ENHANCING THE EFFICIENCY OF GAS-LIQUID-SOLID REACTIONS USING A MONOLITHIC MICROHONEYCOMB CATALYST

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Abstract

Monolithic carbon gels with a microhoneycomb structure were prepared using the Ice Templating method, and Pt nanoparticles were loaded within them. High conversions were achieved in the hydrogenation of 4-nitrophenol even at room temperature and atmospheric pressure when the obtained microhoneycombs were used as the catalyst. These results show the possibility of enhancing the efficiency of various gas-liquid-solid 3 phase reactions by using solid catalysts with a unique microhoneycomb structure.

Keywords

Gas-liquid-solid reactions, Microchannel, Microhoneycomb, Carbon gel, Ice templating.

Introduction

There are various industrially important gas-liquid reactions which are catalyzed by solids, but generally they are difficult to conduct, mostly due to the slow mass transfer between different phases. It has been reported that the efficiency of such reactions can be drastically improved by conducting them in microfluidic devices (Kobayashi et al., 2004). However, catalyst loading into the microchannels of such devices is generally difficult, and the numbering-up of the devices to increase productivity is also a difficult task. These problems can be solved by using a catalytic monolith having straight and aligned micrometer-sized channels within it.

We showed that such monoliths, which can be called "microhoneycombs," can be easily synthesized using ice crystals as the template to introduce micrometer-sized channels into the monolith (Mukai et al, 2004). Microhoneycombs with various functions can be obtained through this method which we named the Ice Templating method (Mukai et al., 2006).

In this work, microhoneycombs of carbon gels were prepared, and Pt nanoparticles were loaded within them. Hydrogenation of 4-nitrophenol was conducted using the obtained microhoneycombs as the catalyst and the results were compared with those obtained using the same catalyst in the form of particles.

Experimental

First, cylindrical microhoneycombs of carbon gels (CMHs), were synthesized through the method previously reported (Mukai et al., 2006). The concentration of resorcinol in the starting solution was set to 0.5 g cm^{-3}, and the ratios between resorcinol and formaldehyde and resorcinol and the catalyst (sodium carbonate) were respectively set to 0.5 mol mol^{-1} and 200 mol mol^{-1}. The carbonization temperature was 1073 K. After carbonization, the microhoneycombs were treated with 65 wt% nitric acid. For comparison, carbon gels in the form of particles were also prepared.

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Pt nanoparticles were loaded within the obtained CMHs and particles through the incipient wetness method using a HNO_3 solution of diammine dinitro Pt(II) as the Pt source. The target Pt loading amount was 5 wt%. Hereafter the CMHs and particles supporting Pt nanoparticles will be referred to as Pt/CMH and Pt/CG, respectively.

The obtained samples were characterized through SEM, TEM, TG and PXRD analyses. The porous properties of the samples prior to and after Pt loading were evaluated through N_2 adsorption experiments.

The obtained Pt/CMH was fixed into a heat shrinkable tube, and then the tube was set vertically. Hydrogenation of 4-nitrophenol was conducted at room temperature and atmospheric pressure. An aqueous solution of 4-nitrophenol was fed to the bottom of the Pt/CMH at a constant flow rate. The concentration of 4-nitrophenol was set in the range of 1.2 - 3.6 mmol L^{-1} and the flow rate of the solution was set in the range of 0.10 - 0.20 mL min^{-1}. Hydrogen was fed to the bottom of the Pt/CMH using 2 modes, a continuous flow mode, and a pulse mode in which hydrogen was introduced as equal-sized pulses every 12 seconds. The average flow rate of hydrogen was set to provide 1 - 4 times the amount required to complete the reaction.

Results and Discussion

Fig. 1 shows a photograph of typical CMHs. Cylindrical monoliths with a diameter of approximately 5 mm and a length of about 10 mm were successfully obtained.

To the obtained CMHs, Pt nanoparticles were loaded. Fig. 2 (a) shows a cross sectional SEM image of a typical microhoneycomb sample after Pt loading. It can be noticed that microhoneycombs having channels with an average equivalent diameter of around 32 μm were obtained, and that Pt loading didn't affect the unique structure of the microhoneycomb. It was confirmed that the amount of Pt loading was about 6.5 wt%. It was also confirmed that the microhoneycombs possessed the unique micro-mesoporous structure common to carbon gels, which hardly changed after Pt loading.

Fig. 2 (b) shows a TEM image of a fragment of a typical Pt/CMH sample. The existence of particles, presumably Pt, with sizes around 2 to 3 nm can be confirmed. PXRD analysis gave a typical pattern of Pt, and the average particle size calculated using the Scherrer equation was 2.3 nm. Therefore, it can be concluded that Pt was efficiently supported within the microhoneycomb.

Hydrogenation of 4-nitrophenol was conducted using the obtained Pt/CMH samples. It was found that the continuous introduction of hydrogen gave slightly better results, therefore experiments at different hydrogen and 4-nitrophenol flow rates were conducted using this mode of hydrogen feeding. Typical results are summarized in Table 1. It was found that a high conversion of 4-nitrophenol exceeding 0.8 could be achieved even at room temperature and atmospheric pressure. It was also confirmed that a high conversion can be maintained even when the flow rate of hydrogen was reduced to the minimum flow rate required to complete the reaction. Such high performances could not be obtained when Pt/CG samples were used as the catalyst, indicating that the efficiency of gas-liquid-solid 3 phase reactions can be enhanced by using monolithic microhoneycombs having catalytic functions.

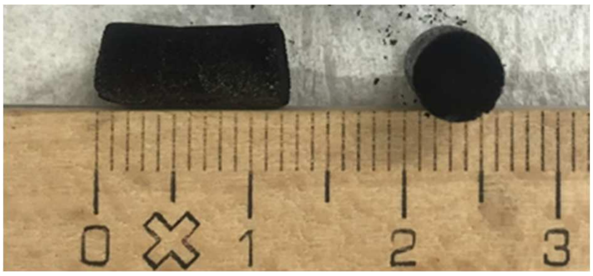

Fig. 1 Photograph of typical Pt/CMHs

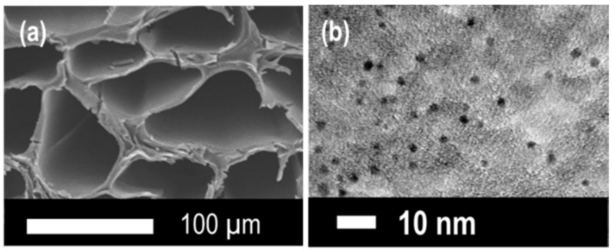

Fig. 2 (a) SEM image of a typical Pt/CMH sample and (b) TEM image of a fragment of a typical Pt/CMH sample

Table 1. Results of hydrogenation of 4-nitrophenol using Pt/CMH

H_2/(3 x 4-nitrophenol) [mol mol^{-1}]	Conversion [-]
4	0.83
2	0.80
1	0.76

Concentration of 4-nitrophenol solution: 3.6 mmol L^{-1}
4-nitrophenol solution flow rate: 0.10 mL min^{-1} (LHSV= 38 h^{-1})

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