



Effect of proximity and support material on deactivation of bifunctional catalysts for the conversion of synthesis gas to olefins and aromatics

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ARTICLE INFO

Keywords:

Catalyst stability
Bifunctional catalyst
Fischer-Tropsch to olefins
Proximity
Synthesis gas to aromatics

ABSTRACT

Synthesis gas conversion to short olefins and aromatics using bifunctional catalysts has gained much attention in recent years. Here, we study the interaction between the components of bifunctional catalysts to design a more stable catalyst system. Mixing α -alumina supported iron (-carbide) promoted with sodium and sulfur with an H-ZSM-5 zeolite to convert synthesis gas to aromatics and short olefins we observed selectivity loss of the iron (-carbide) catalyst as well as the acid function. This was displayed by increasing methane and decreasing aromatics selectivity when the two individual catalysts were mixed in close proximity. We introduced different approaches to understand this selectivity related deactivation. Larger spatial separation of the iron and zeolite allowed a more stable system with constant methane and aromatics selectivity. Alternatively, iron supported on carbon nano tubes mixed with the zeolite in close proximity did not display selectivity related deactivation. We conclude that the selectivity loss was caused by migration of sodium ions that were used next to sulfur as promoters on the iron catalyst over the α -alumina support to the zeolite, which was supported by XPS model experiments. This migration seems hindered on carbon supported iron catalysts.

1. Introduction

Synthesis gas (a mixture of carbon monoxide/carbon dioxide and hydrogen) can be derived from coal [1] and natural gas [2] as well as from biomass [3] and can be converted to valuable chemicals such as short olefins and aromatics. This has received significant interest in the past years in academia and industry [4,5]. Recent publications have shown that bifunctional catalyst systems consisting of a metal oxide catalyst and a zeolite enable direct conversion of synthesis gas towards chemicals such as short olefins [6,7] and aromatics [8]. The intermediates in this reaction are reported to be oxygenates like methanol and dimethyl ether [9,10] or ketene [11].

Alternatively, cobalt carbide catalysts with certain crystal facets exposed or promoted iron (-carbide) based Fischer-Tropsch to olefins (FTO) catalysts can be used to convert synthesis gas to short olefins [12–18]. These catalysts show a selective suppression of methane formation next to an increase in olefins to paraffin ratio in the products and allows to form olefins in the range of C₂–C₄ beyond the Anderson-Schulz-Flory (ASF) distribution. In the case of iron (-carbide) based FTO catalysts, the presence of both sodium and sulfur promoters on the iron

(-carbide) particles is essential for the decrease in methane selectivity [19–21].

In order to further convert the olefins formed on the iron (-carbide) based catalyst to aromatics the iron catalyst can be combined with a solid acid such as H-ZSM-5 zeolites in a single reactor [22–26]. The group of Ding successfully combined iron catalysts with an H-ZSM-5 zeolite to convert synthesis gas to aromatics with high CO conversion (85%) and aromatics selectivity (70% in C₅+). This was achieved by either impregnation of the zeolite with iron precursor or powder mixing of bulk iron catalysts with H-ZSM-5 zeolites [23,26]. Additionally, the group of Dadyburjor studied the effect of addition of H-ZSM-5 zeolite to carbon supported iron catalysts in different catalyst bed designs and observed catalyst deactivation in mixed bed mode, which was assigned to metal migration [24,25].

Typically, deactivation of supported metal catalysts has been ascribed to particle growth, which decreases the number of active sites but does not change their nature [27–30]. However, in bifunctional catalysts other deactivation mechanisms might play a role. For instance, a short distance between the iron (-carbide) and the acid sites of a bifunctional catalyst system may facilitate migration of alkali metal ions

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<https://doi.org/10.1016/j.cattod.2019.02.002>

Received 31 August 2018; Received in revised form 8 January 2019; Accepted 3 February 2019

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from the iron (-carbide) catalyst towards the zeolite [31] due to high mobility of alkali metal ions [32,33]. This could not only lower the activity and selectivity of the FTO catalyst but also neutralize the acid sites of the zeolite with alkali metal ions leading to a decreased selectivity to aromatization of olefins [34].

Here, we want to gain fundamental understanding of the mechanism of selectivity loss, with the final aim to allow design of more stable bifunctional catalysts. Therefore, we combined a Fischer-Tropsch to olefins (FTO) catalyst based on iron promoted with sodium and sulfur with an H-ZSM-5 zeolite to convert synthesis gas to aromatics with short olefins as intermediates [35]. This work focuses on both the influence of proximity [6,8,36] of the two catalytic functions as well as of the nature of the support on the stability. We show how the migration of promoters from the iron catalyst to the zeolite is affected and the resulting increase in methane selectivity and decreased selectivity to aromatics.

2. Experimental

2.1. Catalyst preparation

The promoted iron catalyst was prepared via incipient wetness impregnation of α -alumina (BASF, Al4196E, 7 m²/g surface area, 0.4 mL/g pore volume (determined by water wetting). Prior to impregnation, the alumina powder was dried in a two-neck flask equipped with a vacuum valve adapter and a septum under vacuum at 120 °C for 2 h. After the flask was allowed to cool to 25 °C in vacuum the valve was closed, and the impregnation solution was added with a syringe and needle through the septum while stirring. The impregnation solution was prepared by dissolving ammonium ferric citrate (6.002 g, brown, Acros), sodium citrate monobasic (380.0 mg, Sigma Aldrich) and sulfuric acid (180.4 mg, 10 wt.-% solution in demineralized water) in demineralized water (20 mL). Three impregnation steps were necessary to achieve an iron loading of ~6 wt.-%. Between the impregnation steps the material was dried under vacuum for 2 h at 60 °C. After the third impregnation step the samples were dried at 60 °C for 16 h in static air followed by calcination at 250 °C in static air for 4 h. The calcined iron catalyst was pelletized, ground and sieved to a fraction of 425–630 μ m or 75–150 μ m.

For the CNT supported iron catalyst, iron nano-crystals (Fe-NC) were prepared via colloidal synthesis. 1,2-hexadecandiol (350.9 mg), oleyl amine (214.9 mg), oleic acid (433.1 mg) and 1-octene (10 mL) were mixed in a 3-neck flask, equipped with a reflux condenser, septum and vacuum adapter connected to a Schlenk-line. Vacuum was applied, and the mixture was heated to 120 °C for 30 min. A mixture of iron pentacarbonyl (20.85 mg) and 1-octadecene (1 mL) was prepared in a nitrogen glovebox. The 3-neck flask was flushed with nitrogen three times followed by injection of the iron pentacarbonyl solution at 90 °C. The mixture was heated to 290 °C and kept there for 1 h. Afterwards the mixture was allowed to cool to 25 °C, it was transferred to a vial, to further process in air and mixed with an equal volume of *iso*-propanol. The Fe-NC were placed in a centrifuge (2700 rpm, 15 min) and the supernatant was decanted. 5 drops of toluene were added and the mixture was sonicated for 30 s, followed by a treatment in the centrifuge (2700 rpm, 15 min). The toluene-washing procedure was repeated. The as-synthesized Fe-NC were suspended in 10 mL 1-octadecene.

To attach the Fe-NC to the support the support material (CNT, Bayer BayTubes, 800 mg, surface area 230 m²/g, pore volume 1.6 mL/g) was added into a 100 mL three-neck flask, which was connected to a Schlenk line through a reflux condenser. The suspended Fe-NC were added to the support material by pipetting while simultaneously magnetically stirring at 400 rpm. The mixture was brought under vacuum for 30 min at 120 °C to evaporate the toluene, and subsequently purged with nitrogen. The temperature was increased to 200 °C within 10 min under nitrogen flow and maintained for 30 min. Afterwards, the mixture

was allowed to cool down to 25 °C and further processed in air. Finally, the iron Fe-NP supported on the carbon materials were washed five times with hexane and acetone (hexane/acetone = 1:3 v/v) and dried at 60 °C for 1 h under static air, at 120 °C for 3 h under static air, and at 80 °C for 3 h under vacuum.

The addition of promoters to the CNT-supported Fe-NC was achieved using incipient wetness impregnation of the unpromoted Fe-NC after attachment to the CNT. The unpromoted Fe-NC on CNT were placed in a two-neck flask equipped with a septum and a vacuum valve adapter and heated to 60 °C under vacuum for 1 h. Afterwards the flask was allowed to cool to 25 °C (under vacuum) and the valve was closed. Sodium sulfide nonahydrate (212.5 mg) was dissolved in demineralized water (5.7 mL) and 1 mL of this solution was diluted with a mixture of water and *iso*-propanol (1:1 v/v, 9 mL of mixture). 1.2 mL of the final solution was added per gram of catalyst. The impregnated catalyst was dried under vacuum at 25 °C for 16 h and pelletized, ground and sieved to a fraction of 425–630 μ m.

The ZSM-5 zeolite was transformed from the ammonium form (NH₄-ZSM-5, Zeolyst, Si:Al = 15 at/at) to the proton form H-ZSM-5 by calcination at 550 °C for 4 h in static air (the temperature programmed desorption profile of ammonia can be found in the supporting information, Fig. S1). Afterwards, the powder was pelletized, ground and sieved to a fraction of 425–630 μ m or 75–150 μ m.

The iron catalyst and the zeolite were combined with different proximities. In the stacked bed configuration (denoted as AFe + Z) the zeolite was placed downstream of the iron catalyst with a thin layer of silicon carbide in between. Mixed bed experiments were performed by physically mixing the iron catalyst and the zeolite in the reactor using sieve fractions of 75–150 μ m (denoted as AFe/Z-100) and 425–630 μ m (denoted as AFe/Z-500), respectively. To prepare composite catalysts consisting of the iron catalyst supported on alumina (denoted as AFeZ) and CNT (denoted as CFeZ), respectively, and the zeolite, the powders of the iron catalysts and the calcined zeolite were mixed in a mortar for 5 min to achieve an appropriate distribution within the final grains. The iron catalyst supported on alumina was mixed with the zeolite in a ratio of Fe/Al₂O₃:zeolite = 3:5 m/m, whereas the CNT-based iron catalysts were mixed with a ratio of Fe/CNT:zeolite = 4:5 m/m to compensate for the lower iron loading of the iron catalysts supported on CNT. Subsequently, the mixed powders were pelletized, ground and sieved to a fraction of 425–630 μ m.

2.2. Characterization

The elemental composition of the calcined alumina-supported iron catalysts and the dried CNT-supported iron catalysts was determined with ICP analysis (supporting information, Table S1). Transmission electron microscopy (TEM) images were acquired using a FEI Talos F200X transmission electron microscope in bright field mode operating at 200 kV (supporting information, Figs. S2–S4). To analyze the porosity and surface area of the support materials, nitrogen physisorption was measured at liquid nitrogen temperature using a Micromeritics TriStar 3000 surface area and porosity analyzer. Prior to physisorption measurements, the alumina support was dried in nitrogen flow for 16 h at 300 °C and CNT support at 150 °C, respectively (isotherms and physisorption data can be found in the supporting information, Fig. S5 and Table S2).

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a K-Alpha XP spectrometer (Thermo Scientific) equipped with a monochromatic small-spot (400 μ m) X-ray source operating at 72 W, a 180° double focusing hemispherical analyzer with a 128-channel delay line detector and an Al anode ($E(\text{Al } K_{\alpha}) = 1486.6$ eV). The background pressure inside the analysis chamber was kept below 8·10⁻⁸ mbar reaching maximum of 3·10⁻⁷ mbar during the measurements due to the flow of low energy Ar⁺ ions involved in the charge neutralization process. Samples were handled in ambient air and were fixed on the XPS sample holder by conducting carbon tape. High-resolution spectra

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