Fischer-Tropsch synthesis—Investigation of the deactivation of a Co catalyst by exposure to aerosol particles of potassium salt

Ljubiša Gavrilović[a], Jan Brandin[b], Anders Holmen[a], Hilde J. Venvik[a], Rune Myrstad[c], Edd A. Blekkan[a],*

[a] Norwegian University of Science and Technology, Department of Chemical Engineering, Sem Sælands vei 4, 7491, Trondheim, Norway
[b] Linnæus University, Department of Built Environment and Energy Technology, 351 95, Växjö, Sweden
[c] SINTEF Industry, NO-7465, Trondheim, Norway

ARTICLE INFO

ABSTRACT

The influence of potassium species on a Co based Fischer-Tropsch catalyst was investigated using an aerosol deposition technique. This way of poisoning the catalyst was chosen to simulate the actual potassium behaviour during the biomass to liquid (BTL) process utilizing gasification followed by fuel synthesis. A reference catalyst was poisoned with three levels of potassium and the samples were characterized and tested for the Fischer-Tropsch reaction under industrially relevant conditions. None of the conventional characterization techniques applied (H_2 Chemisorption, BET, TPR) divulged any difference between poisoned and unpoisoned samples, whereas the activity measurements showed a dramatic drop in activity following potassium deposition. The results are compared to previous results where incipient wetness impregnation was used as the method of potassium deposition. The effect of potassium is quite similar in the two cases, indicating that irrespective of how potassium is introduced it will end up in the same form and on the same location on the active surface. This indicates that potassium is mobile under FTS conditions, and that potassium species are able to migrate to sites of particular relevance for the FT reaction.

1. Introduction

Population growth and developments in living standards are drivers for increased energy use. Even with the assumption that the world's population will approach steady-state, future energy supplies will be a constraint in world development [1]. High energy cost is forcing scientists and engineers to think about alternative ways of producing fuels, especially transportation fuels which amount to about one quarter of the overall usage of fossil fuels [2]. One alternative option to produce transportation fuels is by the Fischer-Tropsch synthesis (FTS). The main reaction in Fischer Tropsch synthesis is converting synthesis gas ($H_2 + CO$) into hydrocarbons (mainly alkanes and alkenes with carbon numbers in the range 1–100). Different catalysts can be used in the Fischer-Tropsch synthesis, all based on group 8 and 9 metals, such as ruthenium, iron, or cobalt [3]. Ruthenium has a high activity and selectivity, but is regarded as too expensive and rare for industrial application. Cobalt and iron catalysts are the preferred industrial catalysts since they exhibit good combinations of activity, selectivity and stability during the process as well as favourable costs [4]. The main differences in these two catalysts are in their activity and selectivity.

Relative to Fe, Co catalysts typically has higher activity as well as selectivity towards higher hydrocarbons (C_{5+}), and lower activity towards the water gas shift (WGS) reaction, thus producing less CO_2 [5]. A lower deactivation rate is also generally found using Co under pure synthesis gas [6], but Co is also more sensitive to impurities. Addition of small amounts of Re or other metals (e.g. Ru, Pt) to the Co based systems mainly enhances catalyst reducibility and increases dispersion [7].

Syngas can be produced from different carbon-containing feedstocks. These feedstocks include coal, natural gas and biomass and the corresponding processes are termed CTL (coal to liquid), GTL (gas to liquid) or BTL (biomass to liquid), respectively. While the CTL and GTL processes are well established, the BTL process has issues regarding the scale and complexity of the process, challenging the economic viability of this route. Different biomass feedstocks are considered, including crop residue, agro-crops, and several tree species [8]. Biomass is a very complex material that besides the C, H and O that dominate the composition contains many other elements that may be undesirable in the syngas due to their potential as catalyst poisons, such as alkali, alkaline earth metal impurities, sulphur and nitrogen. Tar formation during gasification can also be an issue. Potassium is an important nutrient

---

essential for the plant growth and one of the major elements in biomass. In most biomass feedstocks, potassium is the dominant alkali element [9]. The potassium concentration in dry biomass varies between different types of biomass feedstock [10]. For example the K content in a typical dry wood biomass (*e.g.* spruce and pine sawdust including bark) is reported to be 560 ppm [11].

The BTL process involves many steps. After pre-treatment (size reduction, drying), the biomass is fed to the gasifier where the syngas is produced. There are a number of gasifier configurations available, but for the subsequent chemical use of the biomass-based syngas the fluid bed or entrained flow gasifiers are considered as the most suitable [12]. In order to satisfy the requirements of the FTS catalysts, the syngas needs to pass a series of cleaning steps in order to remove contaminants and other undesired species. The syngas must be essentially free of tar, particulates and ash components to prevent catalyst poisoning [13]. The syngas cleaning can be divided into conventional gas cleaning and dry hot gas cleaning. During cooling, alkali species condense on particulates at 550 °C [14]. Consequently, alkali elements can be removed with the particulates by cyclones, filters, scrubbers and packed beds with sorbents at 150–250 °C. Alternatively, hot gas cleaning can be considered, where alkali can be removed via chemisorption or physical adsorption at 750–900 °C [15], but at present there is no commercially available technology for the high temperature removal of alkali [16].

The requirement (concentration limit) for the alkali species for FT synthesis over cobalt catalysts has been proposed to be below 10 ppbv [17]. Although gas cleaning will be employed, poor plant design or operational errors can lead to contamination of the downstream catalysts. Thus, it is important to understand the effect of potential poisons on the FT catalyst. Previously it was shown that alkali species act as poisons, severely deactivating cobalt-based FTS catalysts [18,19]. Cobalt catalysts are known as sensitive to sulphur and some nitrogen compounds, together with alkali and some carbonyl species [6]. Catalyst deactivation by poisoning is often discussed in terms of site blocking, also termed a geometric effect, and electronic effects changing the chemical properties of the surface [20]. Alkali species are electropositively charged, so when deposited on the catalyst surface, the charge can be transferred to the surface and influence H_2 and CO adsorption and dissociation [21]. On Fe surfaces this has been attributed to increased adsorption energy of H_2, thereby stabilizing the H_2 molecule and reducing the probability of H_2 dissociation [22]. Blekkan et al. [23] observed rapid desorption of H_2 for K-promoted Co catalyst. The lack of H availability on the Co surface was offered as an explanation for the decrease in activity and increased C_{5+} selectivity. Ma et al. [24] observed increased CO_2 selectivity with increasing potassium loading. This indicates an increase in the WGS activity, which at the outset is low for Co based catalysts.

Previous research in our group [18,19] has been performed using incipient wetness impregnation as a method of deposition of alkali and alkaline earth compounds to Co based catalysts. Although practical, this method differs considerably from the situation in a BTL-plant, where the alkali species are transported to the catalyst surface with the gas phase. In the present work we study the influence of potassium on a Co-based catalyst, introducing aerosol technology as the method for potassium deposition on the Co surface. Potassium nitrate was chosen as a representative salt for this purpose. We aim to show how potassium species in the form of aerosol particles interact with the catalyst, knowledge that can contribute to understanding catalyst deactivation by alkali species. Previous work using this deposition technique showed a decreased conversion of methane in the steam reforming reaction for a Pt/Rh catalyst when exposed to K_2SO_4 aerosol particles compared to the unpoisoned catalyst [25]. As far as we are aware, the technique has not previously been used in relation to cobalt based Fischer Tropsch synthesis. The results are compared to the previous investigation with the same catalyst and poison, but where incipient wetness impregnation was used as the method of alkali deposition.

2. Experimental

2.1. Catalyst preparation

A 20%Co/0,5%Re/γ-alumina catalyst was used as a reference catalyst during these experiments. A one step incipient wetness impregnation of an aqueous solution of $Co(NO_3)\cdot6H_2O$ and $HReO_4$ was used as a technique for the catalyst preparation. The support was Puralox γ-alumina from Sasol (surface area 160 m^2/g, pore volume 0.62 cm^3/g). After impregnation, the catalyst was dried in a stationary oven (393 K, 1 h). To improve homogeneity, the sample in a beaker was stirred every 15 min. After drying, the catalyst was calcined in flowing air in a fixed bed quartz reactor at 573 K for 16 h, using a ramp rate of 2 K/min. The final step was sieving the oxidized catalyst precursors to particles size in the range 53–90 μs. The catalyst prepared like this is considered free from impurities, but the support did contain a minor amount of Na (26 ppm) [26]. Inductively coupled plasma (ICP-MS) was used to determine ppm levels of potassium.

2.2. Catalyst exposure by aerosol deposition of potassium salts

Potassium nitrate were deposited using the aerosol technology in the apparatus shown in Fig. 1 [25]. KNO_3 dissolved in deionized water (0.025 M) was placed in the pneumatic atomizer (Palas GmbH AGK-2000), which produces aerosol particles from the solution. Nitrogen is used as a carrier gas for transporting the generated aerosol particles towards the reactor. On the way, the gas mixture passes an impaction vessel, which separates and traps large particles. In this way a narrow particle size distribution is achieved. The tubular quartz reactor is placed inside an electrically heated oven and the catalyst bed is placed in the middle of the reactor. The lower part of the catalyst bed consists of a glass frit, which allows the gas to pass through, while most of the aerosols are trapped on the catalyst. A continuous gas flow of 4 l/min was passed through the catalyst bed for three different times on stream; 15 min, 60 min and 300 min. The experiments were performed at 300 °C and 1 bar. The drying time of the generated particles at these conditions is in the range of milliseconds, while the residence time of the gas in the oven is in the range of seconds [27].This means that the aerosol particles are completely dry and the salt is transported and deposited in the form of solid particles on the catalyst. Finally the catalyst was calcined *ex-situ* in air at 573 K for 16 h.

A scanning mobility particle sizer (SMPS; TSI Inc.) consisting of a differential mobility analyser (DMA; TSI Inc. Model 3081) and a condensation particle counter (CPC; TSI Inc. Model 3010) were used to physically characterize the aerosol particles according to their electrical mobility [25,27]. The SMPS system was used to measure the particle size in the range from ~20 to 700 nm. A software package with an inversion algorithm is converting the penetration characteristics (aerosol flow of around 0,3l/min) to the particle size distribution. Before entering to the SMPS system, the flow has been dried by a Nafion dryer (Perma Pure Inc., US). To prevent the entrance of larger particles into the system, an impactor device with a cut off size of 805 nm was placed right before the SMPS system. The SPMS system has the upper limit of aerosol concentration of 10 000 particles/cm^3. If the concentration of the aerosol particles exceeds this limit, dry compressed air is used to dilute the aerosol flow before entering the SMPS system [28].

2.3. Catalyst characterization

Volumetric adsorption of N_2 was performed on a Tristar II 3020 to determine surface area, pore volume and average pore dimeter of the support materials and prepared catalysts. Before the measurement at liquid nitrogen temperature, the samples (~70 mg, particle size 53–90 μm) were outgassed in vacuum, first at ambient temperature for 1h and then at 473 k overnight. The Brunauer-Emmet-Teller (BET) isotherm [29] was used for calculation of the surface area and the