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Short Communication

Deactivation of supported skeletal Ni catalyst and effect of regeneration temperature on its catalytic performance

Yanli Wang [a], Guohua Luo [a,*], Xin Xu [a], Jiajia Xia [b]

[a] *Department of Chemical Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, China*
[b] *College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China*

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ABSTRACT

Deactivation and regeneration of supported skeletal Ni catalyst applied to hydrogenation of indene and styrene in fixed-bed reactor were investigated. The significant aggregation of skeletal Ni and formation of coke precursors were the main reasons for deactivation of catalyst. Furthermore, TG-DTA, XRD, SEM, BET and H_2-TPR were utilized to characterize the regenerated catalysts and calcining the spent catalysts in air at 550 °C for 3 h and then reducing in H_2 at 450 °C for 3 h under 240 h^{-1} (GHSV) could recover its activity according to hydrogenation evaluation results.

1. Introduction

Raney Ni (skeletal Ni) catalyst, as a classical catalyst for hydrogenation processes, has been applied in industrial processes for hydrogenation reactions such as hydrogenation of double bonds for several decades [1,2]. Even though skeletal Ni exhibits excellent hydrogenation activity, its inferior compressive strength restricts its application on fixed-bed reactor and it is unable to regenerate [2]. Several approaches have been adopted to enhance the compressive strength (namely, supported skeletal Ni catalyst), implying that skeletal Ni is a kind of potential catalyst which can be applied to fixed-fed reactor [3,4]. However, few further studies are carried out on the deactivation of supported skeletal Ni catalyst.

According to the researches [5–7], there are two reasons for activity decline and deactivation of skeletal Ni catalysts: (a) loss of active Ni surface by aggregation and (b) deposition of organic species produced by side reactions. Several methods can be utilized to regenerate deactivated catalyst and partial or complete regeneration of the catalyst can be achieved [8]. Special methods such as washing the catalyst with organic solvents [9], supercritical fluids or plasmas [10] can remove organic species whereas calcination is the common approach in order to remove coke precursors over the catalyst. Apparently, calcination in air, as a kind of regeneration method, cannot be applied to skeletal Ni while it may be an appropriate regeneration approach for supported skeletal Ni catalyst in terms of removing coke precursors so as to recover hydrogenation activity. Nevertheless, calcination in high temperature may cause sintering which has detrimental influence upon hydrogenation activity. Therefore, the objective of present work is to study the main reasons for supported skeletal Ni catalyst activity decline and deactivation in hydrogenation of indene and styrene and study the effect of calcination in air on catalytic activity of regenerated catalyst.

2. Experimental

2.1. Catalysts preparation

Catalysts were prepared by precursors which were molded by alloy powder (composed of 48/50/2 (mass percentage) Ni/Al/Mo, $D_p < 75$ μm) and pseudo-boehmite powder with mass ratio of 4/6. The extruded precursors were dried at 120 °C for 2 h and then calcinated at 860 °C for 4 h in the atmosphere of the mixture Ar:O_2 (volume ratio = 90:10). Subsequently, leaching process was performed in 20 wt.% sodium hydroxide solution with 70 °C for 5 h with calcinated precursors/solution mass ratio of 1/3.5. After leaching, the obtained supported skeletal Ni catalysts were washed several times with distilled water to neutrality and preserved in water.

2.2. Catalysts regeneration

Supported skeletal Ni catalyst was regenerated by the method of calcinating spent catalyst in air for 3 h. The calcination temperature

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* Corresponding author. Tel./fax: +86 1081292074.
E-mail address: luoguohua@bipt.edu.cn (G. Luo).

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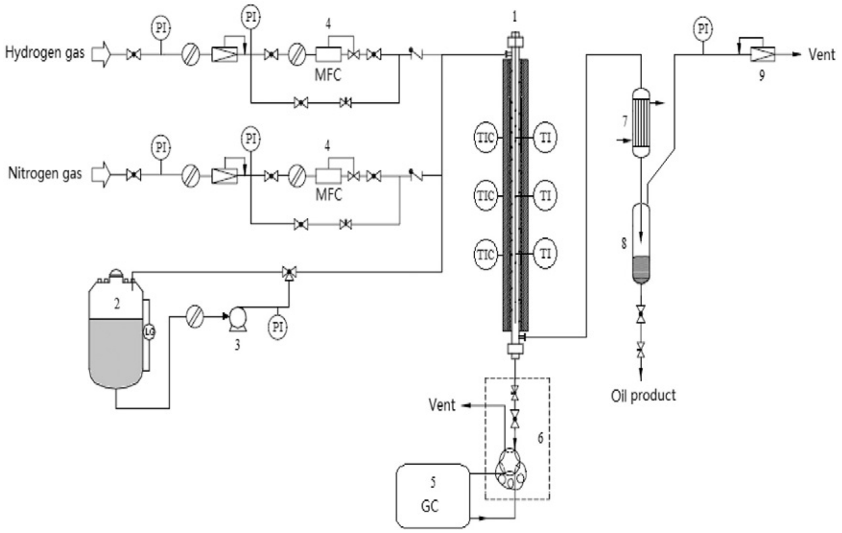

Fig. 1. Schematic drawing of hydrogenation reaction experimental apparatus: (1) hydrogenation reactor; (2) feed tank; (3) pump; (4) gas mass flow meter; (5) gas chromatograph; (6) on-line six-way valve sampler; (7) condenser; (8) high-pressure separation tank; (9) back pressure valve.

rose to 450 °C, 500 °C, 550 °C and 600 °C at heating rate of 5 °C/min in order to investigate the effect of regeneration temperature on properties of catalyst.

2.3. Catalysts characterization

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.

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

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

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) of spent catalyst were performed in dry air atmosphere using a thermal analyzer SDTQ600 (TG–DTA). The temperature was raised from room temperature to 900 °C at heating rate of 10 °C/min and the sample weight was 10 mg.

Temperature programmed reduction (H_2-TPR) was carried out in an automatic equipment (Chemisorb2750, 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:$H_2 = 95{:}5$ (volume ratio).

2.4. Catalytic activity test

Catalytic activity tests for indene and styrene 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 for 3 h under 240 h^{-1} (GHSV) and the reduced temperature rose to 450 °C at heating rate of 5 °C/min before each experimental run. Raw material consisted of 15/5/80 (mass percentage) indene/styrene/dimethylbenzene and hydrogenation experiments were performed at 180 °C under 2.0 MPa with 3.0 h^{-1} (LSHV) and 240:1 (hydrogen-oil ratio). The product was analyzed by GC2010 (SHIMADZU, Japan). The conversions (%) of indene and styrene were calculated according to the following formulas:

$$\text{Indene-conversion}(\%) = \frac{(\text{moles of indene}_{\text{in}})-(\text{moles of indene}_{\text{out}})}{\text{moles of indene}_{\text{in}}} \times 100, \tag{2.4.1}$$

$$\text{Styrene-conversion}(\%) = \frac{(\text{moles of styrene}_{\text{in}})-(\text{moles of styrene}_{\text{out}})}{\text{moles of styrene}_{\text{in}}} \times 100. \tag{2.4.2}$$

3. Results and discussion

3.1. Deactivation of catalyst

The catalyst prepared by the method mentioned in part 2.1 is utilized to hydrogenation of styrene and indene. Furthermore, a 700-hour period successive experiment is performed and corresponding results are listed in Table 1. Conversion rate of styrene and indene drops to 95.35% and 85.22%, respectively, indicating that hydrogenation activity decreases and catalyst deactivates after a 700 h successive run. Therefore, XRD, SEM and BET are applied to characterize the spent catalyst in order to study the reasons of activity decline.

The XRD patterns of the catalysts before and after the test are shown in Fig. 2(a). The XRD pattern of the spent catalyst is different to that of the fresh one around 2θ = 44.5°, 52.0° and 76.5°, which are attached to metallic Ni. Meanwhile, the intensities of the Ni peaks of the spent catalyst increase apparently while full width at half maximum (FWHM) decreases, indicating that the average size of the Ni crystallites rises (amounting to 15.1 nm, according to Table 2) since wider

Table 1
700-h successive experimental run results of fresh supported skeletal Ni catalyst.

Reaction time (h)	Conversion (%)[a]	
	Indene	Styrene
50	98.86%	99.26%
350	93.71%	98.18%
700	85.22%	95.35%

[a] Instantaneous conversion rate of indene and styrene.