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## Investigating the Stability of Ru-promoted Fe-based Fischer-Tropsch Catalyst at high Synthesis Gas Conversion

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### Abstract

The productivity of an iron-based Fischer Tropsch (FT) process strongly depends on the synthesis gas conversion. However, iron is known to oxidize significantly at high CO conversion due to the high reactor water partial pressures. In commercial iron-based FT plant this necessitate operation at low single pass conversion, resulting in high separation and recycling cost of the tail gas and the overall economics of the process. Ruthenium has been reported to demonstrate significant stability in the presence of water, hence the employment of FT catalyst promoted with Ru is expected to permit high CO conversion. In this study the stability of an industrial Fe-based FT catalyst impregnated with ruthenium is investigated. The reactions were carried out at industrially relevant conditions in a 1 dm<sup>3</sup> slurry reactor at 250 °C and 20 bar. It was noted that the Fe promoted with Ru was more stable at high CO conversion implying a significant resistance to deactivation in the presence of water. An increase in CO<sub>2</sub> and CH<sub>4</sub> selectivity and a fall in C<sub>5+</sub> selectivity were also noted.

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### 1. Introduction

Energy security, affordability and sustainability is a topical issue worldwide [1]. The Fischer Tropsch Synthesis (FTS) is used to produce synthetic fuels and high-value petrochemical feedstock from a mixture of hydrogen (H<sub>2</sub>) and carbon monoxide (CO). The process provides an alternative route for the production of clean fuels from coal, natural gas, biomass and other carbonaceous materials. FT process is attracting renewed interest due to the product

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characteristics of the fuel produced with low sulphur and negligible aromatics contents [2] which can be directly substituted for or blended with conventional crude derived fuels.

The FTS employs transition metals as catalyst to convert synthesis gas (the H<sub>2</sub> and CO mixture) to a complex spectrum of products mainly hydrocarbons with water as a major byproduct [3, 4]. One of the main areas of improvement in FT process economics is by improving catalyst properties such as stability, selectivity and activity. Even though the transition metals Ru, Co, Fe and Ni are all active for the FTS reaction, only Fe and Co are employed commercially due to cost considerations [5, 6]. Iron catalysts are active at more severe conditions of pressure and space velocities [7] but the productivity of strongly depends on the CO conversion level [8]. On iron-based catalysts despite the significant water gas shift (WGS) reaction occurring together with the FTS, high per pass synthesis gas conversions will cause high reactor water partial pressures and result in rapid deactivation of the catalyst. This is due to the fact that iron is known to oxidise significantly during FTS at high reactor water partial pressures [8]. This renders iron-based catalyst an unattractive option for such operations.

Ruthenium (Ru) is the most active of the transition metals for FTS but mainly due to its very high price compared to iron or cobalt, it was abandoned as commercial catalyst [6, 9]. The metal however, has demonstrated significant resistance to oxidation by either water or oxygen during FTS [10]. It has been reported that high reactor water partial pressure increases the FT reactions rates on ruthenium as well as increases the chain length of the products [11] from the polymerization reactions. These have led to the claims that high synthesis gas conversions should be feasible on Ru at industrial relevant conditions thereby eliminating the need for tail gas recycling required at the current low conversion process. Studies on Fe-Ru systems have been conducted, in general, Ru was found to improve reducibility and increased conversion was observed with an increase in metals loading. The conclusion was that the catalysts were more stable due to the presence of Ru.

A single pass high synthesis gas conversion over the catalyst that eliminates the separation and recycling of the reactor tail gas in a once-through commercial FT operation will result in an improved overall economics of the FT process. The feasibility of such a process depends on the catalyst stability at such high synthesis gas conversion levels. This study investigates the industrial feasibility of a FT process conducted at a high single pass conversion of the syngas over Fe-based catalyst promoted with Ru. The emphasis is on the stability and activity of the catalyst in the prevailing high water partial pressure in the reactor.

## 2. Experimental

### 2.1 Catalyst preparation and Characterization

The 100 Fe /30 Al<sub>2</sub>O<sub>3</sub>/5 K<sub>2</sub>O precursor was prepared by the method of co-precipitation of the respective nitrate salts with a precipitating agent and incipient wetness impregnation of potassium. Details of the catalyst formulation and preparation steps are reported elsewhere [12]. The calcined K-promoted catalyst was further impregnated with Ru by dissolving the required amount of the sparingly soluble organometallic complex Ru<sub>3</sub>(CO)<sub>12</sub> (Sigma Aldrich, 99%) to achieve a Fe/Ru of 20 in n-hexane and added to the catalyst in a 1 L flask. The flask is sealed and allowed to stand while the change in the colour of the solution was monitored. After 3 days the colour had stabilized to a pale yellow (compared to bright yellow of the fresh solution). The slurry was transferred into a vacuum bowl and the n-hexane slowly evaporated under variable pressure at 110 °C. Since Ru<sub>3</sub>(CO)<sub>12</sub> thermally decomposes to the base metal in an inert atmosphere at 175 °C [13], a calcination step was not deemed necessary. The organometallic complex would be reduced to its metallic state well before the FT activation temperature of 270 °C is reached.

Nitrogen chemisorption using the BET method was done using Micromeritics Tristar II 3020 to determine the morphological properties of the catalyst. The catalyst bulk phases were studied with X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with a cobalt source ( $\lambda_{\text{CoK}\alpha 1} = 1.78897 \text{ \AA}$ ). A scanning range of 10° - 130° a scanning rate of 1 degree per minute was used with a step size of 0.01°. SEM-EDS was carried out on a FEI Nova NanoSEM 230 with an Oxford X-Max silicon drift EDS detector. The TPR profiles were obtained using a Micromeritics AutoChem 2950 to investigate the reducibility of the metal oxides under the reaction conditions. The Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) method was used to confirm the composition of the catalyst as prepared as well as confirm the elemental analysis obtained using SEM-EDS.

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