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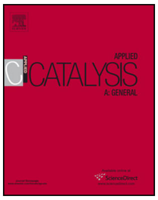

Generalized kinetic model for iron and cobalt based Fischer–Tropsch synthesis catalysts: Review and model evaluation

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ABSTRACT

During the decades of kinetic studies over iron and cobalt based Fischer–Tropsch synthesis (FTS) catalysts, various mechanisms and equations have been proposed with a wide diversity. Literature review indicates that neither general kinetic model nor the same shape for reaction rate equation has been proposed for FTS. In the present paper, a generalized mechanism was developed and verified against reported kinetic data for both iron and cobalt based FTS catalysts. Also it was shown that all various types of the proposed mechanisms can fall under the heading of one general mechanism. The proposed generalized macro kinetic model can be applied simultaneously to both iron and cobalt based FTS catalysts.

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1. Introduction

The major fuel production is currently based on crude oil. The reserves of crude oil are limited and therefore, fuel production from other hydrocarbon sources attracted considerable amount of attention. The XTL (X to Liquid) process can produce fuel from any hydrocarbon containing materials like coal, natural gas, biomass, and even wastes. A typical XTL process involves feed to synthesis gas (syngas), syngas to syncrude and syncrude to product steps. The syngas to syncrude conversion is known as Fischer Tropsch synthesis (FTS).

A typical FTS is catalytic conversion of syngas to a mixture of predominantly linear alkanes and alkenes, with the product distribution displaying a recognizable pattern.

$$\text{Parrafins}: n\mathrm{CO} + (2n+1)\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O} \tag{1}$$

$$\text{Olefines}: n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O} \tag{2}$$

$$\text{Alcohols}: n\mathrm{CO} + (2n-1)\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n-1}\mathrm{OH} + (n-1)\mathrm{H_2O} \tag{3}$$

In FTS, iron and cobalt based catalysts are of commercial interest. The mechanism and kinetics of FTS on iron and cobalt based catalysts has received significant attention. Many attempts have been made to describe the rate of reaction, either by tuning the kinetic data in an empirical equation or driving an equation based on mechanistic assumptions [1]. This leads to different and sometimes conflicting rate equations in literature meaning there are different and conflicting mechanisms which are unfavorable and unacceptable.

It is interesting to propose one reaction rate equation that can cover all reported kinetic data for either cobalt and/or iron catalysts. Table 1 summarizes reported studies that claim to cover a range of kinetic data. From the Table 1, Eq. (1) proposed by Anderson–Dry [2,3] and Eq. (2) proposed by Yates and Satterfield [4] were the first equations that have been studied and used extensively for iron and cobalt catalysts, respectively [5]. Recently Botes et al. performed a macro-kinetic study for cobalt and iron FTS catalysts wherein operating conditions were systematically varied in a wide range [6,7]. They found that Eqs. (1) and (2) show systematic statistical deviations and therefore proposed different equations (Eqs. (3) and (4)) for cobalt and iron, respectively.

In another approach, van Steen and Schulz [8], performed experimental kinetic studies in a wide range of operating conditions for both iron and cobalt catalysts. They derived mechanistically one equation that could present experimental kinetic data for both catalysts (Eq. (5)). But it must be noted that it predicts zero value for FTS rate in case of zero water partial pressure that is contrary to experimental observations [9]. Most recently, Ojeda et al. [10] used density functional theory (DFT) to study FTS mechanism on Co and Fe surfaces. They came to the conclusion that iron and cobalt catalysts kinetic data can be presented with one mechanism and reaction rate equation and so proposed Eq. (6). But Eq. (6), predicts non zero rate for zero hydrogen partial pressure that is not true conceptually.In this work, a generalized kinetic model (kinetic equation and mechanism) that can be applied to both iron and cobalt FTS catalysts was developed. In Section 2, some of the most important aspects of FTS mechanism are discussed. In Section 3, CO consumption rate is modeled (based on Section 2 results), a mathematical procedure for evaluation of CO consumption rate is described and results are discussed.

2. Fischer–Tropsch synthesis mechanism

Several transition metals are active in FTS. Vannice [11] found the following order for transition metals according to the average molecular weight of produced hydrocarbons:

$$\mathrm{Ru} > \mathrm{Fe} > \mathrm{Co} > \mathrm{Rh} > \mathrm{Ni} > \mathrm{Ir} > \mathrm{Pt} > \mathrm{Pd} \tag{4}$$

Pd, Pt, and Ir are mainly selective for methanation and essentially produce methane. Ni as pure metal is very poor in FTS, however when the pressure is increased, it can show FT activity [12]. In other words; Ru, Fe, Co, Rh, and Ni can be considered as FTS active metals. Pricewise, Co or Fe based catalysts are preferred for commercial scale but Ru and Ni are most attractive for academic research [13].

Previous studies confirm certainly that FTS is polymerization type reaction with step wise chain growth [14], but unlike other polymerization reactions, in FTS reaction the feed should be converted firstly to a monomer and initiator, then polymerize into the final hydrocarbon products. Thus, the formation chemistry and form of monomer and initiator are the first points that must be addressed and noticed [15]. This behavior leads to a type of mechanism based on one path monomer and initiator formation. Recently, another type of mechanism appears based on two paths for initiation and propagation steps. In this section, two aforementioned mechanism types are presented and discussed.

2.1. Monomer and initiator formation chemistry

During the decades, several assumptions for FTS monomer and initiator forms and formation chemistry had been made. The general form of the monomer and initiator can be defined as [13]:

$$\mathrm{C}_x\mathrm{H}_y\mathrm{O}_z \tag{5}$$

Historically, the most important proposed monomers were: methylene (CH_2), hydroxyl carbine (CHOH), and CO; that led to three mechanisms for FTS; carbide, the Enol, and CO insertion mechanism, respectively. Another mechanism proposed recently is “formate” mechanism [16]. The differences between proposed mechanisms arise from different assumptions for monomer and initiator forms and formation chemistry. In this regard, the formation chemistry dictates the form of monomer and initiator, so it is sufficient to be investigated.

The previously proposed formation chemistry for monomers and initiators are shown in Table 2. As can be seen, different formation chemistry leads to different FTS mechanisms. In the next subsections, monomers and initiators formation chemistry and dependent FTS mechanism are discussed.

2.1.1. Enol mechanism

As shown in Table 2, CHOH is considered as monomer and initiator in Enol mechanism. Previous studies on Fe catalysts indicate that alcohols and aldehydes can initiate FT reaction [17] whereas, they are weak initiators for Co catalysts [18]. Though alcohols can act as chain initiator, Tau et al. [19] found that they cannot act as propagators. In other words alcohols can act as initiator but not monomer.

Other studies on Fe and Co based catalysts showed that alcohols and aldehydes form alkoxide not CHOH [20–23] and initiation chemistry is well described by the alkoxide structure [22,23]. These results indicate that alkoxide intermediate is responsible for the chain initiation not CHOH. On the other hand anionic polymerization chemistry confirms that alkoxides can act as nucleophilic initiators [24]. As a result for iron or cobalt catalysts, alcohols (or aldehydes) can form alkoxide structure that can act as chain initiators but they cannot create active monomer in the form of CHOH.