Catalysis Letters 34 (1995) 269–284

Study of the deactivation mechanism of Al_2O_3-supported cobalt Fischer–Tropsch catalysts

D. Schanke[b], A.M. Hilmen[a], E. Bergene[b], K. Kinnari[c], E. Rytter[c],
E. Ådnanes[b] and A. Holmen[a,1]

[a] *Department of Industrial Chemistry, Norwegian Institute of Technology,*
University of Trondheim, N-7034 Trondheim, Norway
[b] *SINTEF Applied Chemistry, N-7034 Trondheim, Norway*
[c] *Statoil Research Centre, N-7005 Trondheim, Norway*

Received 31 March 1995; accepted 15 May 1995

The influence of water on alumina-supported cobalt catalysts has been studied. The deactivation of supported Co catalysts was studied in a fixed-bed reactor using synthesis gas feeds containing different concentrations of water vapour. Supporting model studies were carried out using H_2O/H_2 feeds in conjunction with XPS and gravimetry. Rapid deactivation occurs on Re-promoted Co/Al_2O_3 catalysts when $H_2/CO/H_2O$ feeds are used, whereas unpromoted Co/Al_2O_3 shows more stable activity. The results from the gravimetric studies suggest that only a small fraction of the bulk cobalt metal initially present reoxidizes to cobalt oxide during reaction. However, the XPS results indicate significant reoxidation of surface cobalt atoms or highly dispersed cobalt phases, which is likely to be the cause of the observed deactivation. Rhenium is shown to have a marked effect on the extent of reoxidation of alumina-supported cobalt catalysts.

Keywords: Fischer–Tropsch synthesis; cobalt catalysts; deactivation; oxidation; reduction; promoters; rhenium

1. Introduction

The Fischer–Tropsch synthesis is an attractive possibility for conversion of natural gas into high quality liquid fuels. Improved Fischer–Tropsch technology has been demonstrated in commercial [1] and demonstration scale [2] applications. Due to its low water–gas shift activity, good activity / selectivity properties and relatively low price, cobalt is the choice of catalytic metal for natural gas conversion via Fischer–Tropsch synthesis.

In fixed-bed processes, relatively low conversions per pass (high recycle ratios)

---

[1] To whom correspondence should be addressed.

are used to control the highly exothermic Fischer–Tropsch reaction. In contrast, the more favorable heat transfer properties of slurry reactors offer the possibility of operating at high conversions [3]. In the cobalt-catalyzed Fischer–Tropsch reaction, oxygen is mainly rejected as water, and this will generate high partial pressures of water at the reactor exit. As a consequence of extensive back-mixing in large scale slurry reactors, high water concentrations and low reactant concentrations will exist throughout the entire reactor. In the commercial iron-catalyzed Fischer–Tropsch synthesis in fixed-bed (Arge) reactors it is known that the catalyst bed becomes progressively deactivated towards the reactor exit as a result of oxidation of iron by CO_2 and H_2O [4]. Conversion of cobalt carbide into cobalt oxide in CO hydrogenation has been shown to be thermodynamically possible at low temperatures in the special case where the water–gas shift and methanation reactions are in equilibrium [5], while formation of cobalt oxide from metallic cobalt is not favored under Fischer–Tropsch reaction conditions [6]. However, supported cobalt particles or surface layers may behave differently and it has been shown that a cobalt/manganese oxide catalyst lost approximately 50% of its Fischer–Tropsch activity while the water–gas shift activity increased after treatment with water and synthesis gas [7].

The influence of (noble) metal promoters (Re, Pt, Ru) on the catalytic properties of Al_2O_3 and SiO_2 supported cobalt catalysts has been documented in several cases [8–14]. In this paper we describe the influence of water on Al_2O_3 supported cobalt catalysts with emphasis on the role of metal promoters.

2. Experimental

2.1. CATALYST PREPARATION

Alumina-supported cobalt catalysts with 18–30 wt% cobalt loading were prepared by incipient wetness impregnation with aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$. Rhenium containing catalysts were prepared by coimpregnation of $Co(NO_3)_2 \cdot 6H_2O$ and $HReO_4$. The γ-alumina supports used were Vista-B (from Vista Chemicals), 5300 (from Harshaw) and Puralox (from Condea). Some catalysts also contained a small amount of a mixture of rare earth oxides (designated RE, supplied as nitrates under the trade name Molycorp 5247), containing (after calcination) approximately 66% of La_2O_3 and the remainder consisting of other rare earth oxides. RE containing catalysts were prepared by coimpregnation of the Co, Re and RE salts. The catalysts were dried in air overnight at 393 K before calcination in air at 573 K for 2 h. Further pretreatment was done in situ.

2.2. CATALYST CHARACTERIZATION

Cobalt metal dispersions were estimated by temperature programmed desorption (TPD) of H_2 adsorbed during cooling of prereduced (623 K, 14–16 h) catalysts in flowing H_2 from 493 K to ambient temperature. After removal of gas-phase H_2 by purging with Ar, the amount of H_2 adsorbed was determined by TPD (10 K/min to 748 K) in Ar.

Temperature programmed reduction (TPR) experiments were performed in a quartz microreactor heated by an electrical furnace. The maximum temperature was 1203 K, and the samples were studied at a heating rate of 10 K/min in a mixture consisting of 7% H_2 in Ar. H_2-consumption was measured by analyzing the effluent gas by a thermal conductivity detector. Calibration was done by reduction of Ag_2O powder.

2.3. KINETIC EXPERIMENTS

The kinetic measurements were carried out in a 10 mm i.d. stainless steel fixed-bed reactor. 0.5–2 g of catalyst (38–75 μm particle size) was diluted with an inert material (non-porous SiC) in a 1 : 5 or 2 : 5 weight ratio (depending on the catalyst activity) to minimize temperature gradients. The catalyst was reduced in flowing H_2 at atmospheric pressure at the desired temperature for 16–18 h (heating rate from ambient temperature: 1 K/min). After reduction, the catalysts were cooled to 453 K in flowing H_2 and purged with He before increasing the pressure to the desired level and switching to a feed mixture containing 50 mol% synthesis gas with $H_2/CO = 2$ and balance inert gas ($N_2 + He$). The reaction temperature was then slowly increased to the desired initial reaction temperature (in the range 463–493 K). On-line GC samples were taken at regular intervals and analyzed for N_2, CO, CO_2 and C_{1+} hydrocarbons on a HP 5890 gas chromatograph equipped with thermal conductivity (TCD) and flame ionization detectors (FID). N_2 (used as an internal standard), CO, CH_4 and CO_2 were analyzed on the TCD and separated by a Carbosieve packed column. C_{1+} products were separated by a 0.53 mm i.d. GS-Q capillary column and detected on the FID. Space velocity was varied to give 10–30% CO conversion. High water partial pressures were obtained by replacing He with an equal flow of steam, generated by adding liquid water (supplied by a Hi-Tec liquid flow controller) to a vaporizer kept at ca. 573 K before mixing with the synthesis gas feed immediately before the reactor inlet.

2.4. GRAVIMETRIC EXPERIMENTS

Reduction and reoxidation experiments were performed in a Sartorius 4436 high pressure microbalance [15]. Ca. 0.5 g of catalyst (300–425 μm particle size) was placed in a stainless steel perforated basket and hung from one arm of the microbalance by a quartz fibre. The catalyst basket was placed inside a 21 mm i.d. stainless steel reactor connected to the microbalance and a gas supply system. Before reduction, the catalyst was dried for 24 h at a temperature 50 K higher than the reduction temperature to ensure minimal weight losses due to removal of water from the catalyst during reduction. After cooling to ambient temperature, the catalyst was reduced in flowing H_2 (1 K/min to 623 K, 16 h hold time). After reduction, the temperature was adjusted to 523 K and a feed consisting of H_2, He and H_2O (as steam) was added to the reactor for a period of 16–17 h. After H_2O treatment, the catalyst was dried again at 673 K for approximately 24 h. The total pressure and the feed composition were varied in different experiments to study the effect of water partial pressure and the H_2O/H_2 ratio.

2.5. X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

XPS studies were conducted in a VG Escalab MkII instrument using a non-monochromatic Al Kα source (1486.6 eV). All spectra were acquired at 20 eV pass energy, giving an overall resolution of approximately 1 eV. Binding energies were referenced to the Al 2p peak at 74.5 eV. Samples were prepared as pressed powders placed in a 12 mm sample holder. An integrated high pressure pretreatment cell allowed the catalyst samples to be pretreated and subsequently moved to the analysis chamber without exposure to air. After XPS analysis of the sample in the unreduced state, the catalyst was reduced in flowing H_2 at the desired temperature (in the range 623–823 K). After reduction of the catalyst, the cell was evacuated and the sample was analyzed in the reduced state. The catalyst was then moved back to the pretreatment cell and exposed to a feed mixture containing different amounts of H_2, H_2O (as steam) and inert gas (Ar). Pressure and temperature were varied in the range 1–20 bar and 473–513 K. After treatment, the catalyst was again analyzed by XPS.

3. Results

3.1. CO HYDROGENATION EXPERIMENTS

By addition of water (steam) to the feed in a conventional fixed-bed reactor during Fischer–Tropsch synthesis, high conversions can be simulated without using long residence times. The combination of low conversion and steam addition also results in a flat axial water concentration profile in the reactor, thus simulating the uniform bulk concentrations expected in large scale slurry reactors. The synthesis gas/water feeds used in this study result in reactor inlet conditions corresponding to between 55 and 75% conversion. The inlet partial pressure of reactants ($H_2 + CO$) was kept constant during periods without water addition by the use of a diluent (He).

Fig. 1a shows that the catalyst was deactivating relatively slowly before water was added to the feed, but the presence of high water partial pressures caused rapid deactivation of the Re-promoted catalysts to less than 50% of the initial activity. Virtually no further deactivation was observed after the water had been removed

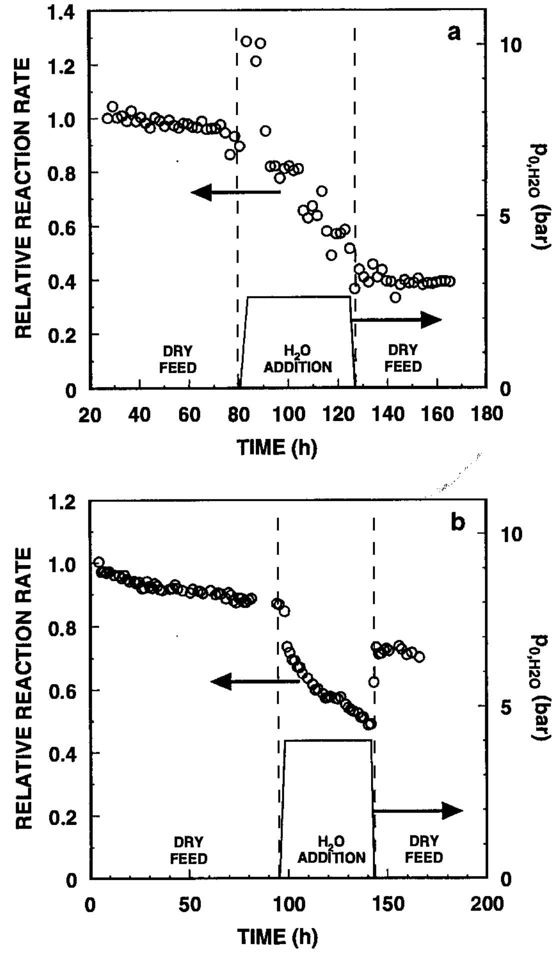

Fig. 1. Observed reaction rate relative to the initial rate for hydrocarbon formation as a function of time during simulated high conversion conditions. p_{0,H_2O} = partial pressure of water at reactor inlet. Feed composition: 50 mol% H_2 + CO, $H_2/CO = 2$, balance N_2 + He or N_2 + He + H_2O. CO conversion before addition of water: 20–28%. (a) Catalyst: 21% Co–1% Re/γ-Al_2O_3 (Puralox). $T = 483$ K, $P = 13$ bar. (b) Catalyst: 20% Co/γ-Al_2O_3 (Vista-B). $T = 493$ K, $P = 8$ bar.

from the feed. The initial increase in the reaction rate during the first 2–4 h after the addition of water (fig. 1a) is a feature that is often observed in these systems. However, this phenomenon and its magnitude appear to be somewhat inconsistent from experiment to experiment. No increase in the reaction rate is observed upon water addition for the unpromoted Co catalyst. It can be mentioned that significant improvements in reaction rate as a result of water addition have been reported also for other cobalt systems, including bulk cobalt catalysts [16].

Some deactivation is also observed on the unpromoted Co/Al_2O_3 catalyst, but this catalyst is still considerably more stable than its Re-promoted analog (fig. 1b).

The initial activity of the unpromoted catalysts is also lower compared to Re-promoted catalysts [8,10]. Some of the drop in the reaction rate is recovered immediately after removing water from the feed. This may be a result of a reversible inhibition effect (rather than deactivation) on the kinetics as described on iron based catalysts [17]. Comparing reaction rates before and after water addition should therefore give the most reliable estimate of the extent of deactivation.

It is known that the nature of the support and the presence of metal promoters can have a significant influence on the reduction properties of supported cobalt catalysts [8–10,12–14,18]. Al_2O_3 supported cobalt catalysts are generally more difficult to reduce than, e.g., SiO_2 or TiO_2 supported catalysts, due to the strong interaction between the Al_2O_3 support and the cobalt oxide phases. Metal promoters like Re and Pt are known to increase the reducibility of Al_2O_3 supported catalysts [8–10]. Typical examples of TPR profiles for Re-promoted and unpromoted Co/Al_2O_3 are shown in fig. 2, illustrating the significant shift in reduction temperatures for the high-temperature peak. As a consequence of the pronounced influence of noble metal promoters on the reduction behavior of Co/Al_2O_3, it was not unreasonable to expect some effect of Re also on the reverse reaction. Water-induced reoxidation of metallic cobalt was therefore investigated as a possible cause of the observed deactivation.

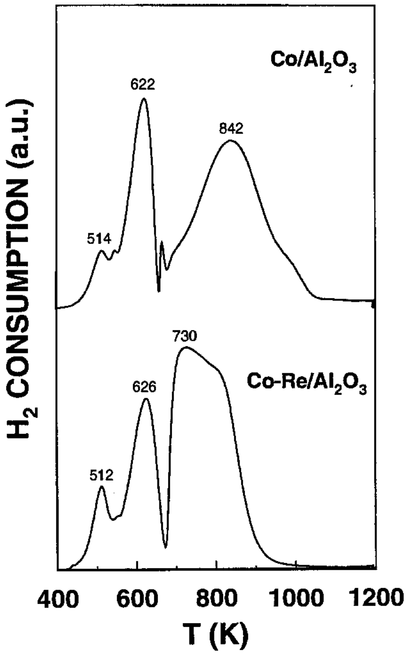

Fig. 2. TPR-profiles of 21% Co–1% Re/γ-Al_2O_3 and 18% Co/γ-Al_2O_3 described in table 1. (Heating rate: 10 K/min.)

3.2. MODEL STUDIES

A series of model experiments under non-reacting conditions with various H_2O/H_2 feeds was carried out. The validity of this approach for simulating Fischer–Tropsch deactivation conditions was confirmed by the low initial activity of reduced $CoRe/Al_2O_3$ treated with a H_2O/H_2 mixture before Fischer–Tropsch synthesis (fig. 3). Furthermore, this catalyst showed only slight deactivation when water was added to the feed during Fischer–Tropsch synthesis, and the final activity level at "dry" conditions (after shutting off the water feed) was approximately equal to the catalyst which had been reduced and deactivated by addition of water. (The horizontal (time) axis in fig. 3 has been slightly modified to allow plotting the data from the two experiments in the same figure. Both catalysts had been operated at 463 and 473 K for 60–70 h with stable activity before the time periods shown in fig. 3.)

The gravimetric studies indicated distinct differences between the behavior of unpromoted and Re-promoted Co/Al_2O_3 catalysts, although these studies are somewhat disturbed by the simultaneous rapid adsorption of water on the porous support during treatment with H_2O/H_2 (fig. 4a). Blank experiments with H_2O/He treatment of calcined (unreduced) catalysts and the support only, showed that the initial, rapid weight increase is caused by physical adsorption of water on the catalyst (fig. 4b). The higher surface area and pore volume of the support compared to

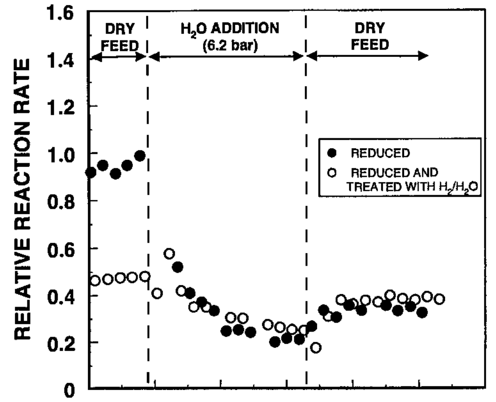

Fig. 3. Comparison of freshly reduced catalyst and catalyst treated with H_2O/H_2 after reduction. Relative reaction rate defined as the observed rate for hydrocarbon formation relative to the initial reaction rate for the freshly reduced catalyst. Catalyst: 20% Co–1% Re/γ-Al_2O_3 (Puralox). $T = 483$ K, $P = 13$ bar. Feed composition: 50 mol% $H_2 + CO$ ($H_2/CO = 2$), balance $N_2 + He$ or $N_2 + He + H_2O$. CO conversion before addition of water: 20–22%. Solid symbols: catalyst reduced at 723 K. Open symbols: catalyst reduced at 723 K and subsequently treated with a 3 : 2 : 1 $H_2O/H_2/He$ mixture at 483 K at 13 bar total pressure for ca. 24 h before CO hydrogenation.

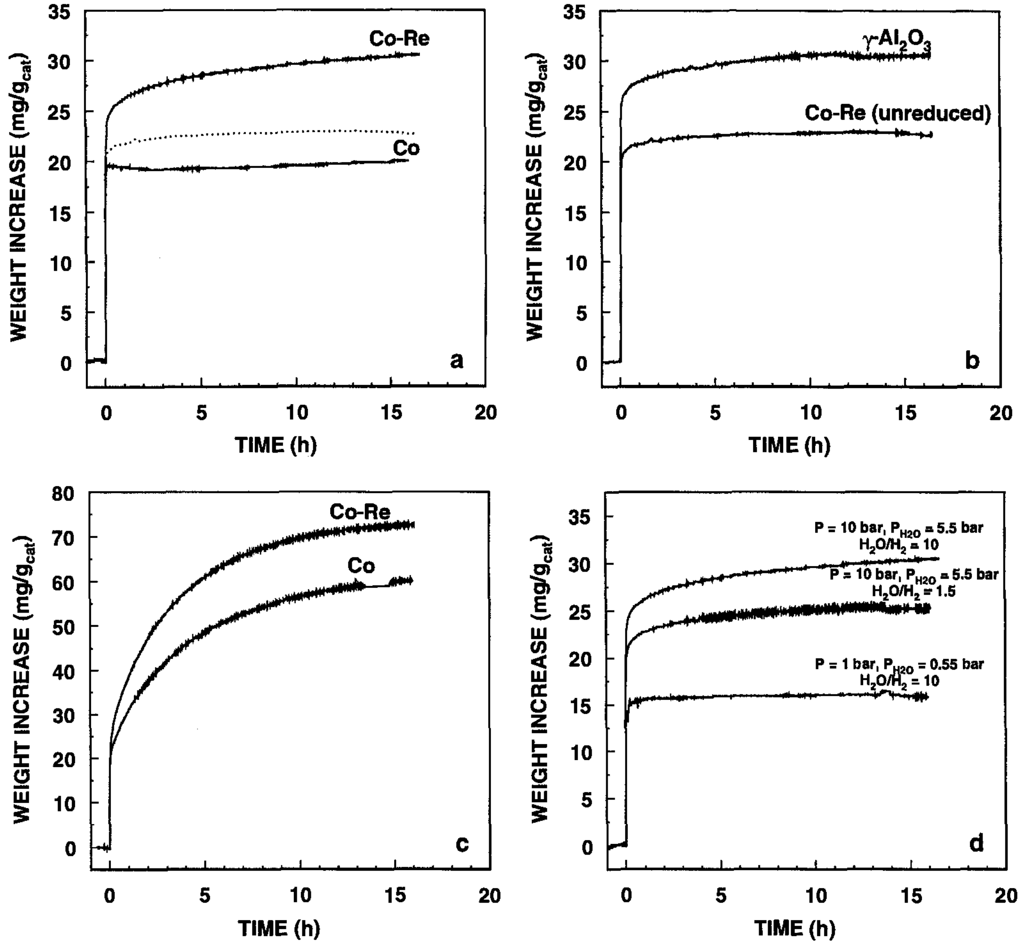

Fig. 4. Weight changes recorded by the microbalance during exposure of γ-Al_2O_3 (Puralox) supported catalysts to H_2O/H_2 or H_2O/He at 523 K. Catalyst composition: 21% Co–1% Re (designated Co–Re) and 18% Co (designated Co). (a) Reduced Co and Co–Re ($P = 10$ bar, $H_2O/H_2 = 10$, $p_{H_2O} = 5.5$ bar, balance He). Dotted line: unreduced Co–Re in H_2O/He ($P = 10$ bar, $p_{H_2O} = 5.5$ bar, balance He). (b) γ-Al_2O_3 and unreduced Co–Re in H_2O/He ($P = 10$ bar, $p_{H_2O} = 5.5$ bar, balance He). (c) Reduced Co and Co–Re in H_2O/He (conditions as in (b)). (d) Exposure of reduced Co–Re/Al_2O_3 to various H_2O/H_2 mixtures.

the calcined cobalt catalyst (table 1) explain the difference in the weight curves for these two materials. However, the physical adsorption equilibrium is quickly established, and we propose that the subsequent, slower weight increase observed on CoRe/Al_2O_3 is caused by reoxidation of metallic cobalt. Drying of the water-treated catalyst to constant weight at 673 K showed that the weight difference between the reduced catalyst and the H_2O-treated and dried catalyst (denoted ΔW_2) was in good agreement with the weight increase corrected for water adsorption on the unreduced catalyst (ΔW_1) (fig. 5 and table 2). Thus, it was established that the

Table 1
Characterization of γ-Al_2O_3 (Puralox) supported cobalt catalysts

Catalyst	BET area [a] (m^2/g)	Pore volume [a] (cm^3/g)	H_{ads} : Co [b]
18% Co/γ-Al_2O_3	138	0.48	0.038
21% Co–1% Re/γ-Al_2O_3	138	0.45	0.066
γ-Al_2O_3	174	0.90	–

[a] From N_2 adsorption at 77 K.

[b] From TPD of H_2 adsorbed between 493 and 298 K after reduction at 623 K, assuming adsorption only on Co atoms.

weight increase observed on reduced cobalt catalysts was not caused by reversible water adsorption on the metal.

If reduced CoRe/Al_2O_3 or Co/Al_2O_3 catalysts are exposed to a H_2O/He mixture (without H_2), both catalysts show large weight increases, corresponding to significant reoxidation of cobalt (fig. 4c and table 2). The presence of H_2 in the feed, even in small amounts ($H_2O/H_2 = 10$), decreases the rate and the extent of weight increase for both catalysts. On the unpromoted Co/Al_2O_3 catalyst, a H_2O/H_2 ratio of 10 resulted in an essentially flat weight curve after equilibration with water, whereas a continuing weight increase was observed on CoRe/Al_2O_3 (fig. 4a). This indicates that the tendency for reoxidation is different for these two catalysts.

Using the same H_2O partial pressure (5.5 bar) but a lower H_2O/H_2 ratio (1.5) resulted in a smaller weight increase, only marginally higher than the baseline curve (unreduced CoRe/Al_2O_3 in H_2O/He) (fig. 4d). The extent of reoxidation evidently depends on the composition and the pressure of the feed gas, and increases with

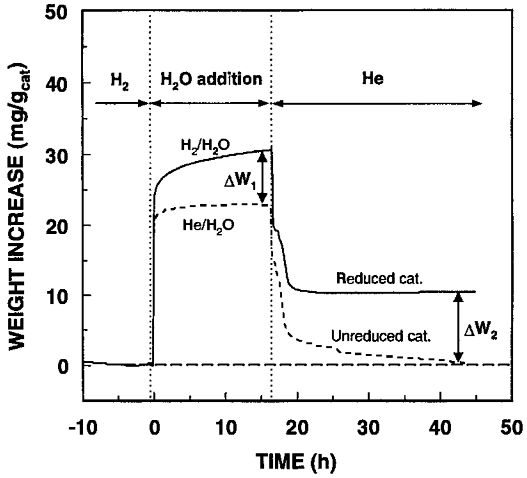

Fig. 5. Illustration of principle for the microbalance experiments ($P = 10$ bar and $p_{H_2O} = 5.5$ bar during H_2O treatment). Catalyst: 21% Co–1% Re/γ-Al_2O_3 (Puralox). Solid curve: reduced catalyst in 10/1 H_2O/H_2. Dashed curve: unreduced CoRe in H_2O/He.

Table 2
Results from gravimetric study of H_2O treatment of Al_2O_3 (Puralox) supported cobalt catalysts after reduction at 623 K. Catalyst composition: 21% Co–1% Re (designated Co–Re) and 18% Co (designated Co). Conditions: $T = 523$ K, $P = 10$ bar

Catalyst	p_{H_2O} (bar)	p_{H_2} (bar)	ΔW_1 [a] (mg/g)	ΔW_2 [b] (mg/g)	O : Co[c]
Co	5.5	0[d]	37.4	34.1	0.77
Co–Re	5.5	0[d]	49.8	45.4	0.87
Co	5.5	0.55	−2.7	−0.7	<0
Co–Re	5.5	0.55	8.1	10.4	0.14
Co–Re	5.5	3.67	2.6	7.3	0.5

[a] Weight increase after ca. 17 h of H_2O treatment, corrected for physical adsorption of water on the catalyst by use of unreduced $CoRe/Al_2O_3$ in H_2O/He as a baseline (see fig. 5 for further illustration).

[b] Weight difference between reduced catalyst and H_2O-treated catalyst dried in flowing He for ca. 24 h (see fig. 5 for further illustration).

[c] mol O/mol Co_{tot} based on ΔW_1.

[d] H_2O/He mixture.

increasing H_2O partial pressure and H_2O/H_2 ratio. The weight curve obtained at 1 bar cannot be compared directly with the curves at 10 bar total pressure, since the amount of physically adsorbed water will be different. However, the absence of a significant weight increase after equilibration with water indicates a very limited extent of reoxidation.

XPS was used for studying the possible oxidation of surface cobalt atoms, in order to assess the impact of reoxidation on catalytic activity. XPS spectra of Al_2O_3 supported cobalt catalysts are shown in figs. 6–9. In the series of XPS experiments shown here, catalysts containing 1 wt% RE (rare earth oxide mixture) have been used. Although this precludes direct comparison of results from the various studies, we have generally experienced that this low level of RE loading does not influence the deactivation behavior significantly. Re in the catalyst samples could not be detected by the XPS.

In the unreduced state, a peak at 781 eV is assigned to various cobalt oxides, and is accompanied by a shake-up satellite at 786 eV representing Co^{2+}. After reduction in H_2, the XPS peak representing cobalt metal is observed at 778 eV, but the oxide peak at 781 eV is still clearly visible in all of the spectra shown in figs. 6–9. The $Co^0/Co^{2+/3+}$ intensity ratio increases with increasing reduction temperature and increasing cobalt loading. In general, the extent of reduction measured by XPS (given as the intensity ratio $Co^0/(Co^{2+/3+} + Co^0)$) is significantly lower than estimated by bulk methods. In addition, the influence of Re on the reducibility, which is well documented by TPR and other bulk methods (fig. 3 and refs. [8,10]), is not easily observed in the XPS spectra (fig. 9). These effects are most likely caused by multiple cobalt oxide phases with widely different dispersion, ranging from large Co_3O_4 crystallites to an atomically dispersed surface cobalt aluminate phase. The

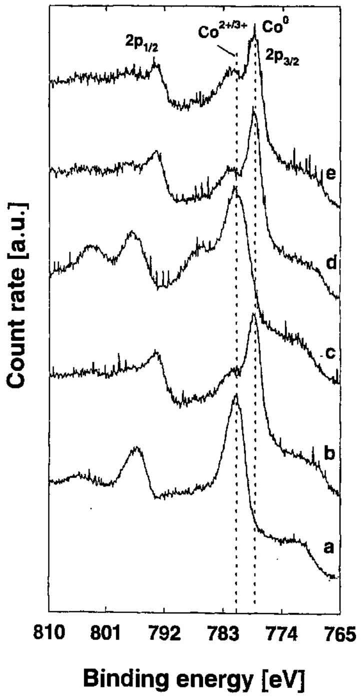

Fig. 6. XPS spectra of 30% Co–1.5% Re–1% RE/γ-Al_2O_3 (5300). (a) Calcined (unreduced). (b) Reduced in H_2 at 823 K. (c) Exposed to ~ 1 vol% H_2O in Ar for 2 h (P = 1 bar, T = 473 K) (after (b)). (d) Rereduced at 723 K for 1.5 h (after (c)). (e) Exposed to ~ 1 vol% H_2O in H_2 for 14 h (P = 1 bar, T = 473 K) (after (d)).

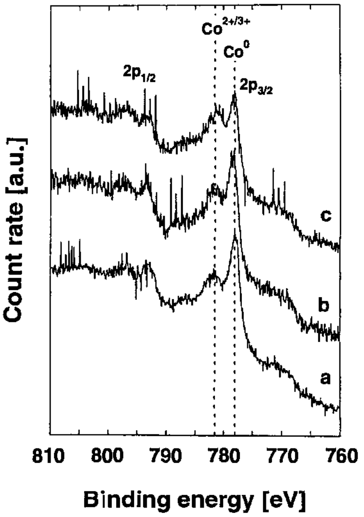

Fig. 7. XPS spectra of 30% Co–1.5% Re–1% RE/γ-Al_2O_3 (5300). (a) Reduced in H_2 at 723 K. (b) Exposed to ~ 10 vol% H_2O in H_2 for 18 h (P = 1 bar, T = 473 K) (after (a)). (c) Exposed to ~ 50 vol% H_2O in H_2 for 22 h (P = 1 bar, T = 473 K) (after (b)).

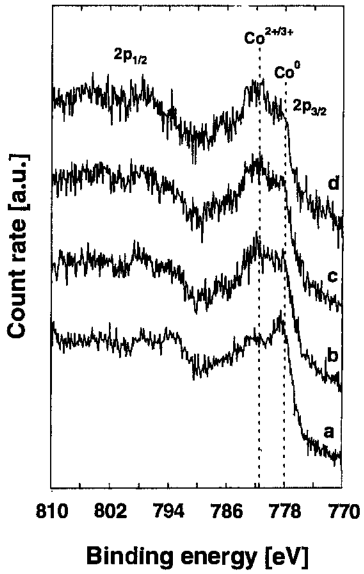

Fig. 8. Co 2p XPS spectra of 30% Co–1.5% Re–1% RE/γ-Al_2O_3 (5300). (a) Reduced in H_2 at 623 K. (b) Exposed to ~ 25 vol% H_2O in H_2 for 16 h ($P = 20$ bar, $T = 513$ K) (after (a)). (c) Treatment described in (b) continued for 20 h (total treatment time 36 h). (d) Treatment described in (b) continued for 68 h (total treatment time 104 h).

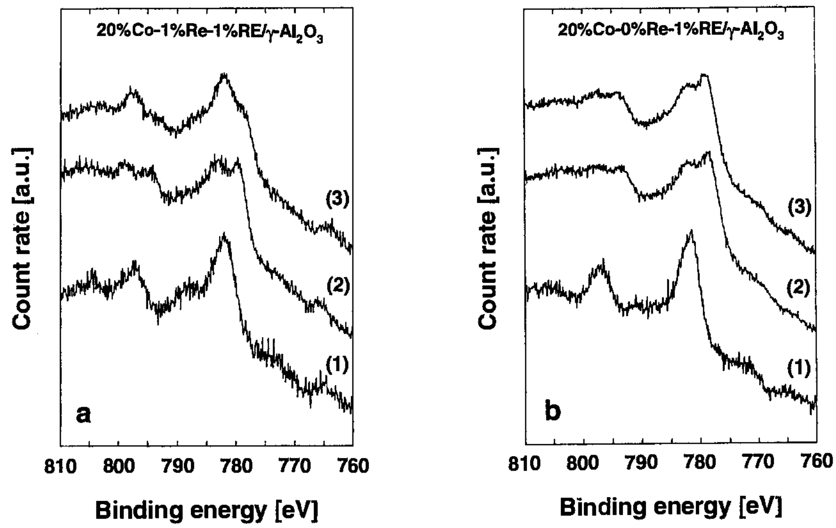

Fig. 9. Co 2p XPS spectra of γ-Al_2O_3 (Vista-B) supported cobalt catalysts. Lower curves (1): calcined. Middle curves (2): reduced at 723 K. Upper curves (3): Exposed to ~ 20 vol% H_2O in H_2 for 16–18 h ($P = 20$ bar, $T = 513$ K). (a) 20% Co–1% Re–1% RE/γ-Al_2O_3. (b) 20% Co–1% RE/γ-Al_2O_3.

latter phase is unreducible at the temperatures used in this study but will dominate the XPS spectrum in reduced Al_2O_3 supported catalysts due to the high dispersion. These conclusions are in agreement with previous work which has shown that the extent of cobalt reduction can be corrected for particle size effects in Co/Al_2O_3 catalysts by use of the Kerkhof–Moulijn model [19] for predicting XPS-intensities at monolayer coverage [20].

After reduction and treatment with various H_2O-containing mixtures, the Re-promoted Co/Al_2O_3 catalysts showed clear signs of reoxidation of cobalt metal to Co^{2+} or Co^{3+} (figs. 6–8). As shown in figs. 6–8, the extent of reoxidation depends on the partial pressure of water and the composition of the feed mixture. Without any H_2 in the feed, a virtually complete reoxidation of the surface occurs after a short time of exposure, even at atmospheric pressure and low water partial pressure ($\sim$ 20 mbar) (fig. 6). The growth of the satellite XPS peak at 786 eV indicates some formation of Co^{2+}. As shown in fig. 6, the catalyst was readily rereduced in H_2 after this treatment. Using the same water partial pressure in H_2 resulted in only slight indications of reoxidation, as shown by the small decrease in the $Co^0/Co^{2+/3+}$ intensity ratio. Increasing the water content of the pretreatment feed to 10 and 50 vol% at atmospheric pressure increased the tendency for reoxidation (fig. 7). At high pressure conditions (20 bar) and $H_2O/H_2 = 0.33$, reoxidation occurs to an even higher extent (fig. 8). The initial $Co^0/Co^{2+/3+}$ intensity ratios (after reduction) are different in figs. 6–8 due to different reduction temperatures. Estimating the extent of reoxidation by XPS is not straightforward, due to difficult deconvolution of the XPS peaks. It was also found that the Co^0/Al and $Co^0/(Co^0 + Co^{2+/3+})$ intensity ratios as indicators for reoxidation resulted in different estimates of surface reoxidation (table 3).

In a similar way as shown by the kinetic and gravimetric experiments, the tendency for reoxidation shown by XPS is strongly influenced by Re. In the case of the catalyst without Re, the XPS spectrum is hardly influenced by the H_2O/H_2-treatment (when compared to the reduced catalyst), whereas a significant reduction in the cobalt metal peak intensity occurs in the catalyst containing Re (fig. 9).

Table 3
XPS intensity ratios from H_2O treatment of 30% Co–1.5% Re–1% RE/γ-Al_2O_3 (5300)

Conditions	$I(Co^0/Al)$	$I(Co^0/(Co^0 + Co^{2+/3+}))$ (%)	Extent of reoxidation [a] (%)
reduced (623 K, 17 h)	0.32	32.6	–
1 : 3 H_2O/H_2 (20 bar, 513 K, 16 h)	0.17	26.2	47 (20)

[a] Defined as $[I(Co^0/Al)_{red} - I(Co^0/Al)_{ox}]/I(Co^0/Al)_{red}$, where the subscript "ox" refers to values measured after H_2O/H_2 treatment. The corresponding value for $Co^0/(Co^0 + Co^{2+/3+})$ is given in parentheses.

4. Discussion

The similarity between the observed deactivation behavior and the results of the model studies (XPS, gravimetry) suggests that reoxidation of cobalt metal to cobalt oxide plays an important role in the deactivation of Re-promoted, Al_2O_3 supported cobalt catalysts. In particular, the consistent difference in the behavior of unpromoted and Re-promoted Co/Al_2O_3 catalysts in all the studies supports this conclusion. The difference in the reoxidation/deactivation trends for unpromoted and Re-promoted Co/Al_2O_3 catalysts may be interpreted in terms of the influence of rhenium on the distribution of metallic and oxidic phases. Rhenium increases the reducibility of Co/Al_2O_3 (fig. 2) and the apparent dispersion (H_{ads} : Co) increases significantly from 0.038 to 0.066 (table 1). However, previous X-ray diffraction results for Co/Al_2O_3 and $CoRe/Al_2O_3$ catalysts have shown insignificant differences in Co_3O_4 particle size on calcined (unreduced) catalysts (typically 15–20 nm [9,10]).

It is well known that cobalt supported on Al_2O_3 consists of multiple oxide phases of different dispersion and reducibility. In temperature programmed reduction studies the large Co_3O_4 particles are readily reduced at temperatures close to the reduction temperature of bulk Co_3O_4 (550–650 K), whereas spinel $CoAl_2O_4$ formed by solid state reactions between cobalt and the support during calcination require reduction temperatures as high as 1200 K. $CoAl_2O_4$ can therefore be considered as virtually unreducible at practical reduction temperatures. Additional cobalt oxide phases, assigned to highly dispersed, amorphous overlayers of Co^{2+} and Co^{3+}, are reduced in the 700–1000 K range on unpromoted Co/Al_2O_3 catalysts [8,9,20–24]. The small peak at 512–514 K in fig. 2 is caused by reductive decomposition of residual nitrate on the catalyst [8]. At the reduction temperature used in the deactivation studies (623 K), the overlayer phases are not completely reduced to the metal in unpromoted Co/Al_2O_3 catalysts. In $CoRe/Al_2O_3$ the reduction temperature of these phases are shifted to lower temperatures by more than 100 K (fig. 2) and are more completely reduced after prolonged reduction at 623 K. The increase in H_{ads} : Co as a result of Re-promotion shown in table 1 is therefore to some extent a result of the reduction of additional cobalt oxide and the observed value is the average of a relatively poorly dispersed Co_3O_4 phase and the more highly dispersed cobalt oxide overlayers.

Thermodynamic calculations show that bulk cobalt metal will not reoxidize in H_2O/H_2 mixtures [6]. However, at high dispersions it is likely that the interaction between support and metal/metal oxides will lead to deviations from bulk behavior. It is likely that the observed deactivation and reoxidation trends for Re-containing catalysts are associated with the instability of the highly dispersed metallic cobalt phases formed by Re-assisted reduction of cobalt oxide overlayers. In addition, a direct influence of Re on reoxidation cannot be excluded if Re promotes reoxidation of metallic cobalt in a similar way as shown for the reduction of cobalt oxide. Discrimination between these two possible explanations is not possible from the present results.

The difference in the results obtained from bulk and surface sensitive techniques is emphasized. The gravimetric studies indicated a relatively small extent of bulk reoxidation of $CoRe/Al_2O_3$ at $H_2O/H_2 = 10$, and an even more modest effect at $H_2O/H_2 = 1.5$ (table 2). The latter conditions are probably more representative of the conditions used in the fixed-bed deactivation studies. In contrast, the XPS studies indicated significant reoxidation at $H_2O/H_2 = 0.33$ (table 3). Due to differences in pressures, H_2O/H_2 ratios, catalyst composition and the properties of the Al_2O_3 supports, the results from the model studies reported here are not directly comparable. In spite of this, the available data from kinetic studies and model studies suggests that surface oxidation or oxidation of highly dispersed phases occurs in H_2O/H_2 or $H_2O/H_2/CO$ mixtures, leading to deactivation of the catalysts.

5. Conclusions

Co/Al_2O_3 catalysts have been shown to deactivate in $H_2O/H_2/CO$ feeds, with Re-promoted catalysts showing the highest rate of deactivation. Model studies, using gravimetry and XPS, show that reoxidation of cobalt can occur in H_2O-containing mixtures. The extent of reoxidation depends on the partial pressure of water and the H_2O/H_2 ratio. Comparison of results from surface and bulk techniques suggests that surface oxidation or oxidation of highly dispersed cobalt phases are responsible for the observed deactivation.

Acknowledgement

The authors gratefully acknowledge Statoil for financial support and for the permission to publish these results.

References

[1] M.M.G. Senden, S.T. Sie, M.F.M. Post and J. Ansorge, in: *Chemical Reactor Technology for Environmentally Safe Reactors and Products*, eds. H.I. de Lasa, G. Dogu and A. Ravella (Kluwer, Dordrecht, 1992) p. 227.

[2] J.M. Hochman, G.C. Lahn, R.F. Bauman and B. Eisenberg, in: *Eurogas '92*, Proc. European Applied Research Conf. on Natural Gas, eds. A. Holmen, B.F. Magnussen and F. Steineke (Trondheim, 1992) A125.

[3] J.M. Fox, Catal. Rev. Sci. Eng. 35 (1993) 169.

[4] M.E. Dry, Catal. Lett. 7 (1990) 241.

[5] P.E. Højlund-Nielsen and J. Bøgild-Hansen, J. Mol. Catal. 17 (1982) 183.

[6] R.B. Anderson, in: *Catalysis*, Vol. IV, ed. P.H. Emmett (Rheinhold, New York, 1956).

[7] F.M. Gottschalk, R.G. Copperthwaite, M. van der Riet and G.J. Hutchings, Appl. Catal. 38 (1988) 103.
[8] A. Hoff, E. Blekkan, A. Holmen and D. Schanke, *Proc. 10th Int. Congr. Catal.* (1992) p. 2067.
[9] D. Schanke, S. Vada, E.A. Blekkan, A.-M. Hilmen, A. Hoff and A. Holmen, J. Catal., accepted.
[10] S. Vada, A. Hoff, E. Ådnanes, D. Schanke and A. Holmen, Topics in Catalysis 2 (1995) 155.
[11] S. Eri, J.G. Goodwin Jr., G. Marcelin and T. Riis, US Patent 4,880,763 to Statoil (1989).
[12] L. Guczi, T. Hoffer, Z. Zsoldos, S. Zyade, G. Maire and F. Garin, J. Phys. Chem. 95 (1991) 802.
[13] L. Bruce, M. Hoang, A.E. Hughes and T.W. Turney, Appl. Catal. A 100 (1993) 51.
[14] E. Iglesia, S.L. Soled, R.A. Fiato and G.H. Via, J. Catal. 143 (1993) 345.
[15] A. Holmen, D. Schanke and G. Sundmark, Appl. Catal. 50 (1989) 211.
[16] C.J. Kim, US Patent 5,227,407 to Exxon Res. Eng. Co. (1993).
[17] C.N. Satterfield, R.T. Hanlon, S.E. Tung, Z.-M. Zou and G.C. Papaefthymiou, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 407.
[18] A. Lapidus, A. Krylova, V. Kazanskii, V. Borovkov, A. Zaitsev, J. Rathousky, A. Zukal and M. Jancalkova, Appl. Catal. 73 (1991) 65.
[19] F.P.J.M. Kerkhof and J.A. Moulijn, J. Phys. Chem. 83 (1979) 1612.
[20] M.A. Stranick, M. Houalla and D.M. Hercules, J. Catal. 103 (1987) 151.
[21] P. Arnoldy and J.A. Moulijn, J. Catal. 93 (1985) 38.
[22] H.-C. Tung, C.-T. Yeh and C.-T. Hong, J. Catal. 122 (1990) 211.
[23] W.-J. Wang and Y.-W. Chen, Appl. Catal. 77 (1991) 223.
[24] Y. Okamoto, T. Adachi, K. Nagata, M. Odawara and T. Imanaka, Appl. Catal. 73 (1991) 249.