



Ruthenium silica nanoreactors with varied metal–wall distance for efficient control of hydrocarbon distribution in Fischer–Tropsch synthesis

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ARTICLE INFO

Article history:

Received 2 May 2018

Revised 24 June 2018

Accepted 25 June 2018

Keywords:

Fischer–Tropsch

Ruthenium

Nanoreactors

Chain length distribution

ABSTRACT

We report here a new strategy for the control of hydrocarbon selectivity in Fischer–Tropsch (FT) synthesis using silica yolk–shell ruthenium nanoreactors prepared in water/oil (W/O) microemulsions. The sizes of nanoreactors have been varied by changing the microemulsion composition. Nanoreactors prepared with the smallest internal volume exhibited a restriction of hydrocarbon chain length growth during FT synthesis. An increase in the nanoreactor volume resulted in a gradual shift of the hydrocarbon distribution to longer-chain hydrocarbons till a distribution of hydrocarbons reached that observed over the reference catalysts prepared by deposition of non-encapsulated metal nanoparticles on silica supports. The observed remarkable modifications of hydrocarbon selectivity over Ru nanoreactors have been explained by shape selectivity effects on hydrocarbon growth due to decrease in entropy in comparison with infinite growth and increase in the Gibbs energy for growing hydrocarbon chains located inside the limited volumes of nanoreactors.

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1. Introduction

Fischer–Tropsch (FT) synthesis is a surface polymerization reaction that produces a wide range of hydrocarbons and oxygenates from syngas (mixture of H₂ and CO), which might be manufactured from different types of resources such as coal, natural gas, or biomass. Low-temperature FT synthesis takes place at 220–240 °C, 20 bar, and a H₂/CO molar ratio of 1–2 over cobalt-, iron-, and ruthenium-based catalysts [1,2]. One of the main problems of this process is efficient control of hydrocarbon selectivity. The distribution of the products in low-temperature FT synthesis obeys the Anderson–Schulz–Flory (ASF) law and is very broad in range, from 1 to 80 carbon atoms [3]. Large industrial facilities including cracking, isomerization, and separation are needed for transformation of this hydrocarbon mixture to value-added products such as diesel (C₁₀–C₂₀) or gasoline (C₅–C₁₂) fuels. The state-of-the-art GTL and CTL technologies include three major stages: syngas generation,

FT synthesis, and hydrocracking/isomerization of the produced hydrocarbons. They have been developed principally for large-scale facilities. Utilization of waste and biomass feedstocks will certainly require technology scale-down. The process complexity and capital costs in small-scale BTL units will certainly be important cost drivers for combining FT synthesis and cracking/isomerization in a single-step process [4].

Direct and selective synthesis of specific hydrocarbon fractions from syngas would provide a great opportunity for broad implementation of FT synthesis. Several strategies have been used to restrict the broad FT hydrocarbon distribution to a specific hydrocarbon range. The most obvious is a combination of FT synthesis with cracking and isomerization. The acid cracking catalyst transforms the linear long-chain hydrocarbons produced in FT synthesis into short-chain isomerized counterparts. Composites of acidic zeolite catalysts with metallic catalysts based on Co or Ru have been found the most efficient for this application [5–7]. However, besides the main reaction of cracking, deactivation is a serious issue for metal–acid bifunctional catalysts.

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Another possible way to control the hydrocarbon chain distribution in FT synthesis is syngas cofeeding, with different compounds interacting with metal surfaces and intermediates. It has been shown that FT synthesis in the presence of a small amount of water leads to higher chain growth probability and lower methane selectivity [8]. The presence of a carboxylic acid leads to stabilization of olefins from further hydrogenation and decreases the contribution of long-chain hydrocarbons [9]. The hydrocarbon distribution can be also controlled efficiently by conducting FT synthesis in a reaction medium consisting of organic and aqueous phases [10]. The distribution of reaction products under these conditions is affected by the composition of the medium. The presence of organic phase in the two-phase system leads to high chain growth probability, while the selectivity to long-chain hydrocarbons can be reduced in the presence of the aqueous phase. A selectivity shift to heavier hydrocarbons has also been observed by application of supercritical conditions for FT synthesis [11].

Steric restriction of the growth of hydrocarbon chains due to the effect of shape selectivity appears as an efficient tool to control the hydrocarbon distribution. The shape-selectivity effect in FT synthesis has been observed earlier in zeolites and micro- and mesoporous materials [12–15]. Variation of the pore size in SBA-15 in Co/SBA-15 from 11 to 5 nm resulted in a decrease in the contribution of long-chain hydrocarbons [16]. Note that in these porous materials, the growth of hydrocarbons is only restricted in the direction perpendicular to the pore.

Nanoreactors containing metal nanoparticles surrounded by a porous shell represent a 3D material where the growth of hydrocarbons will be restricted in all directions [17]. Our recent work demonstrated that encapsulation of Co nanoparticles in silica nanoreactors prepared by the microemulsion method leads to restriction of the growth of hydrocarbons with an increase in the contribution of diesel-range hydrocarbons (C_{20} – C_{30}) [18].

The present work proposes a new strategy for control of the hydrocarbon distribution in FT synthesis by variation of the distance between Ru nanoparticles and silica surface in nanoreactors. The microemulsion technique gives a perfect opportunity to control this parameter simply by variation of the concentration of the aqueous phase in the microemulsion. The structure of nanoreactors is monitored in this paper by a combination of characterization techniques at different stages of catalyst preparation and reaction. The catalytic tests in FT synthesis were conducted in a high-throughput setup operating under high pressure.

2. Experimental

2.1. Catalyst preparation

The reference Ru/SiO₂-10 and Ru/SiO₂-50 catalysts were synthesized via incipient wetness impregnation using aqueous solutions of ruthenium chloride (RuCl₃·H₂O) to obtain 10 and 50 wt% of Ru in the final samples, respectively. The catalysts were dried at 100 °C and calcined at 450 °C and are denoted as REF-10-Ru/SiO₂ and REF-50-Ru/SiO₂, respectively.

The Ru@SiO₂ catalysts were prepared using the w/o microemulsion technique. Initially, 3 g of CTAB (cetyltrimethylammonium bromide) was dispersed in 5 g of hexanol with vigorous stirring. Afterward, 0.8 g of water containing 0.5 M RuCl₃ was added. An optically transparent microemulsion system (M1) was obtained. A separate microemulsion (M2) was prepared by mixing 0.113 g NaBH₄ in 0.8 g of water, 3 g of CTAB, and 5 g of hexanol. Microemulsion M2 was then added drop by drop to microemulsion M1. The resulting microemulsion was then stirred for 30 min. The prepared microemulsion with Ru nanoparticles is denoted as

Table 1

Composition of CTAB/hexanol/water microemulsions for preparation of the silica shells and Ru nanoreactors.

No.	Name	CTAB/g	Hexanol/g	Water/g	Water content
1	WOM-0.08	1.0	8.2	0.8	0.08
2	WOM-0.20	3	5	2	0.20
3	WOM-0.45	2.5	3.0	4.5	0.45

WOM-0.08-Ru, where 0.08 indicates the water content. Afterward, the composition of the microemulsion was adjusted by addition of water and CTAB to prepare microemulsions WOM-0.2-Ru and WOM-0.45-Ru, defined in Table 1.

The pH was adjusted to 9 by addition of ammonia. Then 0.5 g of TEOS (tetraethyl orthosilicate) was added with subsequent hydrolysis during 1 h. The prepared product was separated by centrifugation and subsequently washed with water. After drying, the samples were calcined at 450 °C for 5 h. The obtained nanoreactors were denoted as WOM-0.08-Ru@SiO₂, WOM-0.20-Ru@SiO₂ or WOM-0.45-Ru@SiO₂ depending on the content of aqueous phase (Table 1).

2.2. Catalyst characterization

The elemental composition of the catalysts was determined with an M4 TORNADO energy-dispersive micro-X-ray fluorescence (XRF) spectrometer (Bruker). The TEM analysis of the samples was performed using a Tecnai instrument, equipped with a LaB₆ crystal operated at 200 kV. Prior to the analysis, the samples were dispersed in ethanol for 5 min, and a drop of solution was deposited onto a carbon membrane located on a 300 mesh copper grid. The HAADF-STEM (high-angular annular dark field scanning transmission electron microscopy) analyses were carried out using a JEOL 2100 FEG (field emission gun) STEM microscope operated at 200 kV equipped with a spherical aberration corrector on the probe-forming lens.

For electron tomography (ET), the tilt series was acquired by the tomography plug-in of the Digital Micrograph software using the ADF and BF detectors. The specimen was tilted in the angular range of ±70° using an increment of 2° in the equal mode. The recorded images of the tilt series were aligned spatially by cross correlating consecutive images using IMOD software. For the volume calculation, we used the algebraic reconstruction technique (ART) implemented in the TomoJ plugin working in the Image J software.

The Brunauer–Emmett–Teller (BET) surface area, pore volume, and average pore diameter were determined by N₂ low-temperature adsorption using a Micromeritics ASAP 2000 automated system. The samples were degassed at <10 mm Hg at 523 K for 3 h prior to N₂ physisorption. The surface area was calculated using the BET equation. The micropore and mesopore size distributions were determined according to the Horvath–Kawazoe (HK) and Barrett–Joyner–Halenda (BJH) methods, respectively.

The catalyst reducibility was studied using H₂ temperature-programmed reduction (H₂ TPR) using an AutoChem II 2920 apparatus from Micromeritics. A sample of 50 mg was put into a quartz reactor, and then reduced in a flow of 5% H₂/Ar (60 ml/min) and heated to 900 °C with a ramp rate of 10 °C/min.

Small-angle X-ray scattering (SAXS) analysis of the microemulsion samples was performed at the Laboratoire de Physique des Solides (Orsay, Université Paris-Sud). The SAXS instrument works on a rotating anode X-ray generator with the wavelength of the X-ray radiation equal to 1.540 Å (Cu source). The sample-to-detector distance was 0.425 m and was calibrated using a reference sample (SBA-15 silica mesoporous material with 2D-hexagonal lattice spacing $a = 114.5$ Å). The beam size (about 0.8 × 0.8 mm at the sample) is defined by scatterless homemade

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