



Further insights into methane and higher hydrocarbons formation over cobalt-based catalysts with γ -Al₂O₃, α -Al₂O₃ and TiO₂ as support materials



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ABSTRACT

A range of cobalt-based catalysts varying in Co loading and prepared by incipient wetness impregnation of traditional support materials (γ -Al₂O₃, α -Al₂O₃ and TiO₂), have been studied in the Fischer-Tropsch reaction at industrially relevant process conditions (483 K, 20 bar, H₂/CO = 2.1). A high selectivity to C₅₊ hydrocarbons (S_{C5+}) is to a great extent connected with a high site activity, but not exclusively. We propose that the ratio of monomer-production rate to C–C coupling rate of a catalyst determines chain-growth probability by means of governing the coverage of the monomer on the cobalt surface. We speculate that this ratio depends on e.g. shape, strain and size of the Co crystallites and, therefore, is highly dependent on the choice of support material. No general relationship between Co particle size and S_{C5+} is found, but individual correlations exist for each support material.

Within each support material, there are indications of negative correlations between the chain-growth probability of the C₁^{*} surface intermediate (α_{C1}) and the higher α_{Cn} values. This can be rationalized by assuming that the majority of methane is formed by a different mechanism, separate from chain growth, but connected with chain growth through a common carbon pool. We propose that the monomers and the majority of methane are produced at sites different from the ones involved in chain growth. There is no general correlation between α_{C1} and S_{C5+} for catalysts with different support materials, possibly due to small differences in cobalt surface coverage of hydrogen.

For the TiO₂-supported catalysts, a dramatically increased α_{C1} value observed for catalysts with Co particles smaller than approx. 15 nm, is probably associated with strong metal-support interactions (SMSI). This phenomenon apparently limits the effect (reduction) on the S_{C5+} when moving toward smaller Co particles.

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1. Introduction

In Fischer-Tropsch (FT) synthesis, hydrocarbons (HCs) are produced from synthesis gas (H₂ + CO) at elevated pressure, typically over a cobalt or iron-based catalyst. Traditionally, coal or natural gas has been used as feedstocks for the synthesis gas. However,

in recent years, due to concerns about global warming and fuel security, the interest for using biomass as feedstock has increased.

Provided that the synthesis gas has the appropriate H₂/CO ratio (approx. 2), supported cobalt catalysts are preferred in the FT process when middle distillates are the desired products, due to high activity, high selectivity to higher HCs and low water-gas shift (WGS) activity. High selectivity to higher HCs (e.g. C₅₊), as well as a low methane selectivity, is critical in achieving high overall plant profitability [1], and the literature on proposed selectivity-governing parameters of Co-based catalysts is vast.

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It has been verified that when supported on carbon nanofibers (CNFs) – an essentially inert carrier material – a positive correlation between Co particle size and selectivity to C_{5+} ($S_{C_{5+}}$) exists up to ~ 6 nm at atmospheric pressure [2] and up to ~ 8 – 10 nm at industrial pressures (35 bar) [3]. For larger Co particles, the $S_{C_{5+}}$ levels off with increasing particle size. By steady-state isotopic transient kinetic analysis (SSITKA) it was found that the smaller Co particles have higher surface coverages of hydrogen, which explains the lower $S_{C_{5+}}$ and higher methane selectivities (S_{CH_4}). What parameters govern the $S_{C_{5+}}$ of more traditional, low-dispersed Co catalysts with metal oxide carriers (e.g. Al_2O_3 , SiO_2 , and TiO_2), however, still is a matter of debate.

The differences in $S_{C_{5+}}$ between such Co-based catalysts, when compared at similar conversion levels, have been attributed to e.g. different extents of α -olefin re-adsorption (followed by further chain growth) [4,5], the extent of α -olefin re-adsorption in turn being governed by the degree of mass transfer restrictions on product removal determined by a structural parameter (χ , composed of the physical properties pore size, catalyst pellet size, average active site density and porosity). The importance of such secondary reactions on the $S_{C_{5+}}$ has, however, been questioned [6–11] and Co particle size effects [8,12–14], as well as effects of the chemical nature of the support material [15–17], on the intrinsic chain-growth probability and, accordingly, on the $S_{C_{5+}}$ have been presented. Differences in surface coverages have also been suggested to govern the $S_{C_{5+}}$ for catalysts with Co particles larger than 6–8 nm, e.g. indirectly by hydrogen spillover from the support (typically γ - Al_2O_3) affecting the amount of α -olefins available for reinsertion [18], or directly by variations in surface coverage of active carbon species as observed from SSITKA [19]. Recently, Rytter and Holmen [17] proposed that the often observed relationship between inert supports, large pores and high $S_{C_{5+}}$ [7,15] is due to less strained Co crystallites as a result of the large support-crystallite size of such materials.

In our previous work [10], we presented the findings of linear correlations between methane selectivity (and other lower HC selectivities) and $S_{C_{5+}}$ of a range of low-dispersed Co-based supported catalysts varying in chemical and physical properties with γ - Al_2O_3 , α - Al_2O_3 and TiO_2 as support materials. In a later work [20], we showed that also SiO_2 and SBA-supported catalysts follow the same trend, under conditions free from reactant mass transfer limitations. The above-mentioned observations made us conclude that, for the investigated catalysts, no pure methanation sites existed, but both methane and higher HCs originated from a common precursor/carbon pool, as also found for lower pressures by Mims and McCandlish [21] and by van Dijk et al. [22] applying SSITKA at 1.2 bar.

For the same catalysts [10,20] we also reported on a more or less constant chain-growth probability of the C_1^* surface intermediate, α_{C_1} , at industrially relevant process conditions, while the chain-growth probabilities of the C_{2+}^* surface intermediates increased with increasing $S_{C_{5+}}$. The rather constant α_{C_1} at typical industrial process conditions was speculated to be caused by two parallel routes of methane formation downstream of the monomer formation – one at a “general” cobalt surface, responsible for CO activation and hydrogenation of C^* to monomers and for the overall turnover frequency (TOF), and one at specific chain-growth sites. The majority of the catalysts had apparent CO-TOF values (mol CO converted per mol surface Co and second, estimated from syngas flow and conversion and *ex situ* hydrogen chemisorption) in a relatively narrow range, and the TOF values (measured after 10 h on-stream at low CO conversion) were found not to correlate with the HC selectivities (measured at 40% CO conversion, approx. after 1.5 days on-stream). This, together with a more or less invariant α_{C_1} – a parameter being dramatically influenced by changes in process conditions affecting cobalt surface coverages and rates – suggested that potential differences in the general cobalt surface, such

as coverages of reactants and reaction intermediates as well as intrinsic rates, were not the main causes for the different HC selectivities of the catalysts in that study. The lack of a (negative) correlation between TOF and $S_{C_{5+}}$ also made us assume monomer formation to be the rate determining step (RDS), in agreement with others [21,22]. This has later been supported by a combination of steady-state and transient kinetic modeling with DFT [23], pointing out hydrogen-assisted CO dissociation as the dominating CO activation pathway and proposing hydrogenation of the surface intermediate HCO^* to be the rate determining elementary step. Furthermore, possible differences in extent of α -olefin re-adsorption as a primary C_{5+} selectivity-governing parameter for these small pellet-size catalysts were discarded.

In the current paper we are revisiting the data for the majority of the catalysts included in our more general previous paper Ref. [10], with the aim of increasing the understanding of the $S_{C_{5+}}$ governing parameters for traditional low-dispersed Co catalysts (typically with Co particle sizes >6 nm). One important difference in the analysis of the data is that in the present study, potential correlations between HC selectivities and TOFs (or more correctly: site-time-yields (STYs)) have been sought after by looking at selectivity and activity data at the same time-on-stream in the FT run.

2. Experimental

2.1. Preparation of catalysts

A range of supported Co-based catalysts were prepared by incipient wetness impregnation of three different carrier materials (γ - Al_2O_3 , α - Al_2O_3 , TiO_2) with aqueous solutions of cobalt nitrate. The Co loading varies between 4 and 30 wt%, and Re (0.5 wt%) is included in three of the catalysts. Boron (B) is included in one γ - Al_2O_3 -supported catalyst and in two TiO_2 -supported catalysts. The number in front of the element (Co, Re or B) indicates the loading in wt%. Two 6Co/ γ - Al_2O_3 catalysts, prepared at two different occasions, are included in the study and illustrate the variance related to catalyst preparation.

The γ - Al_2O_3 (Puralox SCCa-5/200 from Sasol) and TiO_2 (Evonik Degussa P25) support materials were dried at 393 K for 6 h and then calcined in flowing air for 10 h at 773 K and 973 K (ramp = 1 K/min), respectively. This was done in order to purify the γ - Al_2O_3 , and to transfer most of the TiO_2 to the rutile form. The α - Al_2O_3 support was prepared from the γ - Al_2O_3 support by calcining it in flowing air at 1373 K for 10 h. The support materials were impregnated with aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ (ACS reagent, $\geq 99.0\%$, Fluka) and, in some cases, $HReO_4$ (Alfa Aesar) or B_2O_3 ($\geq 98.0\%$, Fluka). Naturally, a higher Co loading of the final catalyst and/or a lower pore volume of the support material imply a higher concentration of the precursor salts in the aqueous solution. Three impregnations, with intermediate drying at 373 K for 1 h in static air, were used. The powder was then dried at 393 K for 3 h, and calcined in air at 573 K for 16 h (ramp = 1 K/min) in a crucible standing in an oven. For one catalyst (20Co/ TiO_2 (LW)), less water (LW) was used in the impregnations (i.e. 60% of the amount used in preparing the 20Co/ TiO_2).

One of the calcined catalysts (12Co + 0.5Re/ TiO_2) was treated further: reduction in hydrogen at 623 K for 16 h, passivation at room temperature in N_2 5.0 for 0.5 h and in 0.5 vol% O_2 in N_2 for 1 h, calcination in air at 573 K for 16 h. This catalyst is referred to as 12Co + 0.5Re/ TiO_2 RO (RO = RedOx).

2.2. Catalyst characterization techniques

Brunauer-Emmet-Teller (BET) surface area and porosity measurements [24] for the γ - Al_2O_3 -supported catalysts were per-

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