Relating the effects of water partial pressure to crystallite size in Co/Al_2O_3 Fischer-Tropsch catalysts using a novel *in-situ* XRD cell

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Introduction and Objectives

The paper utilises a newly designed *in situ* cell to help correlate the effects of water partial pressure (P_{H_2O}) to cobalt crystallite size whilst monitoring the Fischer-Tropsch Synthesis (FTS) conversion of H_2 and CO to hydrocarbons with online gas chromatography (GC). The cell design is such that it can be mounted on any commercial. This *in situ* cell allows for real-time analysis of the catalyst whilst being subjected to harsh conditions. In regards to application for this work, cobalt mediated FTS is reported to be a size dependent reaction for cobalt crystallite less than 10 nm [1] while increasing P_{H_2O} has been linked to both positive and negative changes in selectivity and activity (based on the system studied), and the deactivation by either oxidisation, sintering and/or surface reconstruction ([2] and citations therein). This experimental approach allows for monitoring all possibilities to link activity, selectivity and phase changes to increasing P_{H_2O} and crystallite size. The phase changes of two industrially-relevant alumina-supported cobalt catalysts (average initial Co_3O_4 crystallite sizes of 6.7 and 11.1 nm) were analysed throughout reduction (H_2 at 1°C/min → 450 for 6h) and FTS reaction conditions (220°C, H_2:CO = 2, P_{H_2O} = 0-3 bar, and P_{H_2O}/P_{H_2} ratios = 0-5).

Results and Discussion

The size-controlled cobalt crystallites were prepared via the microemulsion preparation technique as developed by Fischer et al [2]. The narrow size distribution resulting from this preparation method provided ideal model-like catalysts for this investigation. Catalyst reduction and FTS experiments have been completed using the *in situ* cell, with the catalyst crystallite phase changes having been successfully monitored. Figure 1 gives a representative view of the continuous XRD measurements during the reduction of the 11.1 nm catalyst. The loss of the 43.1°, 70.2° a nd 77.5° Co_3O_4 peaks at 350°C give rise to the 49.7° and 72.8° CoO peaks, which disappear during the 450°C holding period to form fcc-Co^0 (51.8° and 91.1°). Immediately following reduction, the catalysts were exposed to FTS conditions and continuously monitored as the P_{H_2O} of the system was increased to simulate high conversions (up to 95%). While oxidation has been suggested to occur, these reports are based on indirect techniques [3]. The design of this *in situ* reaction cell

provided the ability to observe the rapid structural changes as they happened that led to determining the oxidation threshold of the Co/Al_2O_3 catalysts.

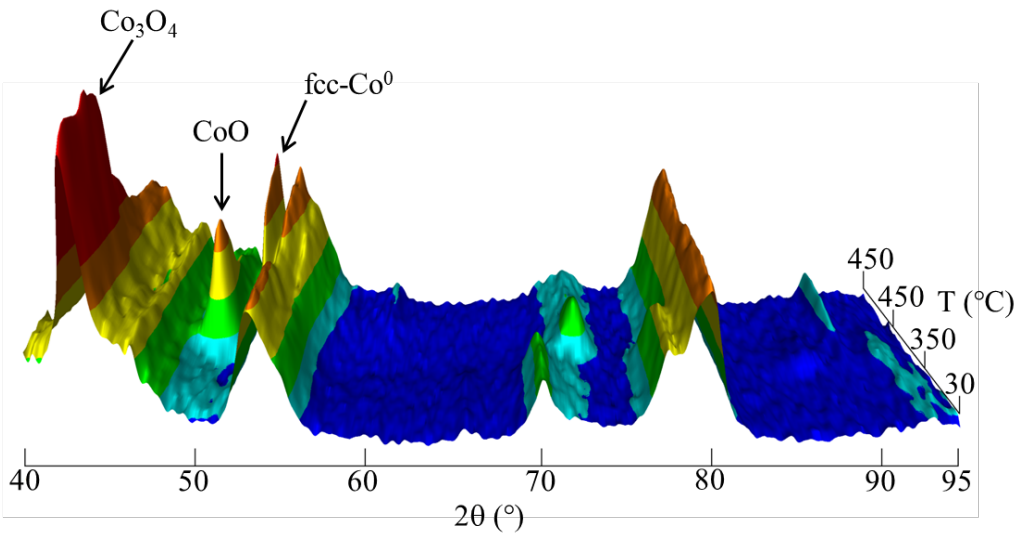

Figure 1. *In situ* XRD reduction of the 11.1 nm Co/Al_2O_3 catalyst.

Conclusions

Factors that were addressed include catalyst activity and product selectivity (by online and offline GC), metal crystallite size effects and water effects. The most significant results revealed the phase changes leading to the catalyst's oxidation with increasing partial pressure and concluding it is indeed related to the catalyst's crystallite size.

References

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