Monolithic catalysts with Pd deposited on a structured nickel foam packing

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ABSTRACT

Catalyst activity and selectivity of the multiphase catalytic reactions may be strongly reduced by mass transfer limitations. A rotating packed bed (RPB) reactor can intensify the mass transfer process by 1–3 orders magnitude compared to the traditional reactors, which has great potential for catalytic reactions. The first step of the RPB reactor applied to catalytic reactions is to prepare a monolithic catalyst with excellent mechanical strength. This work selected the structured nickel foam packing as the catalyst substrate and then deposited palladium on the surface of the porous nickel foam packing. The above monolithic catalyst was then characterized by FESEM, EDS, TEM, XRD, ICP, and 3D-CT. In order to know the coating adhesivity, the monolithic catalyst was tested by the ultrasonic vibration in an ultrasonicator tank and scouring experiments in a RPB reactor. Hydrogenation of α-methylstyrene was employed to test its catalytic performance.

1. Introduction

Conventional multiphase reactors, such as trickle-bed reactors, slurry reactors, and slurry bubble column reactors, play a significant role for the chemical catalytic reactions [1]. A major drawback of many conventional multiphase reactors is that both activity and selectivity of the catalyst may be strongly reduced by mass transfer limitations [2]. Efforts on the mass transfer enhancement between the multiphases in a gas-liquid-solid reaction with monolithic catalysts or in a novel reactor have attracted considerable attention in recently years [3,4].

Higee (high gravity) technology, one of the process intensification technologies, was regarded as a promising technology for the modern chemical industry [5]. A rotating packed bed (RPB) reactor is the core device of Higee technology. For a gas-liquid or gas-liquid-solid system, thin liquid films, tiny liquid droplets, and chaotic gas flow are yielded when the fluid flows through the high-speed rotor under the centrifugal force, thus generating large interfacial area to enhance the mass transfer process.

Based on 35 years' researches, Higee technology has been widely applied to reaction and separation process intensification and has been proved to be excellent, especially for the processes limited by micro-mixing or mass transfer [6–9]. Owing to these distinctive advantages of RPBs, they have been successfully applied not only to gas-liquid reaction systems, but also liquid-liquid, gas-solid, and gas-liquid-solid reaction systems, such as CO_2 absorption [10], sulfonation [8,11], Fischer-Tropsch synthesis [12], nanomaterials preparation [13] and catalytic hydrogenation [14]. One of the catalytic hydrogenation examples is that Rao et al. [15] conducted the α-methylstyrene (AMS) hydrogenation reaction in a Higee device. Experimental results showed that because of the mass transfer enhancment, the reaction rate was in the range of 30–40 times in a centrifugal force field of about 450 times the gravitational force field and an industrial reactor of $60 \, m^3$ could be replaced with a Higee device $<1.5 \, m^3$ in volume. It demonstrated that the Higee device has great potential for the catalytic reactions.

In general, conventional pellet catalysts are randomly packed inside the reactor. Commercial pellet catalysts, like sphere-shaped particles, may be not much suitable for the RPB reactor since catalyst particles loaded in the RPB reactor will be under a high centrifugal filed and easily debunked at the outer edge of the rotor, which is not favorable for the dynamic balance of the RPB reactor for a long-time running. Structured packings, such as nickel (Ni) foam [16], silicon carbide (SiC) [17], are excellent candidates for the RPB reactor because they have good mechanical strength. Mono-

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Nomenclature

X_{AMS}	Conversion of AMS
$V_{AMS,in}$	The initial volumetric flow rate of AMS
$V_{AMS,out}$	The volumetric flow rate of AMS in the reactor outlet
D	The crystallite size
k	The dimensionless shape factor
λ	The X-ray wavelength
β	The line broadening at half the maximum intensity (FWHM)
$\cos\theta$	The cosine of diffraction angle

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Table 1
Dimension of the Ni foam substrates.

Properties	Specification 1	Specification 2
Color	Silver gray	Silver gray
Estimated avg. pore diameter, mm	0.6	0.6
Specific surface area, m²/m³	2916	2916
Material	Nickel	Nickel
Porosity	0.96	0.96
Dimensions of the packings		
OD, mm	80	10
ID, mm	35	–
Axial thickness, mm	18	18

lithic catalyst with an active component deposited on a structured packing seems therefore a potential application to the RPB reactor for the catalytic reactions. The catalytic packing has double functions of fluid shearing and catalytic action. The first step of the RPB reactor applied to the multiphase catalytic reactions is to prepare a monolithic catalyst with good mechanical strength and catalytic performance. This work is the first part of a project that intends to prepare a monolithic catalyst with palladium (Pd) deposited on the structured nickel foam packing. The standard characterization techniques and coating adherence test were conducted. Though the monolithic catalysts will be eventually applied to the RPB reactor in the further, we used a tubular reactor as the first trial to test the catalytic activity of the above monolithic catalyst by the AMS hydrogenation reaction, which is a mass transfer limited reaction.

2. Experimental

2.1. Catalyst preparation

Nickel foam packing (Jilin Zhuoer Technology Co., Ltd., China) was used as the substrate for catalyst deposition, and its parameters are given in Table 1. First, in order to remove the oil, primary oxides, and other superficial impurities, the nickel foam cylinders were ultrasonically cleaned in the acetone (Beijing Chemical Works, 99.5%), alkaline (Beijing Chemical Works, 96.0%), and acidic (Beijing Chemical Works, 36–38%) solution, respectively, and then thoroughly rinsed in de-ionized water. Wetness impregnation method was used to deposit Pd. The treated metal foams were soaked into hydrochloric acid solution (Beijing Chemical Works, 36–38%) which contains 0.2 mol/L $SnCl_2\cdot2H_2O$ (Beijing Chemical Works, 98.0%) for 30 min. Nickel foams were then taken out and were blown by nitrogen carefully to assist filling of the pores or channels. The foams were immersed in $PdCl_2$ (Tianjin Fuchen Chemical Reagents Factory, 99.5%) solution for 30 min. After that, $SnCl_2\cdot2H_2O$ solution was added slowly into $PdCl_2$ solution and stirring at the same time. Different Pd loadings were controlled by the concentration of $PdCl_2$. The solution was stirred with a magnetic stirrer to eliminate gas bubbles and to maintain uniform composition in the holes and crevices of the foams. To avoid non-uniform coating, the excess

liquid trapped is removed by blowing nitrogen. During the deposition, the Sn(II) is oxidized to Sn(IV) while Pd(II) is reduced to Pd(0) [18]. After the deposition, the foams were rinsed thoroughly with distilled water (Sn(0) would be removed) and dried in a stream of hot air. As shown in Table 1, the big size Pd/Ni foam catalyst would be used for the scouring test in the RPB reactor, and the small one was used for ultrasonic vibration test in an ultrasonicator tank and hydrogenation in tubular reactor.

2.2. Catalyst characterization

The surface morphology of the samples was observed by a field emission scanning electron microscope (FESEM) (JSM-7100F), and energy dispersive X-ray spectroscopy (EDS) was used to examine the samples' element information. The morphologies of obtained Pd catalysts were examined by transmission electron microscope (TEM) (Tecnai G2 20). The crystals of the catalysts were studied by X-ray diffraction (XRD) using a 2500VB2 + PC instrument with Cu Kα radiation (λ = 1.5418 Å, tube voltage 45 kV, tube current 150 mA). The active component distribution on the nickel foam surface was scanned by an X-ray microtomography (μCT) as a non-invasive characterization method to obtain realistic 3D images of a porous medium. The catalyst adherence was qualitatively measured by an ultrasonic vibration test [19]. The catalyst adherence and mechanical strength was also tested by liquid scouring experiment in a RPB reactor.

2.3. Experimental setup and procedure

The schematic diagram of the experimental setup for AMS hydrogenation is shown in Fig. 1(a). A mass flow controller was used to control the flow rate of hydrogen (Shiyuan Co., 99.999%) to the reactor. The exhaust gas that came from the outlet of the reactor went through a cooling trap and was discharged for post-processing. A tubular reactor (inner diameter 10 mm, length 700 mm, length of monolithic catalysts 150 mm) was designed for the hydrogenation experiments. These experiments were conducted in a semi-batch mode of operation with a circulating liquid flow. The liquid feed was pumped from bottom reservoir of the reactor into the head of the reactor by a pump. The entire setup was well insulated and kept at operating temperature during the experiments. In order to enhance the gas and liquid distribution, several bare monolith pieces were stacked at both upper and lower of the catalyst bed. The model reaction for activity study of Pd/Ni foam catalyst is described as follows:

$$\text{(1)}$$
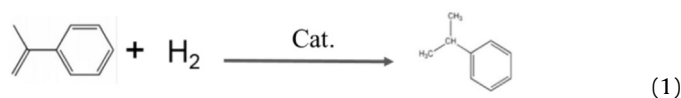
Since reactant impurities have an important impact on the rate and deactivation behavior of the reaction system [20], the polymerization inhibitor 4-ter-butylcatechol would be removed by the activated Al_2O_3 (2 g/L, neutral alumina) and molecular sieves (4 g/L, 3 Å) for at least two hours before the hydrogenation. Considering the polymerization of AMS, an upper concentration limit is given by the ceiling temperature of the mixture which depends on the reaction temperature. According to the correlation of Stein et al. [21], the mixture should not exceed 23% (w/w) AMS in cumene when working without polymerization inhibitor at room temperature. In order to avoid any polymerization of AMS, an AMS (Aladdin, 99%) concentration of 5% (v/v) in cumene (Beijing Chemical Works, 99.7%) was applied in this study. Samples were taken from the liquid inlet of the reactor at regular intervals. The samples were analyzed by a gas chromatography (Shimadzu 2014C) with a flame ionization detector to determine the composition.