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Fischer-Tropsch catalyst deactivation in commercial microchannel reactor operation

Andre P. Steynberg, Soumitra R. Deshmukh, Heinz J. Robota*

Velocys, 7950 Corporate Boulevard, Plain City, OH 43064, USA

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ABSTRACT

Deactivation pathways for supported cobalt catalysts in Fischer-Tropsch (FT) synthesis have been found to comprise a number of independent mechanisms. The degree to which the various mechanisms apply is expected to be specific to each particular catalyst formulation and operating condition. The highest activity FT catalysts, finding industrial application, are used in microchannel reactors. Such catalysts provide a useful benchmark for FT catalyst performance comparisons. Deactivation mechanisms are grouped according to the methods used to manage them for typical industrial applications and then quantified to provide for the proposed benchmark catalyst behaviour.

1. Introduction

Deactivation mechanisms in supported cobalt catalysts used in the Fischer-Tropsch (FT) synthesis have been identified and discussed extensively with a view to designing catalysts with improved stability [1]. Nel [2] has described how the consequences of catalyst deactivation can be managed in an industrial slurry phase reactor. Similarly, LeViness et al. [3] have described how catalyst deactivation is handled in fixed bed microchannel reactors. In both cases, a temperature ramp is used to maintain constant conversion. In the former case, additional catalyst is added to the reactor when a maximum temperature is attained, while in the latter case, an *in situ* catalyst regeneration or rejuvenation procedure is periodically applied. From an industrial perspective, it is important to characterize the deactivation mechanisms according to the methods used to manage their impact. This leads to three main categories: 1) irreversible deactivation by an external agent, e.g. due to sulfur poisoning; 2) reversible deactivation by an external agent, e.g. due to active nitrogen species poisoning and; (3) intrinsic deactivation with time on-stream. In this paper, we present data quantifying the intrinsic deactivation for a highly active and stable commercial FT catalyst operated under intensified operating conditions in microchannel reactors.

The University of Cape Town, in collaboration with Sasol Technology, has recently developed an *in situ* magnetometer which allows ferromagnetic catalysts to be studied at industrial conditions [4]. This allows for the quantification of the two primary "intrinsic" deactivation mechanisms, namely, sintering of a cobalt FT catalyst as a function of process conditions [5] and the formation of deactivating carbon species. The role of carbides [6] and the role of crystallite size-dependent oxidation of cobalt FT catalysts under typical operating conditions [7] have been studied and found to be less significant than either deposition of deactivating carbonaceous species or the sintering-derived deactivation mechanisms.

Intrinsic deactivation, observed under microchannel operating conditions, is reversible with a three-step catalyst regeneration procedure comprising of wax removal, oxidation, and reduction. This is the case whether operating with synthetic syngas under laboratory conditions or using highly scrubbed steam methane reformer-derived syngas in pilot scale multichannel operations. Regeneration is conducted *in situ* within the microchannel reactors. The time evolution of activity follows a two-phase profile, with a more rapid and extensive deactivation occurring over a roughly 20 day period followed by a much slower activity loss rate thereafter. Ascribing specific deactivation mechanisms to each of these phases is outside the scope of this discussion. However, the slow, longer term deactivation is consistent with activity loss primarily resulting from the slow but continuous accumulation of carbonaceous species. A model of a commercial operating cycle has been developed by combining the details of the intrinsic deactivation rate with the impact of poisons likely to be encountered in commercial syngas. H_2S is used to represent all possible S-bearing contaminants and is a permanent, non-regenerable deactivating species. NH_3 is used to represent all reactive nitrogen species, the effects of which can be fully reversed in a regeneration process.

* Corresponding author.
E-mail address: heinz.robota@velocys.com (H.J. Robota).

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2. Experimental

The detailed time-evolution of activity data presented were acquired in an experiment conducted using a single microchannel with dimensions which are representative of commercial-scale reactor channels [8,9]. A proprietary commercial supported cobalt catalyst [10] was operated for 2 months at the following conditions after an *in situ* regeneration procedure:

Contact time: 288 ms (defined as packed channel volume/feed flow at STP)

Inlet pressure: 357 psig (24.6 bar(g))

Feed gas inert content: 31.6 mole%

Feed gas H_2/CO ratio: 1.73

Per-pass CO conversion is kept close to 70% using a temperature ramp.

Separate experiments were performed in which controlled and verified quantities of contaminants were dosed into the feed gas. Hydrogen sulfide was used to quantify the impact of non-regenerable poisons relative to the intrinsic deactivation profile. Ammonia was dosed into the feed gas to quantify the impact of regenerable poisons. The combined effects were then incorporated into what is referred to as the catalyst life-cycle model to provide a useful prediction for the time-dependant catalyst performance. The catalyst life-cycle model is further validated by comparison with data from pilot plant operations.

3. Results

The experimental data from the single channel reactor test using a clean synthesis gas feed, from high purity industrial cylinders (the CO stream being further scrubbed using a commercial carbonyl trap) with operating conditions described in Section 2 are presented in Fig. 1a. The per-pass CO conversion was adjusted by increasing temperature to stay within a 70 ± 2% window. As shown in Fig. 1b, CH_4 selectivity increases with temperature but is ≤6% over this entire period.

Using data from Fig. 1a, the deactivation rate, reported as normalized CO conversion rate loss, is shown in Fig. 2. This intrinsic deactivation rate starts out at a fairly high rate, but decreases asymptotically toward a very slow subsequent deactivation rate within approximately 20 days on stream. The test was repeated after a further *in situ* regeneration (indicated as Test 1 – cycle 2 in Fig. 2) and also with separate fresh catalyst charges (indicated as Test 2 and Test 3 in Fig. 2). The same pattern of high initial normalized CO conversion loss rate followed by an asymptotic approach to a very slow deactivation rate was observed in all experiments.

Poisoning experiments were performed in a single channel test reactor [8,9] using a synthesis gas feed doped with H_2S and NH_3, as representative S- and N- based poisons. Poisons were fed to the reactor through lines with inert coatings to avoid transmission losses through surface equilibration. Fig. 3 shows one illustrative example (from many such tests) of the decrease in CO conversion as a function of time on stream under synthesis conditions similar to those described in Section 2 with a syngas feed composition of H_2:CO = 1.79, 28 mol% inerts and ~0.1 ppm(v) NH_3 or ~0.3 ppm(v) H_2S. While the starting CO conversions are slightly different, both catalysts had operated steadily in clean syngas prior to the start of exposure. Shown for comparison in the figure is the change in CO conversion with time for a freshly regenerated catalyst, the period of most rapid activity decline, as shown in Fig. 2. It illustrates that the contaminant-induced deactivation rate, at these high contaminant concentrations, is substantially greater than even the most rapid intrinsic deactivation rate. This allows for a more accurate determination of the incremental deactivation caused by each "unit" of contaminant than if the contaminants were dosed at closer to our specification levels. On this catalyst, the impact of NH_3 poisoning is greater than that of H_2S poisoning. Data from this and additional supporting tests were used to quantify the impact of poison exposure and accumulation on the catalyst performance which is incorporated into the catalyst life-cycle model.

4. Discussion

By combining the temporal characteristics of the various deactivation modes: intrinsic, S-related, and N-related; into a catalyst life-cycle model, a net activity evolution can be modeled for a given syngas poison profile. We believe it is appropriate to treat the individual sources of deactivation as independent when modeling a catalyst operating under commercial conditions. When subjected to regular regeneration procedures, the only cumulative effect stems from S deposition. Throughout a substantial majority of a charge's commercial life, the fraction of the bed meaningfully impacted by S is modest. As reported elsewhere [11], analysis of the S content on a catalyst subjected to a 1-year equivalent exposure at 5 ppb(v) allows us to anticipate that about 80% of the catalyst charge remains largely unaffected by S at the end of the charge's commercially useful life. Consequently, that large fraction of the bed is expected to behave in a manner comparable to a laboratory charge operating in clean syngas. Similarly, we have observed that the temporal rate of CO conversion decline with exposure to NH_3 is the same whether using a charge subjected only to clean syngas or following exposure to a 1-year equivalent dose of H_2S at 5 ppb(v). At short exposures of the catalyst charges to low NH_3 exposures, with concentrations on the order of 10 ppb(v), we observe a near-linear decline in CO conversion with time which is directly proportional to the moles of NH_3 dosed. Such exposures were specifically started after the initial rapid intrinsic activity decline, to best quantify the response to the reactive N compound. Since the intrinsic deactivation rate seen in Fig. 2 is quite non-linear, and the actual temporal decline in CO conversion caused by NH_3 at 10 ppb(v) will be much slower than the rate shown in Fig. 3, we believe treating each of these individual deactivation mechanisms as independent is a reasonable assumption.

Fig. 4 shows how CO conversion would decline as a function of time, at a constant operating condition, if only one of the deactivation modes were operative with H_2S or NH_3 present at the 5 ppb(v) concentration. Following either fresh activation or regeneration, the initial period of activity loss is dominated by the intrinsic deactivation mechanisms operative for this catalyst. However, for the time following this initial period of high intrinsic deactivation, the impact of exposure to poisons, particularly reactive nitrogen contaminants, becomes quite readily apparent. Further, the N-poisoning dominates the deactivation associated with the accumulation of carbon species between regenerations. Clearly, if much higher concentrations of either or both H_2S and NH_3 were present, extrinsic poisoning would dominate the activity decline over all times. This suggests that catalyst developments aimed at retarding the rapid initial intrinsic deactivation would have the most potential to improve the FT process performance when syngas can be held to high purity standards by limiting the contaminants in syngas feed to near or sub 10 ppb(v) levels.

Net catalyst deactivation behavior under commercial operating conditions can, thus, be modeled using a linear combination of the effects of intrinsic deactivation working concurrently with poisoning from contaminants in the feed gas. Model data shown in Fig. 5 were generated using feed gas conditions which correspond to synthesis gas typically produced by an autothermal reformer (ATR) when an internal recycle ratio (molar recycle flow to fresh feed flow) in the range from 0.5 to 0.6 is applied to the FT reactor in order to achieve an overall CO conversion greater than 90%. These data are in general agreement with previous observations reported by LeViness et al. [3] at somewhat different operating conditions. The operating profile consists of a series of temperature increases over a span of approximately 2 years of operational time with a regeneration cycle every 60 days. Temperature increases are used to maintain the CO conversion as the catalyst deactivates due to intrinsic and extrinsic factors. The methane selectivity tends to increase with increase in operating temperature. As the catalyst

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