

# Hydrophobic Catalyst Support Surfaces by Silylation of $\gamma$ -Alumina for Co/Re Fischer-Tropsch Synthesis

Erling Rytter,<sup>a,b</sup> Ata ul Rauf Salman,<sup>a</sup> Nikolaos E. Tsakoumis,<sup>a</sup> Rune Myrstad,<sup>b</sup> Jia Yang,<sup>b</sup> Sara Lögberg,<sup>c</sup> Anders Holmen<sup>a</sup> and Magnus Rønning<sup>a\*</sup>

<sup>a</sup> Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Sem Sælands vei 4, NO-7491 Trondheim, Norway

<sup>b</sup> SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway

<sup>c</sup> Royal Institute of Technology (KTH), Chemical Technology, SE-100 44 Stockholm, Sweden

[\\*magnus.ronning@ntnu.no](mailto:magnus.ronning@ntnu.no)

## Abstract

Eight different silanes with chloro or methoxy active ligands have been examined to modify the surface of a standard  $\gamma$ -alumina support to investigate the effect of surface acidity and hydrophobicity in Fischer-Tropsch synthesis (FTS) at common operating conditions (210 °C; 20 bar; H<sub>2</sub>/CO=2.1). Silanes were impregnated prior to cobalt (*Pre*) or after cobalt impregnation and calcination (*Post*). Samples were characterized by standard techniques (FTIR, XRD, TPD, TPR, TGA, BET). In the *Post* series, cobalt crystallite size is maintained, while it is reduced when cobalt impregnation is performed on a partly hydrophobic surface. Both series of catalysts have FTS performances that deviate significantly from a reference catalyst and, in combination with characterization data, the silanes have modified all the 15 examined catalysts. The *Pre* series offer options for improved selectivity to higher hydrocarbons in FTS. The effects of silylation on FT performance mechanisms are discussed in terms of gas diffusion limitations, strain on cobalt particles and partial blocking of CO activation sites.

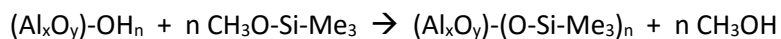
## Introduction

Fischer-Tropsch Synthesis (FTS), using supported cobalt catalysts, is characterized by high activity, high polymerization probability and low content of byproducts like oxygenates and isomers. Industrial support materials comprise  $\gamma$ -alumina, titania and silica. These supports exhibit large variations in catalytic responses, particularly in the selectivity to methane and  $C_{5+}$  products. The reason for these differences is still being investigated, and theories comprise acid-base properties, pore size effects, diffusion and/or condensation of water, and strain induced on the active metal.<sup>1</sup>

As to  $\gamma$ -alumina supports, there are large variations in properties obtained through calcination of Boehmite 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.<sup>2</sup> Comparison has previously been made of 13 different  $\gamma$ -alumina supports from different suppliers with large variations in pore sizes and purity.<sup>3</sup> The present discussion focuses on high purity samples of Puralox SCCa series materials from Sasol GmbH.

Transitional aluminas have acidic properties which have significant importance in use as supports for metals in catalysis. The presence of a significant concentration of hydroxyl groups on the surface of  $\gamma$ -alumina gives rise to acidic sites. These hydroxyl groups are formed either during precursor decomposition or by subsequent interaction with atmospheric water. The dehydrated surface is a Lewis acid whereas Brønsted acidic character is exhibited by surface Al-OH groups. The ability of  $\gamma$ -alumina to disperse the active phase during deposition or impregnation is attributed to its acid-basic character. It has been shown that high surface area  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibits strong Lewis acid sites compared to low surface area  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>4</sup>

Various studies have been conducted to convert hydrophilic alumina into hydrophobic alumina. Chemical modification of the surface has been carried out by using different modifiers like trimethoxy methyl silane, tetraethyl orthosilicate, stearic acid and trichloro methyl silane.<sup>5,6,7</sup> All these modifiers have been applied for near complete substitution of the surface -OH groups to induce hydrophobicity. The modification reaction of alumina with methoxy trimethyl silane can be depicted as



During the reaction, the methoxy group picks up hydrogen from the alumina surface to form methanol while an oxygen bridge is formed to silicon with the organic group inducing hydrophobicity. In the same fashion almost all of the surface hydrogens of Al-OH groups can be replaced by -Al-O-SiR<sub>3</sub> bonds making the surface hydrophobic.<sup>8</sup> The surface hydroxyl can be of three different types; terminal (-Al-OH), vicinal where one hydroxyl forms a hydrogen bond to its neighbor hydroxyl (-Al-OH-O(H)-Al-) and a minor amount of geminal (-Al-(OH)<sub>2</sub>). Highly reactive vicinal groups are formed upon heat treatment. Alkoxy-silanes have increased reactivity with free hydroxyl as compared to chloro-silanes. The extent to which surface hydroxyl groups react depends upon several factors:<sup>9</sup>

- The ability of the silane to penetrate to inaccessible hydroxyl groups. The smaller size of reactant, the more surface groups are modified.
- Bi-or tri-functional ability of the reactant leads to a higher degree of silylation.
- The higher the steric hindrance is, due to bulky ligands of silicon, the more the silylation is prevented.

Other important parameters are reaction conditions like temperature, time and concentration. Aqueous solutions are to be avoided to prevent hydrolysis with subsequent condensation/polymerization of the silanes. Surface coating of silane consists of chemisorbed as well as physisorbed molecules. Heat treatment, generally at 80-200 °C, is required for chemical stabilization of the silane layer.

In the present study we have explored a number of different silanes to modify the surface of a standard alumina support to investigate the effect of surface acidity and hydrophilicity/hydrophobicity in Fischer-Tropsch synthesis. Silica supports modified with different silanes have been studied for cobalt Fischer-Tropsch synthesis and are reported to have a positive influence on C<sub>5+</sub> selectivity,<sup>10,11,12,13</sup> although due consideration was not taken to the effect of conversion and/or diffusion on selectivity.<sup>14</sup> However, use of silane modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as support for cobalt Fischer-Tropsch synthesis has not been studied until now. With silane modification, two effects can be studied simultaneously:

- Effect of hydrophobic nature of catalysts as water affects the activity and selectivity of Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in FTS.<sup>15,16</sup>
- Effect of concentration of surface hydroxyl groups.

One hypothesis is that silylation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> makes the surface to more resemble hydroxyl free  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, a support known for high selectivity to higher hydrocarbons.

## Experimental

The  $\gamma$ -alumina support used is a specially prepared sample in the Puralox SCCa series. All catalysts have 20 wt% cobalt and 0.5 wt% rhenium prepared by one-step incipient wetness (IW) impregnation with aqueous solutions of cobalt nitrate hexahydrate and perrhenic acid, followed by drying for 2 h and calcination for 16 h at 300 °C. Catalysts were sieved to the size range of 53-90  $\mu$ m in order to ensure elimination of diffusion limitations during the Fischer-Tropsch reaction.<sup>17</sup>

Details on BET, pore characterization, XRD (CuK $\alpha$ ), hydrogen chemisorption, temperature programmed reduction (TPR) and Fischer-Tropsch synthesis can be found in previous reports.<sup>2,3,10</sup> FTS was run at 210 °C, 20 bar and H<sub>2</sub>/CO=2.1 after reduction at 350 °C, and selectivities are reported at 50 $\pm$ 1% conversion. Attenuated total reflection (ATR) FTIR spectra were recorded using a Nicolet IS50 FTIR KBr Gold Spectrometer using a diamond crystal. A 60 psi pressure tower was used to increase contact between crystal and sample. Thermogravimetric analyses (TGA) were performed using Netzsch STA 449. The

samples, approximately 10 mg, were heated from room temperature to 800 °C at a rate of 10 °C/min with an air flow of 75 ml/min. A mass spectrometer was coupled with the TGA and analysis was performed for chlorine, methane, silicon, water and carbon dioxide.

A list of employed silanes is given in Fig. 1. They comprise variations in: type of functional group, 3 are methoxy and 5 are chloro; mono-(5), bi-(1) or tri-(2) dentate functional groups; and methyl(5) or octyl/methyl(3) hydrophobic alkyl groups. One of the mono-chloro complexes contains a methylene bridge to silicon. Note the acronyms introduced where the functional group is given first and then the type(s) of alkyl.

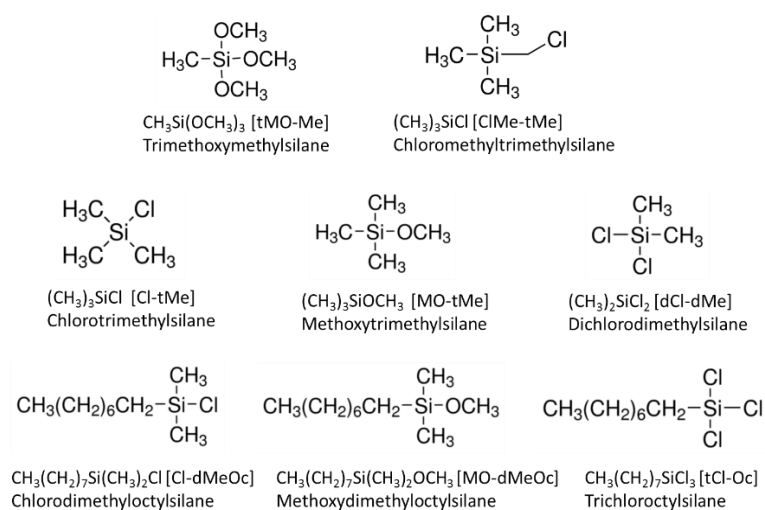


Fig. 1. Employed silanes in modification of  $\gamma$ -alumina.

Several procedures for impregnation of the silane were explored, but they can be divided into two main groups:

- Impregnation of alumina with silane before impregnation with Co/Re (*Pre*)
- Impregnation of silane on calcined Co/Re/ $\gamma$ -alumina catalyst (*Post*)

Methoxy dimethyloctyl silane and trichloro octyl silane were prepared by post modification only as they yielded completely hydrophobic supports prohibiting incipient impregnation with aqueous Co/Re

solution. Note that the silane of the *Pre* catalysts has been heated to 300 °C during catalyst calcination before FT testing, while the silane in the *Post* catalysts have only seen 50 °C prior to catalyst reduction at 350 °C.

Table 1. Prepared CoRe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts impregnated with silanes before (*Pre*) or after (*Post*) cobalt.\*

<i>Silane</i>	<i>Silane acronym</i>	<i>Silane impregnation method</i>	<i>Variations</i>
No silane	-	-	Reference catalyst; Ref1
No silane	-	-	Reference catalyst; Ref2
Trimethoxy methyl silane	<i>tMO-Me</i>	<i>Post</i>	
----“----	<i>tMO-Me</i>	<i>Post</i>	10x concentration of impregnation solution
----“----	<i>tMO-Me</i>	<i>Post</i>	0.1x concentration of impregnation solution
----“----	<i>tMO-Me</i>	<i>Post</i>	----“----
----“----	<i>tMO-Me</i>	<i>Post</i>	Reduced at 350 °C and passivated before imp.
----“----	<i>tMO-Me</i>	<i>Post</i>	Reduced at 250 °C and passivated before imp.
----“----	<i>tMO-Me</i>	<i>Post</i>	Reduced at 200 °C and passivated before imp.
Chloromethyl trimethyl silane	<i>ClMe-tMe</i>	<i>Post</i>	
----“----	<i>ClMe-tMe</i>	<i>Pre</i>	
----“----	<i>ClMe-tMe</i>	<i>Pre</i>	Calcined at 250 °C (after CoRe impregnation)
Methoxy trimethyl silane	<i>MO-tMe</i>	<i>Pre</i>	
Chloro trimethyl silane	<i>Cl-tMe</i>	<i>Pre</i>	
Dichloro dimethyl silane	<i>dCl-dMe</i>	<i>Pre</i>	
Chloro dimethyloctyl silane	<i>Cl-dMeOc</i>	<i>Pre</i>	
Methoxy dimethyloctyl silane	<i>MO-dMeOc</i>	<i>Post</i>	
Trichloro octyl silane	<i>tCl-Oc</i>	<i>Post</i>	

\* Standard calcination temperature after cobalt and rhenium impregnation is 300 °C.

A modified version of the method of Bao *et al.*, aimed at complete substitution of the surface hydroxyl groups, was adopted.<sup>6</sup> Surface modification was carried out by immersing 5 g of solid sample in 100 ml of 1% v/v solution of silane in n-hexane, contained in a three-neck round bottom flask, placed in an oil bath preheated to 50 °C, and magnetically stirred. Any evaporating n-hexane was condensed in order to keep the concentration of the modification mixture constant. After 24 hours of operation, the reaction mixture was cooled down, the solid sample was separated from the silane/n-hexane solution by centrifugation, subsequently washed with n-hexane three times and dried at 120 °C. The prepared catalyst samples are summarized in Table 1.

## Results

### *Surface areas and pore characterization*

It is to be expected that the surface area (SA) and pore volume are reduced after impregnation of silanes in the  $\gamma$ -alumina pores followed by centrifugation and drying at 120 °C; the reduction is fairly modest with SA 173→163 m<sup>2</sup>/g on average for 6 silanes reported in Table 2. This reduction is not significant taken into account mass change during impregnation. There are larger variations in subsequent water intrusion as measures by the incipient wetness saturation point. In particular, two silanes made the support completely hydrophobic. This complies with general experience,<sup>9</sup> as these silanes have one long substituent combined with high steric hindrance. They are therefore not expected to penetrate into other than large pores; they rather block the pore mouths. The dCl-dMe silane shows a strongly reduced IW, possibly because it is bidentate with enhanced ability to silylation. It is rational that the bi- or tri-dentate silanes dCl-dMe and tCl-Oc have stronger propensity for bonding to the surface or being cross-linked. It is more difficult to explain why MO-dMeOc shows the same property, although the long alkyl chain may be a factor.

The most striking result for pore characteristics of *Post*-silane impregnated catalysts is that the surface areas have been reduced by an average of  $14 \text{ m}^2/\text{g}$  independent of silane used; from  $127$  to  $113 \text{ m}^2/\text{g}$ . The reduction is doubled to  $101 \text{ m}^2/\text{g}$  by using a more concentrated solution while there is no effect if a 10 times diluted solution is used. Although there is a weight change during silylation to be corrected for, the reduction in surface area is larger than for impregnating the neat alumina. *Post*-modified catalysts are expected to contain physisorbed silane, primarily affecting the smaller pores, that is only partly removed by degassing the samples at  $200 \text{ }^\circ\text{C}$  prior to BET measurements. There is also a parallel reduction in pore volume. Similar decreases in surface area and pore volume were found for silane modified silica supports.<sup>13,18</sup> No significant effect is seen for the sample where the silylation has been performed on a reduced and passivated catalyst. The reason might be that the passivated sample before silane impregnation has a higher surface area than a calcined catalyst.

*Pre*-impregnation of silane before catalyst preparation does not influence the pore structure of the catalyst to the same degree. This is to be expected as there is no physisorbed material and some of the silane has decomposed during calcination. However, there is a slight tendency towards increased surface area ( $127 \rightarrow 134 \text{ m}^2/\text{g}$ ), reduced pore volume ( $0.44 \rightarrow 0.39 \text{ cm}^3/\text{g}$ ) and narrower pores ( $13.7 \rightarrow 11.6 \text{ nm}$ ). This can be understood in terms of grafting of the surface with silane, making rougher surface and taking up space inside the pores. The silane with a bi-dentate ligand, dCl-dMe, shows the largest response, possibly due to a more robust bond structure to the support.



Table 2. Pore characteristics of  $\gamma$ -alumina, pre-impregnated alumina and Co/Re catalysts.

Silane ligands	Impregnation method	Surface area [m <sup>2</sup> /g]	Pore volume* [cm <sup>3</sup> /g]	Pore diameter* [nm]	Incipient wetness [ml/g]	Comment
<b>Support (after silane impregnation and drying at 120 °C)</b>						
Reference $\gamma$ -alumina		173	0.69	15.9	1.33	
MO-tMe	<i>Pre</i>	164	0.71	17.4	1.39	
Cl-tMe	<i>Pre</i>	160	0.62	15.4	1.22	
dCl-dMe	<i>Pre</i>	160	0.66	16.5	1.06	
Cl-dMeOc	<i>Pre</i>	168	0.66	15.8	1.35	
MO-dMeOc	<i>Pre</i>	166	0.63	15.3	Hydrophobic	
tCl-Oc	<i>Pre</i>	158	0.54	13.6	Hydrophobic	
<b>Catalysts</b>						
<i>Reference catalyst Ref1</i>		126	0.43	13.8		
<i>Reference catalyst Ref2</i>		129	0.44	13.6		
tMO-Me	<i>Post</i>	111	0.42	15.3		
tMO-Me	<i>Post</i>	101	0.37	14.6		10x silane
tMO-Me	<i>Post</i>	128	0.47	14.7		0.1x silane
tMO-Me	<i>Post</i>	125	0.47	14.3	Silylation on passivated catalyst	
ClMe-tMe	<i>Post</i>	130	0.47	14.4		
ClMe-tMe	<i>Pre</i>	133	0.40	12.0		
ClMe-tMe	<i>Pre</i>	134	0.40	11.9		Calcined 250 °C
MO-tMe	<i>Pre</i>	133	0.42	12.5		

Cl-tMe	<i>Pre</i>	127	0.38	12.0		
dCl-dMe	<i>Pre</i>	139	0.37	10.7		
Cl-dMeOc	<i>Pre</i>	135	0.38	11.2		
MO-dMeOc	<i>Post</i>	117	0.39	13.3		
tCl-Oc	<i>Post</i>	112	0.35	12.5		

\* Based on BJH desorption isotherm.

### *FTIR spectroscopy*

FTIR spectra were only used in qualitative assessments. As expected,  $\gamma$ -alumina impregnated samples containing octyl chains show the characteristic 4 bands of C-H stretching modes of  $\text{CH}_x$  groups.

Specifically, antisymmetric and symmetric stretch of methylene are strong at  $2923$  and  $2853\text{ cm}^{-1}$ , respectively, with weaker features for corresponding modes of methyl at ca.  $2960$  and ca.  $2875\text{ cm}^{-1}$ .<sup>19</sup>

Methylene bending is seen at  $1466\text{ cm}^{-1}$ . Somewhat sharper peaks for tCl-Oc compared to MO-dMeOc points to a multilayer due to cross-bonding. This is confirmed by a broad band at ca.  $1050\text{-}1100\text{ cm}^{-1}$  that is assigned to Si-O-Si bonds.<sup>20</sup> The rest of the investigated samples are dominated by the antisymmetric stretch of methyl at  $2960\text{ cm}^{-1}$ . A peak at  $1252\text{ cm}^{-1}$  is assigned to the symmetric  $\text{CH}_3$  bending mode in Si- $\text{CH}_3$ ; absent in the tCl-Oc impregnated sample.

*Post*-impregnated catalysts have the same IR features as the impregnated alumina. In contrast, it is apparently significant that catalysts *Pre*-impregnated with silane show no sign of alkyl features in the FTIR spectra, indicating decomposition to Al-O-Si-O on the support of the catalyst during calcination. Few organic groups may have survived, although this is in contrast to the TGA measurements below. It is likely that the ATR method is not sensitive enough for low concentration samples.

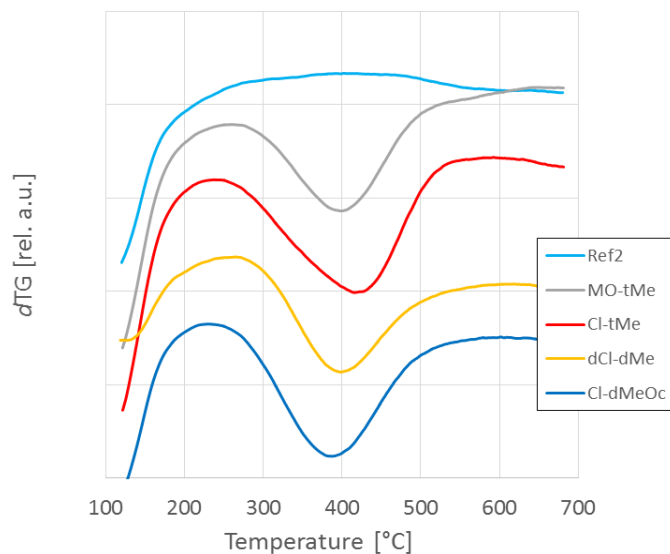


Fig. 2. TGA in  $O_2/N_2$  derivative of CoRe catalysts on  $\gamma$ -alumina impregnated with silane by the *Pre* method.

#### Thermogravimetric analysis

The stability of the silanes impregnated on  $\gamma$ -alumina was studied for selected samples by TGA-MS, notably those that later were impregnated by the FT metals. The data shows that combustion of alkyl groups takes place in the temperature range of 450-500 °C, and they are therefore stable against oxygen at the calcination temperature. Decomposition of Si-C bonds is inconclusive from these measurements, although weight loss between 200 and 300 °C in some samples gives an indication.

The derivatives of 4 silane *Pre*-impregnated catalysts are shown in Fig. 2. All catalysts, confirmed by MS of water and  $CO_2$ , have a combustion profile around 400 °C. We therefore safely conclude that all *Pre*-catalysts have silyl groups retained after calcination, and they also probably survive reduction at 350 °C. Weight loss between 300 and 500 °C, corrected for reference catalyst, is between 1.0 and 1.5 %.

*Post*-impregnated catalysts have larger combustion weight losses; ca. 3 wt% for MO-dMeOc and 6 wt% for tCl-Oc. This is consistent with the low temperature exposure during preparation and the longer octyl

chain. Grafting of the tridentate trichloro octyl silane is particularly successful with insignificant weight loss around the boiling point of 233 °C. This is in contrast to methoxy dimethyloctyl silane which combusts at a significantly lower temperature peaking at 300 °C. Possibly, this is close to the combustion temperature of free silane.

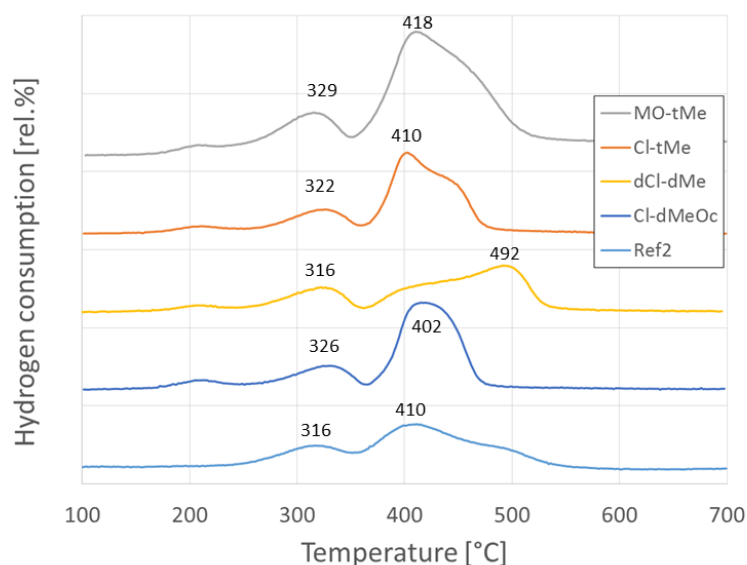


Fig. 3. TPR of selected silane *Pre*-modified catalysts.

#### *Temperature programmed reduction*

TPR profiles of selected catalysts are shown in Fig. 3. The reference CoRe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has three peaks that are well understood in terms of reduction of Co<sub>3</sub>O<sub>4</sub> to CoO (316 °C), further reduction to metallic cobalt (410 °C), and a shoulder around 500 °C that is attributed to well dispersed oxide on the  $\gamma$ -alumina surface.<sup>21</sup> All *Pre*-modified catalysts maintain the first reduction step. The three mono-dentate silanes have induced easier reduction of the dispersed cobalt oxide, probably a result of blocking alumina support sites for cobalt interaction due to the silylation. Most easily reduced is Cl-dMeOc. A similar shift has previously been seen by going from narrow, through medium, and to wide pore  $\gamma$ -alumina,<sup>22</sup> *i.e.* toward larger alumina crystals and a less reactive surface. It has been reported that smaller cobalt particles, typical for the chloro-silane *Pre*-impregnated catalysts, are more challenging to reduce.<sup>22,23</sup> This

effect is not observed, probably due to decrease in cobalt-support interaction when the support has been impregnated with a silane. The most remarkable change in TPR profile is observed for dichloro dimethyl silane that has its most prominent peak at 490-500 °C. This can be related to decomposition of cross-linked silane or to cobalt oxide that is stabilized against final reduction; like cobalt silicate. The latter seems to be the case from the peak intensities. Control TPR experiments with the support impregnated by the silanes only show very weak signals and no features above 300 °C. Note also a weak peak for *Pre*-modified catalysts at ca. 210 °C that remains unexplained. However, the mentioned control experiments with silanes indicate silane hydrogenation, possibly to HCl and CH<sub>3</sub>OH, around 200 °C.

The *Post*-modified catalysts are more challenging to reduce. Both cobalt reduction steps are shifted to higher temperatures for MO-dMeOc silane, indicating more difficult access of hydrogen. This temperature shift is very pronounced for cross-linked tCl-Oc silane. That the first reduction step of Co<sub>3</sub>O<sub>4</sub> is shifted by a formidable 110 °C is a strong indication of blocking of cobalt oxide; physically by pore filling of -Si-O-Si- cross-linked silanes; or chemically by either grafting to cobalt oxide or decomposition of the silane that leaves -Si-O-Si- structures directly on cobalt oxide

#### *XRD and hydrogen chemisorption*

X-ray diffractograms of calcined catalysts show the well-known features of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>,<sup>3</sup> with the only significant variation between samples being the half-height full-width of the cobalt oxide peaks. The (311) reflection at  $2\theta = 36.9^\circ$  was used to estimate the crystallite size of the oxides as well as of reduced cobalt. Results are shown in Table 3.

Table 3. XRD and hydrogen chemisorption data for CoRe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts modified with silanes.\*

Silane ligands	Impregnation method	XRD			Chemisorption	
		Crystallite size Co <sub>3</sub> O <sub>4</sub> [nm]	Crystallite size Co** [nm]	Dispersion *** [%]	Dispersion [%]	Nanoparticle size; Co*** [nm]
<i>Reference catalyst Ref1</i>		-	-	-	7.59	12.7
<i>Reference catalyst Ref2</i>		13.4	10.7	8.9	7.37	13.0
tMO-Me	<i>Post</i>	-	-	-	5.90	(16)
tMO-Me	<i>Post 10x</i>	-	-	-	4.90	(20)
tMO-Me	<i>Post 0.1x</i>	-	-	-	6.14	(16)
tMO-Me	<i>Post passivated</i>	-	-	-	5.02	(19)
ClMe-tMe	<i>Post</i>	-	-	-	7.05	13.6
ClMe-tMe	<i>Pre 250 °C</i>	-	-	-	8.14	11.8
MO-tMe	<i>Pre</i>	13.4	10.7	9.0	8.36	11.5
Cl-tMe	<i>Pre</i>	8.6	6.9	13.9	2.22	(43)
dCl-dMe	<i>Pre</i>	9.7	7.8	12.4	5.63	(17)
Cl-dMeOc	<i>Pre</i>	10.7	8.6	11.2	3.49	(27)
MO-dMeOc	<i>Post</i>	14.6	11.6	8.2	5.41	(18)
tCl-Oc	<i>Post</i>	14.6	11.7	8.2	0.66	(145)

\* Not corrected for degree of reduction

\*\* Estimated from the oxide

\*\*\* Based on  $D [\%] = 96/d_{Co}$

*Post*-impregnated catalysts have XRD based Co crystallite size within the accuracy of the standard catalyst on which they are based. The same is the case for *Pre*-impregnation with the methoxy silane

MO-tMe, again showing no or weak anchoring of this silane after calcination. The situation is different for chloro silanes which significantly enhance cobalt dispersion. Cobalt crystallites are formed by precipitation from super-saturated droplets during drying, and it is reasonable that, at least partly, a hydrophobic surface makes these droplets smaller. Note that there is a link to pore diameter that is reduced simultaneously, see Table 2,

Hydrogen chemisorption is significantly reduced for most catalysts, with the exception of three catalysts, including the MO-tMe *Pre*-impregnated one discussed above. The other exceptions are for the silane with MeCl as reactive ligand. As indicated under the discussion on TPR measurements, there is evidence that hydrogen transport is diffusion limited either by blocking of pores or a surface layer on cobalt. The tri-dentate chloro octyl silane is extreme in this respect. The low hydrogen chemisorption for the three *Pre* catalysts of the mono- or dichloro- silane types is astonishing. At least two of them are easily reduced (Fig. 3), XRD shows small crystallites, transport limitations of hydrogen are expected to be smaller than for the *Post* catalysts, and they have high initial reaction rates; see Table 4 below. This indicates that the cobalt surface is partially blocked during chemisorption conditions, but still not affecting the FTS rate that is dictated by CO activation.

#### *Fischer-Tropsch synthesis*

Precision of the data is good as can be seen from three reproducible pairs in Table 4: the two reference catalysts from separate catalyst preparations; two FT runs of tMO-Me *Post*-impregnated catalyst with reduced concentration of silane reduced at 350 and 425 °C before chemisorption and FT measurements; and the ClMe-tMe silane used for *Pre*-impregnation (calcination of 300 and 250 °C, respectively).

Average spread in selectivities is 0.1 C% for CH<sub>4</sub>, C<sub>2</sub>-C<sub>4</sub> and C<sub>5+</sub>; 0.1 units in C<sub>3</sub>=/C<sub>3</sub>; with somewhat larger spread in STY due to uncertain dispersion measurements.

The catalyst performances are compared with characterization data and discussed in the next section.

Table 4. Fischer-Tropsch synthesis at 210 °C, 20 bar and H<sub>2</sub>/CO =2.1 of silane modified CoRe/Al<sub>2</sub>O<sub>3</sub> catalysts.

Silane ligands	Impregnation method	rCO			Selectivities [C%] <sup>****</sup>			Olefin/paraffin ratio C <sub>3</sub> =/C <sub>3</sub>
		initial* [10 <sup>-3</sup> mol CO/g <sub>cath</sub> ]	CO conv. [%]**	STY [10 <sup>-3</sup> s <sup>-1</sup> ] ***	CH <sub>4</sub>	C <sub>2</sub> -C <sub>4</sub>	C <sub>5+</sub>	
Reference catalyst Ref1		52	~50	56 <sup>Δ</sup>	7.5	6.8	85.7	2.5
Reference catalyst Ref2		58	50.2	53	7.4	6.9	85.7	2.5
tMO-Me	Post	37	~50	51 <sup>Δ</sup>	8.7	8.4	82.9	2.0
tMO-Me	Post 10x	35	~50	59 <sup>Δ</sup>	9.2	9.5	81.4	1.8
tMO-Me	Post 0.1x	49	~50	65 <sup>Δ</sup>	8.8	7.5	83.7	1.8
tMO-Me	Post 0.1x	40	~50	49 <sup>Δ</sup>	8.6	7.4	84.0	1.9
tMO-Me	Post red350°C + p.	39	~50	63 <sup>Δ</sup>	8.5	8.5	83.0	2.0
tMO-Me	Post red250°C + p.	42	~50	68 <sup>Δ</sup>	8.7	8.9	82.4	1.9
tMO-Me	Post red200°C + p.	40	~50	65 <sup>Δ</sup>	8.8	8.6	82.6	1.9
CMe-tMe	Post	54	~50	53 <sup>Δ</sup>	8.0	7.6	84.4	2.1
CMe-tMe	Pre	61	~50	-	7.2	6.1	86.7	2.4
CMe-tMe	Pre 250 °C	60	~50	60	7.1	6.1	86.8	2.6
MO-tMe	Pre	72	49.3	66	9.0	5.8	85.2	1.4
Cl-tMe	Pre	80	50.2	47	8.0	6.0	86.0	1.7
dCl-dMe	Pre	68	49.8	45	7.8	6.0	86.2	1.8
Cl-dMeOc	Pre	62	50.4	45	8.8	6.5	84.8	1.8
MO-dMeOc	Post	47	49.9	47	8.7	8.3	83.0	1.9
tCl-Oc	Post	23	53.7	23	7.2	7.0	85.9	2.2



\* At 20 h TOS with constant GHSV

\*\* At ca. 50% after adjustment of GHSV and ca. 70 h TOS

\*\*\* Site-time-yield at 50% conversion. Black: from XRD dispersion; Red  $\Delta$ : from chemisorption

\*\*\*\* CO<sub>2</sub> free selectivities

## Discussion

From the results section and interpretations of support and catalyst characterization therein, we conclude that

- Grafting with chloro-silanes is more efficient than with methoxy-silanes.
- Grafting with multi-dentate silanes is more efficient than with mono-dentate ones, indicating better anchoring to the surface and/or cross-linking.
- Longer alkyl groups induce more hydrophobic materials.
- Grafted Si-alkyl groups are stable during typical calcination and reduction conditions of the catalysts. (Possible exception for methoxy dimethyl octyl silane).
- *Pre*-impregnation prevents formation of highly dispersed cobalt oxide interacting with alumina.
- On the other hand, *Pre*-impregnation with chloro silanes increases cobalt dispersion; with cobalt crystallite size reduced typically from 11 to 7-8 nm.
- Silane impregnation *Post* catalyst calcination leaves larger amounts of silanes.
- *Post* impregnation makes reduction more challenging, particularly for multi-dentate chloro silanes.

The seven catalysts marked in green in Table 4 have approximately equal performance in Fischer-Tropsch synthesis. They are characterized by the reactive silane group being methoxy and different variations of *Post*-synthesis: reduction at temperatures between 200 and 350 °C followed by passivation; and reduced silane concentration. In other words, calcination or pre-reduction at different temperatures has no

influence on the FT results as long as the silane is *Post*-impregnated. Performance of this series of catalysts is inferior as to activity and  $C_{5+}$  selectivity compared to the reference catalysts. That these catalysts have reduced dispersion measured by hydrogen chemisorption and reduce at higher temperatures, point to diffusion restrictions on syngas in the pores as a likely explanation. Further support is found from the lower olefin/paraffin ratio, presumably due to slow diffusion of products leading to secondary hydrogenation. Inadequate cobalt reduction is less likely as increasing the reduction temperature to 425 °C has no effect. This interpretation concurs with the experiment where 10 times the concentration of tMO-Me silane was employed, giving even lower reaction rate and selectivity to longer chains. That diffusion may play a role when pores are deliberately filled is not surprising as catalyst particles above 300  $\mu\text{m}$  in size show clear signs of increased  $\text{H}_2/\text{CO}$  ratio in FTS.<sup>17</sup> Nevertheless, an alternative interpretation in terms of partial silylation of the cobalt or cobalt/alumina interphase cannot be excluded; see the discussion below on interpretation of  $\alpha$  chain propagation probabilities. From the present characterization of *Post*-impregnated catalysts, it is not possible to conclude whether the alumina surface has been grafted with alkyl silane or not. In any case, the predicted positive effect on selectivity is not observed.

Methoxy silane is used in only one other experiment; with MO-tMe. This is the only combination of methoxy silane and *Pre*-impregnation. FTS shows slightly improved reaction rate and site-time-yield, and low o/p ratio. More remarkable are the selectivities. Although  $C_{5+}$  is on par with the reference catalyst, methane is highest of all catalysts and  $C_2\text{-}C_4$  is lowest. XRD and chemisorption data are close to the reference catalyst. The data appear conflicting; particularly that grafting has had no influence on cobalt particle size. TGA shows for certain that alkyl combustion takes place.

There are two more *Post*-impregnated silanes, ClMe-tMe and tCl-Oc, that have rather different properties. The former of these is similar to the references in performance and might have been included in the list of seven highlighted in green in Table 4. Implications are that the silane in this catalyst

is present in low concentration, as also inferred from the pore characteristics. The tri-dentate silane, however, has an extremely low hydrogen chemisorption value, by far the lowest STY, a highly displaced TPR profile to higher temperatures, a very strong TGA-MS signal, and the lowest surface area and pore volume. Evidently, alkyl silane is present in high concentrations with efficient grafting, cross-linking and with a partly silica covered cobalt surface. It might seem astonishing that all selectivity parameters are close to the reference catalysts and do not show the pore transport limitation effects described above. A plausible explanation is found in the very low reaction rate that allows syngas transport to take place in the pores unaltered.

Four *Pre*-impregnated catalysts contain chloro functional groups. We exclude ClMe-tMe from further discussion as it, similar to its post impregnated analogue, shows minimal sign of silylation or silane presence in the pores. Evidently, the methylene bridge efficiently separates silicon from the surface hydroxide and prevents grafting. The remaining three chloro silane based catalysts have reduced cobalt crystallite size, presumably due to an induced hydrophobic  $\gamma$ -alumina surface. Hydrogen chemisorption values are low as well, and the o/p ratio is reduced. Pore characterization (Table 2) and TGA (Fig. 2) confirm silylation. Fig. 3 show that an octyl ligand slows down reduction of cobalt. In line with the MO-tMe type *Pre*-modified support, methane selectivity is high and C<sub>2</sub>-C<sub>4</sub> is low.

It is frequently observed that selectivities to C<sub>5+</sub> and CH<sub>4</sub> follow a straight line for variations in catalyst formulation or process variables.<sup>24</sup> The plot in Fig. 4 is somewhat different in that two separate lines clearly are visible corresponding to *Pre*- and *Post*-impregnation. The reference catalysts are included in the *Post* dataset. That the *Post* catalysts with low silane concentrations follow an intermediate response-line seems reasonable. The origin of the two lines lies in differences in distribution of propagation probabilities,  $\alpha$ -values, as discussed below. Another observation to be made from Fig. 4 is that the only catalysts with significantly improved selectivity to higher hydrocarbons, are *Pre*-impregnated with ClMe-tMe; chloromethyl trimethyl silane. As described above, this silane is not efficient in changing catalyst

properties as measured by the characterization techniques. For comparison,  $C_{5+}$  selectivity for a Co/Re on  $\alpha$ -alumina catalyst with 12 nm cobalt crystallites has been report to 89%.<sup>25</sup>

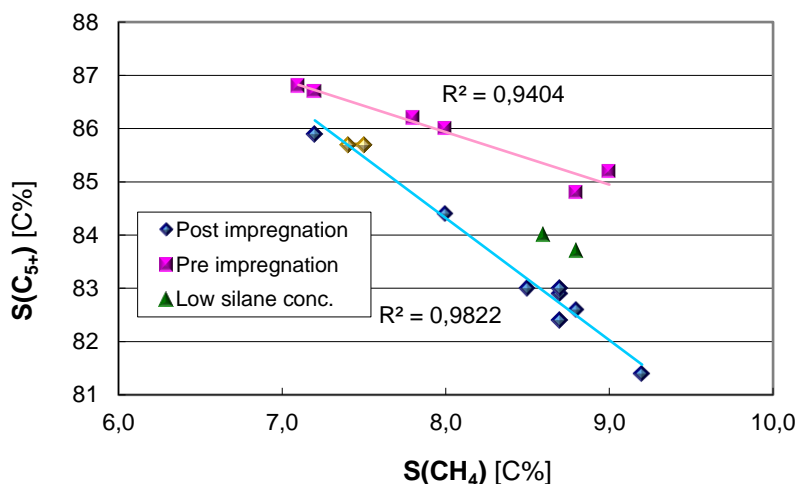


Fig. 4. Selectivity to  $C_{5+}$  as a function of selectivity to  $CH_4$  for *Pre* and *Post* silane impregnated CoRe/ $\gamma$ - $Al_2O_3$  catalysts. Reference catalysts are marked yellow.

Olefin to paraffin ratio is a powerful tool for identifying hydrogenation environment during FT synthesis. Several groups have found that secondary hydrogenation of primary olefins is the main reaction path to paraffins.<sup>17,26</sup> As formation of methane also is a hydrogenation reaction, it is reasonable to see an inverse correlation between these parameters, as indeed is shown in Figs. 5 and 6 for *Post* and *Pre* silane impregnated catalysts. This is a confirmation of silylation as a tool to vary and enhance hydrogenation conditions. Note the outlier for *Post*-impregnation with tCl-Oc silane. Not only is this presumably cross-linked silane at least as selective as the reference catalysts, but it also provides an improved environment for olefin hydrogenation. The very low ethene to ethane ratio, and its independence of hydrogenation conditions, points to a different mechanism for initiation of the chain before regular chain growth commences.

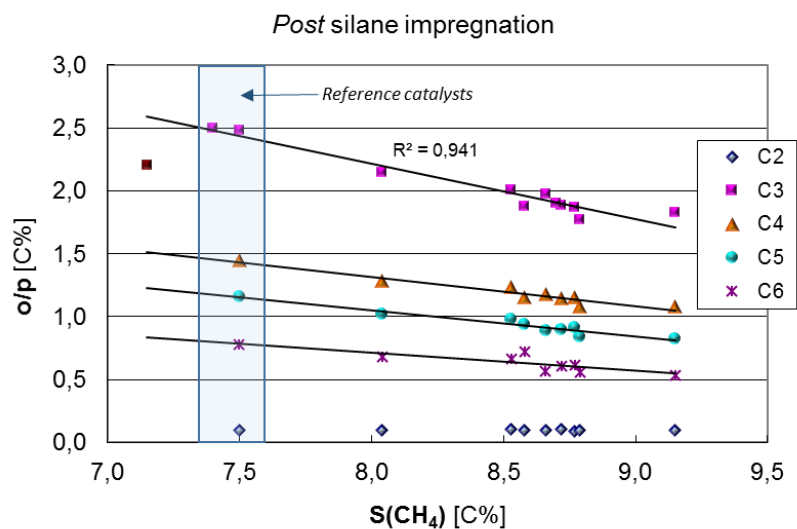


Fig. 5. Olefin to paraffin ratio as a function of selectivity to CH<sub>4</sub> for *Post* silane impregnated CoRe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Outlier at lowest S(CH<sub>4</sub>) is impregnated with tCl-Oc.

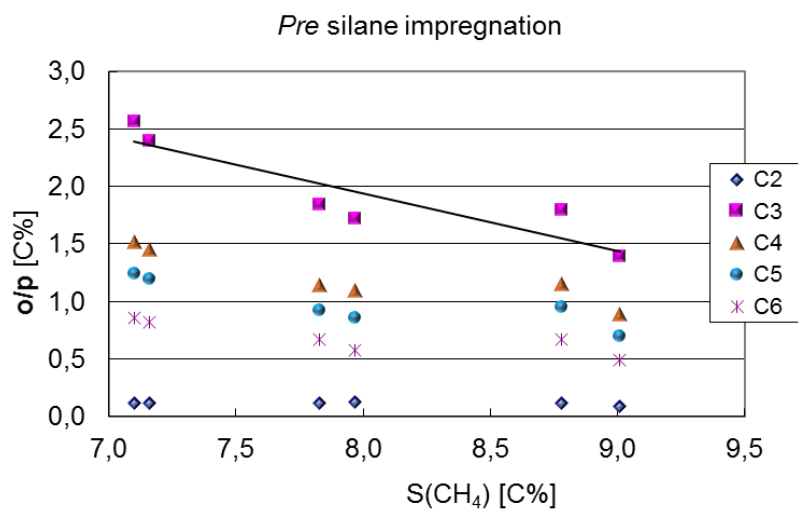


Fig. 6. Olefin to paraffin ratio as a function of selectivity to CH<sub>4</sub> for *Pre* silane impregnated CoRe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

The peculiar selectivity responses are analyzed further by calculating the chain propagation probabilities  $\alpha_{C1}$  and  $\alpha_{C2+}$ ;  $\alpha_{C1}$  being the probability for growth to C<sub>2</sub> over methanation. Fig. 7 shows these two

parameters as a function of  $C_{5+}$  selectivity. Clearly, there is a major difference between *Post*- and *Pre*-impregnated catalysts. The trends for *Post* type catalysts are similar to what is seen in other investigations.<sup>26</sup> It was inferred above that the observed variations in  $C_{5+}$ ,  $o/p$  ratio *etc.* for *Post* catalysts are due to diffusion restrictions giving an enhanced  $H_2/CO$  ratio. However, in such a case a significant reduction in  $\alpha_{C1}$  is expected as the surface  $CH_x$  pool will be shifted towards methane. Although a slight reduction in  $\alpha_{C1}$  is seen for lower  $S(C_{5+})$ , it is more the  $\alpha_{C2+}$ , representing chain growth probability, that varies. A possible interpretation is that there is a silylation of part of the stepped cobalt surface, or at the interphase with alumina, that suppresses CO activation. This is in line with reduced catalyst activity. Fewer  $CH_x$  monomers are then generated per growing chain, and  $\alpha_{C2+}$  declines compared to the reference catalyst.

*Pre*-modified catalysts are characterized by smaller cobalt particles presumably residing on a partly Si-alkyl surface on alumina. The  $\alpha_{C2+}$  value is lifted to some extent, *i.e.* toward  $\alpha$ -alumina and titania supports,<sup>27</sup> and stays constant. This is compatible with the hypothesis that less strained cobalt crystals promote chain growth.<sup>1</sup> The implication is that lower  $S(C_{5+})$ , *i.e.* going left in Fig. 7, in its entirety resides in more facile hydrogenation of  $CH_3^*$  to  $CH_4$ .

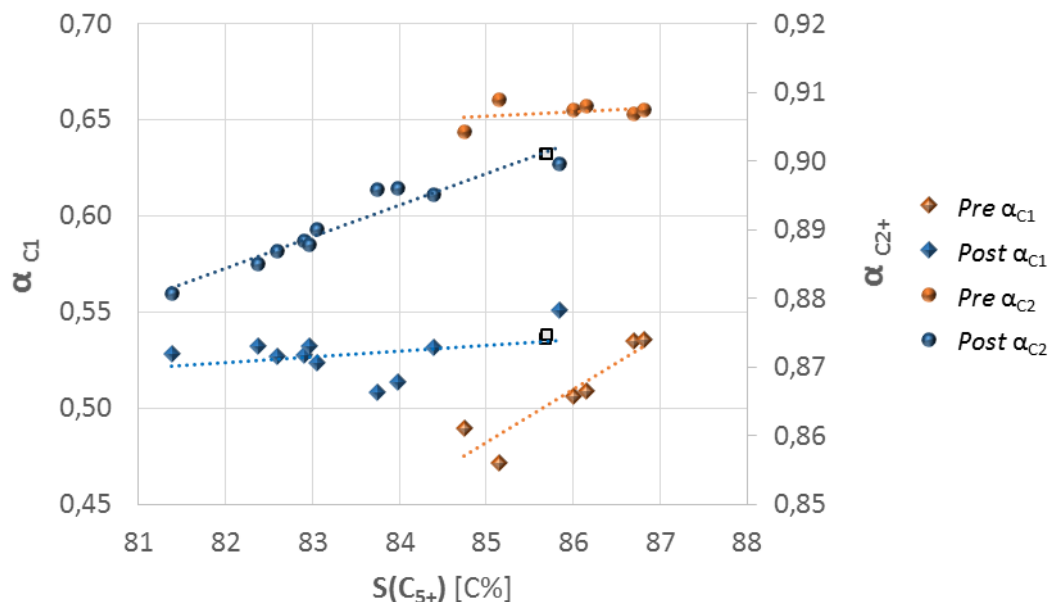


Fig. 7. Propagation probabilities  $\alpha_{C1}$  and  $\alpha_{C2+}$  for *Pre* and *Post* silane impregnated CoRe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Reference catalysts are marked with a black square.

## Conclusions

We conclude that *Post*- or *Pre*-impregnation, *i.e.* after or before cobalt and rhenium calcination, of a reference CoRe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with a number of selected silanes induce the following responses to Fischer-Tropsch synthesis conditions:

- *Post*-impregnation leaves to varying degree silanes in the pores without detectable silylation of the support surface. The observed responses are compatible with diffusion limitations, resulting in higher effective H<sub>2</sub>/CO ratio and lower selectivities to C<sub>5+</sub> products. Interplay with partial silylation of cobalt oxide, suppressing CO activation, is inferred from decoupling the selectivity data. Special effects are seen for trichloro octyl silane indicating cross-linking and silica deposits on cobalt.
- *Pre*-impregnation with chloro or methoxy alkyl silanes leads to silylation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, a hydrophobic surface and smaller cobalt crystallites. There are anomalies in measured product

selectivities, with higher CH<sub>4</sub> and lower C<sub>2</sub>-C<sub>4</sub> fractions than expected. A coupling to the chain growth mechanism is offered in terms of high and constant chain propagation  $\alpha$ -value combined with low, but increasing  $\alpha_{C1}$  as a function of rising C<sub>5+</sub> selectivities.

- The hypothesis that silylation of  $\gamma$ -alumina renders a support surface that resembles  $\alpha$ -alumina, due to a hydrophobic surface, is proven partly correct through an improved chain growth probability ( $\alpha_{C2+}$ ). Particularly interesting is chloro trimethyl silane that has a slightly improved selectivity coupled with significantly improved activity, meaning that the temperature can be reduced for further benchmarking of selectivity. Further studies are needed to explain why *chloromethyl* trimethyl silane, as the only one of five silanes impregnated before cobalt, yields improved C<sub>5+</sub> selectivity in spite of low detectable residues found in the final catalysts.

### Acknowledgements

This publication forms a part of the inGAP (Innovative Natural Gas Processes and Products) Centre of Research-based Innovation, which receives financial support from the Norwegian Research Council under contract no. 174893.

### References

---

<sup>1</sup> E. Rytter and A. Holmen, *On the support in Fischer-Tropsch synthesis – emphasis on alumina and aluminates*, Catal. Today 275 (2016) 11-19.

<sup>2</sup> C.M. Balonek, A.H. Lillebø, E. Rytter, L.D. Schmidt and A. Holmen, *Effect of alkali metal impurities on Co-Re catalysts for Fischer-Tropsch synthesis from biomass-derived syngas* Catal. Lett. 138 (2010) 8-13.

<sup>3</sup> Ø. Borg, S. Eri, E.A. Blekkan, S. Storsæter, H. Wigum, E. Rytter and A. Holmen, *Fischer-Tropsch synthesis over  $\gamma$ -alumina-supported cobalt catalysts: Effect of support variables*, J. Catal. 248 (2007) 89-100.

<sup>4</sup> G. Busca, *The surface of transitional aluminas: A critical review*, Catal. Today 226 (2014) 2–13.

<sup>5</sup> E. Richard, S. Aruna and B. J. Basu, *Superhydrophobic surfaces fabricated by surface modification of alumina particles*, Appl. Surf. Sci. 258 (2012) 10199–10204.



- 
- <sup>6</sup> W. Bao, F. Guo, H. Zou, S. Gan, X. Xu and K. Zheng, *Synthesis of hydrophobic alumina aerogel with surface modification from oil shale ash*, *Powd. Techn.* 249 (2013) 220–224.
- <sup>7</sup> L. J. Jallo, M. Schoenitz, E. L. Dreizin, R. N. Dave and C. E. Johnson, *The effect of surface modification of aluminum powder on its flowability, combustion and reactivity*, *Powd. Techn.* 204 (2010) 63–70.
- <sup>8</sup> L. Wu, Y. Huang, Z. Wang, L. Liu and H. Xu, *Fabrication of hydrophobic alumina aerogel monoliths by surface modification and ambient pressure drying*, *Appl. Surf. Sci.* 256 (2010) 5973–5977.
- <sup>9</sup> E. F. Vansant, P. Van Der Voort and K. C. Vrancken, *Characterization and chemical modification of the silica surface*, Elsevier, 1995.
- <sup>10</sup> L. Shi, J. Chen, K. Fang and Y. Sun, *CH<sub>3</sub>-modified Co/Ru/SiO<sub>2</sub> catalysts and the performances for Fischer-Tropsch synthesis*, *Fuel* 87 (2008) 521 – 526.
- <sup>11</sup> L. Shi, D. Li, B. Hou and Y. Sun, *Organic modification of SiO<sub>2</sub> and its influence on the properties of Co-based catalysts for Fischer-Tropsch synthesis*, *Chin. J. Catal.* 28 (2007) 999 – 1002.
- <sup>12</sup> L. Jia, L. Jia, D. Li, B. Hou, J. Wang and Y. Sun, *Silylated Co/SBA-15 catalysts for Fischer-Tropsch synthesis*, *J. Sol. State Chem.* 184 (2011) 488 – 493.
- <sup>13</sup> M. Ojeda, F. J. Prez-Alonso, P. Terreros, S. Rojas, T. Herranz, M. Lopez Granados and J. L. G. Fierro, *Silylation of a Co/SiO<sub>2</sub> Catalyst. Characterization and Exploitation of the CO Hydrogenation Reaction*, *Langmuir* 22 (7) (2006) 3131–3137.
- <sup>14</sup> E. Rytter, N. Tsakoumis and A. Holmen, *On the selectivity to higher hydrocarbons in Co-based Fischer-Tropsch synthesis*, *Catal. Today*, 261 (2016) 3-16.
- <sup>15</sup> S. Storster, Ø. Borg, E. Blekkan and A. Holmen, *Study of the effect of water on Fischer-Tropsch synthesis over supported cobalt catalysts*, *J. Catal.* 231 (2005) 405 – 419.
- <sup>16</sup> Ø. Borg, S. Storster, S. Eri, H. Wigum, E. Rytter and A. Holmen, *The effect of water on the activity and selectivity for  $\gamma$ -alumina supported cobalt Fischer-Tropsch catalysts with different pore sizes*, *Catal. Letters* 107 (2006) 95–102.
- <sup>17</sup> E. Rytter, S. Eri, T. H. Skagseth, D. Schanke, E. Bergene, R. Myrstad and A. Lindvåg, *Catalyst particle size of cobalt/rhenium on porous alumina and the effect on Fischer-Tropsch catalytic performance*, *Ind. Eng. Chem. Res.* 46 (26) (2007) 9032–9036.

- 
- <sup>18</sup> M. Capel-Sanchez, L. Barrio, J. Campos-Martin and J. Fierro, *Silylation and surface properties of chemically grafted hydrophobic silica*, *J. Coll. Interface Sci.* 277 (1) (2004) 146 – 153.
- <sup>19</sup> R. G. Snyder, S. L. Hsu and S. Krimm, *Vibrational spectra in the C-H region and the structure of the polymethylene chain*, *Spectrochim. Acta* 34A (1978) 395-406.
- <sup>20</sup> M. Scarlete, S. Brienne, I. S. Butler and J. F. Harrod, *Infrared spectroscopic study of thin films of poly(methylsilane), its oxidation and its transformation into poly(carbosilane) on the surface of silicon single-crystal wafers*, *Chem. Mater.* 6 (1994) 977-982.
- <sup>21</sup> Ø. Borg, M. Rønning, S. Storsæter, W. van Beek and A. Holmen, *Identification of cobalt species during temperature programmed reduction of Fischer-Tropsch catalysts*, *Stud. Surf. Sci. Catal.* 163 (2007) 255–272.
- <sup>22</sup> Ø. Borg, N. Hammer, S. Eri, O. A. Lindvg, R. Myrstad, E. A. Blekkan, M. Rønning, E. Rytter and A. Holmen, *Fischer-Tropsch synthesis over un-promoted and Re-promoted  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported cobalt catalysts with different pore sizes*, *Catal. Today* 142 (2009) 70 – 77.
- <sup>23</sup> A. Khodakov, J. Lynch, D. Bazin, B. Rebours, N. Zanier, B. Moisson and P. Chaumette, *Reducibility of cobalt species in silica-supported Fischer-Tropsch catalysts*, *J. Catal.* 168 (1997) 16 – 25.
- <sup>24</sup> E. Rytter, T. H. Skagseth, S. Eri and A. O. Sjøstad, *Cobalt Fischer-Tropsch catalysts using nickel promoter as a rhenium substitute to suppress deactivation*, *Ind. Eng. Chem. Research* 49 (2010) 4140-4148.
- <sup>25</sup> Ø. Borg, P.D.C. Dietzel, A.I. Spjelkavik, E.Z. Tveten, J.C. Walmsley, S. Diplas, S. Eri, A. Holmen and E. Rytter, *Fischer-Tropsch synthesis: Cobalt particle size and support effects on intrinsic activity and product distribution*, *J. Catal.* 259 (2008) 161-164.
- <sup>26</sup> B. Shi and B. H. Davis, *Fischer-Tropsch synthesis: The paraffin to olefin ratio as a function of carbon number*, *Catal. Today*, 106 (2005) 129-131.
- <sup>27</sup> S. Løgdberg, M. Lualdi, S. Järås, J. C. Walmsley, E. A. Blekkan, E. Rytter and A. Holmen, *On the selectivity of cobalt based Fischer-Tropsch catalysts: Evidence for a common precursor for methane and long-chain hydrocarbons*, *J. Catal.* 274 (2010) 84-98.