Journal of the Taiwan Institute of Chemical Engineers 43 (2012) 704–710

Contents lists available at SciVerse ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Effect of lanthanum doping on the lifetime of Co/γ-Al_2O_3 catalysts in Fischer-Tropsch synthesis

Mohammad Reza Hemmati [a,b], Mohammad Kazemeini [a,*], Jamshid Zarkesh [b], Farhad Khorasheh [a]

[a] Department of Chemical and Petroleum Engineering, Sharif University of Technology (SUT), Tehran, Iran
[b] Research Institute of Petroleum Industry (RIPI), National Iranian Oil Co (NIOC), Tehran, Iran

ARTICLE INFO

Article history:
Received 24 November 2011
Received in revised form 22 January 2012
Accepted 2 March 2012
Available online 10 April 2012

Keywords:
Cobalt catalyst
Fischer-Tropsch synthesis
Deactivation
Lanthanum doping

ABSTRACT

Cobalt-based catalysts were prepared on gamma alumina supports, and their behaviour for different Fischer-Tropsch synthesis (FTS) conditions was assessed. Although Co/γ-Al_2O_3 is a well-known FTS catalyst, its durability ought to be improved to make the industrial process economically feasible. The effect of lanthanum doping on the catalyst lifetime was examined utilising reactor tests and catalyst characterization techniques including TPR, ICP and N_2 porosimetry. Reactor test results revealed that an optimum amount of lanthanum improved catalyst activity and selectivity. Increasing amounts of lanthanum doping up to about 1.1 wt% seemed to modify the chemical composition of the support resulting in improved catalyst selectivity and lifetime. Further increase in lanthanum doping up to 2.7 wt% only marginally enhanced the catalyst selectivity and lifetime. TPR results revealed that the high temperature peak due to cobalt aluminate phase shifted to lower temperatures with increasing amount of doped lanthanum possibly due to the formation of lanthanum/aluminium mixed oxides.

1. Introduction

Cobalt and iron are the most widely used active metals for the preparation of the Fischer-Tropsch synthesis (FTS) catalysts [1]. Iron catalysts are more selective toward the olefin and gasoline cuts, produce more CO_2, have lower durability and a lower price. The research field is still wide open to investigate all aspects of iron-based FTS catalysts including the effects of feed impurities that are of considerable importance in commercial plants [2]. Both catalysts can be used in different reactors and recent investigations have reported the benefits and disadvantages of various reactors for each catalyst [3]. Cobalt-based catalysts result in a wide range of product distributions, produce water as a major product, and are more expensive than iron-based catalysts. Thus, cobalt-based catalysts need to have a longer lifetime to overcome their negative price trade-off and be economically competitive with iron-based catalysts. The most important deactivation agent for cobalt catalysts is water with both reversible and irreversible effects [4–7]. Another important deactivating agent for the system undertaken is carbon deposition for which mechanism of composition as well as origin and effects are considered elsewhere in detail [8,9]. Other factors such as reactor type and H_2/CO ratio have a lesser effect on the deactivation of cobalt catalysts [10]. Catalyst preparation conditions, support properties, support modifications prior to impregnation, conditions and number of calcination steps, and the type of precursor are other important factors affecting the catalyst selectivity and lifetime. Due to repetition of calcination steps, for example, porosimetric properties and also particle size and particle size distribution deteriorated [11]. The type and properties of alumina and silica, which are most commonly used as the support for cobalt-based catalysts, alter the deactivation behaviour of the catalyst [12–15]. The reduction procedure can also affect the primary activity and the deactivation behaviour [16]. The cobalt dispersion and crystal size are important properties affecting the behaviour of the catalyst [17–20]. There is an optimum range for cobalt crystal size as smaller crystals deactivate rapidly by oxidative effect of water and larger crystals lead to lower cobalt dispersion. It should be noted that cobalt crystal oxidation is a function of some interacting parameters such as the H_2O/H_2 (molar) ratio in the reaction media [9] as well as the type of support. Furthermore, crystal size also has effects on activity and selectivity of the catalysts. In fact, studies showed that smaller crystals led to more methane and less C_{5+} species. On the other hand, smaller crystals might have not provided the required active sites for a reaction to take place [21].

---

* Corresponding author at: Department of Chemical and Petroleum Engineering, Sharif University of Technology, Azadi Avenue, Tehran 11365-9465, Iran.
Tel.: +98 21 66165425; fax: +98 21 66164823.
E-mail addresses: hemmatimmr@ripi.ir (M.R. Hemmati), kazemini@sharif.edu (M. Kazemeini), zarkeshj@ripi.ir (J. Zarkesh), khorashe@sharif.ir (F. Khorasheh).

1876-1070/$ – see front matter. Crown Copyright © 2012 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jtice.2012.03.002

Ultimately, smaller crystals might be more prone toward sintering and their reduction could be more troublesome.

This investigation deals with possible modification of the support prior to cobalt impregnation. The properties of γ-alumina support may be modified by doping with elements such as molybdenum [22] and lanthanum [23–26]. In addition to modifying the alumina support, lanthanum can also be utilised as activity and selectivity promoter for cobalt based FTS catalysts. The influence of La loading on Zr-Co/activated carbon (AC) catalysts was reported recently [24]. The experimental results showed that when a low La loading of 0.2 wt% was added to the Zr-Co/AC catalyst, CO conversion and C_{5+} selectivity increased while methane selectivity decreased. However, high loadings of La resulted in a decrease in catalyst activity and C_{5+} selectivity and an increase in methane selectivity. The results also indicated that lanthanum loading had no significant effect on cobalt dispersion. The addition of a small amount of La increased the reducibility of the Zr-Co/AC while excess amount of La led to the decrease of the reducibility of Co catalyst thus resulted in higher methanation activity [24]. These types of catalysts were also used to investigate the effect of La on the production of α-alcohols in the C_1–C_{18} range under mild processing conditions. The selectivity towards alcohols was improved by La doping. The reducibility of the catalyst decreased and the Co dispersion improved due to the strong interaction between Co and La_2O_3 species. La_2O_3 might promote the formation of cobalt carbides (Co_2C) which are postulated to play an important role in the syntheses of the mixed linear α-alcohols [26]. Albeit such species formation was still a route led to losses in activity (and perhaps caused permanent deactivation) by excluding fractions of available carbons on the surface as active sites while also increased in methane selectivity [27]. Thus, a compensating (*i.e.*, optimum) amount of La_2O_3 doped onto the catalyst was indeed necessary to prolong its lifetime through making it more deactivation resistant. On the other hand, high Co dispersion and an appropriate ratio of Co^{2+}/Co^0 can enhance the activity of CO hydrogenation [26].

In another investigation [25], alumina was doped with La_2O_3 by either impregnation or co-precipitation. The doped and undoped alumina were then used as supports for the preparation of cobalt catalysts by incipient wetness impregnation. The results of reactor test and physicochemical characterizations indicated that catalysts prepared from La_2O_3-doped support showed better reducibility, activity and product selectivity [25].

The major goal of the present study was to investigate the effects of La doping on γ-alumina supports before Co impregnation on the catalyst lifetime. For comparison, an in-house recipe for catalyst preparation [11,16] was utilised as a baseline. Four different catalysts with different lanthanum loadings were prepared and tested in a microreactor and characterised by techniques including ICP, TPR and N_2 porosimetry.

2. Materials and methods

2.1. Catalyst preparation

Lanthanum nitrate hexa-hydrate ($La(NO_3)_3{\cdot}6H_2O$, Art. No. 105326, assay 99%) obtained from Merck Chemicals, was dissolved in distilled water. The γ-alumina support was produced from calcination of a bohmite sample provided by the Research Institute of Petroleum Industry (RIPI). To investigate the effects of lanthanum loading, four different catalysts were prepared by dry impregnation (C.1, C.7, C.8 and C.9 with 0.61, 0.0, 1.1 and 2.7 wt% of lanthanum, respectively). Lanthanum impregnation was followed by drying at 120 °C (from ambient temperature using a 1 °C/min ramp) for 2 h and subsequent calcination at 450 °C (2 °C/min ramp) for 3.5 h to complete the support preparation process. The prepared support was cooled to room temperature prior to cobalt impregnation. Cobalt (II) nitrate hexa-hydrate was obtained from Merck Chemicals ($Co(NO_3)_2{\cdot}6H_2O$, Art. No. 102534, assay 97%) and ruthenium (III) nitrosyl nitrate solution, which provided the activation promoting effects of ruthenium on the final catalyst, was obtained from Acros ($Ru(NO)(NO_3)_x(OH)_y$, $x + y = 3$, Art. No. 365041). Cobalt (II) nitrate hexa-hydrate and ruthenium (III) nitrosyl nitrate solutions were diluted in concentrated nitric acid and dissolved in distilled water; yielding a solution suitable for making a 10 wt% cobalt catalyst (based on the catalyst weight) with 0.5 wt% ruthenium (based on the existing cobalt on the catalyst). After 3 impregnations of this solution onto the support, the final catalyst was expected to be loaded with 14–17 wt% Co and 0.5 wt% Ru. Because of the low solubility limit of cobalt nitrate in water at ambient temperature, the solution was heated to 70 °C to ensure complete dissolution. All impregnations were performed using the dry impregnation (incipient wetness) method. The drying and calcination procedures were similar to those performed after lanthanum impregnation.

2.2. Reactor test

All catalysts were tested in a fixed bed microreactor for more than 200 h, to obtain sufficient experimental data to measure their primary catalyst activity, decrease in catalyst activity with time-on-stream, methane selectivity, and liquid product yields, including water and hydrocarbons. The fixed bed microreactor was a 3/8 in. stainless steel tube, into which the catalyst was poured and reduced *in situ*. The reactor was placed in a molten salt bath with a stirrer, to ensure uniform temperature along the catalyst bed. A schematic of the microreactor laboratory setup is shown in Fig. 1.

The reactor was loaded with 3 g of fresh catalyst, which was dried at 70 °C in an oven for 2 h and milled until it was able to pass through a 30-mesh, but not through a 60-mesh sieve. Catalyst powder was diluted before loading into the reactor by inert materials with 1:3 ratio to facilitate heat transfer and preventing hot spots to occur. The catalyst bed was placed in the middle of the reactor in between layers of inert materials to ensure a uniform temperature. To reduce the catalyst, H_2 (60 cc/min g.cat) at atmospheric pressure was passed through the reactor, while the reactor temperature was increased from ambient temperature to 400 °C using a 1–2 °C/min ramp. Once the final temperature was reached, temperature, H_2 flow and pressure were kept constant for at least 8 h to complete the reduction reaction. Then, while maintaining H_2 flow, the electric heater was turned off and the reactor temperature was allowed to drop from 400 °C to the reactor test temperature of 230 °C over a period of approximately 10–12 h. Although 220 °C has been reported to be the optimal temperature for FTS with this catalyst, the higher temperature of 230 °C was used in this study to accelerate the deactivation process, thereby reducing data acquisition time. Once the reactor temperature was stabilised at 230 °C, a feed with an H_2/CO molar ratio of 2.0 and a total flow of 60 cc/min g.cat was introduced into the reactor at 20 bars of pressure, while the backpressure valve simultaneously blocked the outlet flow until the reactor pressure reached 20 bar. At this pressure, continuous flow of the feed into the reactor was maintained for between 170 and 220 h, depending on the deactivation rate of the catalyst. The start-of-the-run was considered to be the instant when the first flow of gaseous products from the reactor was detected. During the reaction, all products from the reactor were directed into a hot trap at 95 °C to collect the heavy components (which were nearly solid at room temperature), followed by a cold trap at 0 °C to collect the light liquid fractions. The remaining gaseous products were directed into a gas chromatograph instrument for further analysis. A Varian 3800 Gas Chromatograph with three channels used for the