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Short Communication

Preparation of supported skeletal Ni catalyst and its catalytic performance on dicyclopentadiene hydrogenation

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ABSTRACT

Preparation and catalytic performance of skeletal Ni catalysts supported on Al_2O_3 were studied. The effects of alloy powder/pseudo-boehmite powder mass ratios and calcination temperatures of precursors on surface properties, compressive strength and catalytic performance were investigated. It was found that catalysts prepared by precursors which were molded with alloy powder/pseudo-boehmite powder mass ratio of 4/6 and calcinated at 860 °C in air atmosphere exhibited excellent compressive strength (16.11 N/mm), high dicyclopentadiene conversion (>95%) and appropriate THDCPD selectivity (>50%) during 1000-hour evaluation. The operational conditions were obtained as following: $T = 120$ °C, $P = 2.0$ MPa, LSHV = 2.0 h^{-1} and hydrogen–oil ratio =300:1.

1. Introduction

Due to its high efficiency and selectivity in molecular hydrogen activation [1], the Raney Ni catalysts have been applied in industrial processes for hydrogenation reactions for several decades since they were introduced in 1925 [2]. The starting Ni–Al (50/50 wt.%) alloy contains a mixture of eutectic phases such as Al_3Ni_2 and AlNi according to the binary phase diagram [3]. In addition, a promoter (such as Mo) is included to enhance the activity and selectivity of the catalyst. Conventionally, the Raney Ni catalyst is prepared by leaching a Ni–Al alloy using sodium hydroxide solution at certain temperature [4]. Even though traditional Raney Ni exhibits high activity for hydrogenation of double bonds [5], one of its most important drawbacks is its inferior compressive strength, which restricts its application on fixed-bed reactor. Thus, several attempts have been adopted to improve the compressive strength [6–8]. In this paper, a supported skeletal Ni catalyst with excellent compressive strength and high catalytic activity is prepared by alkali leaching of calcinated precursors obtained by Ni-Mo-Al alloy powder and pseudo-boehmite powder. As molding procedure, calcination procedure and activation process are of crucial significance for the structure and catalytic performance of the catalyst [9,10], effects of calcination temperature and mass ratio of alloy powder/pseudo-boehmite powder are also investigated.

2. Experimental

2.1. Catalysts preparation

Precursors were prepared by alloy powder (composed of 48/50/2 (mass fraction) Ni/Al/Mo, $D_p < 75$ μm) and pseudo-boehmite powder. Two kinds of powder were mixed uniformly with different mass ratios (50 g per time) and peptized by 10 g 5% nitric acid solution. Then the mixture was extruded to little strip precursors and dried at 120 °C for 2 h. The dried precursors were calcinated at different temperatures for 4 h in air atmosphere. Leaching process of calcinated precursors was performed in an excess of 20 wt.% sodium hydroxide solution at 70 °C for 5 h. After leaching, the supported skeletal Ni catalysts were obtained and washed several times with distilled water to neutrality.

2.2. Catalysts characterization

Nitrogen adsorption–desorption isotherms of the catalysts were obtained with a ASAP 2020 (micromeritics) instrument. The samples were degassed under vacuum at 200 °C for 4 h. BET surface areas were determined by the Brunauere Emmette Teller (BET) method and total pore volume and sizes were evaluated by the standard Barrett Joyner Halenda (BJH) treatment.

The compressive strength of samples was measured using the YKHC-3A (YinHe Corporation, China) equipment.

The morphology of the catalysts was analyzed by scanning electron microscopy using QUANTA 400F (FEI corporation, The United States) equipment.

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Powder X-ray diffraction patterns of samples were obtained by XRD (D-Max2500-PC, Rigaku) measurements using CuK$_\alpha$ radiation operated at 40 kV and 20 mA, performing from 10° to 90° at 4°/min speed.

Temperature programmed reduction (H_2-TPR) was carried out in an automatic equipment (Chemisorb 2750, Micromeritics). The sample (0.1 g) was submitted to a heat treatment (from room temperature to 900 °C with 15 °C/min) in a gas flow (20 mL/min) of the mixture N_2: H_2 (volume ratio = 95:5).

2.3. Catalytic activity test

Catalytic activity tests for dicyclopentadiene (DCPD) hydrogenation were carried out in the fixed-bed reactor (φ12 mm, reactor diameter), which was shown in Fig. 1. 10 mL catalyst was loaded in reactor and the catalyst was situ pre-reduced using H_2 at 450 °C for 3 h under 240 h^{-1} (GHSV) before each experimental run. Hydrogenation experiments were performed at 120 °C under 2.0 MPa with 2.0 h^{-1} (LSHV) and 300:1 (hydrogen–oil ratio). The product was analyzed by GC2010 (SHZMAZU, Japan). The DCPD conversion (%) and THDCPD selectivity (%) were calculated according to the following formulas:

$$\text{DCPD-conversion}(\%) = \frac{(\text{moles of DCPD}_{\text{in}}) - (\text{moles of DCPD}_{\text{out}})}{\text{moles of DCPD}_{\text{in}}} \times 100$$

$$\text{THDCPD-selectivity}(\%) = \frac{\text{moles of THDPD}}{(\text{conversion (DCPD)}) \times (\text{moles of DCPD}_{\text{in}})} \times 100.$$

3. Results and discussion

3.1. Effect of precursor calcination temperature on properties of supported skeletal Ni catalyst

Supported skeletal Ni catalysts and corresponding precursors are prepared with alloy powder/pseudo-boehmite powder mass ratio of 4/6. Precursors are calcinated at different temperatures (800–880 °C) in order to investigate the effect of calcination temperature on physicochemical properties of catalysts. The characterization results are summarized as follows.

The textural properties of the five catalysts are given in Table 1. Remarkable decrease of surface areas shall be attributed to the sintering of catalysts which may result in the decrease of Ni active sites with the increase of calcination temperature. Since mean crystallite diameters raise with the temperature increasing, larger particles can block part of micropores of alumina [11], which decreases the pore volume of the catalysts. Meanwhile, between particles may form some pores to increase the pore volume of the catalysts [12]. Thus, the pore volume fluctuates between 0.218 cm^3/g and 0.226 cm^3/g. According to Table 1, pore size and compressive strength increase with the higher calcination temperature (from 800 °C to 860 °C) and peak at 8.99 nm and 16.11 N/mm, respectively when the temperature amounts to 860 °C. The results demonstrate that larger particles will block the pores with smaller size, which can preserve the larger-size pores in the catalysts [13]. However, it is apparent to note that the catalyst exhibits inferior textural properties, especially lower compressive strength with the temperature rising to 880 °C. Therefore, precursor shall be calcinated at 860 °C due to its best compressive strength and appropriate textural properties.

The morphological properties of the catalysts are investigated utilizing SEM method and SEM images of these samples are illustrated in Fig. 2. The SEM observations (Fig. 2a–e) imply that catalyst samples calcinated for different temperatures have completely different morphological features. The SEM images show that sample "a" is comprised of the dispersed grains with different sizes and low dense agglomeration (Fig. 2a). The sample "b" has a higher dense agglomerate compared with the sample "a" since there are more larger grains (Fig. 2b). Sample "c" (Fig. 2c) is made up of several blocks with different-sized particles inserting on them. Sample "d" exhibits that not only do grains embed on the blocks but also apparent aggregation of particles on blocks can be observed (Fig. 2d). Similarly, sample "e" (Fig. 2e) has the highest dense agglomerate in comparison with other samples. Thus, according to the results of SEM and Table 1, increasing in the particle size in samples calcinated at higher temperature may be due to sintering phenomena during calcinating process.

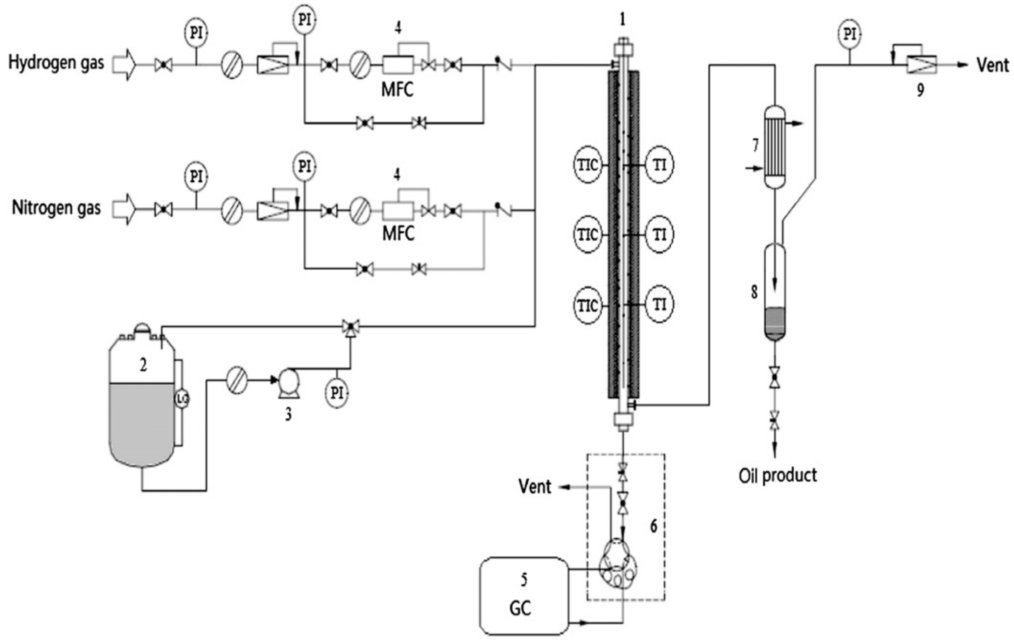

Fig. 1. Schematic drawing of hydrogenation reaction experimental apparatus:(1) hydrogenation reactor; (2) feed tank; (3) pump; (4) gas mass flow meter; (5) gas chromatograph; (6) online six-way valve sampler; (7) condenser; (8) high-pressure separation tank; (9) back pressure valve.