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Co catalysts supported on oxidized CNTs: Evolution of structure during preparation, reduction and catalytic test in Fischer-Tropsch synthesis

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ABSTRACT

CNT oxidation, Co/CNT preparation and transformation of both catalyst and support in Fischer-Tropsch synthesis (FTS) were thoroughly studied. CNTs functionalized by nitric acid for 1–15 h were used as supports for Co catalysts for FTS at 190 °C and atmospheric pressure. Co supported on CNTs with the highest specific surface area and oxygen content showed the highest activity and C_{5+} yield. According to TEM results after 70 h of FTS this catalyst was the most stable to Co sintering due to the large number of surface defects and oxygen groups on a support surface combined with the preserved integrity of CNTs. Activity of catalysts increased and selectivity to C_{5+} decreased when the particle size diminished from 26.5 to 4.3 nm. Study of the evolution of CNT support revealed that most of the carboxylic groups decomposed at calcination. Etching of support surface during the catalyst reduction and partial pore blocking after FTS were detected.

1. Introduction

Surface oxidation of carbon nanotubes (CNTs) is the most commonly used method to transform hydrophobic CNT material into hydrophilic substance covered with a large number of functional groups [1]. Oxidized CNTs are used in the different areas of science and engineering such as synthesis of polymer composites [2], catalyst supports and electrochemistry [3,4]. Surface groups allow using the polar solvents during the synthesis of composites, metal and metal oxide catalysts. Various oxidizing agents, such as acids, $KMnO_4$, H_2O_2, RuO_4, oxygen plasma, ozone, are used for the oxidation of the CNT surface [5–7]. The most common method of CNT oxidation is the nitric acid treatment since it provides the greatest number of oxygen groups on the CNT surface [6].

The degree of CNT oxidation significantly influences the structure of CNT based composites or catalysts. Properties of CNT based composite strongly depend on the nature and number of functional groups on the CNT surface. In the case of catalysis applications, surface modification affects the metal-support interaction and stability of catalyst in different reactions [3,8].

Co based catalysts supported on CNTs are effective materials for hydrogenation of carbon oxides [9,10], electrocatalysis [11,12], catalytic oxidation of pollutants [13], hydroformylation and hydrodesulphurization reactions [4]. Fischer-Tropsch synthesis (FTS) is an industrial process for production of liquid fuels, lubricants and other chemicals by CO hydrogenation into hydrocarbons. Co and Fe based catalysts are commonly used in FTS. Co systems are more expensive than Fe, but at the same time more stable and less active in water gas shift reaction [14]. Oxide materials such as Al_2O_3, SiO_2 and TiO_2 are usually used as catalyst supports for FTS [15]. In the last decade CNTs have been seen as an effective alternative to oxide supports due to the lower degree of metal-support interaction, ability to tune the surface properties in a wide range, rigid structure that prevents metal agglomeration and the permanent price reduction [16–18]. FTS is highly sensitive to the structure of catalyst: porosity of support and Co particle size can significantly affect the catalytic performance [19,20]. Surface oxidation of CNTs is a powerful technique to modify the structure of CNT based catalyst. Several studies have been dedicated to the influence of CNT surface groups on the catalytic performance of Co/CNT catalysts but their results are contradictory: either positive [21] or

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negative [22] effects of the CNT oxidation on the activity and selectivity of catalysts were detected. In our previous work we showed that the oxidation effect can also depend on the type of CNT support and may increase or decrease the activity and selectivity of Co-based catalysts [18].

In the present study we try to assess the impact of the CNT surface state on the structure of Co/CNT catalyst for FTS and trace the evolution of support and Co at different stages of process (catalyst calcination, reduction and catalytic reaction). The main aim of this work is to reveal the effect of functionalization, defectiveness and porosity of CNT surface on the stability, activity and selectivity of Co/CNT catalyst in FTS. For this purpose CNTs are oxidized by nitric acid for different time and resulted materials are investigated as supports for Co-based FTS catalysts. Changes in Co particle size and composition/defectiveness of the support surface during the catalyst preparation, reduction and FTS are discussed.

2. Experimental

2.1. CNT synthesis and oxidation

Multiwall CNTs were synthesized using catalytic chemical vapor deposition method via the technique described in our previous works [9,18]. Hexane and Co-Mo/MgO were used as carbon source and growth catalyst, respectively. Synthesis temperature was 750 °C. Synthesized material was annealed at 400 °C in air flow, washed by HCl and distilled water to remove amorphous carbon and metal impurities. Obtained sample of pristine CNTs was named as “CNTp”. CNTs were oxidized by refluxing in concentric HNO_3 (Chimmed, Russia, ~70%, density–1.4 g/cm^3, purity–99.999%) at acid-to-CNT ratio of ~20 ml/g under vigorous stirring (~400 rpm) for 1, 3, 6, 9, 12 and 15 h. The obtained material was filtered and washed with distilled water to neutral pH and finally dried at 130 °C. It was named as “CNTn” where n is the refluxing time in hours.

2.2. Catalyst preparation

Catalysts were prepared by impregnation of CNT supports with $Co(NO_3)_2{\cdot}6H_2O$ (Vecton, Russia, 99% purity) ethanol solution for metal loading of 15 wt.%. After the solvent evaporation at 70 °C samples were dried at 130 °C for 16 h. Catalysts were named as Co/CNTn (CNTp in the case of pristine CNTs).

2.3. Catalytic tests

FTS was performed in a quartz tubular flow fixed bed reactor with the inner diameter of 10 mm. Catalyst was placed on a layer of fiberglass fitted on a quartz grid and then reduced in situ in H_2 flow (60 ml/min) at 400 °C for 4 h. CO hydrogenation was carried out at 190 °C and atmospheric pressure for 70 h. Metachrom mass-flow controller was used to deliver a gas mixture of H_2:CO:N_2 = 2:1:0.7 with the velocity of 2200 ml/(h g). N_2 was used as an internal standard gas. The catalyst loading was 1 g. The reaction products were analyzed on an Agilent Technologies 6890N gas chromatograph. CO, N_2, CH_4 and CO_2 gases were separated in 5 m HayeSep column filled with Porapaq R and analyzed using TCD detector. Hydrocarbons were separated in 50 m DB-Petro capillary column and analyzed by FID detector. CO conversion, product selectivity (S) and C_{5+} fraction yield (Y_{C5+}) were measured at steady state similarly to that described in Ref. [18]. TOF was calculated using TEM data for average particle size assuming spherical Co particles, with only a half of their surface being available for the reaction.

2.4. Study of CNT evolution

In order to study the evolution of CNT support, additional samples of Co/CNT9 catalyst were prepared after calcination, reduction and FTS. For the calcination CNT9 support impregnated by Co nitrate was heated up to 400 °C (10°/min heating rate) in nitrogen flow of 30 ml/min and then slowly cooled. Reduced catalyst was prepared the same way with the additional treatment in hydrogen flow of 60 ml/min for 4 h at 400 °C. After reduction, catalyst was slowly cooled in hydrogen flow and then passivated in O_2/Ar mixture with 1 vol.% of O_2. Catalyst after 70 h of FTS was cooled in nitrogen flow and also passivated. Obtained samples were treated with concentrated HCl solution in ultrasonic bath for 2 h in order to remove Co.

2.5. Characterization

Textural properties (specific surface area (S_{BET}), average pore radius (R_{BJH}) and total pore volume (V)) were measured by nitrogen adsorption using Quantachrome AUTOSORB-1C/MS/TPR gas sorption analyzer. Prior to analysis, samples were degassed at 250 °C for 3 h under vacuum. Raman spectra were registered using LabRam HR800 UV (Horiba Jobin Yvon, Japan) microscope-spectrometer using 5 mW argon laser excitation with 514.5 nm wavelength and 50 × Olympus lens. The chemical composition of the surface and the nature of chemical bonds were determined using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer (XPS) with a monochromatic Al Kα source ($h\nu$ = 1486.6 eV, 150 W). The pass energy of the analyzer was 160 eV for the survey spectra and 20 eV for the high-resolution ones. X-ray diffraction patterns were recorded using a Stoe Stadi P instrument equipped with Ni-filtered CuKα X-ray tube in the 2θ range from 10 to 70°. Temperature-programmed reduction (TPR) was performed on a home-made system that consisted of a gas preparation stage, quartz reactor, tube furnace and TCD-detector. Gas mixture (Ar + 5% H_2) at a flow rate of 23 ml/min was used for the reduction. Heating rate was 12°/min. Before XRD and TPR analyzes catalysts were heated to 400 °C (10°/min heating rate) in nitrogen flow of 30 ml/min and then slowly cooled. Morphology of the catalysts was studied using transmission electron microscopy (TEM, JEOL 2100F). Samples for TEM study were reduced in hydrogen (60 ml/min) for 4 h at 400 °C and then passivated in O_2/Ar mixture with 1 vol.% of O_2. Catalysts after reaction were also passivated before TEM analysis.

3. Results and discussion

3.1. CNT oxidation

TEM images of CNTp, CNT6 and CNT15 are shown in Supplementary material (S1). Oxidation of CNTs gradually destroys their walls (Fig. S1b) which finally results in highly damaged material (Fig. S1c). This trend is common for the oxidation of CNTs by liquid nitric acid that was shown elsewhere [21,23–26].

The changes in the textural properties of CNTs during oxidation are presented in Fig. 1a. S_{BET} value shows a maximum at 9 h of oxidation due to defects formation on the surface and then decreases probably because of the strong destruction of CNTs. Similar trend was observed in the oxidation of N-doped CNTs for 2–20 h, but the maximum S_{BET} was found at 2 h of oxidation [26]. Such a difference in the position of maximum S_{BET} can be explained by higher defectiveness of N-doped CNTs (see below the discussion of Raman data): oxidation of more defective tubes takes less time. Pore volume maximum at 1 h in the present study corresponds to the opening of CNT channels, partial cutting of nanotubes and removing of residual growth catalyst [23]. Further decrease of pore volume during