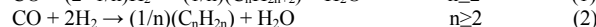
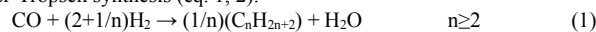


The influence of Ru and ZrO₂ addition to Co/SiO₂ catalysts on composition and distribution of liquid products obtained in Fischer-Tropsch synthesis

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Introduction

Supported cobalt catalysts are preferred for the Fischer – Tropsch synthesis of high – quality diesel fuel from synthesis gas (CO + H₂). Many studies of Co – based Fischer – Tropsch synthesis catalysts have been made in order to improve their physico–chemical properties as well as activities and selectivities [1]. Catalyst activity mainly depends on the density of surface metallic cobalt sites, which is usually correlated to its dispersion and reducibility of supported cobalt metal oxide. The structure of cobalt catalysts results from both textural and surface chemical properties of support, as well as metal precursor identity and preparation method [1]. The synthesis gas (CO + H₂) can be converted to paraffins and olefins via Fischer-Tropsch synthesis (eq. 1, 2):



Also aromatic hydrocarbons and oxygenates (alcohols, ketones, aldehydes) can be produced in FT synthesis [2]. In many studies the influence of reactions conditions, such as reaction temperature and synthesis gas pressure and the choice of appropriate catalysts were investigated.

In our work the effect of catalysts chemical composition (20%Co/SiO₂, 10%Co/8.5%ZrO₂/SiO₂ and 10%Co/0.5%Ru/8.5%ZrO₂/SiO₂) on the distribution of liquid products in Fischer-Tropsch synthesis under high pressure conditions were studied.

Materials and Methods

Supported catalyst containing metal active phase 10% Co and 10% Co/0.5 wt % Ru were prepared by incipient wetness impregnation and coimpregnation of SiO₂ with aqueous solutions of cobalt(II) nitrate Co(NO₃)₂ · 6H₂O and ruthenium(III) nitrosyl nitrate Ru(NO)(NO₃)₃. The support was prepared by impregnation of SiO₂ (271 m²/g, Aldrich) with aqueous solution of zirconyl nitrate (ZrO(NO₃)₂ · 6H₂O) to produce 8.5% ZrO₂/SiO₂ support. Then the support was dried at 120°C and calcinated at 400°C. After active phase impregnation the catalysts were dried in air at 120°C and then calcined in air at 400°C for 4 h. The catalysts were reduced at 350°C prior the reaction. Carbon monoxide hydrogenation was carried out in stainless reactor at temperature 220°C under high pressure (30atm) applying gas mixture with molar ratio H₂:CO equal 2:1. Gaseous reaction products were analyzed on-line by mass spectrometer (Hidden Analytical), whereas liquid products were cold trap and hydrocarbon products distribution was estimated by gas chromatography (Schimadzu 14B) and hydrocarbons were separated on capillary column (HP-1) and analyzed with a flame ionization detector (FID). The GC/MS analysis was carried out on an Agilent Technologies 6890N

Network GC coupled to 5973 Network Mass Selective Detector, used in 70eV electron impact (EI) mode. Analytes were separated using an Agilent HP5MS capillary column of 30m x 0.25mm with a phase thickness of 0.25 µm GC-MS and FTIR (Nicolet 6700) method.

Results and Discussion

FTIR spectrum presented in Fig. 1 a) for the oil fraction was obtained by using 20%Co/SiO₂ catalyst showed the products being aliphatic unsaturated hydrocarbons with adsorption bands located at 720 cm⁻¹ - (CH₂)_{n-6} and essential absence bands located at 724-740 cm⁻¹ of side chain methyl branching bands indicated the hydrocarbons (paraffins - (CH₂)_{n<5}) contained at least C₄ linear sections [2]. Moreover acknowledgment of unsaturated hydrocarbons were bands located at 888, 908, 964, 992, 1642, 1822 cm⁻¹ (RCH₂=CH₂R). Wave number bands at 1340, 1378 cm⁻¹ confirmed the presence of terminal methyl groups –CH₃. GC chromatogram representing the distribution of hydrocarbons in oil fraction is presented in Fig. 1 b). The condensed hydrocarbon products showed significant aliphatic hydrocarbon peaks beginning with C₅ up to C₁₇ [3]. The liquid products were also studied by GC/MS analyses.

Significance

The FTIR and GC analysis of the condensed liquid products showed aliphatic unsaturated hydrocarbons which can be assigned to with C₅ up to C₁₇.

Addition of Ru and ZrO₂ to Co supported catalysts resulted in growth of selectivity to heavier hydrocarbons C₅₊ due to better dispersion and reducibility degree of cobalt metallic phase.

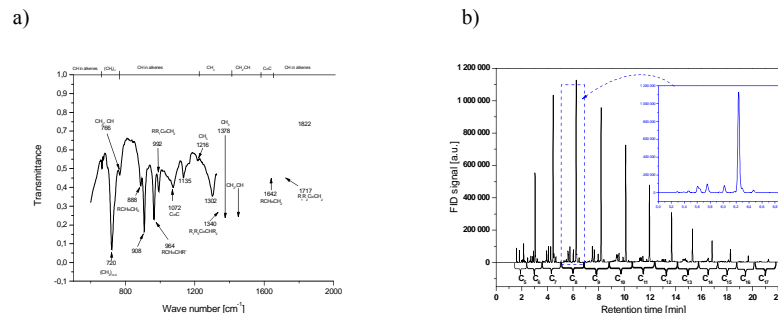


Figure 1. IR spectrum (a) and CG chromatogram (b) for liquid products obtained in FTS reaction for 20%Co/SiO₂ catalyst.

References

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