

Multi-functional alumina–silica bimodal pore catalyst and its application for Fischer-Tropsch synthesis

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Abstract

A multi-functional bimodal pore catalyst support, alumina–silica bimodal pore support, was prepared from a polymer complex solution and silica gel. The obtained bimodal pore support had two kinds of main pores; the pore volume was decreased and the specific surface area was enlarged, comparing with the original silica gel. This kind of bimodal pore support was applied in slurry phase Fischer-Tropsch synthesis, where cobalt was supported as active metal. Alumina–silica bimodal pore catalyst exhibited high catalytic activity and favorite selectivity, due to the spatial effects of bimodal pore structure and chemical effects of coexisting alumina, which formed the new small pores inside SiO₂ large pores. Alumina–silica bimodal pore catalyst showed higher activity than silica–silica bimodal pore catalyst with similar pore structure, proving that hetero-atom bond between alumina and silica was important to promote the performance of the dispersed cobalt. The various catalysts were characterized by XRD, chemisorption, in situ DRIFT, TPR, and TPSR. It was found that alumina in alumina–silica bimodal structure improved cobalt dispersion significantly while keeping the reduction degree almost the same. TOF of alumina–silica bimodal catalysts was the highest, supported by the largest bridge-type adsorbed CO peak in DRIFT observation of this catalyst, as bridge-type adsorbed CO was the active intermediate in FTS.

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1. Introduction

The F-T synthesis (FTS) for the production of hydrocarbons from synthesis gas is well known and well documented; it is one of the major gas conversion routes. The production of fuels that can substitute the natural petroleum is an interesting way of the FTS. Cobalt-based catalysts attract most of current attention for the direct conversion of syngas in FTS because of their high activity, high selectivity for long chain paraffins, and low water gas shift activity [1]. Besides cobalt, some supports such as SiO₂, Al₂O₃ and TiO₂, are indispensable. The chemical and texture properties of the support influence the catalytic activity and product selectivity

of Co catalysts, via their modifications on the reducibility and dispersion of cobalt or the formation of well-fined phases. Synthesis of highly dispersed Co catalysts requires strong interaction between the support and the Co precursor, but in turn such strong interactions generally lower the reducibility of such precursors [2]. Alumina is one of the most employed supports for cobalt FT catalysts due to its favorable mechanical properties and adjustable surface properties. The supports like Al₂O₃ have significant support interaction, contributing to formation of a smaller supported metal cluster, while supports such as silica always yield a large supported metal cluster size and high reduction degree. However, unlike the cobalt silica catalyst, Co/Al₂O₃ catalysts have limited reducibility because the support can interact with the active phase by the diffusion of cobalt ion into the structure of alumina to impede the reduction [3,4].

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On the other hand, the activities and selectivities of the FTS catalysts are markedly dependent on their pore structure. Generally, the metal dispersion is enhanced with the increased surface area of the support. But, if the support has large surface area, it usually has small pores. Undoubtedly, the intrapellet diffusion efficiency is poor for small-pore catalysts, especially in the multi-phase reactor. A support with a distinct bimodal pore structure has excellent advantages in solid catalysis reaction because the large pores provide pathways for rapid molecular transportation and small pores provide a large area of active surface, contributing to high diffusion efficiency and enhanced dispersion of supported metal simultaneously, as theoretically proved by Levenspiel [5].

The present authors reported that silica–silica and silica–zirconia bimodal pore supports remarkably promoted the catalytic activity of cobalt catalysts in FTS reaction, due to their spatial and chemical effects [6]. The bimodal pore catalyst supports were obtained by building up nano-particles from silica or zirconia sol to form small pores, inside tailor-made large silica pores. In the present study, because the polymer complex solution can form homogeneously distributed oxide particles and homogeneous packing of the particles, a multi-functional alumina–silica bimodal pore support was prepared by impregnating a polymer complex solution of aluminium into the original silica gel. As an application of this kind of bimodal pore support, it was used for slurry-phase FTS reactions as the support of cobalt catalysts. This kind of support is estimated that it cannot only realize higher supported cobalt dispersion by spatial effects of bimodal pore structure and chemical effects of alumina, but can also obtain a high reduction degree of supported cobalt by coexisting silica and alumina, and is also expected to realize high catalytic activity via higher diffusion efficiency of reactants and products via bimodal pore structure.

2. Experimental

The aluminium nitrate was dissolved in a 0.3 mol/l polyethylene glycol (PEG, average molecular weight of 200) aqueous solution to prepare the polymer complex solution. After stirring at 353 K for 1 h, the solution was impregnated into original silica gel (Cariact Q-50, Fuji Silysia Chemicals Ltd., specific surface area: 70 m²/g, pore volume: 1.2 ml/g, pellet size: 74–590 μm and mean pore diameter: 50 nm) by incipient-witness method. After the impregnation, the support was calcined in air at 673 K for 2 h. The alumina loading of the obtained bimodal pore support was 10 wt.%. The preparation method of silica–silica bimodal pore support was reported elsewhere [6].

Cobalt-supported catalyst with 10 wt.% metal loading was prepared by incipient-witness impregnation of different supports, including the two bimodal pore supports, with cobalt nitrate aqueous solution. The catalyst precursors were dried in air at 393 K for 12 h, and then were calcined in air from room temperature to 673 K with a ramping rate of

2 K/min and kept at 673 K for 2 h. After calcination, the catalysts were activated in flowing hydrogen at 673 K for 10 h, and at last passivated by 1% oxygen in nitrogen. As comparison, a 10 wt.% metal loading cobalt-supported alumina catalyst was prepared using a JRC-ALO-5 alumina support (JRC-ALO-5, Reference catalyst, Catalysis Society of Japan, specific surface area: 233 m²/g, pore volume: 0.41 ml/g, pellet size: 74–590 μm and mean pore diameter: 5.6 nm), in the same method.

FTS reaction was carried out in a flow type slurry-phase semi-batch autoclave, with the inner volume of 80 ml. The passivated catalyst (1.0 g, under 149 μm) and 20 ml liquid medium (*n*-hexadecane) were loaded in the reactor. During the reaction, effluent gas released from the reactor was analyzed by on-line gas chromatography. CO and CO₂ were analyzed by using an active charcoal column equipped with a thermal conductivity detector (TCD). The hydrocarbons were also analyzed using FID for C₁–C₅ (Porapak Q, on-line) and for C₆–C₃₀₊ (SE-30, uniport), respectively. Argon was employed as an internal standard with concentration of 3% in the feed gas. The reaction conditions were P (total) = 1.0 MPa, CO/H₂ = 1/2, W/F (CO + H₂ + Ar) = 5 g-cat. h mol⁻¹, T = 513 K.

Pore size distribution, BET surface area and pore volume were determined by adsorption method (Quantachrome Autosorb-1, Yuasa Ionics), where nitrogen was used as adsorbent. The supported cobalt crystalline size of the passivated catalysts was detected by XRD (Rigaku, RINT2000). The supported cobalt crystalline average size was calculated by $L = K\lambda / \Delta(2\theta) \cos \theta_0$ for XRD data, where *L* is the crystalline size, *K* a constant (*K* = 0.9–1.1), λ the wavelength of X-ray (Cu K α = 0.154 nm), and $\Delta(2\theta)$ is the width of the peak at half height.

Temperature-programmed reduction (TPR) experiments were carried out in a quartz microreactor using 0.2 g calcined catalysts. The gas stream, 5% H₂ diluted by nitrogen as reducing gas, was fed via a mass flow controller. After the reactor, the effluent gas was led via a 0.3 nm molecular sieve trap to remove the produced water, before reaching TCD.

Chemisorption experiments were carried out in a static volumetric glass high-vacuum system (Quantachrome Autosorb-1, Yuasa Ionics). Research grade gases (H₂: 99.9995%, Takachiho Co.) were used without further purification. Before adsorption of H₂, the catalysts, previously reduced by H₂ and passivated, were treated in H₂ at 673 K for 1 h, followed by evacuation. H₂ adsorption isotherms were measured at 373 K. The calculation of chemisorption uptake (at 373 K), dispersion percentage and average crystalline diameter were described elsewhere [7].

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectra were collected on a Nexus 470 FT-IR spectrometer equipped with a diffuse reflectance attachment and with a MCT detector. The catalyst powder of 14 mg was contained in a diffuse reflectance infrared cell with a ZnSe window, which can work at high temperature and high pressure. In situ absorbance spectra were collected using

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