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Higher alcohols synthesis from syngas over carbon-nanotube supported Iron-Chromium catalysts

Qiongxiao Wu¹, Trine M. H. Arndal¹, Lars L. Jensen¹, Jakob M. Christensen¹; Anker D. Jensen^{1}, ¹Department of Chemical and Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark; Linus D. L. Duchstein², ²Center for Electron Nanoscopy, Technical University of Denmark, Lyngby, Denmark; Burcin Temel³, ³Haldor Topsøe A/S, Lyngby, Denmark; Jan-Dierk Grunwaldt^{1,4}, ⁴Institute of Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany*

Introduction

Higher alcohols synthesis (HAS) from syngas has recently drawn considerable attention for its application in the field of biofuel and bioadditive production [1-3]. Higher alcohols may be produced directly from syngas, which may be obtained by gasification of renewable sources such as biomass and waste. In the 1980s van der Riet et al. [4] studied the HAS with a K/Fe/Cr₂O₃ catalyst and achieved a high total selectivity to C₂₊ oxygenates of 83.4 wt% at 5 mol% CO conversion, but after these very promising, initial results there have been no subsequent reports on HAS with the K-Fe-Cr system. Recently, carbon-nanotubes (CNTs) have been reported as a novel interesting carrier for catalysts due to the unique chemical and physical properties of the nanotubes [5]. Here, CNT-supported K-Fe-Cr catalysts have been investigated. The investigations include high pressure (100 bar) activity evaluations, BET surface area measurements, X-ray diffraction (XRD) studies, and transmission electron microscopy (TEM) evaluations.

Experimental

Fe-Cr supported on CNTs or silica were prepared by co impregnating the supports with a precursor solution containing the metal salts. Additionally, CNTs were purified by refluxing CNTs in 37 wt% nitric acid at 110 °C for 5 h, followed by filtering, washing and drying. Performance of catalysts for HAS from syngas has been evaluated in a fixed-bed continuous-flow reactor with a GC-FID/TCD detection system [6]. Prior to the reaction the catalysts precursor were in-situ subjected to a reducing treatment in a flow of 20% H₂ in N₂ for 12-14 h at 400 °C. Typical operating conditions are: P = 100 bar; T = 250-400 °C; GHSV = 5000 h⁻¹; Feed: H₂/CO=1 (v/v).

Results and Discussion

Table 1 shows the catalytic properties of K₂CO₃/Fe₁Cr₂/CNTs catalyst in CO hydrogenation at steady state. From 300 °C to 400 °C the selectivity to alcohols decreased from 83.7 % to 68.9 %, while the hydrocarbon (HC) selectivity increased from 13.4 % to 30.3 %. The selectivity to C₂₊-oxygenates reached 42.8 mol% at 300 °C. The alcohol space time yield reached 87 g·kg_{cat}⁻¹·h⁻¹. The production of alcohols or hydrocarbons followed Anderson-Schulz-Flory (ASF) distributions. The chain growth probabilities for both alcohols and hydrocarbons are different, which may indicate that the intermediates for the alcohols and hydrocarbons are different. Figure 1 shows that the catalytic particles mainly are spread inside the CNTs. In the calcined catalyst, Fe₃O₄ particles were identified by XRD. No chromium-related reflections were observed in the XRD patterns indicating that Cr compounds in the catalyst were amorphous or finely dispersed. The particle sizes are in the range of 3-10 nm.

Additionally, the opened/impregnated CNTs did not seem to have agglomerated compared to the raw CNTs.

Table 1. Behavior of $K_2CO_3/Fe_1Cr_2/CNTs$ catalyst in CO hydrogenation at steady state at $P = 100$ bar, $H_2/CO = 1.0$ vol/vol, and $GHSV = 5000$ h^{-1} .

T [°C]	CO conv. [mol%]	Space time yield [g/ kg _{cat} h ⁻¹]	Carbon based, CO ₂ -free selectivity [mol%]				Chain growth probability (α)		
			alcohol	Overall alcohols	Hydro- carbons	C ₂₊ - oxygenates	MeOH	α _{Alc}	α _{HC}
300	3.6	11		83.7	13.4	42.8	43.8	0.32	0.42
325	4.4	26		85.0	13.2	31.8	55.0	0.26	0.41
350	4.7	32		81.9	17.7	26.0	56.3	0.26	0.29
400	8.2	87		68.9	30.3	22.5	47.2	0.29	0.30

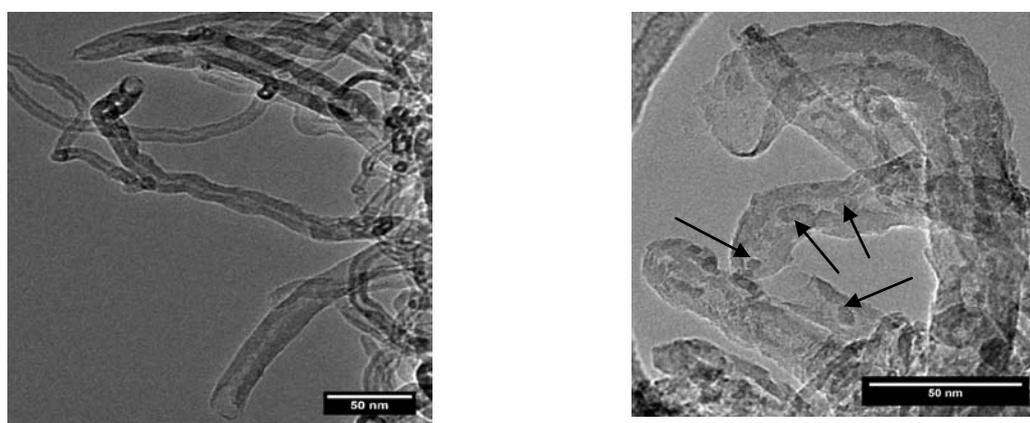


Figure 1. TEM images of the raw CNTs (left) and the fresh $K_2CO_3/Fe_1Cr_2/CNTs$ (right, the individual catalytic particles highlighted with black arrows).

Conclusions

A carbon-nanotube supported iron-chromium alcohol synthesis catalyst was synthesized, tested and characterized. At 300 °C it showed up to 43.8 mol% and 39.9 mol% selectivity to methanol and higher alcohols, respectively (3.6 mol % CO conversion). The production of alcohols or hydrocarbons followed ASF distributions. Chromium compounds in the catalyst were in the form of either amorphous or finely dispersed particles. Fe_3O_4 particles are mainly spread inside of the CNTs.

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