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Alumina-supported cobalt-molybdenum catalyst for slurry phase Fischer–Tropsch synthesis

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Abstract

An evaluative investigation of the Fischer–Tropsch performance of two catalysts (20%Co/Al_2O_3 and 10%Co:10%Mo/Al_2O_3) has been carried out in a slurry reactor at 2 MPa and 220–260 °C. The addition of Mo to the Co-catalyst significantly increased the acid-site strength suggesting strong electron withdrawing character in the Co-Mo catalyst. Analysis of steady-state rate data however, indicates that the FT reaction proceeds via a similar mechanism on both catalysts (carbide mechanism with hydrogenation of surface precursors as the rate-determining step). Although chain growth, α, on both catalysts were comparable ($\alpha \cong 0.6$), stronger CH_2 adsorption on the Co-Mo catalyst and lower surface concentration of hydrogen adatoms as a result of increased acid-site strength was responsible for the lower individual hydrocarbons production rate compared to the Co catalyst. The activation energy, E, for Co (96.6 kJ mol^{-1}), is also smaller than the estimate for the Co-Mo catalyst (112 kJ mol^{-1}). Transient hydrocarbon rate profiles on each catalyst are indicative of first-order processes, however the associated surface time constants are higher for alkanes than alkenes on individual catalysts. Even so, for each homologous class, surface time constants for paraffins are greater for Co-Mo than Co, indicative that the adsorption of CH_2 species on the Co-Mo surface is stronger than on the monometallic Co catalyst.

Keywords: Fischer–Tropsch synthesis; Bimetallic catalyst; FT kinetics; Co-Mo oxide; Slurry reactor

1. Introduction

Depleting resources and a dramatic increase in price of crude oil has encouraged renewed interest in the development of efficient Gas-to-Liquid (GTL) technology for clean fuels production via Fischer–Tropsch synthesis (FTS). Abundant stranded gas fields as well as coal resources, form reservoirs of synthesis gas feedstock ($CO + H_2$), due to well-established processes such as natural gas steam reforming and coal gasification. While the technology has matured over the past half century, it still struggles to compete with the crude oil market, with catalyst deactivation being a major area of concern.

Research has revealed that supported cobalt is the preferred choice for a commercial catalyst, principally due to its high activity, better selectivity to higher hydrocarbons, and low conversion to CO_2 compared to iron catalysts [1,2]. The focus recently has been on the need for better carbon resilient catalysts than conventional Co catalysts (which suffer from on-line carbon induced deactivation) and improved reactor design and operation for superior alkene selectivity. Pairing traditional FT catalysts (Co, Fe, and Ru) with other metals such as Pt, Mn, and K, has often been used to enhance activity [3–7]. Kogelbauer et al. [2], and Hosseini et al. [8,9] have studied the Ru-promotion of Co/Al_2O_3 catalysts, and its effects on catalyst reducibility and CO hydrogenation activity. Satterfield and Stenger [10], and Bukur et al. [11] have investigated the effects of K- and Cu-promotion of precipitated Fe catalysts, on hydrogenation activity and selectivity. Jacobs et al. [12–16] have carried out extensive work on several noble metals and metal cations promotion of Co (including Pt, Ru, Re, La, Zr, and K), and their effects on the physicochemical properties, and deactivation behavior of the catalysts.

The advantages of improved heat transfer, minimisation of hot-spots and side-reactions, and better catalyst longevity make the slurry reactor more attractive than the fixed bed system [17–23]. Isothermal operability, and longer contact time of reactant gases with catalyst in the slurry reactor, endow it with the potential to produce very high molecular weight hydrocarbons:

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these may potentially accumulate as the liquid phase in the reactor. A major drawback though, is the need for product separation from the solid catalyst: both online, as well as of the spent catalyst at the conclusion of a run. Even so, its significant advantages over the fixed and to a lesser extent fluidised bed systems, and a more favourable market for high molecular weight FT products, make the slurry reactor the preferred choice for recent as well as new FT plants. Combined with a supported cobalt catalyst, it forms the latest generation of Sasol's FT reactors for the production of middle distillates and liquid fuels [19,21,24]. Ultimately however, the formulation of a high activity, stable catalyst, is at the heart of the process, if maximal benefits of the slurry reactor are to be enjoyed [25].

Since Mo carbide is known to be active for hydrogenation/dehydrogenation reactions [26,27] and also used as a desulfurisation catalyst [28], the addition of Mo to a Co catalyst for FT reaction should endow it with carbon-resilient attributes especially for sulfur-containing natural gas conversion processes. This constitutes the rationale for this evaluation study of the Co-Mo catalyst. Moreover, ethylene re-adsorption reportedly takes place during FTS [29–32], hence the use of a well-stirred slurry reactor will favour olefin selectivity.

2. Experimental

2.1. Catalyst preparation

Two catalysts (monometallic 20%Co/Al_2O_3, and bimetallic 10%Co-10%Mo/Al_2O_3) were prepared via pH controlled wet impregnation on commercial γ-alumina support (Saint-Gobain Norpro Corporation) using $Co(NO_3)_2.6H_2O$ (Aldrich Chemicals) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Ajax Finechem) as the respective Co and Mo precursors. Accurately weighed amounts of precursor(s) required to make a 20 wt% total metal loading catalyst, were dissolved in ultra pure H_2O to make the precursor solution. The support was ground and sieved to 38–147 μm particle size, before adding to the precursor solution to make the impregnating slurry. Impregnation was carried out at 25 °C for 3 h under constant stirring, constant pH (=2) conditions, using 5 M HNO_3 solution as the pH control. The sub-isoelectric pH impregnation was adopted to create a positively charged support surface, and hence an alike-charged support-impregnating species pair, which would enhance catalyst dispersion, while simultaneously reducing detrimental metal–support interactions [33–36]. Impregnated catalysts were dried in an oven at 120 °C, for 24 h.

The dried catalysts were ground and calcined in flowing dry air, at 400 °C, for 5 h, using a heating rate of 5 °C min^{-1}. The air used was passed through a series of gas purifiers to remove moisture, hydrocarbons and organics. Calcined catalysts were finally ground and sieved to 38–147 μm size before charging 7.5 g (calcined, unreduced basis) in a 1/2 in. diameter stainless steel fixed bed reactor to carry out ex situ activation at 350 °C, for 16 h, with a heating rate of 5 °C min^{-1} in 3:1 H_2:CO mixture, and total GHSV of 1.5 l(STP) $g_{cat}{}^{-1}$ h^{-1}, with 50% N_2 diluent to dissipate the heat of reaction and minimise generation of hot spots which may lead to coking and catalyst deactivation. High purity research grade H_2 (99.99%), CO (99.97%), and N_2 (99.99%) supplied by Linde Gas were used throughout. Gas flowrates were controlled by Brooks 5850E Series electronic mass flow controllers.

2.2. Catalyst characterisation

The BET surface areas of the calcined catalysts and the γ-alumina support, were obtained from liquid N_2 physisorption at −196 °C, in a Micromeritics AutoChem 2910 unit. Temperature-programmed NH_3 desorption (TPD) was also performed in the same unit after solid pretreatment at 500 °C with H_2 for 3 h. NH_3 (10%NH_3/N_2, Linde Gas) adsorption occurred at 150 °C for 60 min, while desorption was performed in He (99.996%, Linde Gas) flow at heating rates of 10, 15, 20, and 30 °C min^{-1}.

Thermogravimetric analysis of the calcination and reduction behavior of the catalysts was performed using a ThermoCahn TG 2121 system. Temperature-programmed calcination was carried out at 400 °C, for 5 h, with heating rates of 1, 5, and 20 °C min^{-1}, using 55 ml min^{-1} high purity air. Temperature programmed reduction (TPR) was performed up to 700 °C, for 1 h, at 5 °C min^{-1}, in 55 ml min^{-1} of 50% H_2/N_2 mixture. Helium purge (55 ml min^{-1}), and a 3-h initial drying step at 120 °C were incorporated for both calcination and reduction experiments.

2.3. Reaction

Slurry phase Fischer–Tropsch synthesis was performed in a 2 l magnetically-stirred Parr reactor (model 4522). Catalyst activated ex situ in the fixed bed reactor as detailed in Section 2.1, was pneumatically transferred (in flowing N_2) through a ball valve and a dip tube, into the slurry reactor containing 600 g of molten wax, which was also pre-purged with N_2 to eliminate possibility of re-oxidation of the activated catalyst. The dip-tube arrangement prevented catalyst from accumulating on the inside walls of the reactor, above the liquid level, as well as being carried out of the reactor in the gas phase. Paraffin wax from Ajax Finechem with a melting point between 56 and 58 °C, was used as the start-up medium. Following catalyst transfer, the reactor temperature and pressure were increased in N_2 flow to 2 MPa pressure, and the required reaction temperature (220–260 °C) in a two-step isothermal–isobaric process. Syngas flow was then introduced at H_2/CO of 2, with 25% N_2 diluent, and a total GHSV of 3 l(STP) $g_{cat}{}^{-1}$ h^{-1}. Reactor outlet gases passed through a series of high pressure, hot and cold traps at 80 and 0 °C, respectively. Reactant gases and uncondensed products passed through a back-pressure regulator, located downstream of the cold trap. The flowrate was measured using a soap-film flowmeter, while gas phase products were analyzed on a Shimadzu GC-17A gas chromatograph, using a 30 m GS-Q capillary column and a Flame Ionization Detector (FID).

3. Results and discussion

3.1. Physicochemical attributes

The presence of different oxide phases in the Fischer–Tropsch catalyst and their reducibility is a determinant of the