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The long-term performance of Co/SiO_2 catalysts in CO hydrogenation

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The activity in terms of conversion of carbon monoxide was determined for Co/SiO_2 catalysts in CO hydrogenation over a reaction time of 120 h. The catalysts were prepared from nitrate (N) and carbonyl (CO) precursors. The conversion decreased rapidly during the first five hours, and thereafter moderately at a rate related to dispersion, i.e. the higher the dispersion the higher the rate of decrease. The active sites were blocked by wax and coke formed in the reaction, although some agglomeration of particles probably took place on the $Co(CO)/SiO_2$ catalysts. More carbon was accumulated on $Co(CO)/SiO_2$ than on $Co(N)/SiO_2$ during the reaction suggesting a need for frequent regeneration. The reduction–oxidation–reduction treatments indicated, however, that the regenerability of the $Co(CO)/SiO_2$ in terms of hydrogen uptake is poor, although the amounts adsorbed still remained higher than those for $Co(N)/SiO_2$.

Keywords: catalyst characterization; cobalt; silica support; carbon monoxide hydrogenation; synthesis gas

1. Introduction

Supported cobalt catalysts are highly active in synthesis gas reactions. Both the support and the identity of the metal precursor have a decisive effect on the characteristics of the catalyst. Conventional preparations have been difficult to reduce especially at low cobalt loadings [1]. Cobalt carbonyls have, in general, produced well-reduced catalysts with high dispersions [1–3] resulting in higher activities compared to the nitrate-derived catalyst [1–8]. The superior performance of the carbonyl-based catalysts has been closely related to the percentage of reduction [9], although the working surface of the Co/SiO_2 catalysts of different origin has been similar in the presence of the $H_2/CO/H_2O$ system, i.e. the catalysts with a low original state of reduction were reduced further and vice versa [10].

The high initial activity of the carbonyl-derived catalysts does not, however, guarantee good long-term performance. An important aspect of deactivation during the first few days of commercial operation is the deposition of carbon [11], although some growth of the highly dispersed metallic particles has also been observed under the conditions of CO hydrogenation [12]. Lisitsyn et al. [7] studied the conventional and $Co_2(CO)_8$ based catalysts at 180°C under atmospheric pressure. They found [7] that the deactivation was more pronounced for the conventional catalysts as well as for the carbonyl ones with a low cobalt content, although the reaction rate only decreased by a factor of two or less 20 h after the beginning of the experiment. The stability of the highly dispersed and well-reduced $Co_4(CO)_{12}$ carbonyl-derived catalysts has also been very good [1]: the turnover number dropped by only 13% after 24 h of reaction at atmospheric pressure and 200°C.

Another important aspect of catalyst deactivation in industrial operations is stability in the cyclic reaction regeneration mode. During regeneration, the carbonaceous residues are removed and the activity of the catalyst is reproduced. For example, Agrawal et al. [11] have been able to restore the activity of the carbon-deactivated (< 300°C) Co/Al_2O_3 catalysts by treating with hydrogen at 400°C. On the other hand, the oxidative regenerations of cobalt–thoria–zeolite catalysts have not succeeded in returning the catalyst to its initial activity due to sintering of the cobalt [13].

The reported activity and selectivity data for the carbonyl-based catalysts have been recorded at different reaction times, resulting in contradictory findings [1,7]. Our previous results [4] have also shown that deactivation continues after 24 h of reaction time. Therefore, we determined the true steady-state performance of the Co/SiO_2 catalysts in syngas reaction, characterized the used catalysts, and studied the regeneration durability using reduction/oxidation sequences – qualities relevant to the industrial applicability of the catalysts.

2. Experimental

2.1. Catalyst

The following abbreviations have been used for precursors in conjunction with the catalyst: N for nitrates and CO for carbonyls. For example, 2-$Co(CO)/SiO_2$ refers to a catalyst derived from $Co_2(CO)_8$, and 4-$Co(CO)/SiO_2$ to one prepared from $Co_4(CO)_{12}$. The preparation of the catalysts with approximately 5 wt% metal loading has been described in detail in our previous publications [4,5]. The $Co(N)/SiO_2$ catalysts were

Table 1

The characteristics of the Co/SiO$_2$ catalysts after reduction by hydrogen [5]

Catalyst on SiO$_2$	H_2 uptake (μmol)/g_{cat}	Reduction, XPS (%)		Dispersion [c]		Size XRD (nm)	Size chemisorption (nm)	
		a	b	a	b		a	b
Co(N)	12.5	63	42	4.8	7.1	14	17	13
2-Co(CO)	46.2	32	15	38	80	2.3	2.6	1.2
4-Co(CO)	52.2	66	41	20	32	3.4	4.6	3.0

[a] Shirley background correction.

[b] Linear background correction.

[c] Corrected with the extent of reduction.

reduced in situ at 400°C, and the 2-Co(CO)/SiO$_2$ and 4-Co(CO)/SiO$_2$ catalysts at 300°C under hydrogen flow for 7 h [4,5]. The results of the characterizations of the catalysts are presented in table 1 [4,5]. After the reaction, the catalyst samples were analysed by SIMS at the University of Florida [14] using a Perkin-Elmer 6600 with a 6 keV Cs^+ primary ion beam and negative secondary ion detection. The masses monitored were $^{12}C^-$, $^{32}O^-$, $^{35}Cl^-$, $^{30}Si^-$, $^{59}Co^-$ and $^{118}Co^-$. The total amount of carbon on the used catalysts was determined after toluene wash using a LECO SC-444 analyser. The used catalyst samples were also extracted with chloroform, and the extracts were analysed by IR and MS at the Neste Corp. Analytical Division [15].

2.2. Reactor system

The deactivation studies were carried out in an automated fixed-bed tubular reactor at 0.5 MPa and 235–290°C using a 3 : 1 : 3 volume ratio of Ar : CO : H_2, and a GHSV of approximately 5200–7800 h^{-1}. The catalyst (1 g/2.7 ml) was diluted with glass beads in 1 : 1 volume ratio. The deactivation data was recorded as conversion of CO vs. time for 120 h. The control point temperatures inside the reactor typically remained within ±0.5°C with respect to the setpoint value. Steady-state temperature profiles were determined from each run, and the temperature of the catalyst bed was maintained within ±1°C with respect to the setpoint value. The product analysis was carried out by two, on-line HP 5890 gas chromatographs: one equipped with a DP-1 and DB-WAX of J&W Scientific, and the other equipped with a packed column filled with activated carbon coated with 2% squalane. The response factors published by Diez [16] were used in quantitative determinations.

3. Results and discussion

3.1. Deactivation studies

The catalysts react intensively with the synthesis gas during the first few minutes of reaction time forming reactive surface species, various products and coke, which deactivates the active sites. The data recorded every hour did not allow us to follow this very rapid initial deactivation and thus we concentrate only on long-term performance, i.e. on the activity data recorded for 2–120 h at 235–290°C. It should also be noted that the temperature of the fixed bed of the carbonyl catalysts could not be controlled in our reactor system at high temperatures due to extensive heat release, i.e. the carbonyl-based preparations appeared to be very active.

In accordance with our previous work [4], the reactivity was measured as conversion of CO instead of turnover rates, because the number of active metallic sites could not be unambiguously determined. Namely, the extent of reduction for the freshly reduced catalysts depended strongly on the method of interpreting the XPS data [5], see table 1. Furthermore, the extent of reduction has been reported to change during the reaction [10,17]. According to Rosynek and Polanski [10],

Table 2

The experimental conditions and the performance of the catalysts after 2 h of time-on-stream in the CO hydrogenation reaction at 0.5 MPa

Catalyst on SiO$_2$	Temp. (°C)	GHSV (h^{-1})	X (%)	α	Oxygenates (mol%)	CH_4 (mol%)	Co$_2$ (mol%)
Co(N)	235	5200	15.0	0.81	6.0	57.9	0
Co(N) [a]	260	5200	21.1	0.70	6.0	59.3	0
Co(N)	290	6500	37.3	0.54	2.7	65.5	13.6
2-Co(CO)	235	5200	12.2	0.77	7.5	57.8	0
2-Co(CO)	245	6500	20.7	0.72	5.8	62.4	0
4-Co(CO)	235	6500	11.2	0.69	7.3	60.7	0
4-Co(CO)	245	7800	20.0	0.73	6.7	59.4	0

[a] The data after 6 h of reaction time.

cobalt catalysts of different origin developed a similar working surface under the synthesis gas reaction atmosphere, i.e. the ones with a low extent of reduction were reduced further and vice versa – an observation supported by our previously published data [17]. Therefore, the number of active sites is very difficult to determine during the course of a long reaction, and the use of conversion appeared more appropriate.

The initial activity of the catalysts at 235°C was fairly similar, see table 2. The deactivation was approximately the same for 4-Co(CO)/SiO_2 and 2-Co(CO)/SiO_2, whilst Co(N)/SiO_2 was slightly more stable, see fig. 1. Thus, the results suggest that Co(N)/SiO_2 was less susceptible to the effects of deactivation than the catalysts of carbonyl origin. This contrasts with the findings of Lisitsyn et al. [7] and Johnson et al. [9]. Their [7,9] results were, however, obtained under more moderate and less hydrogen-rich conditions: at 180–200°C under atmospheric pressure with a 2 : 1 ratio of H_2 : CO.

The performance of the most stable Co(N)/SiO_2 catalyst was also evaluated at 260 and 290°C, see fig. 2. The results indicate that the stability of the catalyst was similar at 235 and 260°C, whereas it was clearly less stable at 290°C, although the amount of carbon on the used catalyst decreased respectively. In principle, the deposition of carbon is enhanced at high reaction temperature, and the increase in conversion also increases the formation of coke [18]. However, carbon deposition is a strong function of partial pressures of CO (P_{CO}) and H_2 (P_{H_2}) in the gas phase. Thus, the greater conversion at higher temperatures results in a corresponding decrease in P_{CO} and P_{H_2}, and may therefore lead to smaller amounts of carbon on the catalyst [19]. On the other hand, at high reaction temperatures shorter hydrocarbon chains are formed and rapidly desorbed [20]. The rate of accumulation is thus slower – an argument supported by the decreasing values for chain growth with increasing temperature, see table 2 and fig. 5.

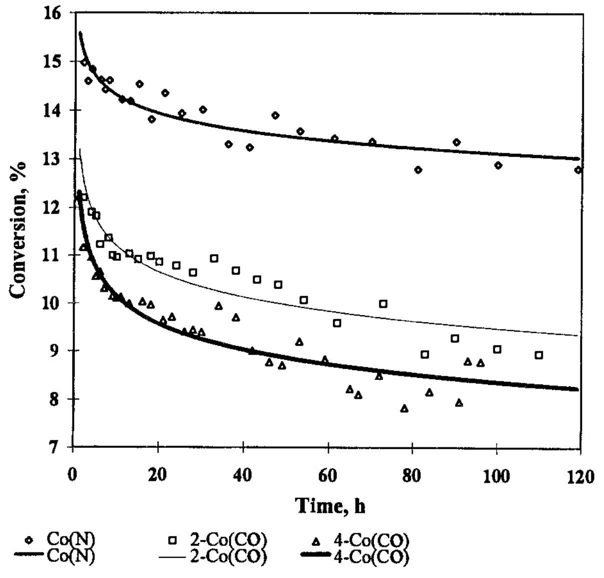

Fig. 1. The activity of Co/SiO_2 at 235°C for 120 h of reaction time.

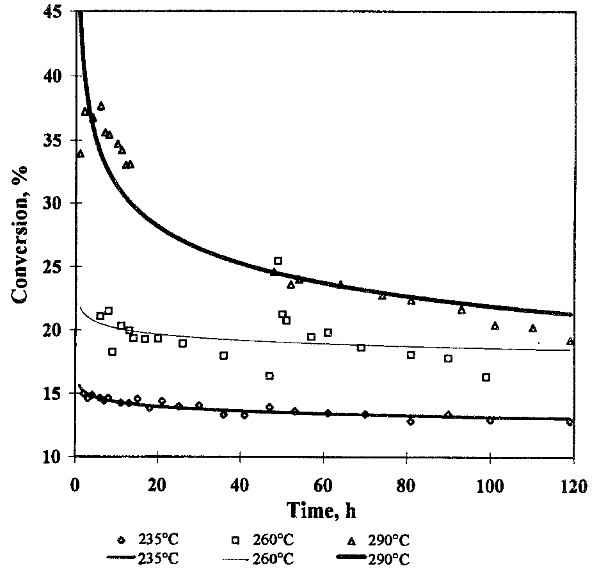

Fig. 2. The activity of Co(N)/SiO_2 for 120 h of reaction time.

The heat release of the highly reactive Co(CO)/SiO_2 catalysts was excessive at 260°C, resulting in an oscillating reaction temperature, i.e. the testing was limited to lower temperatures. At 245°C, the conversion for 4-Co(CO)/SiO_2 dropped at the same rate as for Co(N)/SiO_2 at 260°C, whereas 2-Co(CO)/SiO_2 appeared less stable, see fig. 3. Thus, the carbonyl catalysts seem more susceptible to the effects of deactivation. In fact, the conversion decreased more rapidly, the more dispersed the catalyst was.

The probability of chain growth, α, remained constant or decreased slightly for Co(N)/SiO_2 over the 120 h of reaction time, whereas for the carbonyl-based cat-

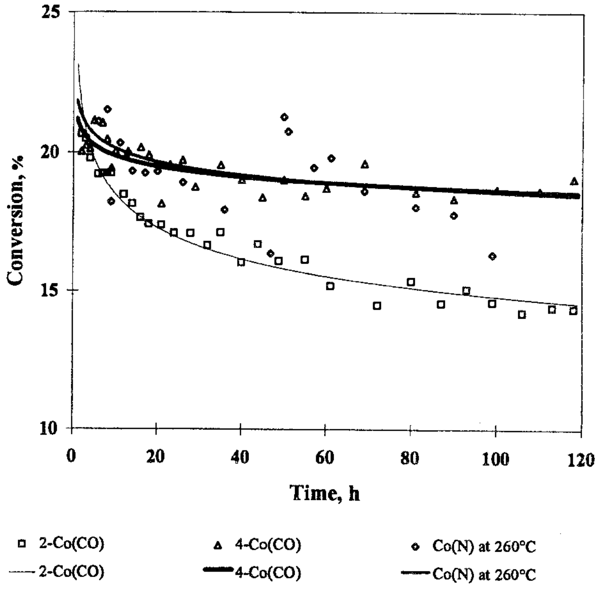

Fig. 3. The activity of Co(CO)/SiO_2 at 245°C and Co(N)/SiO_2 at 260°C for 120 h of reaction time.

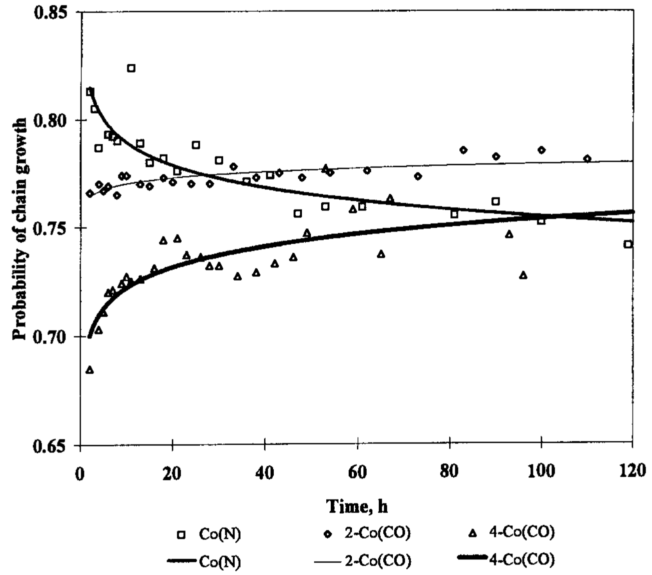

Fig. 4. The probability of chain growth at 235°C for Co/SiO_2 as a function of reaction time.

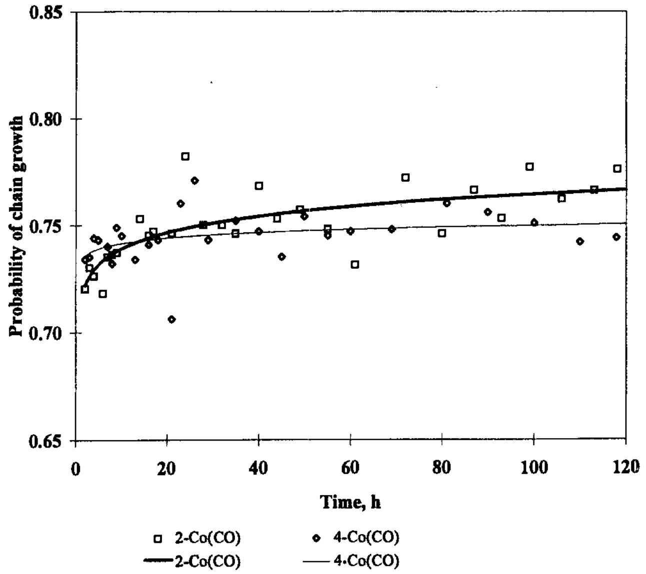

Fig. 6. The probability of chain growth at 245°C for Co(CO)/SiO_2 as a function of reaction time.

alysts it increased with time as illustrated in figs. 4, 5 and 6. In fact, the probability of chain growth for reaction times above 100 h was highest for 2-Co(CO)/SiO_2. Previously, Mukkavilli et al. [19] have reported that the relative turnover number for the C_{2+} species may increase significantly during the initial phase of carbon deactivation due to preferential blockage of the narrowest of the catalyst pores. Thus, the high molecular weight products probably blocked some of the active sites of the highly dispersed Co(CO)/SiO_2 catalysts, in particular those of 2-Co(CO)/SiO_2, see also table 1. The cobalt species on Co(N)/SiO_2 are located mainly on the outer surface of the silica particle [4], thereby being more accessible to the reacting gas and less susceptible to site blockage.

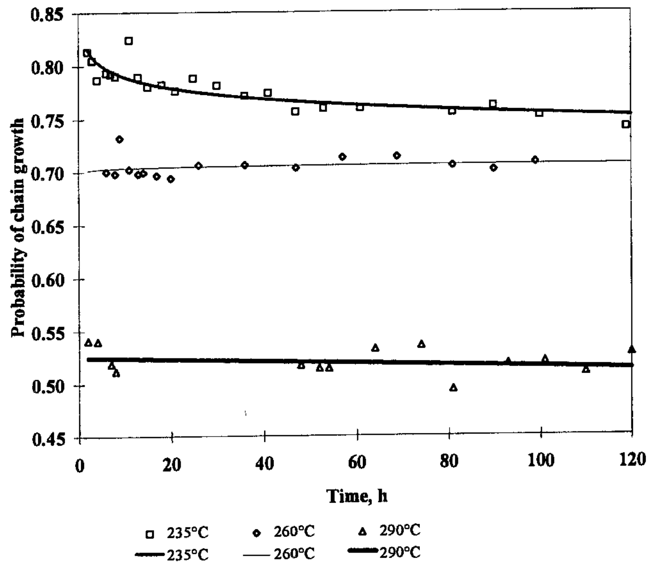

Fig. 5. The probability of chain growth at 235–290°C for Co(N)/SiO_2 as a function of reaction time.

The results shown in tables 2 and 3 also indicate that with time-on-stream the amount of methane formed on Co(N)/SiO_2 increased, remained more constant on 4-Co(CO)/SiO_2, and decreased on 2-Co(CO)/SiO_2. Our previous results [5] also suggested that 4-Co(CO)/SiO_2 resembled Co(N)/SiO_2 rather than 2-Co(CO)/SiO_2 in pulse micro reactor experiments with very short time-on-stream. The 2-Co(CO)/SiO_2 catalyst produced more methane, less ethane and less water than the others [5]. We presumed that the differencies in the product distribution were due to the higher dispersion and lower extent of reduction of 2-Co(CO)/SiO_2 compared to the other catalysts, see table 1. During the long-term experiments, however, the performance of 2-Co(CO)/SiO_2 was more similar to 4-Co(CO)/SiO_2 than to Co(N)/SiO_2 in terms of deactivation and α, although the formation of oxygenates was highest for 2-Co(CO)/SiO_2 as we assumed in our previous paper [5]. Thus, some growth of the highly dispersed cobalt sites present on the 2-Co(CO)/SiO_2 probably occurred within the first hour of reaction time, leaving the catalyst surface more similar to that of 4-Co(CO)/SiO_2.

3.2. Characterization of catalysts

The surface areas of the catalysts were determined after use. In addition, the carbon content and depth profile of cobalt and carbon in the catalysts were measured after the reaction to get more insight into the causes of deactivation. The sensitivity of the Co/SiO_2 catalysts to oxidation and rereduction was also evaluated in order to estimate their stability in industrial reaction–regeneration cycles.

Table 3
The performance and the characteristics of the catalysts after 95 h on stream in the CO hydrogenation reaction at 0.5 MPa. (Note: CO_2 0 mol% for all)

Catalyst on SiO_2	Temp. (°C)	X (%)	α	Oxygenates (mol%)	CH_4 (mol%)	BET (m_2/g)	Carbon (wt%)
Co(N)	235	12.8	0.74	6.5	60.1	239	2.7
Co(N)	260	16.3	0.71	3.6	60.4	224	2.2
Co(N)	290	19.2	0.53	2.6	79.4	247	0.4
2-Co(CO)	235	9.0	0.78	7.3	54.3	53	16
2-Co(CO)	245	14.3	0.78	7.0	55.3	216	1.4
4-Co(CO)	235	7.8	0.73	6.4	60.2	203	3.3
4-Co(CO)	245	19.1	0.74	5.8	57.6	275	1.6

After CO hydrogenation, the catalysts were washed twice with toluene and dried, and the BET surface areas and the amount of carbon on the catalysts were determined. The results depicted in table 3 indicate that more carbon was retained on the $Co(CO)/SiO_2$ catalysts than on $Co(N)/SiO_2$. The SIMS results indicated that carbon was located mainly on the outer surface of the silica particles, i.e. the signal decreased considerably with increasing depth. The amount of accumulated carbon was extremely high, and the BET very low, for 2-$Co(CO)/SiO_2$. We suspect that some waxes must have been retained into the catalyst pores. In accordance, Fredriksen et al. [20] have reported that the weight gain increased with decreasing reaction temperature (300–200°C) for Co/SiO_2, and attributed the increase to adsorbed reaction products. Dry [21] and Agrawal [22] have also noted that the selectivity towards higher hydrocarbons increases at low reaction temperatures.

For illustrative purposes, some samples of the coked $Co(N)/SiO_2$ (235 and 290°C) and 4-$Co(CO)/SiO_2$ (245°C) catalysts were extracted with chloroform, and the extracts were analysed to determine the type of carbonaceous compounds on the used catalysts. The IR and MS analysis of extracts of 4-$Co(CO)/SiO_2$ (245°C) and $Co(N)/SiO_2$ (235°C) contained C_{15-30} paraffins, C_{10-20} primary and secondary alcohols and C_{10-20} ketones. After reaction at 290°C only C_{15-30} paraffins and traces of ketones were detected on $Co(N)/SiO_2$. Thus, the results suggest that more of reactive intermediates were present on the catalyst surfaces at low reaction temperatures, and hence the assumption of wax build up at low reaction temperature is certainly plausible.

Since rather large amounts of carbon were accumulated during the reaction particularly on the 2-$Co(CO)/SiO_2$ catalyst, it was essential to study the effects of carbon removal on the characteristics of the catalyst. Therefore, the Co/SiO_2 catalysts initially reduced were allowed to oxidize under ambient conditions, and the catalysts were thereafter rereduced by hydrogen at 300–400°C for 2 h. The effect of rereduction on hydrogen uptake was determined, see table 4. The results indicate that the hydrogen uptake of $Co(CO)/SiO_2$ after rereduction at 300°C was only approximately 23–36% of the initial hydrogen uptake, i.e. the oxidized species required higher reduction temperatures. However, even after the rereduction at 400°C, the hydrogen uptake of 4-$Co(CO)/SiO_2$ was only 36% of the initial value, whereas that of $Co(N)/SiO_2$ was 60% of its initial value. Similarly, Hucul [23] has studied the hydrogen uptake of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ supported on alumina. The initial hydrogen uptakes decreased to approximately 60% of their original values when the catalysts were rereduced at 500°C after their use in the methanation reaction at 250°C. Moreover, the subsequent oxidation and reduction of these catalysts at 500°C resulted in hydrogen uptakes that were 40% of the respective initial values. It should be noted, however, that high-temperature calcination generates particle growth [24]. In all, the regeneration durability of the $Co(CO)/SiO_2$ catalysts is poor, although the hydrogen uptakes of the oxidized and rereduced $Co(CO)/SiO_2$ catalysts remained higher than that of the similarly treated $Co(N)/SiO_2$.

4. Summary and conclusions

The initial activity of the catalysts in CO hydrogenation decreased in the order 4-$Co(CO)/SiO_2$, 2-$Co(CO)/SiO_2 > Co(N)/SiO_2$. The activity of all catalysts decreased very rapidly during the first two hours and thereafter decreased moderately at a rate related to dispersion: the higher the dispersion the higher the rate of deactivation. The probability of chain growth for the

Table 4
Hydrogen chemisorption of the Co/SiO_2 catalysts

Catalyst on SiO_2	T_{red} (°C)	T_{rered} (°C)	H_2 uptake ($\mu mol/g_{cat}$)
Co(N)	400	–	12.5
Co(N)	400	400	7.5
2-Co(CO)	300	–	46.2
2-Co(CO)	300	300	16.7
4-Co(CO)	300	–	52.2
4-Co(CO)	300	300	11.8
4-Co(CO)	300	400	18.7

Co(CO)/SiO_2 catalysts increased during the reaction, whereas that for Co(N)/SiO_2 remained constant or decreased. Therefore, we suggest that the deactivation of Co(CO)/SiO_2 was partly due to agglomeration of the cobalt crystallites and mainly due to the formation of wax and coke, whereas the deactivation of the Co(N)/SiO_2 catalyst was most likely due to the formation of wax and coke.

More carbon was accumulated on the Co(CO)/SiO_2 catalysts than on Co(N)/SiO_2 during the 120 h of CO hydrogenation, suggesting a frequent need for regeneration. The reduction–oxidation treatments of the Co(CO)/SiO_2 catalysts indicated that the carbonyl-based catalysts require high rereduction temperatures; the reduction at 400°C reproduced only 36% of the initial hydrogen uptake of the 4-Co(CO)/SiO_2 catalyst initially reduced at 300°C, whereas 60% of the initial uptake was reproduced for Co(N)/SiO_2. Yet, after the oxidation rereduction treatment the hydrogen uptakes of the Co(CO)/SiO_2 remained higher compared to the conventional catalyst.

In conclusion, the results clearly demonstrate that long-term testing is necessary for the evaluation of the performance of the catalysts, since significant changes in product distributions were still observed after 50 h of time-on-stream.

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References

[1] B.G. Johnson, M. Rameswaran, M.D. Patil, G. Muralidhar and C.H. Bartholomew, Catal. Today 6 (1989) 81.

[2] K. Takeuchi, T. Matsuzaki, T. Hanaoka, H. Arakawa and Y. Sugi, J. Mol. Catal. 55 (1989) 361.

[3] K. Takeuchi, T. Matsuzaki, H. Arakawa, T. Hanaoka and Y. Sugi, Appl. Catal. 48 (1989) 149.

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

[5] M.K. Niemelä, A.O.I. Krause, J.J. Kiviaho and M.K.O. Reinikainen, Appl. Catal., in press.

[6] T. Matsuzaki, K. Takeuchi, T. Hanaoka, H. Arakawa and Y. Sugi, Appl. Catal. 105 (1993) 159.

[7] A.S. Lisitsyn, A.V. Golovin, V.L. Kuznetsov and Yu.I. Yermakov, C_1 Mol. Chem. 1 (1984) 115.

[8] C.H. Bartholomew, *New Trends in CO Activation*, Studies in Surface Science and Catalysis, Vol. 64 (Elsevier, Amsterdam, 1991) p. 158.

[9] B.G. Johnson, C.H. Bartholomew and D.W. Goodman, J. Catal. 128 (1991) 231.

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

[11] P.K. Agrawal, J.R. Katzer and W.H. Manogue, J. Catal. 69 (1981) 312.

[12] A.S. Lisitsyn, A.V. Golovin, A.L. Chuvilin, V.L. Kuznetsov, A.V. Romanenko, A.F. Danilyuk and Yu.I. Yermakov, Appl. Catal. 55 (1989) 235.

[13] H.W. Pennline and S.S. Pollack, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 11.

[14] P. Holloway and M. Puga-Lambers, University of Florida, private communication (1995).

[15] O. Jylhä, A. Toivo and K. Wikström, Neste Corp., private communication (1995).

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

[17] M.K. Niemelä and A.O.I. Krause, Book of Abstracts, Europacat-II, Maastricht, 4–8 September 1995, p. 671.

[18] H. Schulz, Pure Appl. Chem. 51 (1979) 2225.

[19] S. Mukkavilli and C. Witman, Ind. Eng. Chem. Proc. Des. Dev. 25 (1986) 487.

[20] G.R. Fredriksen, E.A. Blekkan, D. Schanke and A. Holmen, Chem. Eng. Technol. 18 (1995) 125.

[21] M.E. Dry, in: *Catalysis Science and Technology*, Vol. 1, eds. J.R. Anderson and M. Boudart (Springer, Berlin, 1981) p. 195.

[22] P.K. Agrawal, PhD Dissertation, University of Delaware, USA (1979) p. 400.

[23] D.A. Hucul, PhD Dissertation, Wayne State University, Detroit, USA (1980).

[24] R.L. Chin and D.M. Hercules, J. Phys. Chem. 86 (1982) 360.