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Molecular structure of inorganic supramolecular compounds and its application as a precursor in producing hydrocarbons

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A B S T R A C T

The thermal decomposition of two inorganic polymers with the formula of $[Mn(O)_2Ni(dipic)_2]_n$ (**1**) and $[Mn(O)_2Co(dipic)_2]_n$ (**2**), resulted in the preparation catalyst of Co-Ni-2Mn. The structure of the catalyst was characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), powder X-ray diffraction (XRD), BET specific surface area, and transmission electron microscopy (TEM). The catalytic performance of Co-Ni-2Mn, supported by silica was compared in producing hydrocarbons using the Fischer-Tropsch reaction within a temperature range of $160\,°C$–$260\,°C$ with two reference catalysts prepared by co-precipitation and impregnation methods. Simultaneously, the effect of temperature and preparation methods on the catalytic activity of these nanocatalysts was investigated. Temperature studies confirmed that at $220\,°C$ catalytic activity was at its highest. Also, a comparison of data showed that nanocatalyst derived from inorganic complexes had higher catalytic performance. In another study, the length of time for which the catalyst stays stable and maintains its catalytic performance was investigated. It was found that all catalysts were stable after 12 h from the start of the reaction.

1. Introduction

Fischer-Tropsch (F-T) reaction is an important chemical process for converting hydrogen and carbon monoxide into various hydrocarbon products and high-value liquid fuels [1–4]. This reaction is a heterogeneous catalytic process which involves a network of parallel and consecutive reactions occurring on the surface and in the pores of a catalyst [5]. The Fischer-Tropsch process has three important steps: gasification, synthesis, and product upgradation. The synthesis step is controlled by important parameters. By optimizing them, can increase the number of products and reduce energy inputs into the overall process. Various factors such as temperature, operating pressure, catalyst stagnation, and apparent gas velocity have a significant impact on the amount of gas synthesis and synthesis distribution of hydrocarbon products. Nanostructured and homogeneous dispersed particle catalysts offer many advantages such as a lot of active sites and easy accessibility to reactants [6]. It has been found that new nanocatalysts can be a good alternative to conventional catalysts. The nano-sized metal clusters are known to exhibit size dependent physical properties [7]. One of the most important factors to increase the activity or selectivity of the product in carbon hydration monoxide is the application of two-metal catalysts [8–11]. It has been made clear that bimetallic catalysts include Ru, Ni, Co, and Fe. These have a higher percentage of carbon monoxide conversion and considerably better selectivity for valuable products like olefins and heavier hydrocarbons compared to single metal catalysts. Also, the use of tri-metallic catalysts made from transition metals are common in recent years [12,13]. Metal organic frameworks have unique capabilities in the field of catalysts, magnetism, and photochemistry. They can act as efficient catalysts in oxidation processes because they have the ability to oxidize and reduce [14–21]. Metal-organic compounds have a unique ability to act as effective precursors in the preparation of Fischer-Tropsch nanocatalysts. Therefore in this study, for the first time, two new supramolecular inorganic complexes with interesting structures, $[Mn(O)_2Ni(dipic)_2]_n$ (**1**) [22] and $[Mn(O)_2Co(dipic)_2]_n$ (**2**) [23] were used as new precursors in producing hydrocarbons. So the main objective in this study is 1) Synthesize the precursor of $[Mn(O)_2Co(dipic)_2]_n$ + $[Mn(O)_2Ni(dipic)_2]_n/SiO_2$; 2) Calcination of this precursor for the preparation nanocatalyst of Co-Ni-2Mn/SiO_2; 3) Preparation of Co-Ni-2Mn/SiO_2 nanocatalyst as references catalyst by co-precipitation and

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impregnation; and 4) Study and comparison of the catalytic performance of these catalysts in the Fischer-Tropsch reaction at 160 ºC-260 ºC.

2. Experimental

2.1. Materials and methods

All the chemicals used in this study were purchased from Aldrich Company and were used as received. All the synthetic work was performed at room temperature. An FT-IR JASCO 460 spectrophotometer recorded the FT-IR spectrum with KBr pellets in the 4000-400 cm^{-1} regions. Elemental analyses of complexes were done by a CHNSO (vario EL III) elemental analyzer. The thermal behavior of the precursor was studied by thermal analysis methods (TGA and DSC) using TGA-PL England equipment. For this purpose, 3 mg of the precursor was placed in a Pt cell and the temperature was increased from room temperature to 700 ºC with the heating rate of 10 ºC/min. Differential scanning calorimetry (DSC) of the precursor was recorded on a Netzsch DSC 200 F3 at a heating rate of 10 ºC/min in the presence a flow of dry air. The morphology of the catalyst was studied by scanning electron microscopy (SEM) using a scanning probe microscope device, VEGA\\TESCAN-LMU instrument, operating with an accelerating voltage of 10 kV. To prepare a thin film of the sample, 1 mg of powder sample was added to a solution of ethanol (10 mL). The resulting solution was dispersed under ultrasonication for 10 min at 30 ºC. In the next step, 0.1 mL of this solution was placed on a carbon coated copper grid and then completely dried. The surface of the sample was coated with a thin layer of conductive carbon. For elemental analysis of catalyst, an EDX (RONTEC's EDX system, Model QuanTax 200, Germany) coupled to the SEM was used. The size and shape of the nanoparticles were studied by transmission electron microscopy (TEM). The TEM images were recorded on a Philips CM200-FEG instrument, operated at 200 kV. To prepare the sample, 1 mg of nanopowder was dissolved in 10 mL of methanol and sonicated for 5 min 0.1 mL of this solution was placed on a carbon coated copper grid. The film was dried on a filter paper and under the infrared lamp.

In order to evaluate and compare the specific surface area of catalysts and precursors, the Brunauer-Emmett-Teller (BET) was measured by nitrogen physical adsorption at −196 ºC using a Quantachrome NS-93 instrument. The sample was dried and degassed under nitrogen atmosphere at 190 ºC for 3 h. The sample was cooled to reach the liquid nitrogen temperature. In the next step, the sample was exposed to a certain amount of nitrogen gas under controlled pressure. With increasing and decreasing pressure, nitrogen adsorption and desorption was measured. Then using adsorption isotherm, the surface area of the nanoparticles was determined. XRD data were collected using Cu-Kα radiation and a graphite monochromator with λ = 1.54056 Aº recorded on the Philips X-Pert MPD diffractometer (Philips electronic Co., Netherlands) at 40 kV and 30 mA. The sample was scanned at 4°–90° (2θ) at a step size 0.02°/s. X-ray data of the single crystal were collected on an -IPDS-2T diffractometer, equipped with a graphite monochromator and using MoKα radiation (k = 0.71073 Aº). The structures were refined with the SHELXL-97 program.

2.2. Synthesis polymers of [Mn(O)₂Ni(dipic)₂]ₙ (1) and [Mn(O)₂Co(dipic)₂]ₙ (2)

For synthesis polymer of $[Mn(O)_2Ni(dipic)_2]_n$, 0.5 mmol of Ni(NO₃)₂, 6H₂O and 0.5 mmol of Mn(NO₃)₂·4H₂O were dissolved in 10 mL of distilled water. In another beaker, 1 mmol (0.167 g) of pyridine −2,6-dicarboxylic acid was dissolved in 10 mL of distilled

water. Then an aqueous solution of NaOH (20 mL, 2 mmol) was added dropwise to it. This solution was slowly added to the previous solution of nitrates. The final solution was stirred at room temperature for 3 h. Next, the solution was filtered and left at room temperature for one week. The light green crystals of $[Mn(O)_2Ni(dipic)_2]_n$ were formed after a few days. Yield: 57%. Anal. Cal. for $C_{14}H_6$ NiMn N_2O_{10}: C, 35.30; H, 1.26; N, 5.88 Found: C, 35.06; H, 1.01; N, 5.73. The synthesis of $[Mn(O)_2Co(dipic)_2]_n$ was also performed according to this procedure. Anal. Cal. for $C_{14}H_6CoMnN_2O_{10}$: C, 35.29; H, 1.26; N, 5.88 Found: C, 35.34; H, 1.25; N, 5.83.

2.3. Catalyst preparation

First, 10 mmol (4.75 g) of $[Mn(O)_2Ni(dipic)_2]_n$ and 10 mmol (4.76 g) of $[Mn(O)_2Co(dipic)_2]_n$ were dissolved in 100 mL of water, then 9.2 g of SiO₂ was added to this solution and the solution was stirred at 30 ºC to dryness. Thermal decomposition of $([Ni(dipic)_2Mn(O)_2]_n + [Co(dipic)_2Mn(O)_2]_n)/SiO_2$ was performed at 600 ºC in static air in an electric furnace for 5 h.

2.4. Preparation of Co-Ni-2Mn/SiO₂ by co-precipitation and impregnation as reference catalysts

In order to investigate the effect of the preparation method on the activity of catalysts, reference catalysts of Co-Ni-2Mn/SiO₂, were prepared by co-precipitation and impregnation methods. For co-precipitation, first, 9.2 g of SiO₂ as support was added to a solution containing certain molar ratios of Mn(NO₃)₂·4H₂O (1 mmol), Co(NO₃)₂·6H₂O (0.5 mmol), and Ni(NO₃)₂·6H₂O (0.5 mmol). An aqueous solution of Na₂CO₃ (0.5 M) was added dropwise into the above mixture. The resulting precipitate was filtrated and washed several times with distilled water. The sediment was dried for 10 h at 120 ºC in an oven. The calcination of this catalyst was performed in an electric furnace in static air at 600 ºC for 6 h. For the preparation of this catalyst by impregnation method, first, SiO₂ as support was calcined at 600 ºC for 6 h. Next, the aqueous solution of Mn(NO₃)₂·4H₂O (1 mmol), Co(NO₃)₂·6H₂O (0.5 mmol) and Ni(NO₃)₂·6H₂O (0.5 mmol) was directly dispersed onto the support. The resulting mixture was dried at 120 ºC for 10 h and decomposed at 600 ºC for 6 h in the electric furnace in static air.

2.5. Catalytic performance measurements

In each experiment, 1 g of the catalysts was weighed and placed inside the reactor. Before starting each test, to remove the air from the system, nitrogen gas was pumped inside the reactor for a few minutes. Nanocatalysts reduced at 400 ºC for 20 h under a flow of $N_2/H_2 = 1$ and a flow rate for each gas of 30 mL/min at atmospheric pressure. After reduction of the nanocatalysts, the furnace temperature rose to the desired temperature for the reaction. The hydrogen and carbon monoxide valves were opened and the test was done at GHSV = 3600(h^{-1}), Pressure = 1 (atm), H₂/CO (mL/min) = 2:1, CO (mL/min) = 15, N₂ (mL/min) = 15, H₂ (mL/min) = 30. Fischer-Tropsch reaction was performed on the surface of the nanocatalysts within a temperature range of 160−260 ºC. The catalytic activity of the catalyst was calculated by the following equations.

CO conversion (%) = [(Moles of CO)in-(Moles of CO)out] / (Moles of COin) × 100

The molar selectivity of the product is:
(The number of Moles of the product/[(Moles of COin) − (Moles of COout)]) × 100 [15,24,25]. The device was equipped with two