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# Role of surface carboxylate deposition on the deactivation of cobalt on titania Fischer-Tropsch catalysts

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## ABSTRACT

Operando spectroscopic techniques (Diffusive Reflective Infrared Fourier-Transform and Mössbauer emission spectroscopy) were combined to investigate the role of oxygenates deposition on deactivation of cobalt on titania Fischer-Tropsch catalysts at high pressure. Clear formation of carboxylates was seen for catalysts prepared via both impregnation and precipitation, but more and heavier carboxylates were seen on the impregnated catalyst. This effect is related to a higher olefin content in the products obtained with the impregnated sample, resulting to increased formation of oxygenates through the hydroformylation side reaction. The combined gas chromatography/infrared spectroscopy data demonstrated that the surface carboxylate species are not involved in the catalyst deactivation, being most likely spectator species on the titania support.

## 1. Introduction

Fischer-Tropsch synthesis (FTS) is a catalytic process that converts synthesis gas obtained from natural gas, coal and biomass into liquid fuels [1,2]. Cobalt based catalysts have high activity, high selectivity to linear paraffins and low unwanted water-gas shift activity, but an important research topic is to further improve the catalyst stability. The general deactivation mechanisms of Co FTS catalysts such as poisoning, re-oxidation, sintering of active phase and deposition of carbon and oxygenated compounds have been reviewed extensively earlier [3–8].

Formation of different types of carbon compounds on the catalyst surface and their role on deactivation of Co-based FTS catalysts has been reported [4–6]. Moodley et al. [6] identified polymeric carbon species on spent Co/Pt/Al<sub>2</sub>O<sub>3</sub> catalyst that linked to long-term deactivation. Scalbert et al. [9] found build-up of oxygenated compounds with time on a Co/Al<sub>2</sub>O<sub>3</sub> catalyst using XRD-DRIFT spectroscopy. They proposed that these strongly adsorbed species are responsible for catalyst deactivation by covering the active sites. As part of the mechanism in cobalt based Fischer-Tropsch synthesis, the hydroformylation route, where CO is inserted in an (re-)adsorbed alpha-olefinic chain, results in formation of alcohols and aldehydes [23,24]. The carboxylic acids are also mentioned to be primary Fischer-Tropsch products, obtained via equilibrium interconversion reactions from the alcohols and aldehydes [26]. Pinard

et al. [10] analysed the carbon species present on a spent Co/Ru/Al<sub>2</sub>O<sub>3</sub> catalyst using temperature programmed hydrogenation-infrared (TPH-IR) technique. Atomic carbon, alcohols, carboxylic acids and polymeric carbon were found on the spent catalyst surface. Carboxylates are formed when an acid reacts with surface hydroxyl groups under formation of water, so on titania: RCOOH + TiOH → RCOO<sup>-</sup>Ti<sup>+</sup> + H<sub>2</sub>O. TPH-IR of the spent catalyst indicated that complete removal of carboxylate species required temperatures above 600 °C. They proposed that carboxylates on the catalyst surface cause deactivation, but the exact role of the carboxylates on the catalyst surface is not yet fully understood. Moreover, it appears that conflicting insights about the resistance to hydrogen rejuvenation are proposed. The main aim of this research is to investigate the role of carboxylates in the deactivation mechanism of titania based FTS catalysts.

In order to determine if carboxylates play a role in the deactivation behaviour of the catalysts, we employed two operando characterisation techniques: diffusive reflective infrared Fourier-Transform (DRIFT) and Mössbauer emission spectroscopy (MES) to monitor the changes in the morphology of the catalysts during FTS operation [9,11,12]. In this study, we have investigated two catalysts prepared by incipient wetness impregnation (IWI) and homogeneous deposition precipitation (HDP) methods, uniquely monitoring the surface species with operando DRIFT and the state of the cobalt with operando Mössbauer emission

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spectroscopy during the FTS reaction.

## 2. Experimental

### 2.1. Catalyst preparation

Two Co/TiO<sub>2</sub> samples Co(9.3 %)/TiO<sub>2</sub> - IWI and Co(8.9 %)/TiO<sub>2</sub> - HDP were synthesized by incipient wetness impregnation with aqueous cobalt nitrate and homogeneous deposition precipitation by NH<sub>3</sub> evaporation. Catalyst preparation methods have been described in detail by Eschemann et al. [13] and the catalyst samples were received from Utrecht University. For the MES experiments, the two catalyst samples (75–150 μm) were post-impregnated with typically 0.3–0.4 μg of radioactive <sup>57</sup>Co (as Co(NO<sub>3</sub>)<sub>2</sub> solution) and dried at 120 °C for 6 h in air.

### 2.2. Operando Mössbauer emission spectroscopy (MES) study of Co/TiO<sub>2</sub> catalysts

The Mössbauer emission spectroscopy (MES) measurements were performed under operando conditions in a high-pressure MES reaction cell. The design and details of the MES reaction cell have been described previously by Crajé et al. [12]. <sup>57</sup>Co-MES technique is used to follow the oxidation state and dispersion of supported cobalt particles [12]. After the reduction procedure (at 350 °C in 100 mL/min of H<sub>2</sub> for 2 h), the FTS measurements were carried out at 200 °C, 20 bar and a H<sub>2</sub>/CO feed ratio (FR) of 4 v/v. The catalytic data is reported after 2 days of operation. The products were analysed with a thermal conductivity detector on a Varian Micro-GC CP4900 (Dual channel) gas chromatograph, equipped with molecular sieve and Porapaq Q columns.

The MES spectra were recorded at different temperatures, using a constant acceleration spectrometer in a triangular mode with a moving single-line K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O absorber enriched in <sup>57</sup>Fe. The velocity scale was calibrated with a <sup>57</sup>Co:Rh source and a sodium nitroprusside absorber. The recorded Mössbauer spectra were fitted using the MossWinn 3.0i program [14].

### 2.3. Operando DRIFT study of Co/TiO<sub>2</sub> catalysts

The catalyst samples CoTiO<sub>2</sub> - IWI and Co/TiO<sub>2</sub> - HDP were also investigated using an operando DRIFT spectroscopy setup, equipped with a Thermo Nicolet Nexus 670 FT-IR spectrometer to monitor the presence of adsorbed surface species on the surface of the FTS catalysts under relevant industrial conditions. Infrared spectra were recorded with 128 scans at a resolution of 4 cm<sup>-1</sup>. The Co/TiO<sub>2</sub> catalyst (100 mg) was loaded into the DRIFT reaction cell and reduced at 350 °C in 100 mL/min of H<sub>2</sub> for 2 h. Subsequently the reaction cell was cooled down to 200 °C and a background spectrum was measured in a mixture of Ar/H<sub>2</sub> (75/20 mL/min). After this step, 5 mL/min CO was also introduced into the reactor and the pressure was increased to 20 bar. Catalyst samples were studied at 200 °C and 20 bar with H<sub>2</sub>/CO FR of 4 v/v. After 4 days of reaction, the catalyst was stripped with H<sub>2</sub> at 270 °C for 16 h to remove wax and other products from the catalyst surface and the reaction was restarted at the initial FTS conditions. A ramp rate of 5 °C/min was used for all heating and cooling steps. The reaction products and permanent gases were analysed with a Thermo Scientific Ultra Trace gas chromatograph (GC), equipped with a thermal conductivity detector and a flame ionisation detector.

### 2.4. Transmission electron microscopy (TEM) analysis

The TEM measurements were performed using a FEI Tecnai microscope, with electron beam voltage of 300 kV. TEM samples were ground with a mortar and suspended in ethanol under ultrasonic vibration. A small amount of this suspension was brought onto a copper TEM grid and dried. Spent samples were first cleaned with tetrahydrofuran to remove solid wax in the pores of the catalyst. Surface area averaged

**Table 1**

Performance of IWI and HDP catalysts at 200 °C and 20 bar after TOS 2 days.

Catalyst sample	*Bulk Co <sup>0</sup> (%)	Activity (mol CO.g <sub>Co</sub> <sup>-1</sup> .s <sup>-1</sup> )
Co/TiO <sub>2</sub> - IWI	95	1.1·10 <sup>-5</sup>
Co/TiO <sub>2</sub> - HDP	94	2.8·10 <sup>-5</sup>

\* From the MES data.

**Table 2**

The MES fitted parameters of Co/TiO<sub>2</sub> - IWI and Co/TiO<sub>2</sub> - HDP catalysts, after different treatments.

Treatment	T (°C)	IS (mm·s <sup>-1</sup> )	QS (mm·s <sup>-1</sup> )	HF (Tesla)	SC (%)	Oxidation state
Co/TiO <sub>2</sub> - IWI	25	0.22	0.82	–	89	Co <sup>3+</sup>
Fresh sample		1.10	2.09	–	11	Co <sup>2+</sup>
Co/TiO <sub>2</sub> - IWI		–0.1	–	34.2	97	Co <sup>0</sup>
Reduction (100 % H <sub>2</sub> , 350 °C)	25	0.97	2.21	–	3	Co <sup>2+</sup>
Co/TiO <sub>2</sub> - IWI	200	–0.22	–	32.8	95	Co <sup>0</sup>
FTS reaction, 20 bar, 2 days		0.95	1.99	–	5	Co <sup>2+</sup>
Co/TiO <sub>2</sub> - HDP	25	0.23	0.76	–	97	Co <sup>3+</sup>
Fresh sample		1.06	2.78	–	3	Co <sup>2+</sup>
Co/TiO <sub>2</sub> - HDP	25	–0.1	–	34.2	96	Co <sup>0</sup>
Reduction (100 % H <sub>2</sub> , 350 °C)		1.13	2.42	–	4	Co <sup>2+</sup>
Co/TiO <sub>2</sub> - HDP	200	–0.23	–	32.8	94	Co <sup>0</sup>
FTS reaction, 20 bar, 2 days		0.76	1.62	–	6	Co <sup>2+</sup>

IS: Isomer shift, QS: Quadrupole splitting, HF: Hyperfine field, SC: Spectral contribution.

Experimental uncertainties: IS: ±0.05 mm·s<sup>-1</sup>, QS: ±0.05 mm·s<sup>-1</sup>, HF: ± 1%, SC: ± 3%.

cobalt particle sizes are calculated based on analysis of typically 300 particles.

## 3. Results and discussion

### 3.1. Operando Mössbauer emission spectroscopy (MES) studies

The catalytic performance of IWI and HDP catalysts studied by the operando high-pressure MES reaction cell is presented in Table 1. The activity of the HDP catalyst was 2.5 times higher than the IWI catalyst. Eschemann et al. [13] also found that the Co/TiO<sub>2</sub> catalyst prepared by the precipitation method is ~1.5 times more active than the catalyst prepared by the IWI method. They observed well-distributed metal particles for the HDP catalyst and clustering of similar-size particles for the IWI catalyst that could tentatively explain the observed difference in catalytic performance. Morales et al. [15] studied a Co/TiO<sub>2</sub> catalysts containing Mn promoter prepared by IWI and HDP methods and they also found that the HDP catalyst was more active than the catalyst prepared by the IWI method, due to the better distribution of the Co phase.

The MES fitted parameters obtained with Co/TiO<sub>2</sub> - IWI catalyst are listed in Table 2. The MES spectrum of the fresh catalyst sample consists of two doublets, with about 89 % of the Co atoms present as Co<sup>3+</sup>. After reduction at 350 °C in H<sub>2</sub>, the main contribution is assigned to metallic Co obtained via conversion of Co<sup>2+</sup>/Co<sup>3+</sup> during reduction. A small Co<sup>2+</sup> amount is still present, either unconverted CoO that interacts strongly with the support or the mixed phase CoTiO<sub>3</sub> [15]. No change in the cobalt oxidation state happened during the 2-day Fischer-Tropsch

**Table 3**  
IWI and HDP Co/TiO<sub>2</sub> catalysts at 20 bar and 200 °C after TOS 4 days.

Catalyst samples	Activity (mol CO <sub>2</sub> g <sub>Co</sub> <sup>-1</sup> s <sup>-1</sup> )	Selectivity (%) on carbon basis				O/P
		C <sub>1</sub> -C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5+</sub>	
Co/TiO <sub>2</sub> - IWI	1.4·10 <sup>-5</sup>	5.8	2.1	2.1	90.0	0.7
Co/TiO <sub>2</sub> - HDP	2.2·10 <sup>-5</sup>	5.6	1.9	2.0	90.5	0.4

**O/P ratio:** Olefins C<sub>5</sub> to C<sub>9</sub>/Paraffins C<sub>5</sub> to C<sub>9</sub>.

reaction, confirming the absence of oxidation.

The MES parameters of Co/TiO<sub>2</sub> - HDP catalyst are also listed in Table 2. Similar Mössbauer results were obtained as with the IWI sample, confirming the absence of oxidation in both catalysts, in line with previous observations of the absence of this deactivation mechanism [7, 16]. From Mössbauer spectra, the percentage of metallic Co, hyperfine field and the isomer shift after reduction and during the reaction in both catalysts is nearly equal. Therefore, the large difference in the activity of the catalysts cannot be revealed solely on the basis of the MES results.

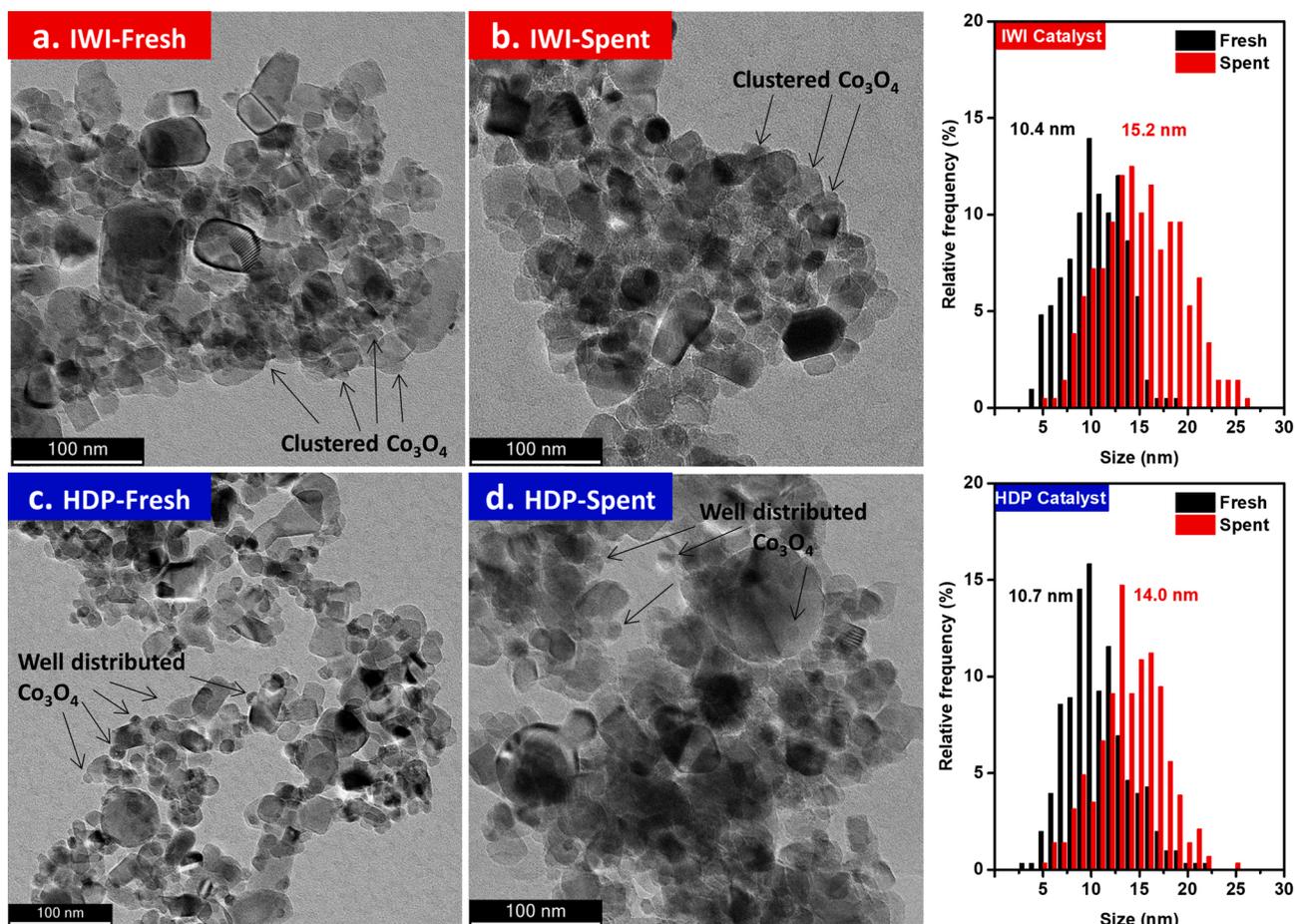
### 3.2. Operando DRIFT and TEM studies

The activity and selectivity of IWI and HDP Co/TiO<sub>2</sub> catalysts measured inside the operando DRIFT cell are shown in Table 3. The HDP catalyst was found to be 1.6 times more active than the IWI catalyst. This ratio is different from the value measured in the MES cell, which is not an optimized plug-flow reactor, having a large dead-volume at the top of the catalyst bed. In order to understand the difference in activity of the

catalysts, both fresh and spent samples were examined with TEM (Fig. 1), where also the particles size distributions are shown. The average particle size of both IWI and HDP spent catalysts is higher than in the fresh samples due to sintering during the reaction. The average particle size of the spent IWI catalyst is higher than for the spent HDP catalyst. As observed in Fig. 1, the HDP preparation method has a significant impact on the cobalt distribution on the TiO<sub>2</sub> support, resulting in well-distributed cobalt active structures having higher accessible surface area and improved activity, as previously indicated by Eschemann et al. [17].

The infrared spectra of IWI and HDP catalysts during FTS at different reaction times are shown in Fig. 2. The intensity of infrared bands corresponding to formate, acetate and high molecular weight (MW) carboxylate species increased with time due to their deposition on the catalyst surface. The band at 1589 cm<sup>-1</sup> and two other bands at 1373 cm<sup>-1</sup> and 1360 cm<sup>-1</sup> are assigned to asymmetric  $\nu_{as}(\text{COO}-)$  and symmetric  $\nu_s(\text{COO}-)$  vibrations of formate species on the catalyst surface. These formate bands level off after one day of FTS for the IWI catalyst, while the spectra are dominated by signals from higher carboxylates. In the case of HDP catalyst, the low molecular weight formate species are always dominant and reached a maximum intensity after 3 days. The presence of formate species on the surface of Co-based FTS catalysts was also reported earlier using DRIFT spectroscopy [18,19]. Lorito et al. [20,21] found two types of formate species (fast and slow reacting) present on the Co-based catalyst, using DRIFT and monitoring the decomposition rates of formate species at different temperatures. They proposed that formate could potentially be an intermediate in the formation of methanol.

The bands at 1554 cm<sup>-1</sup> and 1540 cm<sup>-1</sup> are assigned to asymmetric



**Fig. 1.** TEM micrographs and histograms for cobalt particle size analysis of IWI and HDP catalysts.  
**Note:** Sharp edged particles: TiO<sub>2</sub> & Round shaped particles: Co/Co<sub>3</sub>O<sub>4</sub> [22].

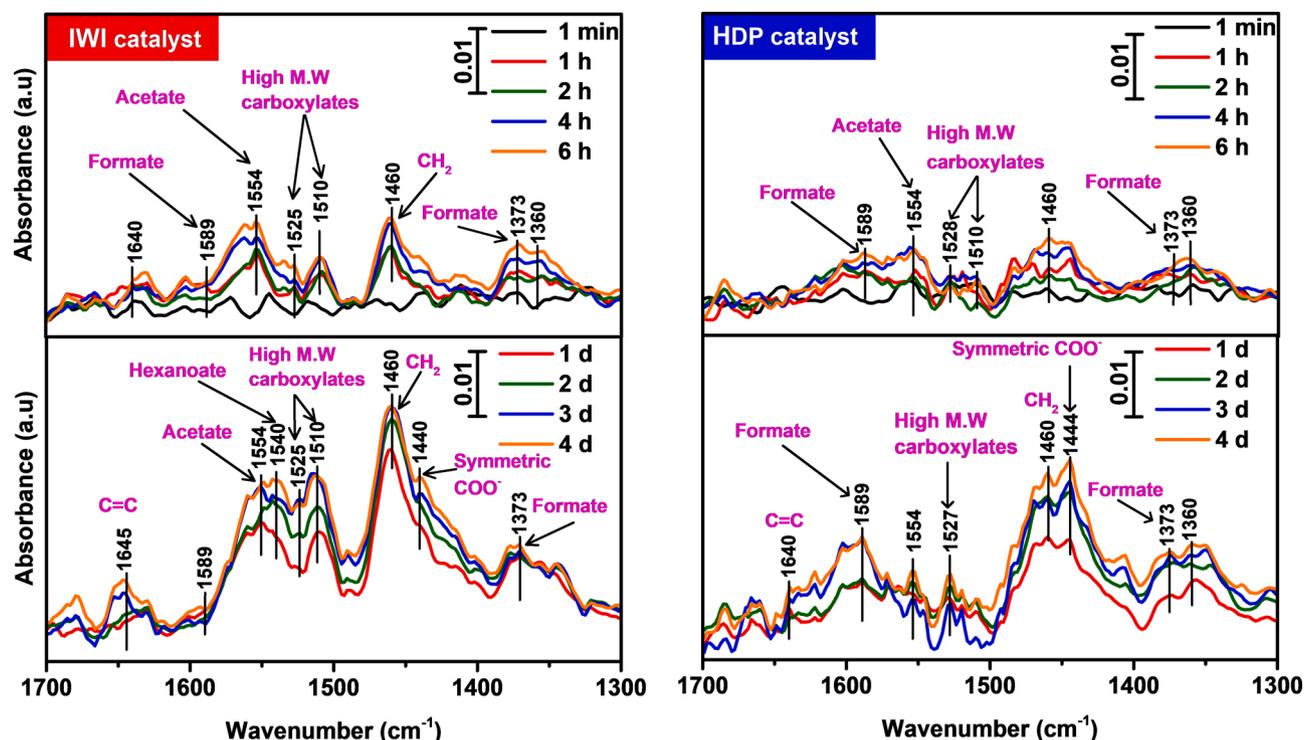


Fig. 2. DRIFT spectra of IWI and HDP catalysts during FTS reaction.

vibrations of acetate  $\nu_{as}(\text{CH}_3\text{COO}^-)$  and hexanoate  $\nu_{as}(\text{C}_5\text{H}_{11}\text{COO}^-)$  on the catalyst [10]. The peaks  $1525\text{ cm}^{-1}$  and  $1510\text{ cm}^{-1}$  correspond to high MW carboxylates. The band at  $1460\text{ cm}^{-1}$  is due to  $\text{CH}_2$  bending vibrations of carboxylates and other hydrocarbons. The band at  $1444\text{ cm}^{-1}$  corresponds to symmetric stretching of  $\text{COO}^-$ . The  $\text{CH}_2$  band at  $1460\text{ cm}^{-1}$  overlaps partially with the  $\text{COO}^-$  band at  $1444\text{ cm}^{-1}$ . The ratio between the bands provides an indication of the carboxylate chain length. In the beginning of the reaction, the IWI catalyst surface is covered by acetate species, with only small amounts of hexanoate and other high MW carboxylates species. After 4 days of reaction, the catalyst surface is dominated by high MW carboxylates species. Like all FT products, also acids follow the ASF chain growth mechanism and hence much fewer heavy acids are made compared to the light acids. The observation that the ratio of lower to higher acids shifts in time, gives insight in the reversibility of carboxylate deposition on the surface. Moreover, a domination by longer carboxylates is contrary their production ratio and indicates the higher stability of long chain acids on the surface.

In the case of the HDP catalyst, at the beginning of the reaction, a very small amount of formate, acetate and high MW carboxylates were present on the catalyst surface. Even after 4 days of reaction, the formate peak still dominates the spectra. This clearly indicates that high MW acids were produced at much lower amounts by the HDP catalyst, resulting in far less heavy carboxylates accumulation.

The band at  $1640\text{ cm}^{-1}$  is corresponding to the  $\text{C}=\text{C}$  stretching vibrations of olefins on the catalyst surface [9,18]. At the beginning of the reaction, a small peak at  $1640\text{ cm}^{-1}$  was observed for the IWI catalyst, while the HDP sample had no band corresponding to  $\text{C}=\text{C}$  stretching vibrations. After 4 days of reaction, there is a very clear band at  $1640\text{ cm}^{-1}$  for the IWI catalyst, whereas for HDP catalyst this band is barely visible. This indicates that the IWI catalyst surface contained more olefins than the HDP catalyst surface, in line with the GC data (Table 3). Also, the intensity of the band at  $1640\text{ cm}^{-1}$  appears to be correlated with the intensity of the carboxylate bands. These results appear to imply a relation between olefins formation and carboxylates compounds present on the catalyst surface. As also the selectivity data indicates an

olefin/paraffin ratio almost twice as high for the IWI sample, we argue that the increased olefin content is related to formation of more carboxylates via a hydroformylation side reaction. The choice of the preparation method resulting in such distinct difference in terms of carboxylates formation is most likely related to the presence of promoters like nitrogen or salts in the HDP sample. The formation of oxygenated intermediates and other products such as alkenes, alcohols and aldehydes can be understood by the CO insertion mechanism of van Santen et al. [23,24]. Compared to iron catalysts, the fraction of oxygenates and acids in the total product is significantly lower. For cobalt on titania catalysts  $\sim 3\text{ mol}\%$  oxygenates were found, the large majority being linear alcohols [27]. From our own work we estimate that acids consist of 5–10 % of the total oxygenates produced.

As most of the products ( $\sim 97\%$ ) in our system are paraffins and olefins, entails that significant amount of wax is produced and filling of the catalyst pores occurs within a few hours. In fact, we ascribe part of the deactivation during the first 24 h to wax filling of the catalyst particles, while most of the deactivation is due to cobalt sintering and is not reversible. After the 24 h period the DRIFT data shows a further build-up of carboxylates for another 2–3 days. Carboxylates can continue to build-up as they have a much stronger ionic interaction with the titania surface compared to the weak forces governing the physisorption of wax. The observation that shorter acids can be replaced by heavier acids does however indicate that also the carboxylates bind reversibly.

The carboxylic acids are believed to have a role in the Co-based FTS catalysts deactivation, with Pinard et al. [10] measuring low catalytic performance with a sample containing surface carboxylates resistant to a rejuvenation treatment with hydrogen. Scalbert et al. [9] found absorption and an increase in the amount of oxygenated and unsaturated compounds with time on a  $\text{Co}/\text{Al}_2\text{O}_3$  catalyst using XRD-DRIFT spectroscopy, species believed to be responsible for catalyst deactivation by covering the active sites. Gu et al. [25] found significant effects on the activity of the  $\text{Co}/\text{Al}_2\text{O}_3$  FTS catalyst in the presence of acetic and butyric acids in the feed. The activity decreased by 50 % in the presence of acetic acid and stabilised afterwards. The low activity was accredited to the formation of inactive cobalt acetate species, which was confirmed

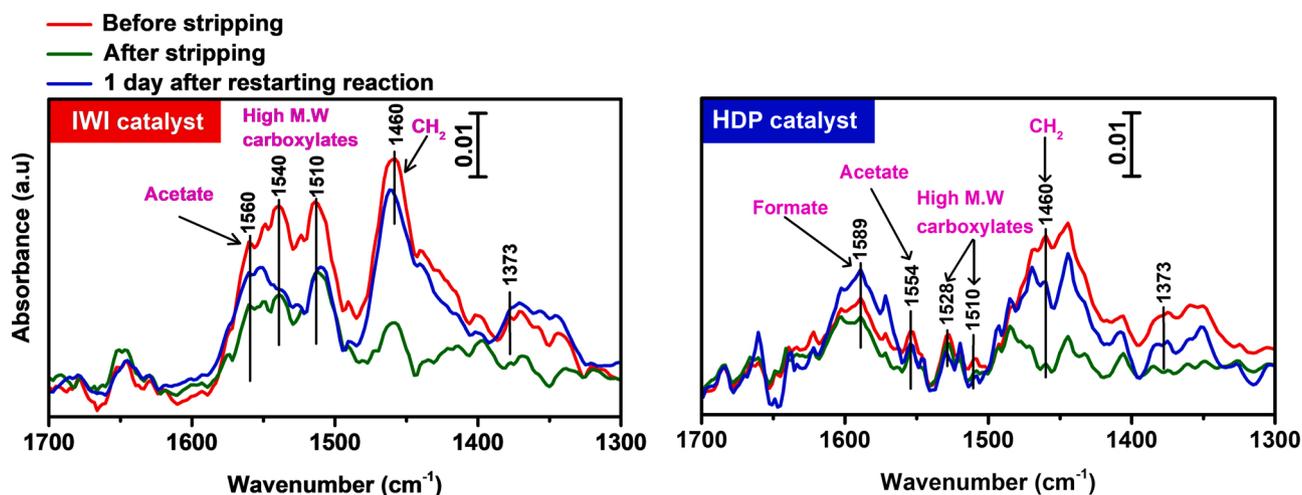


Fig. 3. Effect of H<sub>2</sub> stripping on DRIFT spectra of IWI and HDP catalysts.

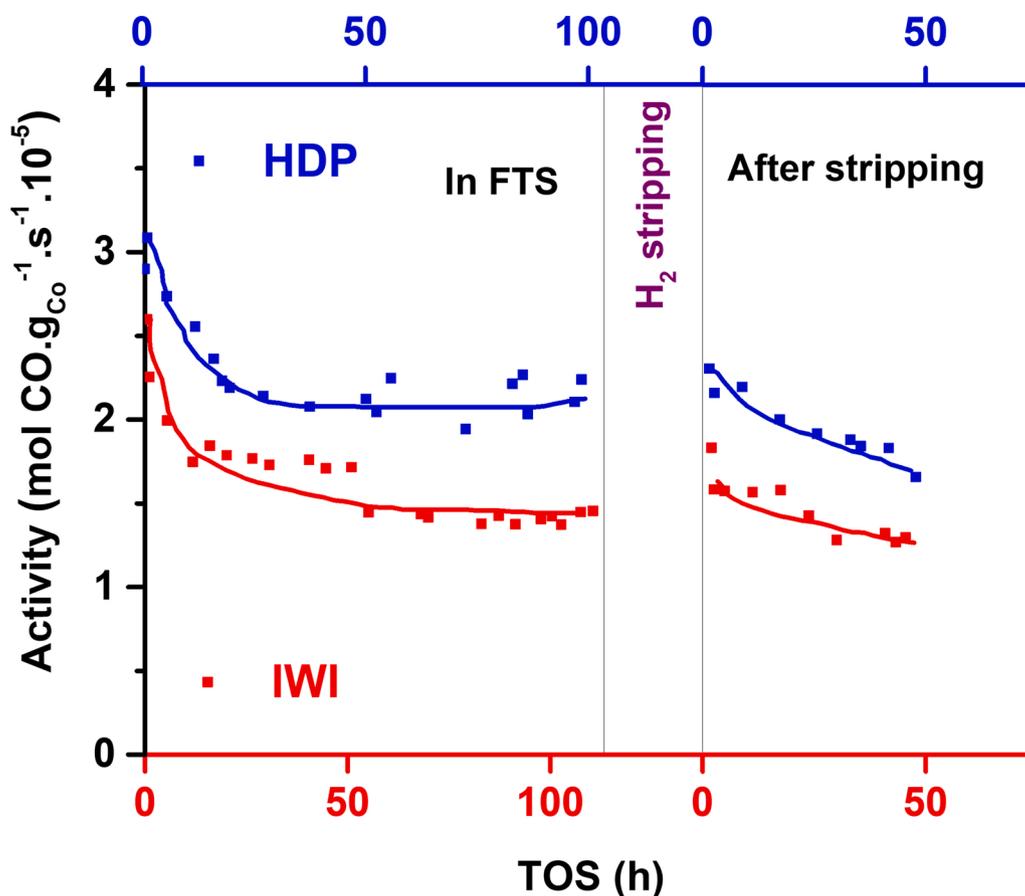


Fig. 4. Effect of H<sub>2</sub> stripping on the performance of IWI and HDP catalysts.

using FTIR and XRD spectroscopy. Addition of butyric acid showed a similar effect on the performance of the catalyst.

To verify the hypothesis that carboxylic acids play a role in the deactivation behaviour of the catalysts, both IWI and HDP samples were stripped under H<sub>2</sub> at 270 °C for 16 h to remove the surface species deposited on the catalysts during the initial 4-day reaction, followed by restarting the FTS reaction for an additional 2 days. Fig. 3 shows the effect of stripping on DRIFT spectra of IWI and HDP catalysts. Acetates, hydrocarbons and part of the high MW carboxylates were removed from the IWI catalyst surface. In the case of HDP catalyst, hydrocarbons were

removed significantly, while the carboxylates (formate being dominant) were partially removed. After restarting the reaction, the hydrocarbons and carboxylates on the surface of both catalysts re-appeared.

As shown in Fig. 4, the H<sub>2</sub> stripping procedure results only in a modest activity recovery for both catalysts, suggesting that the surface carboxylates are not involved in a deactivation mechanism, being most likely spectator species on the titania support. The wax filling of the samples pores is only partly responsible for the catalyst deactivation, as the diffusion limitations are small due to chosen operating conditions with crushed particles and ~4% CO conversion. The similar

deactivation pattern observed in Fig. 4 with the IWI and HDP samples, although on HDP far less carboxylates are present, provides another convincing evidence in support of the preferential location of the carboxylates on the support material. Also, the observed 40 % drop in activity for both catalysts during the FT reaction would be related to significant presence of an oxidized cobalt phase, if carboxylates were associated with the active sites. However, the Mössbauer results (Table 2) showed that this is clearly not the case.

Pinard et al. [10] showed using TPH that in a 100 % H<sub>2</sub> environment the removal of carboxylates from the catalyst surface begins already at 270 °C under transient conditions. Therefore, the static 16 h applied stripping method is expected to remove most of the carboxylic acids. Some high MW carboxylates are still observed in the DRIFT spectra measured with the IWI catalyst after stripping (Fig. 3, left), as carboxylates on cobalt are more easy to remove than on the support, since the removal requires a hydrogenation step. On metallic cobalt the required hydrogen activation is easily accomplished, but on the titania support, without neighbouring cobalt active species, it will take much longer. The presence of the carboxylates preferentially on the support material (before and after the stripping procedure) is backed by Schweicher et al. [19], who showed that the detected oxygenates were not part of the reaction mechanism. Paredes-Nunez et al. [20] demonstrated that the surface formate species present on an alumina-supported cobalt catalyst had two distinct reactivities, both associated to an oxide phase. As the MES results clearly indicate that cobalt oxidation is absent in our samples, we can substantiate the conclusion that most of the carboxylic acids are present on the TiO<sub>2</sub> support, with little influence on the catalytic activity.

#### 4. Conclusions

The combination of operando spectroscopy techniques allowed to further elucidate the role of carboxylates during deactivation of cobalt on titania catalysts at industrial pressure. Carboxylate formation was seen on both precipitated and impregnated catalysts, but more and heavier carboxylates were found on the impregnated catalyst. The Mössbauer emission spectroscopy experiments indicated that almost full cobalt reduction is achieved at 350 °C and that oxidation was absent during the FTS reaction for both samples, regardless of their preparation method, showing that the large majority of the carboxylates are on the titania surface.

The combined gas chromatography/infrared spectroscopy data demonstrated that the surface carboxylate species are not involved in the catalysts deactivation, being most likely spectator species on the titania support. An interesting observation, which warrants further work, is that the formation of long-chain carboxylates was inhibited in the HDP catalyst, this may be due to the presence of impurities like nitrogen or salts introduced by the preparation procedure.

#### CRedit authorship contribution statement

**Prasad Gonugunta:** Investigation, Formal analysis, Writing - original draft. **A. Iulian Dugulan:** Investigation, Formal analysis, Supervision, Validation, Writing - review & editing. **G. Leendert Bezemer:** Conceptualization, Methodology, Resources, Validation, Writing - review & editing. **Ekkas Brück:** Project administration, Funding

acquisition, Supervision, Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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