



# Synthesis of light olefins and alkanes on supported iron oxide catalysts

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## ABSTRACT

Catalytic synthesis of C<sub>1</sub>–C<sub>4</sub> hydrocarbons from clean synthesis gas, representative of natural gas, biomass or coal, was investigated over conventional supported catalyst (FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and FeO<sub>x</sub>/ZrO<sub>2</sub>) and compared with catalytic cartridges made from anodized Al plates (FeO<sub>x</sub>/AAO-Al). Porous aluminum oxide layers (ca. 50 and 100 μm thick) and uniform meso/macro pores (ca. 25–50 nm, 50–75 nm diam.) were established on Al plates by anodization treatment. Iron was supplied by incipient wetness impregnation (particles), wet impregnation and ultrasonic spray deposition (plates). Catalysts were characterized by SEM, XPS, H<sub>2</sub>-TPR N<sub>2</sub>-BET and Hg porosimetry. Synthesis performance was studied at 350–500 °C, H<sub>2</sub>/CO ratios 1–3 and atmospheric pressure. Loading of FeO<sub>x</sub> and its reducibility was favoring gaseous products and determining reaction mode. Conditions were strongly favoring accumulation of carbonaceous material, being governing for performance and limiting lifetime. Low olefins selectivity (< 5%) and yields (< 1%) were obtained. Addition of 1 wt.% K favored syngas conversion and deactivation, 1.2 wt.% Cu caused no effect. Results indicate that large pores favor olefin selectivity and lifetime. The catalyst working state, as evolving during reaction was independent on initial state (calcined oxide, reduced, precursor nitrate salts), indicating that thermodynamics was structure controlling.

## 1. Introduction

Synthesis gas and light olefins (C<sub>2</sub>–C<sub>4</sub>) are major building blocks for the chemical industry. Catalytic synthesis is used for producing ammonia/urea, wax and liquids (naphtha, diesel) via the so-called Fischer-Tropsch synthesis (FTS), as well as methanol, dimethyl-ether or higher oxo-alcohols. FTS interest was strongly related to petroleum availability and was originally developed for coal utilization and liquid fuels production, i.e. mineral oil or synthetic gasoline [1–3]. Now, the general interest is growing due to a politically stimulated shift towards increased utilization of renewables. EU targets to fulfill are 20% increased efficiency, 20% renewable fraction and 20% decreased emissions, typically stated as EU-20-20-20.

A new synthesis route for light olefins constitutes an attractive alternative to the present industrial naphtha cracking or alkane dehydrogenation. While FTS thermodynamics favors formation of CH<sub>4</sub>, carbon, H<sub>2</sub>O and CO<sub>2</sub> as products, the basic mechanism typically follow a slow stepwise approach towards equilibrium via formation of a wide range of alkanes and alkenes, according to the Schulz-Flory-Anderson distribution (C<sub>1</sub>–wax). While light products typically are favored by lowering pressure and increasing temperature, unsaturated products are favored by increasing the CO/H<sub>2</sub> ratio and GHSV, i.e. by lowering

contact time.

Conventional FT-synthesis catalysts are either Co- or Fe-based [3]. Co has superior properties at low-temperature (< 250 °C) enabling high conversions to wax and diesel, and is used for natural gas derived synthesis gas and H<sub>2</sub>/CO ratios of 1.8–2. Fe is used at higher synthesis temperatures (> 300 °C), and for synthesis gas with lower H<sub>2</sub>/CO ratios, benefiting from higher WGS activity. Fe-catalysts tolerate impurities such as sulphur better than cobalt and are well suited for biomass and coal based processes. Since Fe has lower hydrogenation activity than Co it has a potential for higher selectivity to olefins.

Nano-level characteristics of Co and Fe catalysts are determining for the kinetic properties. Intrinsic activity can be correlated to reduced cobalt metal and crystal size, and is stable for larger crystals whereas the activity significantly declines for crystals < 8 nm [4]. The Co crystal morphology also depends on pore structural characteristics of the support [5]. This implies that too small pores and strong support interactions are undesired in a system needing optimization for Co<sup>0</sup> and internal mass transfer. A systematic study of support variables confirms that Co crystal size and properties are depending upon pore dimensions [5,6], and also that there is a correlation between crystal size and reducibility [4,7]. On the other hand, optimization of Fe catalysts are related to carbide formation, i.e. not reduced Fe, and is therefore not

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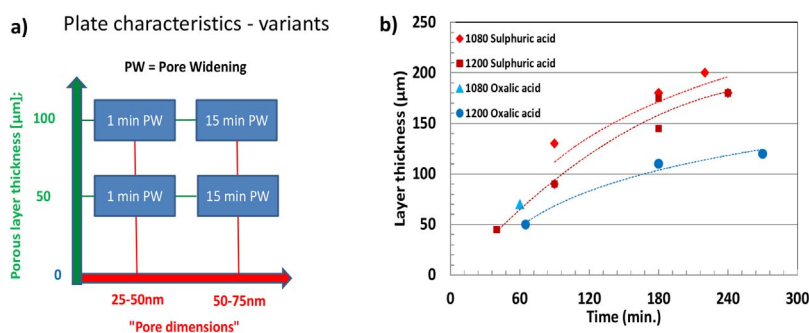


Fig. 1. (a) Matrix of materials established for cartridge assembly; (b) Correlations of obtained layer thickness vs. anodization time (right).

directly comparable to the Co system. However, reduced Fe might play a role as an intermediate in the carbide formation. A few systematic studies of size dependency between Fe crystals and pores have been reported [8–10], but correlations are still not well known. It has been suggested that larger iron particles can lead to a catalyst with a higher fraction of the iron in an active state, suggesting that the Fe system appears as dynamical with complex phase transitions [3]. Carbides (“ $\text{Fe}_2\text{C}$ , Hägg”) are important for activity and considered a key for optimized performance. It is reported that transformation to carbide can proceed more readily in large pores [10]. Carbides can transform further by oxidation by CO or  $\text{H}_2\text{O}$  to form magnetite  $\text{Fe}_3\text{O}_4$ , which is a process followed by crystal growth. Oxide particles are susceptible to carburization and break-up to  $\text{Fe}_2\text{C}$  crystal entities. A large degree of self-organization is involved [11]. In parallel, reduction reactions can cause formation of  $\text{Fe}^0$ . Alkali based promoters and reduction inducing metals like Cu [3,4,12] are used to affect morphology and formation of phases, and thereby performance. A deeper understanding of kinetics and thermodynamics of this interplay is desired for a rational progress to better performing catalysts.

Already in 1976, Büssemeier et al. [2] reported that Fe catalysts could have a lifetime of a few hundred hours at 250–320 °C and 5–20 bar pressure. A high  $\text{CO}/\text{H}_2$  ratio was found favorable for olefin formation, but a disadvantage for catalyst lifetime due to carbon formation. Olefins amounting to 50–80% of total hydrocarbons were claimed [2]. Galvis et al. [13] reported promising  $\text{C}_2$ – $\text{C}_4$  olefin selectivity (40–70%) over Fe based catalysts at low-pressure conditions. However, these values were established at conversion levels below 1% without accounting for  $\text{CO}_2$  and carbon formation. Clarification of the potential at higher conversions at ambient and low-pressure conditions remains. Jiao et al. [14] recently presented more promising results, with 80% olefins in the hydrocarbon fraction at a conversion of 17%, over a  $\text{ZrCrO}_x$  zeolite (mesoporous SAPO) hybrid type catalyst at 2.5 MPa pressure. However, ca. 45% of product carbon was  $\text{CO}_2$ .

The scope of the present investigation is to establish new knowledge about the physicochemical environment of iron and its phases on the performance and potential for olefin formation at low synthesis gas pressure. Fe was hosted in conventional supports and in well-defined meso- and macro-porous supports prepared by anodic oxidation of Al plates, used for constructing a small-scale structured cartridge prototype. Performance of particle based catalysts on conventional supports ( $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ) and cartridges are compared. Materials and conditions suitable for establishing high yields of short-range olefins or alkanes ( $< \text{C}_5$ ), i.e.  $\alpha$ -values  $< 0.5$  was targeted. A well-defined pore system might offer size and structure control for defined properties. It is of obvious interest to investigate a wide range of pore dimensions for the Fe catalyst system (7–100 nm, i.e. meso and macro), since large  $\text{FeO}_x$  crystals is positively size dependent for reduction and potentially for formation of carbide phases. Regarding cartridges, it is also an interesting reactor engineering aspect, since the Al core of the cartridge plates can provide efficient heat transport/distribution for exothermic reactions, thus avoiding detrimental hotspots contributing to approach differential conditions and kinetic measurements.

## 2. Experimental

### 2.1. Anodic oxidation of Al plates

Pre-cut aluminum plates of 1.5 mm thickness (AlMg1, with 1 wt.% Mg) with lengths of 12 cm and different widths (14, 11 and 8 mm) were used for anodic oxidation. Al surface pretreatment was performed by first cleaning in Ridoline to remove fatty materials, then etching in NaOH, and finally desmutting in  $\text{HNO}_3$ . Oxalic acid (0.3 M) was used as electrolyte in the anodization treatment. The applied anodization voltage in the range 75–175 V ( $3 \text{ A}/\text{dm}^2$ ) and duration from 60 to 270 min., was targeting two levels of porous layer thickness (50 and 100  $\mu\text{m}$ ). Different Al plates were used in establishing various pore size and layer thickness distribution. The material matrix with four combinations of pore size and layer thickness as used for assembly of cartridges is shown in Fig. 1a. The bath temperature of either 8 or 15 °C was causing no significant differences. Phosphoric acid was used in a subsequent step for pore widening with duration of either 1 or 15 min, providing two ranges of pore diameters (meso-range 25–50 nm, macro-range 50–75 nm).

Predictive control of the porous anodic oxide layer has been established for both sulfuric and oxalic acid solutions as electrolyte. Correlations of porous layer thickness  $< 200 \mu\text{m}$  and required anodization time is shown in Fig. 1b. This thickness range is relevant for diverse liquid and gas phase catalytic applications [15]. The pore widening (PW) procedure was used to both ascertain accessibility, i.e. ensure open pore mouths (1 min), and to increase pore diameters (15 min).

### 2.2. Impregnation of particles, single plates and cartridges

Saturated aqueous solutions of Fe-nitrate were applied for impregnation. Fe-nitrate was added to the conventional supports ( $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ , 0.3–0.5 mm particle size fraction) by incipient wetness impregnation, drying for ca. 24 h at room temperature and thereafter ca. 24 h at 120 °C. The particle catalysts were finally calcined at 500 °C in flowing air for 3 h. K or Cu were added as potential promoters to the catalysts in a subsequent impregnation step, repeating the procedure, still using nitrate metal salts. Table 1 provides an overview of particle based catalysts and properties.

Cartridges were prepared by two different procedures. A common step for all AAO/Al plates prior to impregnation or assembly was a mild 1 h long precalcination at 300 °C for surface cleaning. Minor weight losses in the range of 0.02–0.09 wt.% was observed, confirming structural stability. Ultrasonic spray deposition (USD) was performed on plates for two cartridges using *ExactaCoat Benchtop* (Sono-Tek, US) with *AccuMist* ultrasonic nozzle with argon as the dispersion (spray) gas. The liquid was fed into the nozzle by a syringe pump at a constant speed of 0.5 mL/min and based on constant movement in XY-direction the coverage was calculated to 0.013 mL/cm<sup>2</sup>. Two liquid layers on each side of the anodized plates were applied with an intermittent drying step of 120 °C for 15 min. All USD impregnated plates were finally calcined at 500 °C for 3 h in ambient air using a heating rate of 3 °C/

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