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High-temperature Fischer-Tropsch synthesis over FeTi mixed oxide model catalysts: Tailoring activity and stability by varying the Ti/Fe ratio

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ABSTRACT

A series of Fe-Ti mixed oxide model catalysts containing different Ti/Fe ratios were synthesized and applied as catalysts for the High Temperature Fischer-Tropsch reaction (HTFTS). XRD, H_2-TPR and *in situ* Mössbauer and XAFS spectroscopy were applied to evaluate the role of Ti on the physical and chemical properties of Fe within the mixed metal oxide. It was observed that the Ti/Fe ratio determines the relative amounts of *hematite*, *pseudobrookite*, and *anatase* in the starting materials. The interplay between these phases is responsible for the HTFTS catalytic performance.

Our results demonstrate that the presence of *pseudobrookite*: i) enhances the dispersion of iron; ii) mediates and controls the reduction and carburization degree during the transformation of Fe (III) species to carbides upon activation, and iii) increases the stability under HTFTS conditions by minimizing the re-oxidation of iron carbides. Highest catalytic activity and stability is achieved for the material with Ti/Fe ratio of 1/2.1.

1. Introduction

Depletion of oil sources and the need to reduce the carbon footprint have directed extensive research efforts into the development of alternative feedstocks and processes to produce chemicals [1–3]. Among these, High Temperature Fischer-Tropsch Synthesis (HTFTS) is a promising alternative technology for the production of short chain olefins from natural gas, coal or biomass [4–7]. This process converts syngas, a mixture of hydrogen and carbon monoxide, to hydrocarbons on a iron catalyst [8,9]. The product distribution from an HTFTS process follows the Anderson-Schulz-Flory (ASF) distribution, making it theoretically impossible to selectively synthesize a narrow product distribution. According to this theoretical model, the maximum selectivity of C_2–C_4 hydrocarbons (including olefins and paraffins) is 58% and is achieved with a chain growth probability (alpha value) between 0.4 and 0.5 [6].

One of the most efficient ways of shifting product selectivity to low carbon numbers (low alpha) is by increasing the reaction temperature. However, a decrease of the chain growth probability also results in an undesired increase of methane selectivity as predicted by the ASF distribution. In addition, catalyst deactivation accelerates at higher temperatures [10,11]. These aspects have been considered to be the major restrictions for the industrial application of this process.

Fe-based catalysts remain the practical catalyst choice for the HTFTS process [8,12,13]. Fe-based catalysts produce less methane and more olefins than Co-based catalysts at high conversion levels (conversion higher than 20%). Furthermore, they are active in the water-gas-shift reaction under typical HTFTS conditions, enabling the *in situ* re-adjustment of the H_2/CO molar ratio for the conversion of hydrogen lean syngas [8].

Extensive research has been carried out to improve the activity and selectivity towards short chain olefins in iron-based catalysts

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while minimizing the formation of methane and mitigating deactivation phenomena. Between mid 1970 and mid 1980 Ruhrchemie (now Johnson Matthey) developed different catalysts for the HTFTS process by mixing iron oxide with oxides of other metals such as Ti, V, Mo, W or Mn [14,15]. Comparable systems were reported by The Dow Chemical Company in the same period [16]. In particular, an important model system composed of bulk iron oxide promoted with titanium, zinc, and potassium oxide was developed for industrial applications [17]. These catalytic systems showed high selectivity towards lower olefins while exhibiting a low methane make (10%) and serve as the reference in bulk HTFTS catalyst development [17]. However, the effect of each catalytic component on the HTFTS performance and their promoting mechanism are still poorly understood.

In a recent work, the phase composition of a Fe-Ti-Zn-K-oxide reference catalyst was studied in the early stages of the HTFTS reaction with *operando* spectroscopy tools [18]. However, this work did not systematically probe the parameters that might affect such transformations. In the current work we therefore focus on simple model systems based on iron-titanium mixed oxides, i.e. without the use of additional promoters like alkali, etc. The purpose of this study is to unravel the role of the Fe-Ti interactions on the HTFTS catalyst performance and stability, by the use of different *in situ* characterization techniques in combination with catalyst performance testing.

2. Materials and methods

2.1. Synthesis

A series of iron-titanium mixed oxides with different Ti/Fe ratios ($0.1 < Ti/Fe < 2.6$) were synthesized as follows: 10 mL of a saturated solution of oxalic acid, an aqueous solution of iron(III) nitrate nonahydrate (2.0 mol/L), and a solution of titanium(IV) bis(ammonium lactato) dihydroxide (50 wt.%) were mixed under vigorous orbital shaking (500 rpm, RT) in such proportions to achieve the Ti/Fe atomic ratio (1/10–3/7–5/5–7/3). Subsequently, the final mixture was heated to 363 K (5 K/min; continuous orbital shaking) and held at that temperature for up to 16 h to evaporate the excess of water resulting in a gel-like residue. Finally, the residue was calcined under static oven conditions (ramp 5 K/min; T = 723 K, hold time 4 h).

2.2. Characterization

2.2.1. X-ray fluorescence (XRF)

X-ray Fluorescence (XRF) data were collected at room temperature (RT) with a PANalytical PW4400 spectrometer using an X-ray tube with a rhodium anode.

2.2.2. X-ray diffraction

X-ray diffraction (XRD) patterns were recorded in a Bragg–Brentano geometry in a Bruker D8 Advance diffractometer equipped with a Vantec position sensitive detector and graphite monochromator. Measurements were performed at room temperature, using monochromatic Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) in the 2θ region between 10° and 90°. Samples were placed on a Si (5 1 0) substrate and rotated during measurements. All patterns were background-subtracted to eliminate the contribution of air scatter and possible fluorescence radiation.

2.2.3. In situ *Mössbauer spectroscopy*

Transmission ^{57}Fe Mössbauer spectra were collected at 300 and 4.2 K with constant and sinusoidal velocity spectrometers using a ^{57}Co(Rh) source. Velocity calibration was carried out at room temperature, using an α-Fe foil. The source and the absorbing samples were kept at the same temperature during the measurements. The low-temperature Mössbauer measurements were performed in a cryostat in which the in-situ cell was fully immersed in liquid helium. The temperatures of both source and sample were continuously monitored using Cryogenic Linear Temperature Sensors (CLTS). The Mössbauer spectra were fitted using the Mösswinn 4.0 program.

The experiments were performed in a state-of-the-art high-pressure Mössbauer *in situ* cell – recently developed at TU Delft [19]. The Mössbauer spectrometer is operated in a vertical configuration – allowing the use of powders inside the sample chamber of the in-situ cell. The catalysts were used in the as-received state, without any additional sample handling. The high-pressure beryllium windows used in this cell contain 0.08% Fe impurity whose spectral contribution was fitted and removed from the final spectra. *In situ* reduction experiments were performed under hydrogen atmosphere at 698 K, 3 bar. A spectrum was recorded after 3 h exposure. *In situ* syngas conversion experiments were carried at 20 bar, 613 K, and H_2/CO ratio of 1. A spectrum was recorded after 5 h exposure.

2.2.4. Temperature programmed reduction (H_2-TPR)

Temperature-programmed reduction (TPR) was used to evaluate the reducibility of Fe on the different catalysts used. These experiments were performed using hydrogen as reducing agent.

In a typical experiment, 50–130 mg of sample was placed in a fixed bed reactor and exposed to a mixture of 10% H_2/He, and heated using a rate of 10 K/min from RT to 1100 K with a flow-rate of 20 cm^3/min (STP). The outlet composition of the gas mixture was measured as a function of time, using a thermal conductivity detector (TCD) and mass spectrometer (MS).

The extent of reduction (ζ) was calculated from the integral consumption of hydrogen within the temperature range of TPR experiment assuming that Fe is in the final reduced form.

2.2.5. In situ *X-ray absorption spectroscopy*

X-Ray absorption spectroscopy was performed at beamline X18A of National Synchrotron Light Source in Brookhaven National Laboratory (NY, USA). The beamline used the Si (1 1 1) channel-cut monochromator and provided an energy range of 5–25 keV. All the measurements were performed in transmittance mode. Incident and transmitted X-rays were detected with ion chambers. EXAFS and XANES data were collected on the K edge of Fe. All Fe-containing samples were measured against the Fe-foil used as a reference.

In a typical *in situ* experiment, the samples were diluted with boron nitrate to achieve a desired edge jump value. Subsequently, the sample was placed in an *in situ* cell, and was continuously purged with a flow of He of 20 cm^3/min (STP) and heating was applied. Once the sample reached 723 K, XAS spectra were collected until no further changes were observed. For the reduction step the cell was cooled to 673 K and exposed to a flow of H_2/He (1:9). The flow rate was 20 cm^3/min (STP) and the cell pressure was 2 bar. The reduction process was monitored by EXAFS/XANES for 3 h. When no further evolution of the spectra was apparent the reduction was discontinued and the reduced catalyst was exposed to Fischer-Tropsch (FTS) conditions. FTS reaction was carried out at 613 K in a flow of CO/H_2 (1:1) mixture at the flow rate of 60 cm^3/min (STP).

The EXAFS data were processed in Athena software package (version 0.8.056). The background subtraction was performed by using the automated single-variable fit implemented in Athena. The Fourier Transform of the reciprocal space data was performed by using the Hanning window in the k range of 2–10 Å^{-1}.