Short communication

Selective hydrogenation of cinnamaldehyde over a rotating stirrer reactor made of SiC foam supported Al_2O_3 and Pt catalysts

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ABSTRACT

A rotating stirrer reactor using aluminum oxide (Al_2O_3) and platinum (Pt) loaded silicon carbide (SiC) foam as both the stirring blade and active catalyst was applied for selective hydrogenation of cinnamaldehyde (CAL). The variations of the catalyst activity and selectivity against the CAL concentration and rotating speed were studied. The reaction rate increased with the increasing of stirring speed and showed a maximum value at 300 rpm, while the highest selectivity of 75% could be achieved at conversion as high as 90% at 100 rpm.

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1. Introduction

Selective hydrogenation of α,β-unsaturated carbonyl compounds to their corresponding unsaturated alcohols is a critical process in chemicals synthesis as the unsaturated alcohols are important intermediates for production of fine chemicals and pharmaceuticals [1]. Noble metals such as Pt [2], Ir [3] and Au [4] are normally used as catalysts to achieve high selectivity of unsaturated alcohols in this process. Among them, Pt is one of the most widely studied metals. The common ways to enhance the selectivity of unsaturated alcohols include using different catalyst supports [5], controlling the catalyst particle sizes [6], constraining the catalyst active site space [7] or decorating the primary metals with a second metal component [8]. However, even with the above mentioned methods, completely pure product of α,β-unsaturated carbonyl that without any other by-products is still difficult to be obtained [9].

To improve the selectivity of unsaturated alcohols, alternative reactors were introduced recently to regulate the mass transfer among the reactants, products and active sites of catalyst. For example, Lee et al. [10] used a continuous flow reactor to replace the batch one and filled the reactor with Pt/SiO_2 heterogeneous catalysts. They found that the CA selectivity could be enhanced by increasing the residence time. At a residence time of 15 min, a 45% conversion and a maximum CAL selectivity of 60% were achieved. This demonstrated that the catalyst activity and selectivity were intimately correlated to the residence time of liquid on the catalyst active site.

Rotating foam stirrer reactors (RFSRs) can control the residence time of liquid in the catalyst active site by changing the rotating speed of their stirring blades. Therefore, they were expected to exhibit better catalyst activity and selectivity than the above mentioned continuous flow reactor. Various porous materials, such as monoliths [11], cloths [12], and fibers [13] have been used as both the supports and stirrer in RFSRs to gain better catalyst activity. As a covalent compound, SiC possesses many outstanding advantages, such as high thermal conductivity and chemical inertness [14–15]. Therefore, it can be a promising and potential catalyst support. In present study, a RFSR with SiC foam stirrer blades was designed for the selective hydrogenation of CAL aiming at achieving a higher yield. The SiC foams were first coated by Al_2O_3 prior to the Pt loading. The factors like hydrogen pressure, cinnamaldehyde concentration and the rotating speed of blades that may influence the selectivity and activity of the catalyst have been systematically investigated and reported in this manuscript.

2. Experimental

2.1. Preparation of SiC foam

The SiC foams adopted in this study were prepared by macromolecule pyrogenation combined with reaction bonding method. The detailed synthesis process of the SiC foams can be found in our previous study [16].

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2.2. Preparation of Al$_2$O$_3$ washcoat on SiC foam

A stable alumina sol was prepared from pseudo-boehmite and de-ionized water in a weight ratio of 1:5. The mixture was vigorously stirred at 80 °C for 1 h, during which a small amount of nitric acid was added slowly to maintain a pH value of 2.0 [17]. Then the SiC foam was immersed into alumina sol for 10 min. After taking out the excessive colloids residue in pores by blowing with an air pump, the SiC foam with wet Al$_2$O$_3$ colloids was dried in an oven at 60 °C. The coating and drying process was repeated several times until a desired loading amount of Al$_2$O$_3$ was obtained. The as-prepared samples were finally calcined in a muffle furnace at 550 °C for 3 h to obtain the structured Al$_2$O$_3$–SiC support. The loading amount of Al$_2$O$_3$ (12 wt%) was calculated from the weight difference between the weight of SiC after Al$_2$O$_3$ loading, and before Al$_2$O$_3$ loading.

2.3. Preparation of Pt/Al$_2$O$_3$–SiC catalyst

Pt catalyst was prepared by successive impregnation using H$_2$PtCl$_6$·6H$_2$O aqueous solution (19.3 mmol/L) as Pt precursor. Briefly speaking, 5 g Al$_2$O$_3$–SiC support was immersed in excessive H$_2$PtCl$_6$·6H$_2$O aqueous solution (20 mL) for 10 min, dried at 110 °C for 2 h, and then calcined at 300 °C in air for 2 h. The same operation was repeated for two times. The catalyst was reduced at 300 °C in hydrogen (50 mL/min) for 3 h prior to the catalytic test. Generally, the metal content in metal supported catalysts is analyzed by ICP, however the SiC is resistant to acid corrosion. Therefore the Pt loading (0.24 wt%) was calculated from the weight difference between the weight of Al$_2$O$_3$–SiC after Pt loading, and before Pt loading, which was similar to that reported by Xu and coworkers [18].

2.4. Catalyst characterizations

The surface morphology of the support and catalyst were examined by scanning electron microscope (Inspect F50). Transmission electron microscopy (TEM) measurements were carried out on a FEI T12 microscope at 120 kV. The Brunauer-Emmett-Teller (BET) specific surface area was determined from N$_2$ adsorption-desorption measurement (Micromeritics ASAP 2020 analyzer) at 77 K. The XRD patterns of the Pt catalysts and support were obtained by a D/MAX-2500 PC X-ray diffractometer with monochromatized CuKα radiation (λ = 1.54 Å). CO chemisorption measurements were carried out on Catlab with a QIC-20 mass spectrometry from Hiden Analytical.

2.5. Catalytic reaction

The hydrogenation experiments were conducted in a 1.0 L autoclave with inner diameter of 90 mm and height of 160 mm, respectively (Fig. 1). The catalyst, which can be used as a foam stirrer (with a dimension of 8 mm × 10 mm × 60 mm), was mounted on a shaft. The hydrogen was introduced from a top port. The reaction was conducted at room temperature and 3 MPa under different rotation speeds in the range of 0–400 rpm. The total volume of CAL 2-propanol (IPA) solution was 100 mL. The reactor was thoroughly purged with H$_2$ before the experiments. A certain amount of the liquid reactant was taken out regularly and analyzed by an Agilent 7890 A gas chromatography (GC) equipped with a HP-5(30 m × 0.32 mm × 0.2 μm) column and FID detector.

3. Results and discussion

3.1. Catalyst characterizations

The SiC foam is an open-celled material consisting of reticulated structure of struts, as shown in Fig. S1a. Fig. S1b and Fig. S1c show the cross section of a foam strut coated by an Al$_2$O$_3$ washcoat layer of approximately 20 μm thick. It was shown from Fig. S1d that the washcoat
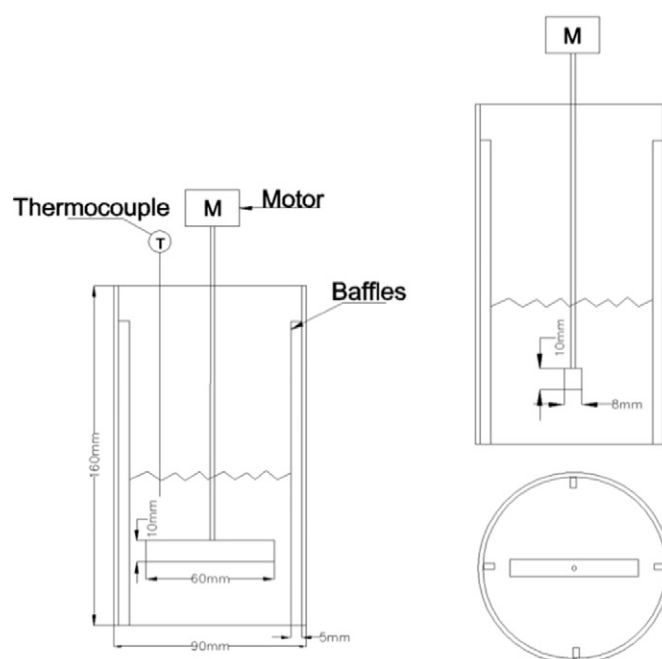

Fig. 1. Schematic illustration of the rotating foam stirrer reactor.

layer was well coated on the SiC foam support. The texture properties of the pristine SiC foam, Al$_2$O$_3$–SiC support and Pt/Al$_2$O$_3$–SiC catalyst were listed in Table 1. It can be seen from the table that the surface area was increased from 1 to 28.4 m^2 g^{-1} after loading the Al$_2$O$_3$ washcoat layer on the SiC foam. The surface area is not obviously changed when Pt is loaded on the Al$_2$O$_3$–SiC support. Only obvious SiC and Si (residues in the preparation of SiC) diffraction peaks could be found in the XRD patterns (Fig. S2). The mean Pt particle size from the TEM images (Fig. S3) is 2.51 ± 0.94 nm, which is similar to that calculated from the CO chemisorption (1.77 nm). The catalyst is very stable even up to 5 recycles, the morphology and surface area of the spent catalyst are not obviously changed.

3.2. Catalytic activity

3.2.1. Effect of reaction time

The products obtained in the hydrogenation of CAL are cinnamyl alcohol (CA), hydrocinnamaldehyde (HCAL) and phenyl propanol (PP) (see Scheme 1 in the supporting information), depending on the reaction conditions used. Other possible reaction products, such as methylstyrene, phenylpropane and acetals, were not detected in present work. The initial H$_2$ pressure was optimized to 3 MPa (Fig. S4). Fig. 2 gives the variations of CAL conversion ratio and products selectivity against reaction time. The CA selectivity stably maintains at 75% within the time range of 120–420 min, whereas after 420 min, it decreases while the PP selectivity increases. Most of the HCAL is formed at the initial reaction stage and thereafter the HCAL selectivity decreases gradually. Finally, only very little CAL is converted to HCAL.

Table 1
Texture parameters of various samples derived from N$_2$ adsorption-desorption.

Sample	BET area [m^2 g^{-1}]	BJH average pore width [nm]	Pore volume [m^3 g^{-1}]
SiC	1.0	–	–
12 wt% Al$_2$O$_3$–SiC	28.4	8.4	0.044
0.24 wt% Pt/Al$_2$O$_3$–SiC	27.1	7.2	0.042
Spent 0.24 wt% Pt/Al$_2$O$_3$–SiC	26.8	6.8	0.041