Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Synthesis of C_{5+} hydrocarbons from low H_2/CO ratio syngas over silica supported bimetallic Fe-Co catalyst

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ARTICLE INFO

Article history:
Received 30 July 2016
Received in revised form
11 November 2016
Accepted 7 December 2016
Available online xxx

Keywords:
Bimetallic catalyst
Fischer Tropsch synthesis
Conversion
Fe-Co phase

ABSTRACT

In the present study, selective synthesis of C_{5+} hydrocarbons from a low hydrogen to carbon mono oxide ratio syngas has been studied over a novel Fe-Co bimetallic catalysts. Fe was added into Co catalyst to increase the H_2/CO ratio internally via increased water gas shift activity. Catalyst with varying Fe/Co composition (Fe/Co (w/w) = 0.25, 0.5, 1) and varying metal loadings were prepared in the laboratory. Catalysts activity were tested in a fixed bed reactor at T–220 °C, P–20 bar, H_2/CO–1.48 and GHSV–1200 mL/h-gcat. Detail characterization of the catalysts were done through different techniques. Quantitative and qualitative analysis of the liquid products were done using GCMS and CHNS analyzers. The presence of Fe in bimetallic catalyst resulted an increase in CO conversion and product selectivity in comparison to that of mono metallic Fe/Co catalysts. Formation of Fe-Co bimetallic phase was confirmed through the detail characterization of fresh and spent catalysts which facilitate the CO adsorption on active metal sites. However, phases for individual iron and cobalt were also evident at higher metal loadings. The CO conversion increases with metal loading and was maximum at 30% metal loading. Optimum ratio of Fe/Co was 0.5 at a total metal loading of 30% (Cat-2) in which maximum (65%) CO conversion was achieved. Enhancement of H_2/CO ratio through WGS reaction was examined over Cat-2 at various temperature and inlet H_2/CO ratio. At 240 °C, C_{5+} selectivity was maximum at the expense of CO_2 and methane production.

1. Introduction

Conversion of coal and natural gas derived syngas into fuel and value added chemicals via Fischer Tropsch synthesis is being accepted widely. In the past few years, the process has been investigated to develop a catalyst system which makes it selective towards desirable products such as gasoline and diesel range hydrocarbons [1,2]. Syngas which is a combination of H_2 and CO can be obtained from natural gas or gasification of biomass and coal. Biomass and coal derived syngas contains lower H_2/CO ratio as compared to syngas produced from natural gas [3]. For the full utilization of syngas with the lower H_2/CO ratio, it is necessary to enhance the water gas shift activity within the reactor with the help of some modification in the catalyst system.

Eqs. (1) and (2) shows the Fischer Tropsch synthesis (FTS) and water gas shift (WGS) reaction respectively. WGS reaction occurs simultaneously with the FTS reaction, which helps in increasing the ratio of H_2 to CO.

$$nCO + 2nH_2 \rightarrow (-CH_2-)_n + nH_2O \quad (1)$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (2)$$

The importance of the WGS reaction in Fischer Tropsch synthesis process automatically increased when feed gas contains low H_2/CO ratio (0.5–1.5) because, the overall CO conversion is not very high without the WGS reaction [4].

The most common metal used in Fischer Tropsch reaction are Fe, Co and Ru. Metals such as Ni and Rh also show high activity towards the Reactions (1) and (2). Among these, Ru shows high activity for CO hydrogenation at comparatively lower temperature (<150 °C). However, high cost of Ru limits its industrial scale application. Both iron and cobalt have been used in industry as active FT catalysts since long time due to their economically acceptable cost. These catalysts are being used separately as they possess specific properties to narrow down the product range in a desired hydrocarbon range. Cobalt based catalyst shows high activity and selectivity towards linear long chain hydrocarbons, however, is more expensive than iron. On the other hand Fe based catalyst is mainly selective towards alkene, oxygenates and olefin range

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http://dx.doi.org/10.1016/j.cattod.2016.12.015
0920-5861/© 2016 Published by Elsevier B.V.

Please cite this article in press as: Sonal, et al., Synthesis of C_{5+} hydrocarbons from low H_2/CO ratio syngas over silica supported bimetallic Fe-Co catalyst, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.12.015

hydrocarbons which are good petrochemical feedstock. The main property of Fe based catalyst is its high activity towards water gas shift activity which widens its application with wide range of H_2/CO ratio of syngas [5]. This is useful for the utilization of the coal and biomass derived syngas which contain low H_2 to CO ratio. In case of Co catalyst, due to its low water gas shift activity its use is restricted for a specific range of H_2/CO ratio. Therefore, modification in the catalyst system is required to get over with these problems.

It has been shown that by mixing two metal catalysts, the activity and selectivity can be changed drastically [6–11]. The performance of catalyst in the terms of WGS activity and FTS activity was compared with their iron or cobalt based monometallic catalyst. Arcuri et al. [8] presented the results for low CO conversion level obtained with a Fe: Co/SiO_2 catalyst in comparison with the supported mono metal catalyst (T–250 °C and P –1 to14.18 bar). They reported that the dependence of selectivity on conversion does not exist at higher pressure and also iron content in the catalyst resulted methanol as main product at the expense of major methane production. If the CO conversion was taken into consideration the performance of bimetallic catalyst resembles supported iron catalyst at atmospheric pressure level and at 14 bar pressure it matches the supported cobalt catalyst. On the contrary, Ishihara et al. [2] found that the silica based Co-Fe bimetallic catalyst with metal ratio 3:1 shows high selectivity towards C_{6+} hydrocarbons at 250 °C temperature and 10 bar total pressure. They reported that after alloying metal catalyst the activity of the catalyst system enhances due to change in electronic properties of metal species. After detail investigation with the silica supported Co-Ni and Ni-Fe bimetallic catalyst systems Arai et al. [7] reported that, in the FT process Co-Ni bimetallic catalyst increased CO conversion fivefold when compared the same over the single metal catalysts. The use of mesoporous support such as HMS and SBA-15 for the bimetallic Fe-Co catalyst does not show a huge difference in their performances in comparison with the monometallic catalyst and the conversion level ranges between 20 and 30% [12]. It was observed that the Fe/Co bimetallic showed different physicochemical properties than the monometallic Co and Fe catalysts. Addition of Fe increases the reducibility of Co and also increases the number of active sites which in turn affect the CO conversion positively, however, hydrocarbon selectivity did not change significantly. Tihay et al. [13,14] observed very different results. They claimed that during the preparation of the bimetallic catalysts only two phase are formed, Fe-Co bimetallic phase and $CoFe_2O_4$ spinel which are solely responsible for catalytic activity. They reported 5% CO conversion and 84.8% C_2-C_4 selectivity at 10 bar pressure and 220 °C temperature when the catalyst were treated with CO/H_2. Some researchers have shown the effect of water on the FT process and found that the addition of water in feed may help in increasing the WGS activity of catalyst but makes the catalyst system highly prone to deactivation [3,15]. However, all these reports lack detailed investigation of results on FT synthesis and water gas shift reaction over bimetallic catalysts.

The purpose of the present work is to examine the effect of addition of Fe in Co catalyst on the same support and to study their effect in the WGS and FT reactions using CO rich syngas (H_2/CO ratio of 1.0–1.5). The combination of Fe-Co catalyst optimized in terms of metal ratio and metal loading. Identification of different individual metallic phases, bimetallic phases and their impact on the performance of catalyst.

2. Experimental

2.1. Catalysts preparation

Seven different catalysts were prepared via combination of co-precipitation and sol-gel method [16]. First batch of catalysts were prepared with different Fe/Co ratio keeping total metal loading constant at 30%. Then the metal loading was varied keeping the ratio of Fe/Co constant at 0.5. Monometallic silica supported cobalt and iron catalysts were also prepared with the same method. Cobalt nitrate hexahydrate [$Co(NO_3)_2{\cdot}6H_2O$] supplied by MERCK and Ferric nitrate nonahydrate [$Fe(NO_3)_3{\cdot}9H_2O$] provided by Fischer Scientific were used as cobalt and iron precursors respectively. In a typical procedure tetraethyl orthosilicate (TEOS) solution was used as silica precursor. Aqueous ammonia solution of concentration of 25% and nitric acid of 70% concentration were used for the precipitation. Metal catalysts precursor were co-precipitated from the aqueous solution of their nitrate salts and mixed at the desired Fe/Co ratio. Both the salt solutions mixed together and heated at 70 °C for one hour. Liquid ammonia solution was added drop wise to maintain the pH 8 ± 0.2. The precipitate of $Fe(OH)_3$ and $Co(OH)_2$ was filtered and washed repeatedly using deionized water to make its pH neutral. The slurry of the filtered precipitate made in water at 80 ± 2 °C. pH of the slurry adjusted at 9.0 ± 0.5 by adding ammonia solution. Further, desired quantity of TEOS was mixed with ethanol and water in a ratio of 1:4:5 (TEOS: EtOH: H_2O) and stirred for 1 h. Then the solution was added gradually in the previous metal precipitate solution under stirring condition and left for one hour. In the next step, nitric acid was added slowly until the pH reached at 6 ± 0.5. Finally, slurry was filtered, washed and dried over night at 110 ± 3 °C. The dried catalyst samples were calcined at 500 ± 2 °C for 5 h. Similar methods of preparation were applied for all catalysts (i) 5%Fe-25%Co/SiO_2 (ii) 10%Fe-20%Co/SiO_2 (iii) 15%Fe-15%Co/SiO_2 (iv) 30%Co/SiO_2 (v) 30%Fe/SiO_2 (vi) 6%Fe-12%Co/SiO_2 (vii) 3%Fe-6%Co/SiO_2 and these are designated as Cat-1, Cat-2, Cat-3, Cat-4, Cat-5 Cat-6 and Cat-7 respectively.

2.2. Catalyst characterization

Micromeritics ASAP 2010 apparatus was used for determining BET surface area. Pore volumes, average pore diameter of the catalysts were also measured in the same apparatus. Prior to gas adsorption measurements, degassing of the sample was done in which catalyst was heated at 150 ± 1 °C under vacuum for a period of 2 h [17]. The final elemental composition of the catalyst was determined using EDS equipped with a ZEISS EVO Series Scanning Electron Microscope EVO 50. HRTEM were performed with PHILIPS CM12 microscope operated at an accelerating voltage of 100 kV. Selected catalysts were subjected to the analysis where TEM images and selected area electron diffraction (SAED) pattern were captured. X-ray diffraction (Rigaku, Miniflex 600) was used to analyze the metal phases of the fresh calcined and spent catalysts at room temperature in the 2θ range from 20° to 80°. CuKα radiation was used as X-ray source generated at 40 kV and 15 mA. Scans were taken with a 2θ step size of 0.02° and a counting time of 1.0 s. The phases of cobalt and iron compounds were identified using database compiled by the Joint Committee on Powder Diffraction Standards (JCPDS). Crystal size of Co_3O_4 and Fe_2O_3 were calculated by the Scherer equation (Eq. (3))

$$d = \frac{0.89\lambda}{\beta\cos\theta} \quad (3)$$

where d is the mean crystallite diameter, λ is the X-ray wavelength (1.54 Å), and β is the full width at half maximum (FWHM) of the diffraction peak [14,15]. Reduction behavior of the catalyst is examined by the temperature programmed reduction (TPR) study, using Micromeritics instrument (Chemisorb 2720, USA) equipped with a thermal conductivity detector (TCD). Same instrument was used for H_2 pulse chemisorption analysis of the samples. Initially 0.1–0.2 g of calcined catalyst was taken in a U tube and degassed at 150 °C for 1 h under flow of argon gas (30 cm^3/min). Then the gas flow switched to H_2 (10.2 vol% H_2 in Argon) with the total flow rate maintained at

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