On the support in cobalt Fischer–Tropsch synthesis—Emphasis on alumina and aluminates

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ABSTRACT

Impact of the support in Fischer–Tropsch synthesis is discussed with emphasis on alumina and aluminates; in particular γ-alumina, α-alumina, Mg-aluminate and Ni-aluminate. Topics covered are the support in industrial type catalysts, pore characteristics, attrition of particles, pore diffusion, loading and heat treatment of aluminates, turn-over-frequency and selectivity to C_{5+} products. Comparison is made between the supports including γ-alumina with narrow, medium, large and ultra-large pore size. An attempt is made to decouple the effects of cobalt crystallite size, pore size and type of support; all of which are important for the degree of polymerization. Selectivity to C_{5+} is favored by supports containing large pores, $i.e.$, pores made up of large crystallites of the support material that also are more inert in nature. Cobalt surface coverage of CH_x reaction intermediates is coupled directly to product selectivity as well as to catalytic activity. A model is suggested to link changes in composition of the surface pool of intermediates with properties of the support. Strain in cobalt crystallites as they extend over several crystallites of the support is expected to play a decisive role. Finally, the effect of conversion and added water on Fischer–Tropsch synthesis is analyzed. It is shown that all supports exhibit a positive selectivity response to water vapor pressure, but more so for the large pore supports titania, Ni-aluminate and γ-alumina with larger pores. Adsorbed water on cobalt may facilitate CO activation and suppress hydrogen coverage. Activity response of water is similar, although an anomalous reduction in activity upon added water for narrow pore alumina is observed. The reduction in activity is ascribed to oxidation of cobalt, possibly due to condensation of water vapor.

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1. Introduction

Fischer–Tropsch synthesis (FTS), using supported cobalt catalysts, is characterized by high activity, high polymerization probability and low content (<5 wt% each) of byproducts like oxygenates and isomers. In contrast, iron catalysts produce considerably more byproducts and are also active for the water–gas shift reaction. Thus, cobalt catalysts are preferred when the synthesis gas (syngas) is based on natural gas and when the main product sought is diesel from hydrocracking/-isomerization of long chain paraffins (wax). Of the longer chains, 1-olefins may constitute up to 10 wt%. These olefins are often hydrogenated to paraffins or alternatively used for more specialized products like LAB (linear alkyl benzene). Process simulations show that maximizing yield of higher hydrocarbons is one factor that contributes significantly to overall plant profitability.

Most catalysts are manufactured either by co-precipitation of a support material with the active phase or by impregnation of the active phase, cobalt in our case, on to the support. Only the latter method is used industrially in FTS, and we will only be concerned with impregnated catalysts. One reason for this preference is that cobalt, and the promoters, are costly and best possible utilization of the metal surface is essential. Other factors that lean toward development of a separate support formulation are optimization of pore characteristics, strength and shape of the catalyst. Key properties of the support and cobalt can thus be optimized separately. The support is normally a porous refractory oxide that is heat treated to elevated temperatures to secure strength and stability of the material. Successive higher calcination temperatures lead to reduction in available surface area and creation of larger pores concurrently with condensation of hydroxyl groups and a more inert surface.

Many support materials have been reported for FTS in the literature, but only titania, silica, alumina, aluminate and zinc oxide have

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Table 1

Formulation of commercial type cobalt catalysts.[a]

Technology provider	Support	Surface area (m²/g)[b]	Support modifier	Pro-moter	Reactor type	Reference
Sasol	*γ-Alumina*	150	Si (TEOS[c])	Pt	Slurry	[2]
Shell	*Titania*	30	Citric acid[d]	Mn; V	Fixed	[3]
GTL.F1	*Ni-aluminate*	40	α-Alumina	Re	Slurry	[4]
ENI/IFP/Axens	*γ-Alumina; aluminate*	180; 40	SiO₂	?	Slurry	[5]
Nippon oil	*Silica*	250	Zirconia	Ru	Slurry	[6]
Syntroleum	*γ-Alumina*	150	Si (TEOS); La	Ru	Slurry	[7]
BP	*ZnO*	50		?	Fixed	[8]
Exxon Mobil	*Titania*	30	γ-Alumina	Re	Slurry	[9]
Conoco-Phillips	*γ-Alumina*	150	Boron	Ru/Pt/Re	Slurry	[10]
Compact GTL	*Alumina?*	150		Re?	Micro	[11]
Oxford cat./Velocys	*Titania–silica*	30		Re	Micro	[12]

[a] Deduced from open literature and patents. Actual commercial formulation may vary.
[b] If actual surface area has not been reported an approximate expected value is shown in italics.
[c] Si from TEOS; tetraethoxy silane.
[d] Extrusion aid.

Table 2

Puralox SCCa γ-alumina types with typical pore properties.

γ-Alumina support	Type	Surface area (BET) (m²/g)	Mean pore diameter (nm)	Pore volume (cm³/g)
Narrow pore	SCCa 40/195	184	7.4	0.48
Medium pore	SCCa series	186	12.3	0.73
Large pore	TH-series	155	20.8	0.98
Ultra large pore	TH series	114	26.7	0.86

been used in pilot or commercial operations, as seen in Table 1. The table is modified from a recent paper on deactivation [1].

The platinum promoted Sasol catalyst is prepared on γ-alumina (Puralox SCCa-2/150 or -5/150: pore volume 0.5 mL/g; surface area 150 m²/g) and stabilized by impregnation with tetraethoxy-silane (TEOS) followed by calcination to give a surface concentration of *ca.* 2.5 Si atoms/nm². This procedure apparently modifies the surface so that the support becomes less prone to dissolution in the acidic product water. The GTL.F1/Statoil catalyst is based on a larger pore diameter γ-alumina modified with nickel and fired at high temperature to produce a nickel-aluminate (spinel)/α-alumina mixture. The pore properties resemble titania based supports, but with very high attrition resistance. Also the ENI/IFP catalyst has a support of modified γ-alumina, but probably strengthened by silanation and calcination giving a final SiO₂ content of 6–7 wt%. Other modification methods have been described by ENI/IFP in earlier patents, including formation of spinel compounds. It is unclear whether the formulation contains a reduction or other type of promoter. In their slurry catalyst development, Nippon has apparently adopted a silica based support formulation similar to that of Shell's previous fixed-bed catalyst, but using ruthenium as a promoter. Zirconia is added, presumably to suppress the acidic properties of silica. No information on attrition resistance has been revealed, as is the case for most other slurry catalysts as well. Syntroleum used a catalyst similar to Sasol's, but also with a ruthenium promoter. Exxon Mobil, that pioneered titania as a support with alumina as binder, BP, Conoco-Phillips and Syntroleum have terminated their developments in FT-technology. However, BP is still licensing FT technology and Exxon Mobil has announced that the technology is ready for commercialization should the right project be prioritized. Note that 7 of the 11 formulations in Table 1 contain alumina or aluminate, six of them as the main support and one case where alumina is used as binder for titania.

The main theme of the paper is mainly concerned with properties of the catalyst support and the effect on FTS performance. Most emphasis is given to selectivity responses, but activity and catalyst robustness have also been covered. The main part of the paper is based on experience gained at Department of Chemical Engineering, NTNU, and Statoil Research Centre during the past 30 years and is divided into three main parts: alumina supports; aluminate supports; and catalytic performance. Most data reported are for lab scale fixed-bed reactors. In addition, support preferences depend on reactor technology applied, but there are unfortunately no comparative studies on this subject.

2. Alumina support materials

The crystal morphology of alumina (Al₂O₃) is rather complex, and a large number of polymorphs exist and are formed upon dehydration as shown in Fig. 1. Transition between the different phases is not as clear-cut as depicted in the figure. Boehmite has the formula AlO·OH while Bayerite is a form of Gibbsite; Al(OH)₃. Starting from Diaspore (AlO·OH) the χ and κ phases can be obtained. Most relevant for the present study are the γ- and α-phases. γ-Al₂O₃ is regarded as a defect spinel in that it is based on the spinel structure, see below, but with a deficit of cations. α-Al₂O₃ contains a closed packed array of oxygen atoms with aluminum distributed symmetrically among the octahedral interstices.

There are large variations in pore structure of γ-alumina supports obtained through calcination depending on factors like crystal size of the original hydroxide, forming technology (spray drying; granulation), heat treatment profiles, *etc.* Another decisive factor is purity of raw materials. Many alumina supports have traditionally been made from natural resources that contain large amounts of sodium and sulfate, both detrimental to FTS [14]. A comparison has previously been made of 13 different γ-alumina supports from different suppliers with large variations in pore sizes and purity [15]. The present discussion focuses on high purity samples of Puralox SCCa series materials from Sasol GmbH. Typical properties of some reference materials are summarized in Table 2. Note that in different reports there can be variation in specifications due to different production lots.

All supports in Table 2 have sufficient surface area to accommodate and distribute cobalt of desired crystallite size (8–15 nm) and amount (20–30 wt%). A two-step impregnation might be needed for low pore volumes and high loadings. For operation in a slurry reactor, a light material is preferred, *i.e.,* large pore volume, to secure proper distribution of catalyst in the reactor column. However, due consideration of the strength of the particles has to be included in the selection criteria. The primary effect of pore diameter for common incipient wetness impregnation is that cobalt particle size increases with pore size. Any direct effect of the pore diameter in itself upon Fischer–Tropsch performance is still being discussed in the literature and is treated below. The medium pore material type is typical for Statoil/GTL.F1's first generation (1G) catalyst while the narrow pore material is similar to the support described in Sasol