

SUPPORT MODIFICATION OF COBALT BASED SLURRY PHASE

FISCHER-TROPSCH CATALYSTS

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INTRODUCTION

Gas-To-Liquids (GTL) processes have received widespread attention as an economically viable route to convert natural gas to liquid transport fuels^(1,2). The GTL process consists of three main steps, i.e. (i) the reforming of natural gas, (ii) the production of hydrocarbons from synthesis gas (i.e. the Fischer-Tropsch synthesis), and (iii) the optimisation to middle distillates. The Fischer-Tropsch synthesis step is preferably performed in a slurry phase bubble column reactor with a suspended cobalt Fischer-Tropsch catalyst of high intrinsic activity^(3,4). For optimum cobalt utilisation, a supported catalyst is selected. The commercial supports of choice are alumina, titania, and silica. In addition to a specification with respect to the mechanical strength of the eventual slurry phase catalyst, it is important to ensure proper cobalt anchoring during the impregnation step of the pre-shaped support material. Insufficient anchoring could result in the washing out of cobalt-rich ultra-fine particulates from the porous support material during commercial slurry phase Fischer-Tropsch synthesis.

Support modification has been reported earlier in the open literature⁽⁵⁻⁹⁾. Zirconia modification of silica supports was used to prevent the formation of unreducible cobalt-silicates⁽⁵⁾. Zr, Ce, Hf, or U modification of titania supports was reported to prevent the formation of cobalt-titanates during regeneration⁽⁶⁾. To increase the porosity of titania supports, they were modified with small amounts of binders, e.g. silica, alumina or zirconia⁽⁷⁾. Lanthanum oxide promotion of alumina was reported to be beneficial for improved production of products with higher boiling points⁽⁸⁾, and zirconia modification of alumina supports was carried out to decrease the interaction of cobalt with alumina⁽⁹⁾. All these modified supports were either used for fixed bed cobalt based Fischer-Tropsch catalysts or they were used for slurry bed cobalt catalysts, but not tested under realistic Fischer-Tropsch synthesis conditions in large scale slurry bed reactors.

This paper will deal with the modification of alumina and titania supports for cobalt based slurry phase Fischer-Tropsch catalysts to ensure the successful operation of slurry phase bubble column reactors on commercial scale.

EXPERIMENTAL

Two alumina-supported catalysts were prepared by means of a two-step slurry phase impregnation method, using an aqueous cobalt nitrate solution⁽¹⁰⁻¹³⁾. After impregnation and vacuum drying, the dried intermediate was calcined in air at 250°C for 6 hours. The calcined catalyst was reduced at 380°C in pure hydrogen using a heating rate of 1°C/min. Platinum was incorporated as a reduction promoter. The catalyst compositions were: catalyst A: 30gCo/0.075gPt/100gAl₂O₃, and catalyst B: 30gCo/0.075gPt/1.5gSi/100gAl₂O₃.

Silicon support modification was performed, prior to the catalyst preparation, in the case of catalyst B, by means of a non-aqueous slurry phase impregnation step using Tetra Ethoxy Ortho Silicate (TEOS) as precursor. TEOS dissolved in dry ethanol was used as impregnation solution. After impregnation, the slurry was dried at 60°C under vacuum for 6 hours. The dried modified support was calcined in air at 500°C for 2 hours⁽¹¹⁾.

The dissolution behaviour of the supports were characterised by monitoring the conductivity of a support in a model acidic aqueous slurry. The support was added to an acidic aqueous medium with a pH of 2 at 25°C. The conductivity was measured continuously for 30 hours under stirring at 25°C. As the dissolution of the support will increase the pH, continuous and automatic titration with a 10% HNO₃ solution was required to fix the pH at 2.0 during the 30 hours dissolution experiment.

Laboratory Fischer-Tropsch synthesis tests were performed in a slurry phase CSTR. The pre-reduced catalyst (20-30 g) was suspended in ca 300 ml molten Fischer-Tropsch wax. Realistic Fischer-Tropsch conditions were employed, i.e.: 220 °C; 20 bar; commercial syngas feed: 50 vol% H₂, 25 vol% CO and 25 vol% inerts; syngas conversion levels in excess of 50%. Use was made of the ampoule-sampling-technique as the selected on-line synthesis performance monitoring method⁽¹⁴⁾.

Larger scale Fischer-Tropsch synthesis runs were performed in a pilot plant slug-flow slurry reactor using 3-8kg catalyst as well as in a slurry phase bubble column demonstration unit using 500-1500kg catalyst. The reaction conditions were similar to those in the laboratory CSTR runs. The reactor wax production varied between 5 and 30kg per day for the pilot plant runs and up to 60bbl/day for the demonstration unit. On-line catalyst samples were taken for particle size distribution measurements and SEM analyses.

RESULTS AND DISCUSSION

The intrinsic Fischer-Tropsch activity as well as the selectivity of the supported cobalt catalysts studied in this paper (i.e. catalyst A and B) is such that these catalysts are economically viable for the GTL process (table 1). Low level silica modification of alumina supports did neither influence the acidity of the support and nor the Fischer-Tropsch synthesis behaviour of the catalysts (table 1).

Table 1: Fischer-Tropsch synthesis data for catalysts A and B, as tested under realistic reactor conditions (refer: Experimental).

	Catalyst A 30gCo/0.075gPt/100gAl ₂ O ₃	Catalyst B 30gCo/0.075gPt/1.5gSi/100gAl ₂ O ₃
Run number	175\$	98F
Time on line (h)	15	20
Syngas conversion (%)	75	76
FT reaction rate (mol/s)	6.8×10^{-6}	7.1×10^{-6}
Productivity (gHC/gcat/h)	0.34	0.36
CH ₄ selectivity (%C-atom)	4	7

Important for slurry phase Fischer-Tropsch catalysts is the mechanical strength, as catalyst break-up will result in (i) loss of catalyst, (ii) difficulties with the catalyst/wax separation, and (iii) undesired contamination of the wax product with cobalt. During extensive Fischer-Tropsch synthesis runs in both pilot plant scale reactors as well as the demonstration unit, the mechanical integrity of the catalyst was monitored by means of Particle Size Distribution (PSD) measurements as well as SEM analyses on extracted catalyst samples. The average particle size did not change even after 8 months of operation, which strongly indicates that catalyst break-up did not occur. This was in agreement with SEM analyses (figure 1).

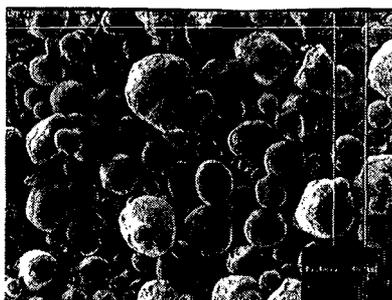


Figure 1: SEM image of alumina-supported cobalt catalyst A after Fischer-Tropsch synthesis test run in the demonstration unit.

The unmodified alumina-supported cobalt catalyst (catalyst A) was tested in the pilot plant slug-flow reactor under realistic Fischer-Tropsch conditions. The produced wax was secondary filtered over a 2 micron filter and analysed for cobalt content. Initially, clean white wax was produced without any cobalt contaminants present. After about 10 days on stream, however, the secondary filtered wax started discolouring and high levels of cobalt containing particulates were

observed (figure 2). This is very undesired, as cobalt contamination of wax may poison the downstream hydroprocessing catalysts. These cobalt containing particulates did not originate from catalyst break up.

The presence of high levels of cobalt-containing particulates in secondary filtered wax was correlated with the dissolution behaviour of the alumina support during the slurry phase impregnation steps of the catalyst preparation procedure. It was reported earlier that alumina supports could (partially) dissolve in aqueous solutions⁽¹⁵⁾, even at pH values close to the isoelectric point⁽¹⁶⁾. Partial dissolution of the alumina used during the preparation of catalysts A and B was experimentally confirmed during the aforesaid model dissolution test (figure 3).

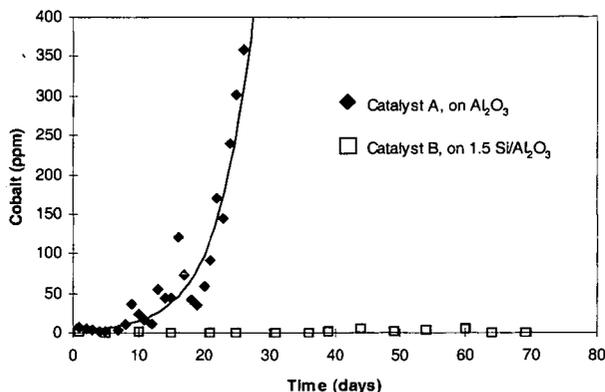


Figure 2: Cobalt content in secondary filtered wax during pilot plant scale Fischer-Tropsch synthesis runs, using catalyst A: 30gCo/0.075gPt/100gAl₂O₃ (run F102), and catalyst B: 30gCo/0.075gPt/1.5gSi/100gAl₂O₃ (run F117).

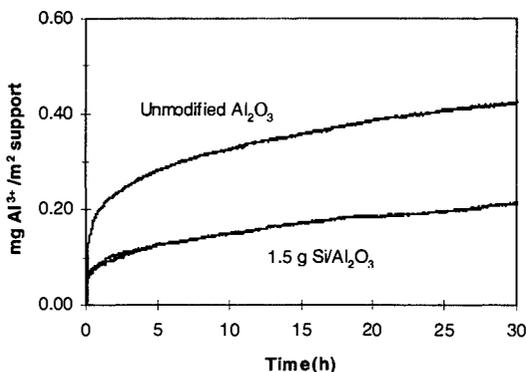
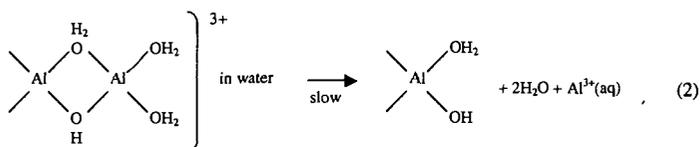
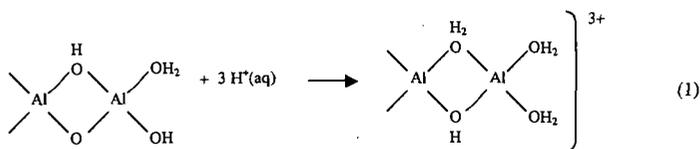


Figure 3: The dissolution behaviour of an alumina support (used to prepare catalyst A) as well as a silica modified alumina support (used to prepare catalyst B).

It can be seen that rapid dissolution occurs within the first hour, followed by a more gradual dissolution that proceeds continuously (i.e. about 30 hours). A mechanism of dissolution is reported in literature⁽¹⁵⁾ (equations 1 and 2). During catalyst preparation, the dissolved aluminium ions can precipitate either as boehmite or in combination with cobalt ions as a cobalt aluminium hydroxalcalcite⁽¹⁷⁾, producing a physically amorphous layer uniformly covering the surface of the bulk support material⁽¹⁶⁾. It is hypothesised that the presence of this amorphous layer, prior to the actual impregnation process, weakens the anchoring of the eventually catalytically active cobalt metal. The cobalt metal crystallites that are weakly anchored to the

alumina support can dislodge and be washed out during slurry phase Fischer-Tropsch synthesis, a process that is enhanced by the increased turbulence associated with large-scale reactors.



To prevent the dissolution of the alumina support during the slurry phase impregnation step of the catalyst preparation procedure, the alumina support was modified with silicon, using Tetra Ethoxy Ortho Silicate (TEOS) as precursor. The support modification step was performed as a slurry impregnation using TEOS dissolved in dry ethanol as impregnation solution. During support modification, TEOS reacts with the hydroxyl groups of the alumina surface. The three remaining ethoxy groups were thermally decomposed during a calcination step at 500°C in air. The maximum amount of silicon that can react with the alumina support depends on the surface area of the alumina support as well as the surface hydroxyl concentration. The dissolution behaviour of the silica-modified alumina was measured (figure 3), and found to be significantly inhibited.

A cobalt catalyst was prepared (catalyst B: 30gCo/0.075gPu/1.5gSi/100gAl₂O₃) on the silicon modified alumina support, using the standard aqueous slurry phase impregnation method. Catalyst B was tested in the pilot plant scale slurry reactor as well as in the semi-commercial demonstration unit under realistic Fischer-Tropsch synthesis conditions during an 8 month continuous test run. Catalyst break-up was not observed during this run, as measured by PSD and SEM analyses. Clean white wax was produced during this entire run, and the cobalt content of the secondary filtered wax remained very low (figure 2). This proved that silicon support modification successfully prevented the generation of cobalt containing ultrafines during large scale Fischer-Tropsch synthesis runs. From table 1, it can be concluded that silicon modification of alumina did not have any substantial effect on the Fischer-Tropsch synthesis performance of the catalyst.

Silicon modification of alumina supports is not only restricted to the utilisation of TEOS. Other silicon precursors can be used, e.g. Tetra Methoxy Ortho Silicate (TMOS). Besides silicon, successful modification of alumina can also be effected with other compounds.

The dissolution of titania supports was also investigated⁽¹¹⁾. Titania also (partially) dissolves in aqueous solutions and silicon modification, using TEOS, effectively inhibited support dissolution.

CONCLUSIONS

It was demonstrated that the production of clean white wax (i.e. free of any cobalt contamination) during large scale slurry phase Fischer-Tropsch synthesis runs, was successfully effected with cobalt catalysts that were prepared on modified supports (i.e. supports displaying inhibited dissolution behaviour in aqueous environments). As an example, the silicon modification of alumina supports was discussed in detail.

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