Available online at www.sciencedirect.com

Catalysis Today 100 (2005) 343–347

www.elsevier.com/locate/cattod

Fischer–Tropsch synthesis over Re-promoted Co supported on Al_2O_3, SiO_2 and TiO_2: Effect of water

S. Storsæter [a], Ø. Borg [a], E.A. Blekkan [a], B. Tøtdal [b], A. Holmen [a,*]

[a] Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway
[b] Department of Physics, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway

Abstract

The activity and selectivity of rhenium promoted cobalt Fischer–Tropsch catalysts supported on Al_2O_3, TiO_2 and SiO_2 have been studied in a fixed-bed reactor at 483 K and 20 bar. Exposure of the catalysts to water added to the feed deactivates the Al_2O_3 supported catalyst, while the activity of the TiO_2 and SiO_2 supported catalysts increased. However, at high concentrations of water both the SiO_2 and TiO_2 supported catalyst deactivated. Common for all catalysts was an increase in C_{5+} selectivity and a decrease in the CH_4 selectivity by increasing the water partial pressure. The catalysts have been characterized by scanning transmission electron microscope (STEM), BET, H_2 chemisorption and X-ray diffraction (XRD).

Keywords: Fischer–Tropsch synthesis; Cobalt; Rhenium; Support; Water

1. Introduction

Water is produced during Fischer–Tropsch synthesis and will always be present in varying quantities during reaction. Different results have been reported on the effect of water on the Fischer–Tropsch activity for cobalt catalysts. Deactivation has been observed for Re-promoted as well as unpromoted Co/Al_2O_3 catalysts [1]. For Co supported on SiO_2 increased activity [2], rapid deactivation [3], as well as activity decrease [4] have been observed. For Co/TiO_2 and $CoRe/TiO_2$ catalysts water has been reported both to increase the activity [5] and decrease the activity [6]. Water apparently influences the activity of various Co catalysts in different ways, but water increases the C_{5+} selectivity and decreases the CH_4 selectivity for all Co catalysts [1,2,5].

The apparently contradictory observations on the effect of water on the performance of Co catalyst using different supports have triggered our interest. Due to different conditions used in earlier studies it is difficult to compare the catalysts directly, and differences may be due to different operation conditions. This forms the basis for the present work, where the effect of water on the activity and selectivity for three cobalt catalysts using different supports has been studied under the same conditions.

2. Experimental

2.1. Catalyst preparation and characterization

Catalysts containing 12 wt.% Co and 0.5 wt.% Re were prepared by incipient wetness coimpregnation of different supports (γ-Al_2O_3, SiO_2 and TiO_2) with aqueous solutions of $Co(NO_3)_2\cdot 6H_2O$ and $HReO_4$. The catalysts were dried in air at 393 K for 3 h, before calcination in air at 573 K for 16 h. Before testing the catalysts were sieved to 53–90 μm. H_2 adsorption isotherms were measured at 313 K in a standard volumetric glass apparatus (Micromeritics ASAP 2010). The catalysts were reduced in situ (623 K for 10 h) before measurement. The dispersions were calculated as described elsewhere [1].

BET surface area measurements were performed in a Carlo Erba Multisampler 1900 apparatus by adsorption of nitrogen. The samples were dried at 423 K prior to analysis.

---

* Corresponding author. Tel.: +47 73594151; fax: +47 73595047.
E-mail address: holmen@chemeng.ntnu.no (A. Holmen).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.09.068

X-ray diffraction (XRD) studies were performed in a Philips PW 1710 spectrometer using monochromatic Cu Kα radiation. The measurements were done on calcined catalysts. Metallic Co particle size was calculated as explained by Hilmen et al. [1].

The catalysts were examined in a dedicated scanning transmission electron microscope (STEM) (VG HB-603) using a Si(Li) detector. Unreduced catalysts were analyzed and the samples were crushed before they were sprinkled on a "holey carbon" film supported on Ti grids.

2.2. Activity and selectivity measurements

The experiments were carried out in a stainless steel fixed-bed reactor surrounded by an aluminium jacket. One to two grams of catalyst diluted with inert SiC (75–150 μm) were loaded to the reactor and reduced in flowing hydrogen at atmospheric pressure at 623 K for 16 h (heating rate: 1 K/min). The temperature was then reduced to 443 K, the reactor purged with helium for 1 h, before increasing the pressure to 20 bar. Synthesis gas (200 ml/min) with a H_2/CO ratio of 2.1 (and about 3% N_2) was then fed to the reactor, and the temperature was slowly increased to 483 K. On-line GC samples of the gaseous products after condensation of water, wax and heavy hydrocarbons in traps, were taken at regular intervals and analyzed for H_2, N_2, CO, CO_2 and C_1–C_9 hydrocarbons. The space velocity was adjusted to give a conversion of about 40–45%. The activity is reported as the reaction rate to hydrocarbons assuming a plug flow reactor and first order reaction. Steam was added by feeding water (distilled) by a liquid flow controller into a vaporizer kept at 648 K. The steam generated was mixed with synthesis gas close to the reactor inlet. The water was degassed with helium for at least 16 h prior to use.

3. Results and discussion

3.1. Catalyst characterization

Catalyst dispersion and particle size for the three catalysts together with BET surface areas are shown in Table 1. The dispersion for the $CoRe/Al_2O_3$ catalyst calculated from chemisorption is almost twice as high as for the $CoRe/SiO_2$ catalyst, and about four times higher than for the $CoRe/TiO_2$ catalyst. The same trend can be seen from the dispersions calculated from XRD. The lower dispersion from XRD compared to chemisorption for the Al_2O_3 supported catalyst is due to the fact that XRD does not measure the smallest particles and the ability of XRD to detect various cobalt phases [7]. For TiO_2 supported noble metal catalysts strong metal-support interactions (SMSI) are observed when the reduction temperature is above 573 K [8]. In this study the $CoRe/TiO_2$ catalyst is reduced at 623 K. SMSI complicates the determination of the Co surface by hydrogen adsorption by diminishing the hydrogen adsorption capacity by site blockage, which could explain the discrepancy. XRD measurements were done on oxide catalysts instead of on reduced catalysts as in volumetric chemisorption.

The STEM pictures shown in Fig. 1 were recorded on calcined catalysts. XRD measurements (not shown here) confirm that the cobalt oxide exists as Co_3O_4. In the case of the $CoRe/Al_2O_3$ catalyst (Fig. 1a and b) and the $CoRe/SiO_2$ catalyst (Fig. 1c and d), it seems like Co_3O_4 deposits are agglomerated in form of large spherical structures, where the spherical structures are largest for the SiO_2 supported catalyst. The distribution of the Co_3O_4 phase on Al_2O_3 and SiO_2 is as reported earlier for high surface area SiO_2 supports [9]. Co_3O_4 is more uniformly distributed on TiO_2, but still it agglomerates into drop-like structures as observed for low surface area SiO_2 [9]. Even at high magnification it is not possible to confirm the particle sizes observed by XRD and chemisorption. Due to limited contrast it is difficult to distinguish between Co_3O_4 and the support. The difficulty in distinguishing the Co_3O_4 from the Al_2O_3 or SiO_2 is in line with earlier findings [10]. Element mapping using energy dispersive spectrometry (EDS) (not shown here) was used to discern the Co particles from the support. On the other hand it was easier to distinguish Co_3O_4 from TiO_2 (at high magnification).

3.2. Effect of water on the activity and selectivity for Co supported catalysts

The activity and selectivity of the catalysts were tested during five periods, using four different conditions. In period I, 200 N ml/min of synthesis gas was fed to the reactor, in

Table 1
Characterization results

Catalyst	Dispersion (H_2-ads.) (%)[a]	Particle size (H_2-ads.) (nm)[b]	Particle size (XRD) (nm)[c]	Dispersion (XRD) (%)[d]	Surface area (m^2/g)[e]
$CoRe/Al_2O_3$	10.2	9.4	11.5	8.3	155
$CoRe/SiO_2$	5.8	16.4	15.8	6.1	302
$CoRe/TiO_2$	2.4	40.0	56.9	1.7	12

[a] Cobalt metal dispersion from H_2 chemisorption at 313 K, assuming adsorption on Co atoms only.
[b] Cobalt metal particle size calculated from H_2 chemisorption using d(Co) = 96/D.
[c] Cobalt metal particle size calculated from XRD of calcined catalyst, using $d(Co) = 0.75d(Co_3O_4)$.
[d] Cobalt metal dispersion calculated from XRD data, using the relation D = 96/d(Co).
[e] BET surface area.

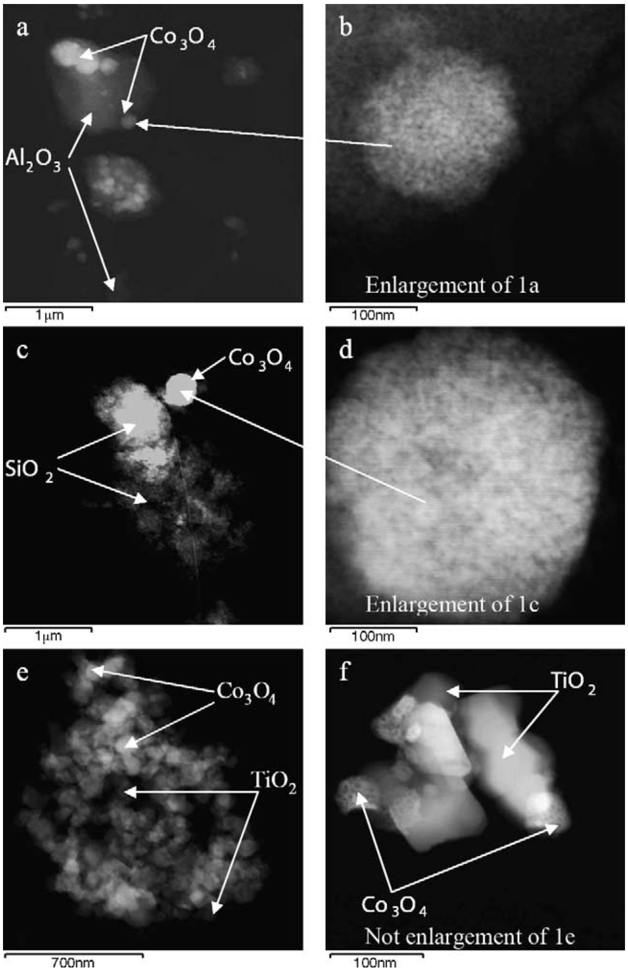

Fig. 1. STEM images of (a and b) CoRe/Al_2O_3 at magnification 20,000 and 200,000 respectively; (c and d) CoRe/SiO_2 at magnification 20,000 and 200,000, respectively; and (e and f) CoRe/TiO_2 at magnification 50,000 and 200,000, respectively.

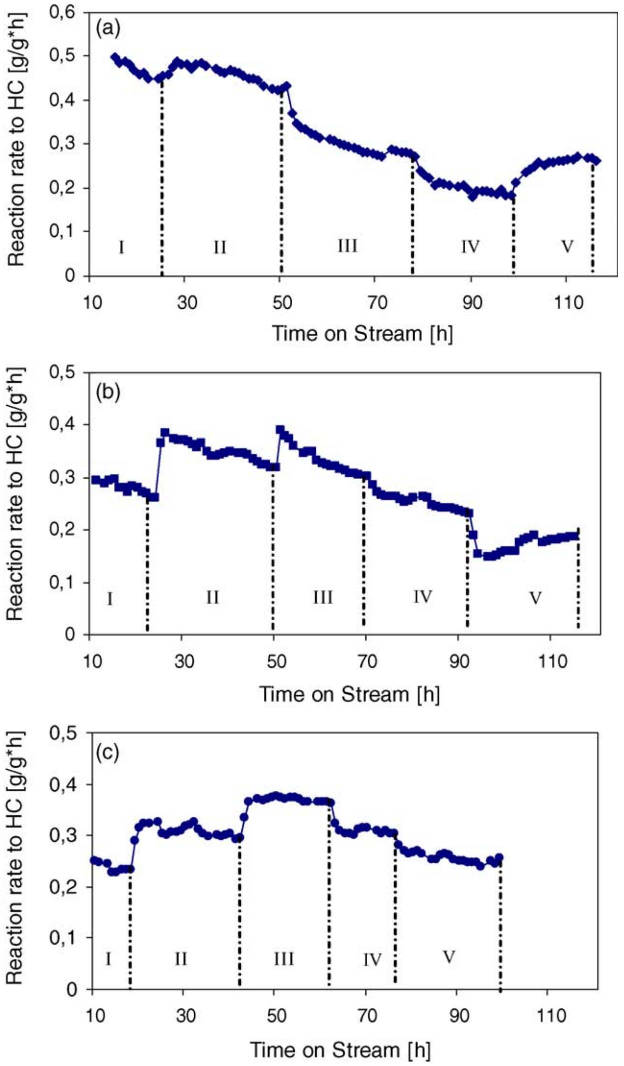

Fig. 2. Observed reaction rate for formation of hydrocarbons as a function of time on stream for CoRe/Al_2O_3 (a), CoRe/SiO_2 (b), and CoRe/TiO_2 (c) at P_{Tot} = 20 bar, T = 483 K, H_2/CO = 2.1.

period II, the GHSV was adjusted to give a CO conversion of about 40–45%, water (inlet $P_{H_2O}/P_{H_2} = 0.38$) was added to the reactor during period III, the amount of water fed was then increased (inlet $P_{H_2O}/P_{H_2} = 0.76$) in period IV, and in period V, the same conditions as in period II were used (before water addition). The results shown in Fig. 2 indicate that the three catalysts behave differently in presence of water.

In the case of CoRe/Al_2O_3 the reaction rate for formation of hydrocarbons (g hydrocarbons formed/g h) as a function of time on stream during the five periods is shown in Fig. 2a. A small increase in the rate is observed when GHSV is decreased (period II) for CoRe supported on Al_2O_3. In accordance with earlier results on Al_2O_3 supported Co catalysts [1], the reaction rate decreases with time on stream and the rate of deactivation increases when water is added (period III), and further addition of water (period IV) increases the rate of deactivation. By returning to the same conditions as before addition of external water (period V), the activity is not completely regained. The deactivation of the Al_2O_3 supported Co catalysts in the presence of water is probably due to reoxidation of metallic cobalt [11].

The reaction rate to hydrocarbons for CoRe/SiO_2 presented in Fig. 2b clearly shows that by increasing the conversion (period II) or adding minor amounts of water (period III) the rate increases, but at the same time the catalyst starts to deactivate. Increasing the amount of water added (period IV) results in even more pronounced deactivation. The activity increase and deactivation presented in Fig. 2b are consistent with the results obtained by Krishnamoorthy et al. [2]. After water addition (period V) only part of the deactivation that occurred during the periods of water addition is recovered. It has previously been reported that the deactivation occurring at high conversions or at high water partial pressures is irreversible [3], and the deactivation has been explained by support collapse and the formation of cobalt silicates.

For the CoRe/TiO_2 catalyst the rate increases with increasing conversion (period II) as seen in Fig. 2c. As for the SiO_2 supported catalyst the rate also increases as small amounts of water (period III) are added to the feed. During period III only a slight deactivation is observed for CoRe/TiO_2, but the catalyst deactivation is increased upon adding more water (period IV). The activity is not completely regained after removal of water (the activity is 15% lower in period V compared to period II). The positive effect of small amounts of water on the activity observed for the TiO_2 supported Co catalysts has also been observed by others [5]. The results showing reaction rate to hydrocarbons for CoRe supported on SiO_2 and TiO_2 (Fig. 2b and c) show that an inlet ratio of $P_{H_2O}/P_{H_2} = 0.38$ gives a higher reaction rate than a inlet ratio of $P_{H_2O}/P_{H_2} = 0.76$, indicating that an optimal ratio between H_2O and H_2 exists to achieve a maximum rate to hydrocarbons.

CH_4 and C_{5+} selectivities are shown in Fig. 3 as a function of the average H_2O partial pressure. For all three catalysts the C_{5+} selectivity increases as the water partial pressure is increased, and the CH_4 selectivity decreases. The observed increase in C_{5+} selectivity as the conversion is increased has partly been attributed to secondary reactions of primary olefins at higher residence times [12]. It has also been shown that water inhibits secondary hydrogenation [13], and this effect may contribute to increased C_{5+} selectivity since more olefins are available for insertion and chain growth at increasing amounts of water in the reactor. Due to the hydrocarbon selectivity being dependent on the conversion level, it is necessary to compare the differences in catalyst selectivities at the same conversion. At partial water pressure of about 2 bar the conversion for all the catalysts is in the range 40–45%. From this point it can be seen that the TiO_2 supported catalyst having the largest Co particles (Table 1) shows higher selectivity to C_{5+} and lower CH_4 selectivity than the corresponding SiO_2 supported catalyst having smaller Co particles, and the SiO_2 supported catalyst achieves higher selectivity to C_{5+} and lower CH_4 selectivity than the Al_2O_3 catalyst with smallest Co particles.

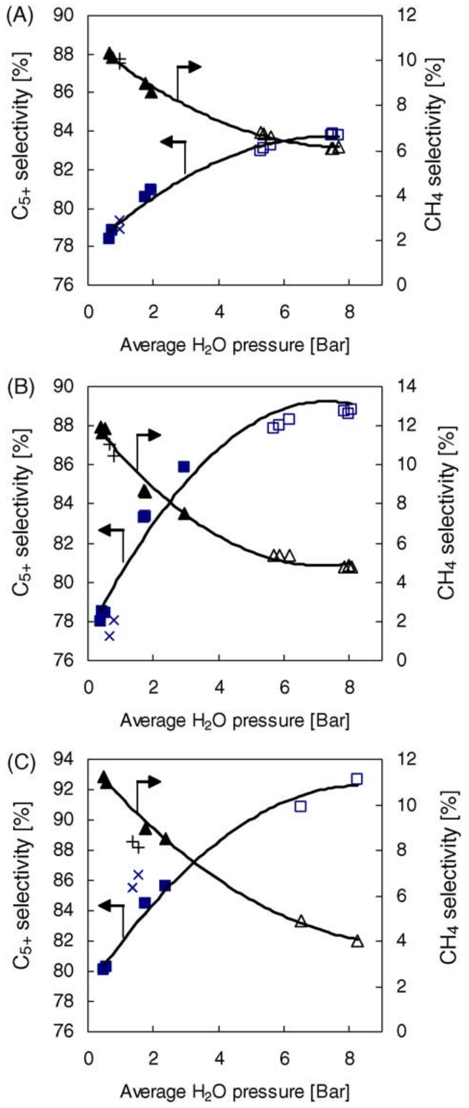

Fig. 3. C_{5+} selectivity (■, □, ×) and CH_4 selectivity (▲, Δ, +) as a function of the average water partial pressure on CoRe/Al_2O_3 (A), CoRe/SiO_2 (B) and CoRe/TiO_2 (C) at $P_{Tot} = 20$ bar, $T = 483$ K, $H_2/CO = 2.1$. Filled symbols represent runs at different GHSV (period I (~0.3 bar) and period II (~2 bar)), open symbols represent water addition runs (period III (~6 bar) and period IV (~8 bar)), and (×, +) is after water addition (period V).

4. Conclusions

The effect of water on the selectivity and activity on 12% Co-0.5% Re supported on Al_2O_3, SiO_2 and TiO_2 has been studied in a fixed-bed reactor by increasing the conversion and adding varying amounts of water to the feed during Fischer–Tropsch synthesis. Water was found to have different effects according to the type of support used for the Co catalyst. For the Al_2O_3 supported catalyst the reaction rate to hydrocarbons was almost unchanged as the conversion was increased, while external water addition deactivated the catalysts. Increased reaction rate to hydrocarbons was observed by increasing the conversion or adding minor amounts of water to the SiO_2 supported and TiO_2 supported catalyst. Further water addition decreased the reaction rate for both. No permanent deactivation was observed for the TiO_2 supported catalysts, while the SiO_2 supported catalyst underwent rapid deactivation during hydrothermal conditions. The presence of water led to a marked increase in C_{5+} selectivity and a decrease in CH_4 selectivity for all the Co catalyst systems.

References

[1] A.M. Hilmen, D. Schanke, K.F. Hanssen, A. Holmen, Appl. Catal. A 186 (1999) 169.

[2] S. Krishnamoorthy, M. Tu, M.P. Ojeda, D. Pinna, E. Iglesia, J. Catal. 211 (2002) 422.

[3] G.W. Huber, C.G. Guymon, T.L. Conrad, B.C. Stephenson, C.H. Bartholomew, Stud. Surf. Sci. Catal. 139 (2001) 423.

[4] J.K. Minderhoud, M.F.M. Post, S.T. Sie, Eur. Pat. Appl. (1984).

[5] C.J. Bertole, C.A. Mims, G. Kiss, J. Catal. 210 (2002) 84.

[6] J. Li, G. Jacobs, T. Das, B.H. Davis, Appl. Catal. A 233 (2002) 255.

[7] J.W. Niemandsverdriet, Spectroscopy in Catalysis, Wiley-WCH, Weinheim, 2000.

[8] Y. Li, Y. Fan, H. Yang, B. Xu, L. Feng, M. Yang, Y. Chen, Chem. Phys. Lett. 372 (2003) 160.

[9] J.M. Jablonski, J. Okal, D. Potoczna-Petru, L. Krajczyk, J. Catal. 220 (2003) 146.

[10] M. Voβ, D. Borgmann, G. Wedler, J. Catal. 212 (2002) 10.

[11] D. Schanke, A.M. Hilmen, E. Bergene, K. Kinnari, E. Rytter, E. Ådnanes, A. Holmen, Catal. Lett. 34 (1995) 269.

[12] E. Iglesia, S.C. Reyes, R.J. Madon, S.L. Soled, Adv. Catal. 39 (1993) 221.

[13] C. Aaserud, A.M. Hilmen, E. Bergene, S. Eri, D. Schanke, A. Holmen, Catal. Lett. 94 (2004) 171.