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Solvent-free synthesis of alumina supported cobalt catalysts for Fischer–Tropsch synthesis

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ABSTRACT

A novel mechano-synthesis method has been elaborated in this work for the design of efficient cobalt-based Fischer–Tropsch catalysts. The process aims to reduce the total number of steps involved in the synthesis of solid catalysts and thus to avoid relevant toxic solutions generated during the catalyst preparation. The mechano-synthesis of the Co/Al_2O_3 catalyst was processed in a low-energy vibratory micro mill and high energy planetary ball mill. Porous spherical γ-aluminas (1860 μm and 71 μm mean particle diameter) were used in this work as host compounds. Co_3O_4 (3 μm mean particle diameter) has provided guest particles for mechano-synthesis. The catalysts were characterized by textural (surface area, porosity and particle size) and structural analyses (X-ray diffraction, TPR, SEM-EDX and microprobe). The microprobe images show deposition of Co_3O_4 on the surface of the alumina and indicated no Co_3O_4 diffusion inside the alumina pores. SEM-EDX mapping illustrated that cobalt coating tended to occur on surface of rounded shape of cracked alumina fragments. After milling, the crystallite size of Co_3O_4 decreased to 15 nm from 30 to 50 nm. The TPR profiles indicated very low concentrations of inactive cobalt aluminate mixed compounds which are usually produced during the catalyst preparation by impregnation. In Fischer–Tropsch synthesis, the catalysts prepared using mechano-synthesis methods showed catalytic performance comparable to the catalysts prepared by impregnation.

1. Introduction

Fischer–Tropsch (FT) synthesis is a promising process for the environmental-friendly industrial production of ultraclean synthetic fuels from syngas in which catalysts play a crucial role. Fischer–Tropsch reaction occurs on supported cobalt nanoparticles. Alumina supported cobalt-based catalysts are currently used commercially in several industrial FT projects [1]. Most of VIII group metals have measurable activity in carbon monoxide hydrogenation [2]. Cobalt catalysts represent the optimal choice for synthesis of long-chain hydrocarbons in the low temperature FT process, because of their stability, higher per pass conversion [3], and high hydrocarbon productivity [4]. Cobalt-supported catalysts for FT synthesis are usually prepared by chemical impregnation. In this method cobalt precursors are first dissolved in the solution and then deposed on the porous supports [5], like alumina and silica. Calcination is an indispensable step in the impregnation method, in which temperature and time of drying are required to be controlled carefully. Otherwise, barely reducible mixed cobalt oxides (for example: cobalt aluminates) [6] inactive in FT synthesis can occur in particular during the calcination. All these preparation steps involve toxic, harmful and corrosive solvents (usually metal nitrate solutions) and catalyst pre-treatments at higher temperatures.

Solvent-free mechano-synthesis has shown potential applications in various areas, including synthesis of new alloys and ceramics, nanocrystalline powders and high diffusivity materials. However, very few works are available in the literature on the mechano-synthesis of solid catalysts for FT synthesis. Delogu et al. [7] prepared $Ni_{40}(ZrO_2)_{60}$ catalysts in a mixermill during 100 h. The system involving milling of the catalysts with the reactant gases was found to yield more active catalysts. In the case of $Ni_{40}(ZrO_2)_{60}$ the CO conversion rate for the milled system was found to be 1.2×10^{-4} mol/h compared to 2.3×10^{-12} mol/h observed on a conventional prepared catalyst. They also reported $(Co_{50}Fe_{50})_{0.2}(TiO_2)_{99.8}$ preparation using $Co_{50}Fe_{50}$

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mechanochemically milled with TiO_2 for CO hydrogenation reactions [8]. The catalyst prepared using milling was found to be approximately 4 orders of magnitude more active. Guczi et al. [9] reported preparation of bimetallic Re-Co/Al_2O_3 catalysts by ball milling in a shaker mill using a tungsten carbide container and tungsten carbide balls. The catalytic performance was tested in CO hydrogenation and methane conversion with 1.7% ethane yield.

In this study, Co/Al_2O_3 catalysts were synthesized using mechano-synthesis method. Al_2O_3 is a common catalytic support with high melting point, high surface area, porosity and thermal stability [10]. Porous spherical γ-alumina particles are used in this work as host particle and Co_3O_4 fine particles are used as guest powders. The catalysts were characterized using a combination of physico-chemical methods. Finally, the solid cobalt-based catalysts are tested in a milli fixed-bed FT reactor. Their catalytic performance is compared with the conventional alumina supported cobalt catalysts prepared by impregnation.

2. Experimental

2.1. Materials

Large and small porous spherical γ-alumina particles (99% Al_2O_3) of mean diameter 1860 μm (labeled as Al_2O_3L) and 71 μm (labeled as Al_2O_3S) were purchased from Sasol. Large γ-alumina particles were selected as host particles in mechano-synthesis to obtain the size of supports after milling around 70–80 μm particle as conventional impregnation supports and to avoid too much fine powders, small γ-alumina particles which were classically used in conventional impregnation method were selected as comparison. Co_3O_4 powders of 3 μm diameter as the guest particles were provided by Sigma-Aldrich.

2.2. Mechano-synthesis processes

The following mechanical processes are utilized in this work for synthesis of catalysts containing 15 wt% cobalt. In a typical mechano-synthesis 2.05 g Co_3O_4 was mixed with 8.5 g γ-Al_2O_3 particles under room temperature and atmospheric pressure.

The vibratory micro mill "Pulverisette 0" (Noted: P0) made by FRITSCH is driven by 50 W power which is much lower than in the universal ball mills, such as planetary ball mill. Therefore, this process is named low-energy process (Fig. 1). A 50 mL agate mortar equipped with a 5 cm agate ball was chosen as accessories in this study. Grinding in "Pulverisette 0" was applied with the operating conditions of interval vibrated amplitude (0.5 mm) and 40 min vibration time at room temperature. The samples are labeled 15%Co/Al_2O_3L-40P0 and 15%Co/Al_2O_3S-40P0 with 1860 μm and 71 μm mean diameter respectively. The amplitude is the height of ball leaving from bottom due to plate oscillations. The coating in P0 is generated by collision and friction phenomena. External impact, vertical force is dominant and produces the collision between ball and particles (Co_3O_4 and Al_2O_3) and the wall of the mortar.

Planetary ball mill mode 100 (Noted: PM) made by RETSCH (Fig. 2) and 750 W driven power named as "high-energy process". Milling time, the rotation speed and ratio of ball to materials are the main parameters controlled for mechano-synthesis in PM. The planetary ball mill was equipped with agate mortar (75 mL) and 25 agate balls of 10 mm diameter. 250 rpm rotation speed was applied to a fixed mass ratio (4:1) of ball to particles (Co_3O_4 and γ-Al_2O_3) adding. The samples are labeled as 15%Co/Al_2O_3L-250PM and 15%Co/Al_2O_3S-250PM for alumina with 1860 μm and 71 μm mean diameter respectively. The mortar was driven by planetary rotation with the speed ratio −2:1 relative to plate speed. The forces for coating in PM are generated from planetary rotation of mortar, as a consequence, tangent shear force between balls/wall and particles accompanied the impact of ball collision and friction owing to the quick movement of balls.

2.3. Chemical preparation

The reference 15 wt% Co/Al_2O_3 catalyst (10 g) was prepared using incipient wetness impregnation with cobalt nitrate solution ($Co(NO_3)_2{\cdot}6H_2O$) (4.7 g, Sigma-Aldrich 98% purity) deposited onto 8.5 g small porous spherical γ-alumina particles (Al_2O_3S) labeled as 15%Co/Al_2O_3S-che. Following this impregnation step the precursor is then dried in a milli fixed bed reactor with 1.75 mm inner diameter under 100 °C then calcined at 400 °C.

2.4. Catalyst characterization

The particle size distributions of the original Al_2O_3, Co_3O_4 powders and 4 samples (15%Co/Al_2O_3L-40P0, 15%Co/Al_2O_3L-250PM, 15%Co/Al_2O_3S-40P0 and 15%Co/Al_2O_3S-250PM) were measured using a light-scattering laser instrument (Beckman-Coulter LS 230). The average diameter (d_p) of powders was calculated according to the definition of "volume-surface" diameter or "Sauter diameter":

$$d_p = \sum N_i {d_i}^3 / \sum N_i {d_i}^2 \quad (1)$$

Where N_i is the number of particles in class i and d_i is the average dimension of the particle in this class.

The range of the particle size distribution was quantified by the uniformity index C_u [11] obtained from the cumulative percentage undersize distribution (in volume) and defined by the following equation:

$$C_u = d_{i60\%}/d_{i10\%} \quad (2)$$

When $C_u < 2$: the particle size distribution is known as uniform; $C_u > 2$: the particle size distribution is known as broad. $d_{i60\%}$ and $d_{i10\%}$ are defined as dimensions of the particles corresponding to 60% and 10% of the cumulative percentage undersize distribution (in volume) [12].

The specific surface area and the pore size of particles were obtained by the BET and BJH methods from the desorption branch of the nitrogen adsorption isotherms using Micromeritics ASAP 2010.

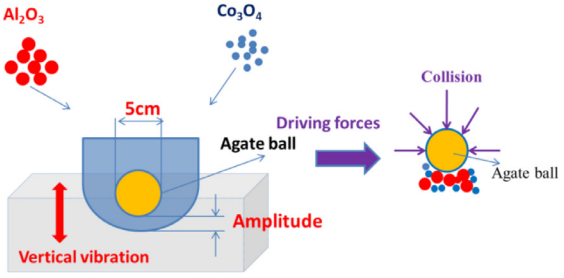

Fig. 1. "Pulverisette0" vibratory micro mill (P0).

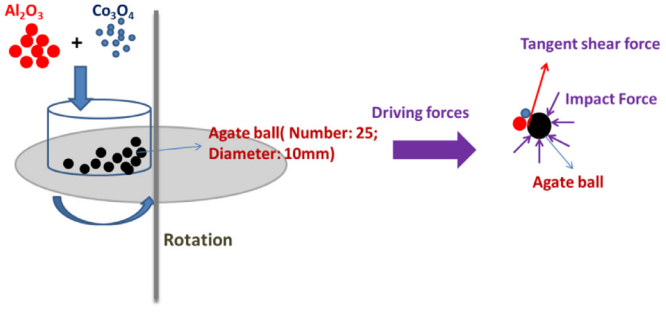

Fig. 2. Planetary ball mill 100 (PM).