Applied Catalysis A: General 470 (2014) 250–260

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Review

Fischer–Tropsch synthesis: A review of the effect of CO conversion on methane selectivity

Jia Yang[a,b], Wenping Ma[b], De Chen[a], Anders Holmen[a], Burtron H. Davis[b,*]

[a] Norwegian University of Science and Technology, NO-7491 Trondheim, Norway
[b] Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, United States

ARTICLE INFO

Article history:
Received 1 July 2013
Received in revised form 30 October 2013
Accepted 31 October 2013
Available online 8 November 2013

Keywords:
Cobalt
Ruthenium
Iron
Fischer–Tropsch synthesis
Methane selectivity
Water effect

ABSTRACT

Methane is the least desired product for the Fischer–Tropsch synthesis so that it is of paramount importance to reduce methane selectivity in the FT process. Despite numerous efforts devoted to the reduction of methane selectivity, the effect of CO conversion on methane selectivity is still not well defined. For cobalt and ruthenium based catalysts, methane selectivity generally decreases monotonically with increasing CO conversion within the range 20–80%, while on iron catalysts, the methane selectivity is more influenced by its water–gas shift activity and potassium promotion. Methane selectivity remains more or less constant at conversion lower than 70% for potassium promoted iron catalysts. Pressure and temperature have a greater influence on methane selectivity for Co and Ru based catalysts. Pressure and temperature change the preference of the secondary reactions of primary olefins and tune methane selectivity at different CO conversions. An increased extent of olefin readsorption may compete with methyl intermediates for surface sites and hence reduce methane selectivity. Water seems to play an important role in determining the dependence of CH_4 selectivity on CO conversion for the Co and Ru based catalysts by either inhibiting the hydrogenation reaction or by increasing the amount of surface carbon for chain growth. Choosing appropriate promoters and process conditions may reduce methane production.

Contents

1. Introduction

Fischer–Tropsch synthesis (FTS) provides an alternative route for the production of clean fuels from coal, natural gas and biomass. FTS is a stepwise polymerization reaction and the products in

* Corresponding author. Tel.: +1 859 257 0251; fax: +1 859 257 0302.
E-mail address: burtron.davis@uky.edu (B.H. Davis).

0926-860X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.10.061

general follow an Anderson–Schulz–Flory distribution. The primary objective is to produce as much transportation fuels as possible [1]. Methane is the least desired product and the amount that is produced needs to be reduced. The product selectivity is strongly related to the process conditions. An increase in temperature shifts the distribution towards the products with lower carbon numbers on iron [2,3], ruthenium [4] and cobalt [4]. An increase in total pressure usually shifts the product selectivity to heavier products [4]. Increasing H_2/CO ratios results in producing more amounts of light hydrocarbons and lower olefins [2,3]. Less well defined is the product selectivity with conversion at one set of reaction conditions. This paper concentrates on the influence of CO conversion induced by varying synthesis gas space velocity on the methane selectivity.

The effect of CO conversion on product distribution strongly depends on the secondary reactions of the primary products, especially olefins. Secondary reactions of primary olefins may include hydrogenation, reinsertion, cracking or hydrogenolysis and isomerization. The dominant secondary reactions of the primary olefins depend on the operating conditions and the catalyst. Cracking or hydrogenolysis is enhanced by high temperature and is strongly inhibited by high CO pressure and water partial pressure [5]. According to Bond [6], the initial step of hydrogenolysis is the loss of hydrogen atoms with the formation of radicals. Generally a negative reaction order with H_2 was found over Co and Fe catalysts. The detailed mechanism is beyond the scope of this work. However, higher temperature should favor the hydrogenolysis of hydrocarbons. Besides, Iglesia et al. [7], Madon et al. [8] and Komaya and Bell [9] concluded that readsorption of an olefin and chain initiation is the most important secondary reaction for Ru, Co and Fe catalysts at typical Fischer–Tropsch conditions instead of hydrogenation or hydrogenolysis reactions. Water has been reported to inhibit secondary hydrogenation and hydrogenolysis [5,7]. The type and extent of secondary reactions may change at different conversion levels and hence cause a selectivity change.

A decrease in syngas space velocity increases the residence time of reactants in the catalyst bed, and hence CO conversion increases. At typical Fischer–Tropsch conditions, the C_{5+} selectivity increases and CH_4 selectivity decreases with increasing CO conversion for the Co and Ru based catalysts. The olefin to paraffin ratio decreases with increasing CO conversion. The increase in chain growth and the decrease in olefin to paraffin ratio has been attributed to the enhanced secondary reaction (readsorption and reinitiation) of α-olefins at prolonged bed residence times [10]. Water may further enhance the effect of α-olefin readsorption on chain growth. Water has been reported to inhibit secondary hydrogenation of olefins [7,11]. Therefore more α-olefin will be available for readsorption and reentering the growing chain (instead of termination as paraffin) at a higher water partial pressure (higher CO conversion). However, the reason for the change of methane selectivity with CO conversion is still not very well defined. In this paper, the dependence of methane selectivity on bed residence time (CO conversion) for typical Fischer–Tropsch Fe, Co and Ru catalysts will be reviewed and the possible mechanisms to account for this will be discussed.

2. Effects of active components

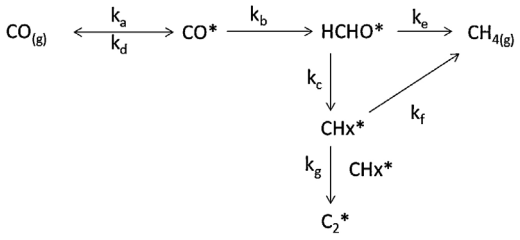
The selectivity of FTS depends primarily on which transition metal (Fe, Co or Ru) is used. Iron based FT catalysts are active for the water–gas-shift (WGS) reaction and are therefore suitable for low H/CO feed. On the other hand, the WGS activities on Co and Ru catalysts are negligible under normal FTS conditions. Therefore the product selectivity of Fe catalyst depends both on FT activity and WGS activity, while Co and Ru depend mainly on their FT activities. Therefore, the change of product distribution with CO conversion is quite similar for both Co and Ru catalysts. Fe behaves differently with increasing CO conversion. The methane selectivity trend with CO conversion for Co, Ru and Fe are discussed respectively.

2.1. Co

Most of the studies on cobalt based catalysts report a decrease in methane selectivity and a concomitant increase in C_{5+} selectivity with increasing CO conversions under typical FTS conditions [12–17]. Holmen and coworkers [12,13] investigated Co catalysts supported on Al_2O_3, SiO_2 and TiO_2 with and without Re promotion in a fixed-bed reactor and observed a common trend with CO conversion 10–50% range for all of the catalysts that were tested. Thus, the support identity and Re promoter did not influence the dependence of selectivity on the CO conversion. Davis and coworkers [14,15] did thorough studies on the unpromoted and Ru promoted Co catalysts on Al_2O_3 support over a wide range of CO conversion (12–90%) both in fixed-bed and slurry phase reactors. In the fixed-bed reactor, using a 15%Co/Al_2O_3, the selectivity to CH_4 decreased, whereas the C_{5+} selectivity increased linearly with increasing CO conversion within the range 35–90%. CO_2 selectivity increased also with increasing CO conversion due to the increased WGS reaction at high water partial pressures. 1-Olefin content of the C_2–C_5 fraction decreased and the 2-olefin content of C_4 hydrocarbons increased with increasing CO conversion. In the slurry phase experiment (Fig. 1), CH_4 and C_{5+} selectivities followed the same trends as those observed in the fixed-bed reactor in the CO conversion range 10–80%. The formation of methane decreased with increasing CO conversion. However, at high conversions (>80%), CH_4 and CO_2 selectivity increased exponentially with increasing CO conversion. The C_{5+} selectivity remained nearly unchanged for CO conversions above 80%. When CO conversion exceeds 80%, part of Co was oxidized as evidenced by XANES results [14], possibly by the high water partial pressure ($P_{H_2O}/P_{H_2} > 0.9$), and cobalt oxide surfaces may contribute to the enhanced WGS reaction and methane formation reactions.

For a 10%Co/TiO_2 catalyst tested in a continuously stirred tank reactor (CSTR) at 493 K, 2.4 MPa, $H_2/CO = 2$ and GHSV 0.75–4 Nl g_{cat}^{-1} h^{-1}, the methane selectivity again decreased (15–7%) and C_{5+} selectivity increased (80–91%) with CO conversion in the range 8–63% (CAER to be published data). The C_2–C_4 selectivity decreased about 2% over the entire range. Therefore the increase in C_{5+} selectivity is mainly due to the decrease in the methane selectivity at higher CO conversion.

Modelling of transient experiments using isotopic labelled ^{13}CO (methanation conditions) has revealed that two reaction pathways via two different carbon pools for methane formation exist for cobalt based catalysts [18,19]. Moreover, a recent study shows that one reaction route is hydrogenation of carbon pool of HCHO* and another is through decomposition of HCHO* to another carbon pool namely CH_x* which can both form methane and undergo chain growth (Scheme 1) [19]. In order to reduce methane formation, the first reaction route for methane formation should be minimized. The relative importance of the two reaction routes depends on the concentration of surface hydrogen. A low hydrogen concentration



Scheme 1. Possible reaction mechanism for methane formation [19].