Catalysis Today 272 (2016) 69–73

Contents lists available at ScienceDirect

Catalysis Today

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

Product distribution change in the early stages of carbon monoxide hydrogenation over cobalt magnesium Fischer-Tropsch catalyst

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ARTICLE INFO

Article history:
Received 5 October 2015
Received in revised form 5 March 2016
Accepted 7 March 2016
Available online 5 April 2016

Keywords:
Fischer-Tropsch synthesis
CO hydrogenation
Cobalt
Transient experiments
Time-resolved
Temporal analysis of products

ABSTRACT

The catalytic hydrogenation of carbon monoxide, known as the Fischer-Tropsch process, is a technologically important, complex multipath reaction which produces long chain hydrocarbons. In order to access the initial kinetics and the mechanism, we developed a reactor that provides information under non-steady state conditions. We tested a CoMgO catalyst and monitored the initial product formation within 2 s of exposure to CO as well as the time dependence of high molecular weight products (in a 60 s window) and found drastic changes in the product selectivity. The probability for forming branched isomers (C_4 and C_5) peaks in the first 25 s, and within that time frame no unsaturated products were detected. The subsequent decline (at ~35 to 40 s) of branched isomers coincides with the detection of olefins (from C_2 to C_5) and the change in carbon coverage at the surface of the catalyst. This indicates a change in the reaction pathway.

1. Introduction

Continuous growth of the worldwide population is increasing the demands in energy leading to the depletion of fossil sources. Crude oil is the primary source for fuel but also for fine chemical production and the plastics industry. Besides the use of conventional alternative sources of energy such as wind, solar, or nuclear power, the synthesis of higher value hydrocarbons from carbon monoxide and hydrogen is an attractive solution. This solution, known as Fischer-Tropsch synthesis, has been around since the early 1900s. Fischer-Tropsch is a perfect example of the greatest challenge heterogeneous catalysis has to face: control of selectivity [1,2]. The major drawback of this synthesis is its vast product distribution and the lack of precise control on the selectivity [3–8]. Subsequent refining processes (hydrocracking, isomerization, reforming, alkylation, etc....) are needed in order to obtain the desired product. Our approach to this problem, until now, has been to use model nanoparticle catalysts in which the synthesis of both the support and the active phase is well controlled [9–11], and to study these model catalysts under high pressure steady state conditions.

Despites their prevalence, steady state experiments are severely limited in that they provide only global kinetics parameters and little to no information on individual reactions steps. Chemical Transient Kinetic experiments and Temporal Analysis of Products are among the most helpful techniques to evaluate the intrinsic kinetic coefficients and give information on the different steps of the reaction [12–17].

In the present paper, we are introducing our findings regarding the initial changes in the product distribution of the FT synthesis. This was made possible by the combination of a new reactor enabling Chemical Transient Kinetics (CTK) experiments with Temporal Analysis of the Products.

2. Material and methods

2.1. Catalyst preparation

Cobalt magnesium oxide catalyst was prepared according to literature using the oxalate route as described elsewhere [14]. Briefly, a bimetallic solution of cobalt nitrate ($Co(NO_3)_2$, Sigma Aldrich) and magnesium nitrate ($Mg(NO_3)_2$, Sigma Aldrich) is prepared in acetone with an atomic ratio of 10:1. The mixed Co-Mg oxalate was obtained by addition of oxalic acid also dissolved in acetone. The

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http://dx.doi.org/10.1016/j.cattod.2016.03.027
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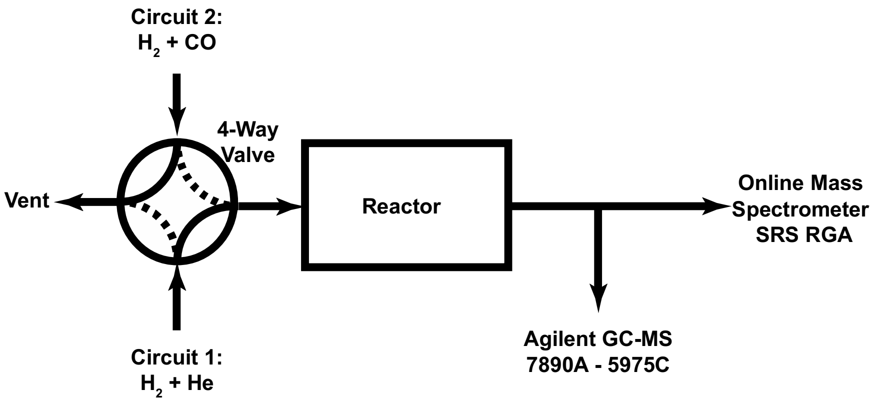

Fig. 1. Schematic of the Chemical Transient Kinetics system used for this study: the 4-way valve allows for quick change of gaseous composition while the outlet is monitored online by a mass spectrometer (SRS RGA). The use of a secondary analytical system, here an Agilent GC–MS, allows for Temporal Analysis of Products during the transient period.

resulting precipitate was centrifuged, washed several times and dried overnight. Subsequently, the dried substance was crushed and sieved to obtain the catalyst precursor (150 μm < particulates size < 250 μm). The final catalyst was obtained by thermal decomposition of the oxalate in hydrogen (10% in argon) at 400 °C.

2.2. *Catalyst characterization*

Physical and metallic surface areas of the catalyst were measured using a Micromeritics ASAP 2020. In both cases the oxalate was decomposed *in situ* with pure hydrogen at 3 °C/min up to 400 °C. Prior to the measurement, the CoMgO sample was evacuated at 150 °C for 2 h. The physisorption measurements were taken using nitrogen as the probe at −196 °C, and the surface area was extrapolated using the BET expression. The metallic surface area was obtained using hydrogen as a probe molecule. The hydrogen chemisorption was carried out at 35 °C and the surface area was extrapolated from the isotherm. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy mapping (EDS) was acquired using an Analytical Field Emission Zeiss Gemini Ultra-55 (at 20 KeV). X-ray Photoelectron Spectroscopy experiments were performed in a PHI ESCA instrument at a base pressure of 7.5 10^{-9} mbar using a non-monochromatic Al Kα radiation. Photoelectron core-level spectra were acquired using a hemispherical analyzer at a pass-energy of 35.75 eV with a 0.05 eV energy step. The spectra were analyzed using the public software package CasaXPS.

2.3. *Catalytic testing*

Transient experiments or Chemical Transient Kinetics experiments were conducted in a home built system described in a previous work [10]. The system is equipped with two independent plug-flow circuits connected to a small volume reactor via a 4-way valve (see Fig. 1 for a schematic).

This 4-way valve enables a fast and reproducible switch of the gaseous composition directed to the catalysts by switching from one circuit to the other. The outlet of the gas reactor is monitored online using a mass spectrometer (RGA, Stanford Research System) equipped with a differentially pumped capillary and valve inlet system (Pfeiffer GES-010). This inlet system allows for a fast sampling rate (max = 0.5 s) while keeping the ionization chamber under molecular flow conditions providing a means for quantitative measurements. In practice, the number of mass/charge ratios monitored using the *multiple ion detection mode* limits the time resolution. In the present work, we have decided to follow 14 m/z ratios giving an optimum time resolution of 2.2 s. In addition to the online mass spectrometer, small aliquots of the gas outlet are analyzed by Gas Chromatography combined with a Mass Spectrometer (Agilent GC–MS). The volume sampled from the outlet corresponds to ~1.3 mL, which given the mass flow rate, is equivalent to a time resolution of 2 s allowing for a Temporal Analysis of Products (TAP).

Table 1
Description of the CoMgO catalyst after decomposition of the oxalate precursor using a temperature programmed decomposition under H_2 (10% in Ar) up to 400 °C at a rate of 6 °C min$^{-1.}$

CoMgO	
Nominal Composition	10:1 Co:Mg
Particle size (nm)	38
BET (m^2/g)	89.5
Metallic surface (m^2/g of catalyst)	4.7

Table 2
Delay times obtained during the transient period or surface build up. The times are given in seconds and evaluated from the time of switch using Ar as an internal standard.

	Transient data
Products	Delay Time (s)
CO & CO_2	21
CH_4	9
C_{2s}	12
C_{3s}	14

Catalytic tests were operated at constant temperature of 230 °C with a ratio of H_2 to CO equal to 3:1. Prior to the testing, the oxalate precursor is decomposed *in situ* as described earlier.

3. Results and discussion

The physico-chemical characteristics of the catalyst are presented in Table 1. According to the metallic surface area obtained from H_2 chemisorption, we evaluated the cobalt particles average diameter to be 38 nm. SEM and EDS mapping evidence a homogeneous distribution of Co and Mg within the catalytic grains (see Fig. 2a). Moreover the post-mortem sample presents an identical homogeneous distribution of both Mg and Co in the grains (Fig. 2b). Nevertheless, surface segregation cannot be ruled out due to the low spatial resolution of the EDS mapping. Finally, the EDS analysis of the samples confirms the atomic percentage to be 89% Co and 11% Mg.

The turnover frequency was evaluated at steady state based on the total cobalt metallic surface area and CO conversion. It was found that the CO conversion at steady state is 32% giving a TOF of 0.066 s^{-1}. In addition, the product distribution at steady state shows high selectivity towards methane and large chain hydrocar-