

REOXIDATION AND DEACTIVATION OF SUPPORTED COBALT FISCHER-TROPSCH CATALYSTS

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Keywords: Fischer-Tropsch synthesis, cobalt catalysts, deactivation

INTRODUCTION

As a result of the highly exothermic nature of the Fischer-Tropsch reaction, heat transfer considerations limit the maximum conversion per pass in fixed-bed processes, whereas slurry reactors can operate at higher conversions (1). During Fischer-Tropsch synthesis on cobalt catalysts, high conversions will generate high partial pressures of water at the reactor exit, due to the low water gas shift activity of cobalt. In addition, the extensive back-mixing in slurry reactors will give a relatively uniform concentration profile in the reactor, characterized by a high concentration of water and low reactant concentrations. From the commercial iron-catalyzed Fischer-Tropsch synthesis in fixed-bed (Arge) reactors it is known that the catalyst deactivates by oxidation of iron by CO₂ and H₂O near the exit of the reactor (2). Although bulk oxidation of cobalt during Fischer-Tropsch synthesis is not thermodynamically favored, it was early speculated that surface oxidation of cobalt could occur during Fischer-Tropsch synthesis (3).

The purpose of the present work is to describe the influence of water on the deactivation behavior of Al₂O₃ supported cobalt catalysts. The possibility of cobalt oxidation during Fischer-Tropsch synthesis was investigated by model studies.

2. EXPERIMENTAL

2.1 Catalysts

Cobalt catalysts containing (by weight) ~20% Co, 1% Re and optionally 1% rare earth oxides (designated RE) on γ -Al₂O₃, were prepared by incipient wetness coimpregnation of the support with aqueous solutions of Co(NO₃)₂·6H₂O, HReO₄ and (optionally) the RE-oxide precursor. The rare earth oxide precursor was supplied as nitrates (Molycorp 5247) and contained 66% La₂O₃ after calcination, the remainder being other rare earth oxides. The catalysts were dried in air overnight at 393 K before calcination in air at 573 K for 2 hours. The alumina supports had a specific surface area of 174 - 182 m²/g and 0.7-0.9 cm³/g pore volume. The extent of cobalt reduction was ~80% after reduction at 623 K for 14-16 hours (measured by O₂ titration at 673 K), and the cobalt dispersion (H_{ads}:Co) was estimated to 7-8% by temperature programmed desorption of H₂.

2.2 Kinetic experiments

Deactivation studies were carried out in a 0.9 cm I.D. stainless steel fixed-bed reactor heated by a fluidized sand bath. 3 g of catalyst (38-53 μ m) was diluted with an inert material (non porous SiC) in a 1:3 weight ratio to minimize temperature gradients. The catalyst was reduced in flowing hydrogen (5000 cm³ (STP)/(g_{cat}·h)) at atmospheric pressure at 623 K for 16 hours (heating rate from ambient temperature: 1 K/min). After reduction, the catalyst was cooled to 443 K in flowing H₂ and purged with He before increasing the pressure to 20 bar and switching to a feed mixture containing 97 mol% synthesis gas with H₂/CO = 2.1 and 3 mol% N₂. The reaction temperature was then slowly increased to the desired initial reaction temperature. On-line GC samples were taken at regular intervals and analyzed for N₂, CO, CO₂ and C₁+ hydrocarbons on a HP 5890 gas chromatograph. Space velocity was varied to give 20-70% CO conversion. High water partial pressures were obtained by addition of steam to the reactor inlet.

2.3 Gravimetric experiments

Reoxidation experiments were performed in a Sartorius 4436 high pressure microbalance (4). Before reduction, the catalyst was dried for 24 hours 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 hours 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 hours.

2.4 X-ray Photoelectron Spectroscopy (XPS)

XPS studies were conducted in a VG ESCALAB MkII instrument equipped with a non-monochromatic Al $K\alpha$ source (1486.6 eV). The catalyst samples were treated in an integrated high pressure pretreatment cell before being transferred to the analysis chamber without exposure to air. The catalysts were analyzed in the unreacted state, after reduction and after treatment with a H_2O/H_2 mixture.

3. RESULTS AND DISCUSSION

3.1 CO hydrogenation experiments

Fig. 1. shows a typical example of the deactivation behavior of an alumina supported, Re-promoted cobalt catalyst. The results are obtained after a 50 h period of stable operation at 463 and 473 K and the CO conversion was adjusted to 31-33% before and after the period where water was added to the feed, in order to allow direct comparison of the catalyst activities. The sharp decrease in reaction rate when water is introduced into the feed is a result of a reversible kinetic effect caused by the change in feed composition and is recovered when water is removed from the feed. The drop in reaction rate is apparently greater than predicted by 1. order kinetics, meaning that the change in reaction rate can only partly be explained by the decreased partial pressure of H_2 when the feed is diluted with H_2O . The reversible part of the decrease in reaction rate must therefore also contain an inhibition term associated with the concentration of water which is not accounted for in the simple 1. order (in H_2) kinetics. Similar behavior has been reported for iron catalysts (5). The contribution of the water inhibition term is likely to be larger than indicated in Fig. 1, since the pressure order for Fischer-Tropsch synthesis on cobalt has been shown to be less than 1.0 (6).

In addition to the inhibition effect, the presence of high water partial pressures also results in relatively rapid deactivation of the catalyst. It is shown that the rate of deactivation is further increased when the inlet partial pressure of water is raised from 5 to 7.5 bar. Virtually no further deactivation was observed after the water had been removed from the feed. From comparison of rates or rate constants before and after the period where water was added to the feed, the catalyst has lost approximately 30% of its initial activity. There is a tendency for decreased rate of deactivation towards the end of the period where water was added to the feed, indicating that the rate of deactivation depends not only on the partial pressure of water, but also on the remaining activity. This is the expected behavior in the case of a parallel poisoning reaction.

The influence of water on the deactivation can also be shown indirectly by monitoring the change in reaction rate at different conversions for a fresh catalyst. Fig. 2. shows that a stable activity is obtained at ~34 and ~52% CO conversion, whereas deactivation is evident when the conversion is raised to an initial value of ~70%. These conversions correspond to H_2O partial pressures of approximately 3, 5 and 7 bar respectively at the reactor outlet. However, these partial pressures are not directly comparable to the situation where water is added to the feed. In the latter case, a uniform concentration profile of water in the reactor is obtained. In the case where all of the water is produced by the Fischer-Tropsch reaction, the concentration of water will be high only near the reactor exit.

3.2 Model studies

Model experiments at non-reacting conditions with various H_2O/H_2 feeds were carried out in order to test the hypothesis of cobalt oxidation as being responsible for the observed deactivation.

Results from the gravimetric studies are shown in Fig. 3. In the series of experiments shown here, catalysts without rare earth oxides (RE) have been used. Although this precludes direct comparison with the deactivation studies, we have generally experienced that this low level of RE loading does not influence the deactivation behavior significantly.

A common feature of all of the curves shown in Fig. 3 is the initial rapid weight increase of ≈ 20 mg/g. Blank experiments using unreduced catalyst (curve 1 in Fig. 3) and the pure support (not shown) also showed the same initial weight increase. It is therefore concluded that the initial behavior is caused by adsorption of water on the porous support. The water adsorption equilibrium is rapidly established and the blank experiments therefore serve as a baseline for measuring weight gains associated with the possible oxidation of cobalt.

Exposure of the reduced $CoRe/Al_2O_3$ catalyst to a H_2O/He mixture (without H_2) resulted in a large weight increase, corresponding to almost complete bulk reoxidation of cobalt (curve 4 in Fig. 3). The situation is markedly different when the feed contains even small amounts of H_2 , as shown for the case with $H_2O/H_2 = 10$ where the weight curve indicates only a limited extent of reoxidation (curve 3 in Fig. 3). This H_2O/H_2 ratio would represent a very high conversion and a stronger deactivation potential than in the kinetic experiments. At the same partial pressure of water but at a higher H_2 partial pressure ($H_2O/H_2 = 1.5$), which could be considered a more realistic case, an even lower weight increase suggests almost negligible bulk reoxidation (curve 2 in Fig. 3).

Significant bulk oxidation of metallic cobalt was therefore considered to be unlikely under Fischer-Tropsch reaction conditions. In view of the strong deactivating effect of water shown in Fig. 1, the possibility of surface oxidation was therefore considered.

XPS spectra of a $20\%Co-1\%Re-1\%RE/\gamma-Al_2O_3$ catalyst are shown in Fig. 4. The peak at 781.5 eV, which is the dominant peak in the XPS spectrum of the calcined catalyst (curve a in Fig. 4), is assigned to cobalt oxides, and is accompanied by a shake-up satellite at 787-788 eV, probably representing Co^{2+} . In the reduced catalyst (curve b in Fig. 4), the XPS peak representing cobalt metal (778 eV) is visible, but the XPS-spectrum is still dominated by the oxide peak at 781.5 eV. 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. This is most likely caused by the presence of multiple cobalt oxide phases with widely different dispersion and reducibility, ranging from large Co_3O_4 crystallites to an atomically dispersed surface cobalt aluminate (7,8). The latter is unreducible at the temperatures used in this study but will dominate the XPS-spectrum due to the high dispersion.

Treatment of the reduced catalyst with a 1:4 H_2O/H_2 mixture, gave clear indications of reoxidation of cobalt metal to Co^{2+} or Co^{3+} , as shown by the decreased $Co^0/Co^{2+/3+}$ intensity ratio (curve c in Fig. 4). The intensity of the satellite peak appears to increase slightly, indicating some formation of Co^{2+} .

Thermodynamic calculations show that bulk cobalt metal will not reoxidize in H_2O/H_2 mixtures (3). However, highly dispersed phases or surface layers can be expected to show deviations from bulk behavior. The gravimetric studies indicated a relatively small extent of bulk reoxidation of $CoRe/Al_2O_3$ even at $H_2O/H_2 = 10$, and an even more modest effect at $H_2O/H_2 = 1.5$. The latter conditions are probably more representative of the conditions used in the fixed-bed deactivation studies. In contrast, XPS indicated significant reoxidation already at $H_2O/H_2 = 0.25$. From the comparison of results from surface and bulk techniques it is reasonable to suggest that surface oxidation or preferential oxidation of highly dispersed phases occurs in H_2O/H_2 or $H_2O/H_2/CO$ mixtures.

4. CONCLUSIONS

The presence of high water partial pressures during Fischer-Tropsch synthesis increases the rate of deactivation of a Co-Re-RE/ γ -Al₂O₃ catalyst. In simulated high conversion conditions using H₂O/H₂ feeds, bulk reoxidation of cobalt occurs only to a very limited extent, even at high H₂O/H₂ ratios. However, XPS studies indicated 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.

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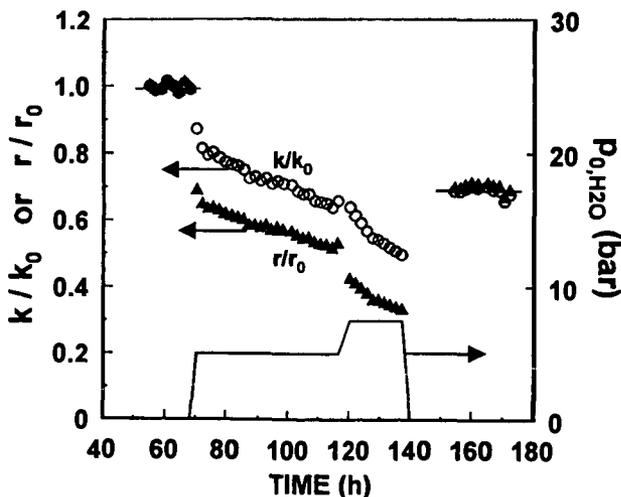


Fig. 1. Activity change during simulated high conversion conditions using a 20%Co-1%Re-1%RE/ γ -Al₂O₃ catalyst. T = 483 K, P = 20 bar, H₂/CO = 2.1.

k/k_0 = (Observed rate constant)/(Initial rate constant at 483 K)
 r/r_0 = (Observed rate)/(Initial rate at 483 K)

k = pseudo 1. order rate constant for H₂ conversion in a plug-flow reactor (contraction factor = -0.5). r = hydrocarbon formation rate (reactor average). P_{0,H_2O} = partial pressure of water at the reactor inlet.

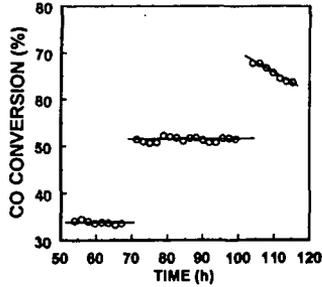


Fig. 2. Conversion vs. time using a 20%Co-1%Re-1%RE/ γ -Al₂O₃ catalyst. Step changes in conversion have been obtained by changing the space velocity. T = 483 K, P = 20 bar, H₂/CO = 2.1.

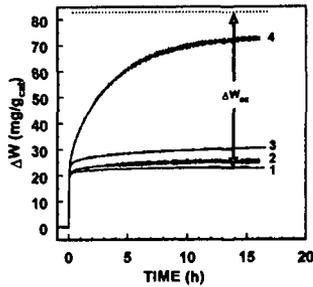


Fig. 3. Weight changes recorded by the microbalance during exposure of 21%Co-1%Re/ γ -Al₂O₃ to H₂O/H₂/He or H₂O/He at 523 K and 10 bar. W_{ox} = weight increase corresponding to total reoxidation of cobalt to Co₃O₄, assuming 80% initial extent of reduction.

1. Unreduced catalyst (P_{H2O}:P_{H2}:P_{He} = 5.5:0:4.5 (bar))
2. Reduced catalyst (P_{H2O}:P_{H2}:P_{He} = 5.5:3.7:0.8 (bar))
3. Reduced catalyst (P_{H2O}:P_{H2}:P_{He} = 5.5:0.55:4.0 (bar))
4. Reduced catalyst (P_{H2O}:P_{H2}:P_{He} = 5.5:0:4.5 (bar))

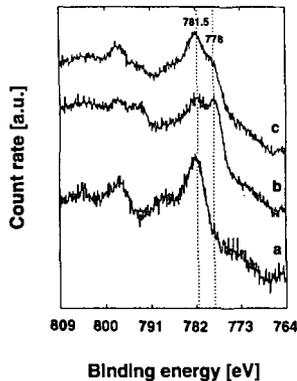


Fig. 4. Co 2p XPS spectra of 20%Co-1%Re-1%RE/ γ -Al₂O₃.
 a. Calcined catalyst.
 b. Catalyst reduced at 723 K for 13 h
 c. Reduced catalyst exposed to -20 vol% H₂O in H₂ for 18 h
 (P = 20 bar, T = 513 K)