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Deactivation of a Co/Al_2O_3 Fischer–Tropsch catalyst by water-induced sintering in slurry reactor: Modeling and experimental investigations

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ABSTRACT

The deactivation of cobalt based catalysts in slurry Fischer–Tropsch reactor has been modeled assuming a sintering mechanism which involves the intermediate formation of cobalt oxide layer on metallic nanoparticles. The mechanism, correlating the crystallite size growth to the water to hydrogen concentration ratio in the liquid phase, has been used to describe the activity decline with time on stream. The effect of operating conditions on the rate of sintering is considered. It is found that at the same initial conversion, sintering rate is higher for lower H_2/CO ratios, whereas higher ratios could lead to larger crystallites once operated at constant gas flow rate. The presence of water in the inlet syngas stream also accelerates sintering. The sintering model is then used to describe the deactivation in laboratory-scale slurry reactor.

1. Introduction

Ultra-clean alternative fuels can be made using Fischer–Tropsch (FT) synthesis which involves intermediate syngas produced from biomass (BTL), coal (CTL) or natural gas (GTL). Recently several FT plants have been built around the world in response to increasing energy demand and high oil prices as well as the higher quality of end products. However, deactivation of cobalt FT catalysts still remains as a major obstacle for further process development as it limits hydrocarbon productivity and process efficiency.

Different mechanisms are proposed for the catalyst deactivation in the literature [1] including sintering, carbon deposition, cobalt oxidation, carbide formation, etc. Several works point to the effect of water on deactivation of FT catalysts [2–4] and [5]. Although thermodynamic calculations have shown that bulk cobalt oxidation is not possible for crystallites more than 5 nm in diameter during FT synthesis [6,7], several research groups reported surface and bulk cobalt oxidation once water is added to the syngas feed [8–20] and [21].

Sintering is suggested as the main source of catalyst deactivation during the first periods of the reaction [22]. Sintering is mainly driven by thermodynamic reasons since larger cobalt crystallites have lower surface energy and therefore higher stability. Larger crystallites however possess lower concentration of active sites for FT reaction, and therefore crystallite growth leads to a decrease in the catalyst activity.

Previous reports suggest [23] that the sintering occurs more readily in the presence of water in FT reactor. Recently Bezemer [23] have observed a correlation between water pressure and sintering rate evaluated from in situ Mössbauer spectroscopy.

Although the sintering in the milli-fixed bed reactors could principally occur during the first few hours on stream, van de Loosdrecht et al. [24] have observed a longer sintering period in the case of slurry reactor which could last up to 3–5 days.

The present work is undertaken to develop a comprehensive mechanistic model for the sintering of cobalt nanoparticles used in the slurry FT reactor which could describe the experimentally observed initial deactivation. The proposed mechanism involves surface oxidation of cobalt metal particles by water and subsequent particle migration and coalescence. This mechanism was previously [25] used to model catalyst deactivation in fixed bed reactor.

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Nomenclature

Latin letters

C_i^L	molar concentration of component *i* in the liquid phase (mol/m^3)
$\bar{d}_S$	surface averaged cobalt crystallite diameter (nm)
E_i	activation energy for the kinetic coefficient *i* (kJ/mol)
F^L, F^G	molar flow rate of liquid and gas phases respectively (mol/s)
GHSV	Gas hourly space velocity (N m^3 kg$_{cat}{}^{-1}$ h^{-1})
H_2/CO	hydrogen to carbon monoxide molar ratio in the syngas (mol/mol)
j	number of carbon atoms in the hydrocarbon (dimensionless)
k_a, k_b, k_d, k_e	kinetic parameters (unit depends on the kinetic law in which they are utilized)
k_i	vapor–liquid equilibrium coefficient (dimensionless)
k_S^L	sintering constant in the slurry reactor (nm^7/s)
m_{Co}	cobalt mass in the catalyst sample (kg)
n	total number of components considered (dimensionless)
n^L	total number of moles in the liquid phase within the reactor (mol)
n_i^L, n_i^G	number of moles of component *i* in the liquid and gas phases within the reactor respectively (mol)
P	pressure (bar)
r_i	production or consumption rate for component *i* in the FT reaction (mol/kg$_{cat}$ s)
t	time (s)
T	temperature (K)
x_i	molar fraction of component *i* in the liquid phase (dimensionless)
y_i	molar fraction of component *i* in the gas phase (dimensionless)

Greek letters

α	ASF probability factor (dimensionless)
ΔH_b	Heat of adsorption for CO (kJ/mol)

Subscripts and superscripts

0	parameter value at *T* = 493 K
em	emulsion phase
G	gas phase
inlet	catalyst bed
L	liquid phase
max	maximum number of carbon atoms
S	solid (catalyst) phase

2. Experimental and methodology

The experimental setup includes a continuous stirred tank reactor (CSTR – 300 cm^3, radial impeller), a gas feeding system, hot and cold condensers, as well as an analytical system for the FT gaseous and liquid effluents (Fig. 1).

The inlet gas is composed of pure hydrogen (99.999%) and a prepared mixture of carbon monoxide (95%) and nitrogen (5%). Nitrogen is used as an internal standard for the analysis of gaseous phase. The inlet H_2 and CO molar flow rates are controlled using Brooks mass flow controllers.

The experiments are conducted using an industrial Co/Al_2O_3 catalyst (15% w/w Co on Al_2O_3, 50 μm, 5 g) reduced in situ at 673 K in the slurry autoclave reactor in a flow of hydrogen during 16 h. The temperature is later reduced to 333 K, the reactor was purged with Ar and the catalyst is wet with 40 g SX70 wax (Shell) for start-up. The premixed syngas replaces the argon flow with an adjusted flow rate. The temperature is then increased to 493 K for reaction start-up.

The absence of external and internal mass transfer limitations has been checked using standard procedures. More details on the experimental set-up and design, and analyses can be found in Refs. [26,27].

Operando XRD experiments [28] and TEM analysis [29] were used recently to follow average cobalt particle size distribution during catalyst sintering in gas-phase fixed-bed reactors. In our previous report [25], a mechanistic sintering model was proposed to correlate the change in the average particle diameter with the operating conditions. The developed mechanistic model [25] has been modified for the slurry reactor to take into account the liquid concentrations. The combined kinetics-deactivation model is built using component mass balance, vapor–liquid equilibria and crystallite growth equations to study the unsteady-state reactor behavior. The vapor–liquid equilibrium coefficients are calculated based on Henry's law for light components (CO, H_2, H_2O, CH_4, C_2H_6, C_3H_8) and Raoult's law for C_{4+} products. Liquid activity coefficients and vapor pressures are obtained by Marano–Holder equations [27]. A derived form of the Yates–Satterfield kinetic equation [30] which includes the effect of particle growth on activity reduction is used for CO consumption rate. The product distribution is given by the ASF model (constant growth factor) with an exception for methane and ethane production. gPROMS® ModelBuilder 3.3.1 is used for model implementation.

3. Model development

The previously developed sintering mechanism includes the effect of water through the formation of surface-oxidized cobalt oxide species in a reversible manner [25]. The CoO surface species could reduce the surface energy of cobalt crystallites by about 80% [7] as well as higher diffusion rates [31]. The surface cobalt oxidation takes place by the reaction of surface cobalt atom and water:

$$Co_{(surface)} + H_2O_{(liquid)} \rightleftharpoons CoO_{(surface)} + H_{2(liquid)} \qquad (1)$$

As the surface CoO formation takes place at the liquid–surface interface, the liquid concentration ratio of water to hydrogen ($C^L_{H_2O}/C^L_{H_2}$) dominates the CoO surface coverage and consequently the sintering rate. Similar approach previously used for description of sintering in fixed-bed reactors [25] has been employed to develop a correlation for the growth rate of surface-average particle diameter ($\bar{d}_S$) in slurry reactor. For the slurry reactor it follows:

$$\frac{d\bar{d}_S}{dt} = k_S^L \frac{C^L_{H_2O}}{C^L_{H_2}} \times \frac{1}{d_S^6} \qquad (2)$$

where k_S^L is the sintering constant.

Table 1 gives the values of the initial parameters used in this study. The previously measured sintering constant of an alumina-supported cobalt catalyst in the fixed bed reactor [25] (Section 4.1) was used as the initial value of sintering constant in slurry phase reactor. The sintering constant was however corrected by the effect of the solubility in the liquid phase in order to be used in Eq. (2). The same approach is used for FT kinetic terms. The sintering and kinetic terms are optimized and fitted to the available experimental data. The set of optimized parameters ($k^L_{s,0}$, $k_{a,0}$, $k_{b,0}$; fitted in 6 experimental runs, 2 further runs used for validation) is listed again in Table 1.

To study the effect of particle growth on catalytic activity a reactor model is also required. Several approaches are available in the