-Co(A)/SiO$_2$ and 11-Co(A)/SiO$_2$ catalysts increased during reaction, the oxo/ethane ratio remained constant (see also figure 3). Therefore, it is rather unlikely that significant changes occurred in dispersion. Perhaps, some of the cobalt sites on the catalysts were reduced under the action of CO [34], and it was the extent of reduction that increased and induced the increase in activity.

The steady or increasing activity of the catalyst with time on stream already indicates that the active metal is not leached or sublimed from the support, and the stability of the catalysts was also confirmed by the metal analyses (see table 2). The results clearly indicate that no metal was lost from the support, since the values before and after reaction were the same within the accuracy of the analyses, considering also the presence of carbonaceous residues in the catalysts before (from acac precursors) and after reaction. Thus, in terms of stability, the present results differ clearly from those obtained for the liquid-phase hydroformylation of 1-hexene, where soluble cobalt species were formed [26].

4. Conclusions

The activity of the 5–16 wt% Co(A)/SiO$_2$ catalysts, prepared by gas-phase deposition, was compared with the activity of the impregnated 4 wt% Co(N)/SiO$_2$ catalyst in ethene hydroformylation at 173 °C and 5 bar.

Active catalysts were obtained after hydrogen treatment: 550 °C was necessary for the reduction of cobalt species on the Co(A)/SiO$_2$ catalysts, whereas for 4-Co(N)/SiO$_2$ 400 °C was adequate. After the reductive treatment, the 5-Co(A)/SiO$_2$ catalyst was three times more active than 4-Co(N)/SiO$_2$, and it yielded a conversion of 9%. Out of the Co(A)/SiO$_2$ catalysts, the most active one was 11-Co(A)/SiO$_2$ with a conversion of 21%, i.e., further increase of metal content from 11 to 16 wt% did not cause increase in activity.

With regard to the selectivity, the more active 5-Co(A)/SiO$_2$ catalyst was similar to the less active 4-Co(N)/SiO$_2$ catalyst: the oxo-selectivities were as good as 39 and 35%, respectively. It is also noteworthy that with increasing metal content (5 → 16 wt%), the oxo-selectivity of the Co(A)/SiO$_2$ catalysts decreased from 39 to 25%, and this decrease appeared to be related to the decreasing dispersion (23 → 8%). Even so, this interrelation is not unambiguous, because the conversion of the Co(A)/SiO$_2$ catalysts varied in the range of 9–20%.

The stability of the catalysts was also evaluated. The activity of the 5-Co(A)/SiO$_2$ and 11-Co(A)/SiO$_2$ increased during the first hours of time on stream and remained almost constant thereafter, whereas the activity of the 16-Co(A)/SiO$_2$ and 4-Co(N)/SiO$_2$ catalysts was the same throughout. Since the selectivities were essentially constant for all the catalysts during the reaction, it was probably the changes in the extent of reduction that induced the increase in activity. It is also very important to note that the good performance of the catalysts with time on stream also indicates that no metal was leached or sublimed from the support – a finding confirmed by the metal analyses of the catalysts.

In summary, highly dispersed catalysts were obtained by gas-phase deposition from Co(acac)$_3$ precursor, and the catalysts were promising in ethene hydroformylation in terms of product selectivity and catalyst stability.

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References

[1] M. Beller, B. Cornils, C.D. Frohning and C.W. Kohlpaintner, J. Mol. Catal. A 104 (1995) 17.

[2] V.A. Likhobolov and B.L. Moroz, in: *Handbook of Heterogeneous Catalysis*, Vol. 5, eds. G. Ertl, H. Knözinger and J. Weitkamp (VCH, Weinheim, 1997) chapter 4.5.

[3] B. Cornils and E. Wiebus, Chemtech (January 1995) 33.

[4] D.L. Hunter, S.E. Moore, P.E. Garrou and R.A. Dubois, Appl. Catal. 19 (1985) 259.

[5] W. Junfan, S. Juntan, Li Hong and He Binglin, React. Polym. 12 (1990) 177.

[6] L. Alvila, J. Pursiainen, J. Kiviaho, T.A. Pakkanen and O. Krause, J. Mol. Catal. 91 (1994) 335.

[7] C.U. Pittman and G.M. Wilemon, J. Org. Chem. 46 (1981) 1901.

[8] J.M. Herman, A.P.A.F. Rocourt, P.J. van den Berg and J.J.F. Scholten, Chem. Eng. J. 35 (1987) 83.

[9] H.L. Pelt, L.A. Gerritsen, G. van der Lee and J.J.F. Scholten, Stud. Surf. Sci. Catal. 16 (1983) 369.

[10] J.P. Arnachet, M.E. Davis and B.E. Hanson, J. Catal. 129 (1991) 94.

[11] I. Guo, B.E. Hanson, I. Tóth and M.E. Davis, J. Organomet. Chem. 403 (1991) 221.

[12] I.T. Horváth, Catal. Lett. 6 (1990) 43.

[13] M.J. Naughton and R.S. Drago, J. Catal. 155 (1995) 383.

[14] C. Andersson, A. Nikitidis, J. Hjortkjær and B. Heinrich, App. Catal. A 96 (1993) 345.

[15] H. Marrakchi, J.-B. Nguini Effa, M. Haimeur, J. Lieto and J.-P. Aune, J. Mol. Catal. 30 (1985) 101.

[16] K.G. Allum, R.D. Hancock, I.V. Howell, R.C. Pitkethly and P.J. Robinson, J. Catal. 43 (1976) 322.

[17] S.C. Chuang and S.-I. Pien, J. Mol. Catal. 55 (1989) 12.

[18] S.S.C. Chuang and S.-I. Pien, J. Catal. 138 (1992) 536.

[19] N. Takahashi, T. Takeyama, T. Yanagibashi and Y. Takada, J. Catal. 136 (1992) 531.

[20] L. Huang, Y. Xu, W. Guo, A. Liu, D. Li and X. Guo, Catal. Lett. 32 (1995) 61.

[21] W.M.H. Sachtler and M. Ichikawa, J. Phys. Chem. 90 (1986) 4752.

[22] M. Ichikawa, J. Catal. 59 (1979) 67.

[23] L. Huang, L. Xu, G. Piao, A. Liu and W. Zhang, Catal. Lett. 23 (1994) 87.

[24] C. Dossi, A. Fusi, L. Garlaschelli, R. Psaro and R. Ugo, in: *New Frontiers in Catalysis*, Proceedings of the 10th International Congress on Catalysis, 19–24 July 1992, Budapest, eds. L. Guczi, F. Solymosi and P. Tétényi (Akadémiai Kiadó, Budapest, 1993) p. 2345.

[25] K. Takeuchi, T. Hanaoka, T. Matsuzaki, M. Reinikainen and Y. Sugi, Catal. Lett. 8 (1991) 253.

[26] T.A. Kainulainen, M.K. Niemelä and A.O.I. Krause, J. Mol. Catal. A 122 (1997) 39.

[27] M. Reinikainen, J. Kiviaho, M. Kröger, M. K. Niemelä and S. Jääskeläinen, J. Mol. Catal. A 118 (1997) 137.

[28] M. Niemelä, Reactions of synthesis gas on silica supported transition metal catalysts, Ph.D. thesis (VTT publications 310, Espoo, 1997) p. 37.

[29] L.B. Backman, A. Rautiainen, A.O.I. Krause and M. Lindblad, Catal. Today, accepted.

[30] M.K. Niemelä, A.O.I. Krause, T. Vaara and J. Lahtinen, Top. Catal. 2 (1995) 45.

[31] W.A. Dietz, J. Gas Chromatogr. 5 (1967) 68.

[32] T. Matsuzaki, K. Takeuchi, T. Hanaoka, H. Arakawa and Y. Sugi, Catal. Today 28 (1996) 251.

[33] M. Reinikainen, Vapor phase hydroformylation of light olefins over cobalt catalysts, Lic. thesis (Espoo, 1995) p. 71.

[34] M.P. Rosynek and C.A. Polansky, Appl. Catal. 73 (1991) 97.