Hydrochlorination of Acetylene Using the Novel SiC Foam with Hollow Structure Supported Au/C Catalysts

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Abstract. Acetylene hydrochlorination using Au/C as catalyst, is an important process to produce vinyl chloride. It is a highly exothermic and diffusion-controlled reaction with local hot spots and poor diffusion process in the fixed-bed reactor, weakening the catalytic performance of Au catalyst. The structuring of catalyst using solid SiC foam ceramic can solve the above problems through optimizing spatial distribution of Au/C, reducing the pressure drop and temperature rise. In order to further disperse Au/C, the novel SiC foam with hollow structure was manufactured to compare with solid SiC foam. The hollow foam structured catalyst has inside and outside surface, thinner catalyst coating and smaller Au particles. Thus it provides more active site accessible to the reactants and further shortens the diffusion distance, then improving the catalytic efficiency. The catalytic lifetime (acetylene conversion above 90%) of hollow SiC foam structured catalyst is 205 hours while that of solid foam is 126 hours at acetylene gaseous hourly space velocity (GHSV) of 120 h⁻¹. In conclusion, the better dispersion of Au/C on hollow SiC foam supported structured catalyst is the main reason for activity and stability enhancement.

1. Introduction
Vinyl chloride monomer (VCM) is an important chemical intermediate for the synthesis of polyvinyl chloride (PVC) which is a kind of polymer widely used in the world[1]. There are two main processes for industrial production of VCM, namely ethylene oxychlorination and acetylene hydrochlorination. Ethylene process based on petroleum resources is a clean and high efficient route, which is widely adopted by developed countries[2]. While due to the coal-abundant resource structure in China, coal-based acetylene process with mercuric chloride supported on activated carbon catalyst, is the dominant industrial route for VCM production[3]. However, due to the strong exothermic process, the catalyst bed is easy to form hot spots, which accelerates the sublimation of mercury chloride in the particle packed bed reactor which has low heat transfer efficiency caused by the high pressure drop. The loss of mercury not only leads to the rapid deactivation of the catalyst, but also causes serious pollution to the environment[4, 5]. Therefore, it is very necessary and urgent to explore alternative green catalysts for acetylene hydrochlorination to replace the toxic mercuric chloride[6-8]. Among metal chlorides, AuCl₃ shows the most catalytic activity for acetylene hydrochlorination, owing to the highest standard electrode potential of the gold cation. But the stability is not well enough to be used...
for long-time running, which increases catalyst cost for its industrialization. Thereby, many efforts to modify active component and support of the catalyst have been carried out recently to improve activity and stability of Au catalyst[9-11].

Structured catalysts, from the point of chemical reaction engineering, have the potential to solve problems of acetylene hydrochlorination with Au catalyst. Among various of structured catalysts, open-cell foam structured catalysts with three-dimension interconnected structure show high surface area per volume that can remarkably increase the exposed active sites and reduce the catalyst loading, especially for noble metal catalysts, and then improving catalytic efficiency[12]. Its open network architecture also provides low pressure drop which is conducive to heat removal, balance the axial-radial temperature and then prevent catalyst particles from sintering[13, 14]. Furthermore, the thin catalyst layer permits the short diffusion distance, enhancing mass transfer and then further improving the catalytic efficiency[15]. Thus, foam structured catalysts possess many advantages that can effectively intensify the reaction processes[16], compared to the particle catalysts, particularly for the strongly exothermic reactions and/or the diffusion controlled processes. SiC foam has excellent thermal conductivity, thermal-shock resistance, antioxidant ability, chemical inertness and mechanical strength which are all important properties for good heterogeneous catalyst supports, and it has been applied to many special reactions as the structural support[15, 17, 18].

The reason for the Au/C deactivation is mainly the result of the reduction and decomposition of AuCl3 catalyst[19, 20], which would be aggravated under the high temperature of catalyst bed. Considering the advantages of SiC foam based structured catalyst, Yang with his coworkers[21] loaded AuCl3 on the SiC foam support coated with activated carbon to improve the catalytic performance of AuCl3 in acetylene hydrochlorination. This structured catalyst not only exhibits superior activity and stability, compared to Au/C granular catalysts, but also greatly reduces the loading of Au, demonstrating that the structured catalyst improves the catalytic performance by enhancing mass/heat transfer.

Taken together, a novel SiC foam ceramic with hollow structure was prepared in this work and used to refine the distribution of Au/C catalyst. The structure of SiC foam was characterized by 3D X-ray micro-CT. The influence of hollow structure on Au/C distribution was investigated by comparing hollow SiC foam with solid foam under the same preparation process and reaction conditions. Moreover, the effect of structural support on the activity and stability of Au/C catalyst in acetylene hydrochlorination reaction was analyzed.

2. Experimental

2.1. Preparation of SiC foam supports

Two kinds of SiC foam supports with solid and hollow structure in circular column shape (40 mm outer diameter, 4.0 mm inner diameter and 25 mm height) were prepared by polymer pyrolysis combined with melt silicon reactive sintering method in our laboratory. The open porosity of different SiC foams was controlled about 75%–80% in order to ensure the load of carbon coating. Prior to be used as structured catalyst support, the SiC foam was treated with boiling NaOH solution (10 mol/L) for 15 min to remove the residual silicon on the surface. At last, the SiC foam was ultrasonically cleaned with deionized water and dried.

2.2. Preparation of structured catalyst

The coating slurry was prepared by ball-milling the commercial activated carbon powder and liquid amino phenolic resin (provided by Beijing FRP Research Institute, China) in ethanol for 2 h. SiC powder was added into the coating slurry at the same time in order to reduce the shrink of coating after pyrolysis. The SiC foam was coated with the slurry and dried at 180 °C repeatedly until the mass increment reach about 5.0 g. Afterwards, the composite was pyrolyzed in the process of heating to 830 °C under high purity nitrogen and activated at 830 °C for 50 min under CO2 with a flowing rate of 200 mL/min. The structural support (denoted as C/SiCfoam) was obtained and the residual mass of
activated carbon was about 2.2 g.

To improve the wettability of activated carbon for efficient adsorption of AuCl₃ in aqueous solution, two C/SiC foam (62.2 mL) was impregnated in 1 mol/L nitric acid solution for 20 min, and then immersed in distilled water. 10.8 mL (solution, 1 g per 100 mL) of HAuCl₄•4H₂O was added dropwise to the above distilled water. Heat the solution until boiling and then add 1.0 g KCl powder in order to improve the stability of AuCl₃. Then the structured catalyst (denoted as Au/C/SiC foam) was obtained after evaporation at 85 °C for 4 h. The actual loading of gold was 0.85 g per L Au/C/SiC foam, determined by inductively coupled plasma (ICP).

2.3. Hydrochlorination of acetylene

The prepared Au/C/SiC foam were tested for acetylene hydrochlorination in a fixed-bed stainless steel reactor of 42 mm inner diameter. In the catalytic tests, Au/C/SiC foam was placed in the isothermal region of the reactor, and it was wrapped with quartz cloth to fill the gap between it and tube wall. Hydrogen chloride (gas, 99.9%) and acetylene (gas, 99.9%) were regulated using calibrated mass flow controllers and fed into the reactor after passing through the drying tube of 5A molecule sieves and silica-gel desiccants to remove trace impurities such as air and water vapor, respectively. The temperature of reactor was initially set at 170 °C. Before the reaction, the reactor was purged with high purity nitrogen to remove water vapor and air in the system. After the catalyst was activated by a certain flowing rate of HCl for 2 h, HCl (137 mL/min) and C₂H₂ (124 mL/min) with the molar ratio of 1.1 were fed through reactor, leading to GHSV (C₂H₂) of 120 h⁻¹. The pressure of the system was kept at 0.05~0.06 MPa.

The product analysis consists of two steps. First, the exit gas mixture from the reactor was passed through a tetrafluoroethylene bottle filled with concentrated NaOH solution to get rid of the excess HCl. Then, the compositions of gas stream were analyzed by gas chromatography (HP 7890A with FID detection, HP-AL/S).

2.4. Characterizations

Three-dimensional morphology of SiC foam with hollow structure was characterized by 3D X-Ray micro-CT system. The maximum X-ray energy is 160 kV and the maximum pixel resolution is 1.0 μm. The sample was rotated through 360° about the axis of rotary table, so that the X-rays were able to penetrate the sample from all directions.

The X-ray diffraction (XRD) patterns were recorded with a D/Max 2500PC Rigaku diffractometer, using Cu Kα radiation, λ=0.15418 nm.

The microstructures of the samples were detected by a Field emission scanning electron microscope (SUPRA 35, SEM).

The morphologies of the Au/C samples were observed by a FEI Tecnai F20 electron microscope. The catalyst was crushed into powder and dispersed in ethanol, then the upper supernatant supported on carbon-film-coated copper grids before characterization by TEM.

3. Results and discussion

3.1. Characterization of SiC foam supports

The optical photographs of the prepared solid SiC foam ceramic and hollow SiC foam ceramic after the treatment with boiling NaOH are shown in figure 1. The color of the surface of foam strut changed from silver to green after removing the residual Si by NaOH. Moreover, it is visible that the strut of hollow SiC foam is tubular while the strut of solid SiC foam is compact.
3D X-Ray micro-CT was used to characterize the three-dimensional structure of the novel SiC foam with hollow structure, and the results are shown in figure 2. Figure 2a indicates the actual 3D morphology of the foam ceramic. The yellow region is completely composed of SiC particles, and the hollow cavity can be seen. The SiC skeleton and the hollow cavity overall diagram is shown in Figure 2b. The red region represents the morphology of the hollow cavity, indicating that the inner channel is an integrated state of 3D connectivity. This result proves that SiC foam with hollow structure has been successfully prepared.

3.2. Characterization of SiC foam structured catalysts

Figure 3. XRD patterns of the fresh Au/C/SiC foam.
Figure 3 shows the XRD patterns of fresh Au/C/SiC foam structured catalyst and standard XRD patterns of Au, KCl and α/β-SiC. According to the standard XRD patterns, the structured catalysts are composed by α/β-SiC, KCl and little Au. The characteristic peaks of Au are weak because of the SiC characteristic peak contained in the coating is too strong. The broad peak in the range of 20 to 30 degrees represents the amorphous carbon. No other phase is observed.

The cross-section of C/SiC foam was observed by SEM and the images are shown in figure 4. A good adhesion between the foam strut and the carbon coating is observed and there is no stratification or gap in the radial direction of the coating, which contributes to the long-term use of structured catalysts. Moreover, carbon coatings on two kinds of SiC foam have no difference in morphology but great difference in distribution. The carbon of solid foam is all loaded around the strut (figure 4a), while the carbon of hollow foam is distributed on both sides of the SiC wall (figure 4b). Therefore, the thickness of carbon coating on hollow foam is less than that of solid foam, which proves that hollow foam plays the role of optimizing the distribution of Au/C.

Prepared by the same process, the hollow foam support has a thinner carbon coating which can supply more area for Au loading than solid foam, and smaller Au particles can be obtained. As can be seen from figure 5, the Au particles (black points in figure 5a) of the catalyst on C/SiC foam with hollow foam are smaller than that on C/SiC foam with solid foam. This result can be confirmed according to that the peaks of Au on hollow foam is weaker than that on solid foam (figure 3). The above discussion demonstrates that the use of hollow SiC foam could significantly disperse the distribution of Au/C, thus enhancing the activity and stability of the structured catalyst.

3.3. Catalytic performance
The catalytic properties of Au/C/SiC foam with different structural support as a function of reaction time
are displayed in figure 6. It is clear that the acetylene conversion of the two structured catalysts rapidly exceeds 99% within a few hours, and the activity of Au/C/SiC泡沫 with hollow foam is slightly higher than that with solid foam. Subsequently, the catalytic activity of both structured catalysts decreased slowly with the reaction time. In particular, the conversion of Au/C/SiC泡沫 with hollow foam decreased to 90% after 205 hours, while the time of Au/C/SiC泡沫 with solid foam was 126 h. Au/C/SiC泡沫 with hollow foam exhibited significantly superior stability than Au/C/SiC泡沫 with solid foam, and its selectivity of VCM is above 99.9% too.

![Figure 6. Acetylene conversion and selectivity of VCM of Au/C/SiC泡沫 with different structural support as a function of reaction time.](image)

4. Conclusion

In this study, we successfully prepared a novel SiC foam ceramic with hollow structure to optimize Au/C catalyst loading. The catalyst can be dispersed on both sides of SiC due to the existence of hollow structure, which can be seen from the micro-CT and SEM analysis. Compared to solid foam, hollow foam results in the smaller size and better dispersion of Au active components, which can be derived from the XRD and TEM results.

Moreover, solid foam and hollow foam were used as supports for Au/C/SiC泡沫 catalysts in acetylene hydrochlorination. The Au/C/SiC泡沫 structured catalyst with hollow foam exhibited the better activity and stability, whose conversion of acetylene decreased to 90% after 210 h at 170 °C with a space velocity 120 h^{-1} and $\frac{V(\text{HCl})}{V(\text{C}_2\text{H}_2)} = 1.1$.

In summary, the hollow foam can further disperse the carbon coating, thus refining and dispersing the Au. The excellent performance of structured catalysts with hollow foam demonstrates that it is a potential alternative to catalysts of acetylene hydrochlorination.

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