Original Article

UV-INDUCED POLYMERIZATION OF SIZE-CONTROLLED PLATINUM/POLY[STYRENE-DIVINYLBENZENE-TRI(PROPYlene GLYCOL) DIACRYLATE] HYDROPHOBIC CATALYST BEADS IN MICROFLUIDICS

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A B S T R A C T
The catalytic exchange of hydrogen isotopes between hydrogen and water has been known to be a very useful process for the separation of tritium from tritiated water. For the process, a highly active hydrophobic catalyst is needed. This study provides an effective fabrication method of size-controlled platinum/poly[styrene-divinylbenzene-tri(propylene glycol) diacrylate] [Pt/poly(SDB-TPGDA)] hydrophobic catalyst beads with a narrow size distribution. Platinum nanoparticles were prepared by γ-ray-induced reduction in the aqueous phase first, and then uniformly dispersed in SDB-TPGDA comonomer after the hydrophobization of platinum nanoparticles with alkylamine stabilizers. The porous Pt/poly(SDB-TPGDA) hydrophobic catalyst beads were synthesized by the UV-initiated polymerization of the mixture droplets prepared in a capillary-based microfluidic system. The size of as-prepared catalyst beads can be controlled in the range of 200–1,000 μm by adjusting the flow rate of dispersed and continuous phases, as well as the viscosity of the continuous phase. Sorbitan monooleate and cyclohexanol were used as coporogens to control the porosities of the catalyst beads.

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1. Introduction
The catalytic exchange of hydrogen isotopes between hydrogen gas and water has been widely applied in producing heavy water, removing tritium from tritiated water, and recovering tritium for fusion reactors [1]. Based on this reaction, a liquid phase catalytic exchange (LPCE) process is employed as the most efficient way to handle tritiated water...
due to lower energy consumption and a higher equilibrium separation factor [2,3]. However, conventional catalysts are largely hydrophilic and they lose catalytic activity when contacting liquid water in the LPCE process [4]. By contrast, hydrophobic catalysts are applied in the LPCE process since their surface properties prevent active centers from being covered by liquid water. This thereby allows the transportation of gaseous reactants to active centers. Platinum/styrene-divinylbenzene copolymer (Pt/SDB) is well suited to the LPCE process [5], because it has strong hydrophobicity, good catalytic activity, high specific area, and shows impressive resistance to irradiation.

In many cases, styrene-divinylbenzene (SDB) copolymer is prepared by the suspension polymerization of monomers in the presence of porogens [6]. Porogens of good solubility produce small pores as phase separation occurs late, while porogens of poor solubility produce large pores. As such, a macroporous SDB copolymer can be formed by using poor solubility porogens after they are extracted. However, these SDB copolymer beads prepared by suspension polymerization have a broad particle size distribution which are predominately too small and exhibit relatively low strength. UV light can lead to the solidification of tri(propylene glycol) diacrylate (TPGDA) in the presence of a photo-initiator. We therefore took advantage of this by adding TPGDA and the photo-initiator into the styrene (St) and divinylbenzene (DVB) as comonomer. Copolymerization then occurs under UV-irradiation. This resulting copolymer is referred to as poly(SDB-TPGDA).

Pt is considered to be one of the most active and efficient catalytic metals for hydrogen isotope exchange [7]. Pt particles loaded on SDB copolymers are conventionally prepared by chemical reduction after applying an incipient wetness method. Unavoidable aggregation of Pt particles commonly occurs due to the reduction mechanism of this approach. Small particle size and a narrow distribution of Pt particles can enhance the catalytic activities of Pt-based hydrophobic catalysts [8,9]. Radiation-induced reduction techniques are useful and effective for preparing metal nanoparticles, which are highly dispersed in the aqueous phase [10,11].

Recently, microfluidic technology has been developed to fabricate uniform monodisperse emulsions and polymer particles [12]. The main advantage of the microfluidic method is that the size and morphology of the polymer particles can be conveniently controlled and the fabrication of droplets is fast. Therefore, we adopted microfluidic technology as a new route for the preparation of hydrophobic catalyst beads.

The Pt/poly(SDB-TPGDA) hydrophobic catalyst beads were fabricated in three steps. First, γ-ray-induced reduction was used to produce uniform Pt nanoparticles dispersed in water. Second, alkylamine stabilizers were used to transfer platinum nanoparticles from aqueous to organic media composed of St, DVB, TPGDA, sorbitan monooleate (Span 80), and cyclohexanol [13]. Third, the hydrophobic catalyst beads were fabricated in a capillary-based microfluidic system under UV-irradiation, allowing size control within a narrow size distribution.

2. Materials and methods

2.1. Materials

Styrene (Analytical Reagent grade; AR), Span 80 (AR), cyclohexanol (AR), ethanol (AR), dimethyl silicone oil (AR), petroleum ether 60–90°C (AR) and sodium dodecyl benzene sulfonate (SDBS; AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, P.R. China. DVB was purchased from Sigma-Aldrich Chemistry Ltd., Steinheim, Germany. TPGDA was purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. 1-hydroxycyclohexyl phenyl ketone (HCPK) was purchased from Bide Pharmatech Ltd., Shanghai, P.R. China. Octadecyamine (ODA) was purchased from Aladdin Industrial Corporation, Shanghai, P.R. China. Hexahydrated chloroplatinic acid (H₃PtCl₆·6H₂O) was supplied by Suzhou Jinwo Chemical Co., Ltd. of China, Suzhou, P.R. China. All reagents were used without any further purification.

2.2. Capillary-based microfluidic device

A capillary-based microfluidic device was employed to prepare Pt/poly(SDB-TPGDA) hydrophobic catalyst beads. It was assembled using fused silica capillary tubing (452/670 μm or 100/162 μm inner/outer diameter; Polymicro Technologies), polytetrafluoroethylene (PTFE) tubing (1.8 mm inner diameter; Fisher Scientific Bioblock), and a T-junction (P-728-01; Upchurch Scientific). As Fig. 1A shows, the fused silica tubing is inserted inside the T-junction along its main axis, and the capillary tip exits the T-junction at the center of a PTFE outlet tube. To deliver the continuous and dispersed phases at a specific flow rate, two syringe pumps (LSP01-1A, Longer pump) were used. The continuous phase was injected perpendicular to the main axis of the T-junction, while the dispersed phase was injected via the capillary. These two different phases meet at the outlet of the capillary, and consequently the dispersed phase is shaped as droplets under the shear force of the continuous phase, as shown in Fig. 1B–1D. The formation of droplets was observed by using a charge-coupled device (CCD) camera (uEye UI-2220SE, IDS) with a microscope (XSP-30E, Shanghai halibut instrument Co. Ltd).

2.3. Fabrication of hydrophobic catalyst beads

2.3.1. Preparation of hydrophobic comonomer dispersible Pt nanoparticles

H₃PtCl₆·6H₂O was dissolved in deionized water followed by the addition of isopropyl alcohol as a radical scavenger and SDBS as a surfactant. The mixed solution was deoxidized by bubbling with nitrogen and then irradiated by a 60Co source at a dose rate of 50 Gy/min for 24 hours. The composition of the solution is listed in Table 1. Pt nanoparticles dispersed in aqueous solution were obtained following γ-ray irradiation by 60Co.

The dispersed Pt nanoparticles were hydrophilic in aqueous solution and were converted to hydrophobic...
nanoparticles by modifying them with ODA. The aqueous solution used to disperse the Pt nanoparticles was added to the same volume of ODA ethanol solution (1.0 wt%). The combined solution was mixed for 20 minutes and then left for another 5 minutes. Subsequently, most Pt nanoparticles modified by ODA floated in the liquid phase spontaneously. The nanoparticles were then separated from the solution by centrifugation. Hydrophobic Pt nanoparticles were separated from the aqueous phase after removing the bottom liquid and drying. Finally, the comonomer organic solution composed of St, DVB, TPGDA, HCPK (as photoinitiator), Span 80, and cyclohexanol (as coporogens), was added to disperse the hydrophobic Pt nanoparticles.

2.3.2. Preparation of Pt/poly(SDB-TPGDA) hydrophobic catalyst beads

The comonomer organic solution was mixed with modified Pt nanoparticles, to produce a dispersed phase. The composition of the mixture is listed in Table 2. The whole mixture was treated by using ball milling for 6 hours to achieve a stable Pt-dispersed organic phase. Dimethyl silicone oil with a viscosity of 1,000 cP was employed as a continuous phase. Comonomer droplets produced in the process were solidified in a collection beaker at the outlet of tubing under UV irradiation. After being washed with petroleum ether and ethanol several times, the beads obtained were placed in a Soxhlet apparatus, equipped with enough ethanol for 24 hours, to extract the coporogens. Finally, 0.5 wt% Pt-loaded Pt/poly(SDB-TPGDA) hydrophobic catalyst beads were achieved after drying at room temperature.

2.4. Characterization

The comonomer droplet formation in the microfluidic device was monitored by a CCD camera (uEye UI-2220SE, IDS) with an optical microscope (XSP-30E, Shanghai halibut instrument Co., Ltd.). The size and dispersion of the Pt particles dispersed in the aqueous phase, the organic phase, and the catalyst beads were determined by transmission electron microscopy (TEM; JEM-2011; Japan Electron Optics Laboratory Co., Ltd., Mitaka, Japan) operated at 120 kV. The microstructure of Pt/poly(SDB-
TPGDA) catalyst beads were observed with a scanning electron microscope (SEM; KYKY-AMRAY 1000B; Scientific instrument factory of Chinese Academy of Sciences, China). X-ray diffraction (XRD) analysis was conducted for the Pt/poly(SDB-TPGDA) catalyst beads using a Cu Ka source (\(\lambda = 0.154056 \text{ nm} \); TTR-III; Rigaku Industrial Corporation, Tokyo, Japan) at a scanning rate of 2°/min from 30° to 90°. The valence state of Pt in the Pt/poly(SDB-TPGDA) catalyst beads was confirmed by X-ray photoelectron spectroscopy (XPS; ESCALAB 250; Thermo-VG Scientific, USA). The special surface area and pore size distribution of the Pt/poly(SDB-TPGDA) catalyst beads were measured by a surface area and porosity analyzer (V-sorb 2800; Gold APP Instruments Corporation, Beijing, China).

3. Results and discussion

3.1. Hydrophobic comonomer dispersible Pt nanoparticles

Radiolysis of water forms radiolytic molecular and radical species due to interaction with high-energy radiation. The produced solvated electrons and hydrogen atoms have a strong reducing capability that can reduce Pt metal ions to lower valences and ultimately to Pt metal atoms. These Pt metal atoms formed Pt particles by self-assembly. The protection by the surfactant, SDBS, limited the excess agglomeration of Pt particles.

The Pt particles which dispersed in water carried negative charges due to the coating of dodecyl benzene sulfonic acid groups from the surfactant. ODA is a long-chain hydrophobic molecule which can be dissolved in ethanol. ODA ethanol solution carries positive charges based on its protonation. After mixing the aqueous dispersing Pt particles and ODA ethanol solution, ODA combined with Pt particles due to electrostatic interaction. The Pt particles then separated from the mixture of ethanol and water due to the hydrophobicity of ODA. Finally, hydrophilic Pt particles changed into hydrophobic ones [14].

Fig. 2A shows the TEM image of Pt nanoparticles dispersed in the aqueous phase while Fig. 2A shows those dispersed in the organic phase. As Fig. 2 shows, the Pt particles had a size range of ~3–8 nm and dispersed well both in the aqueous and organic phase. No obvious agglomeration of Pt particles was observed. It proved that the phase transfer treatment using ODA did not affect the dispersion of Pt particles in organic phase.

3.2. UV-induced polymerization of Pt/poly(SDB-TPGDA) catalyst beads

In conventional methods for the preparation of SDB beads, such as suspension polymerization, the monomer droplets formed by mechanical stirring are solidified by continuous heating for several hours in the presence of a thermal initiator. It is not realistic to apply this heating method due to the fact that the droplets produced in the microfluidic device need to be solidified in a relatively short time so that beads of a uniform size can be formed. In order to solidify the droplets rapidly, HCPK was added as a photoinitiator, which would be decomposed into free radicals under UV-light. However, the efficiency of the polymerization reaction between St and DVB with these free radicals was far too low to meet our requirement. TPGDA is sensitive to the free radicals decomposed by HCPK, and the polymerization of St and DVB was found to be quite rapid by adding TPGDA and HCPK. In our opinion, the free radicals produced by HCPK caused the polymerization of TPGDA, and new free radicals were produced in this reaction, which promoted the polymerization reaction speed between St and DVB. The specific reaction mechanism needs further research. The whole UV-induced polymerization time for every comonomer droplet is within 10 minutes.

The UV-induced polymerization of the comonomer droplets containing TPGDA and HCPK was fast enough to keep the uniformity of solidified beads with the capillary-based microfluidic device. Fig. 3 shows different sizes of Pt/poly(SDB-TPGDA) catalyst beads with narrow size distribution in different conditions by our method.

The Pt/poly(SDB-TPGDA) catalyst beads were prepared by solidifying the uniform droplets produced by the capillary-

Fig. 2 – TEM images of Pt nanoparticles. (A) Pt nanoparticles in aqueous with a scale bar of 20 nm; (B) Pt nanoparticles in comonomer with a scale bar of 20 nm. Pt, platinum; TEM, transmission electron microscopy.
based microfluidic device. The size of the comonomer droplets can be controlled by changing operating parameters, such as the flow rate ratio of the continuous phase to the dispersed phase and the viscosity of the continuous phase. The relationship between the diameter of beads and the flow rate ratio of the continuous phase to dispersed phase for different continuous viscosities has been researched in our previous work [15].

Fig. 4 shows the XRD pattern for the Pt/poly(SDB-TPGDA) catalyst beads without eliminating background. The characteristic diffraction peaks of Pt (111), Pt (200), Pt (222) and Pt (311) were observed at $2\theta = 40.2^\circ$, $46.3^\circ$, $67.5^\circ$, $81.2^\circ$, respectively. These results are consistent with the face-centered cubic structure of platinum (Joint Committee on Powder Diffraction Standards; JCPDS Card No. 04-0802). The XRD results indicated that the reduction of the platinum precursor to its metallic form was successful and Pt particles were deposited in the poly(SDB-TPGDA) beads successfully.

In our experiment, the reduction of Pt was performed in water under $\gamma$-rays, and the Pt/poly(SDB-TPGDA) catalyst beads were fabricated and handled below 100°C without contacting any oxidant. Thus, it was reasonable to assume that Pt was in the zero valence state in the as-prepared catalyst beads. The XPS spectra of the as-prepared catalyst beads were obtained to identify the surface chemical states of the metal particles. As Fig. 5 shows, there is only one doublet in the Pt 4f XPS spectra. Comparing the result in Fig. 5 to the standard XPS spectra of Pt base peak in the Handbook of X-ray Photoelectron Spectroscopy [16], the result in Fig. 5 was found to be identical to the latter. The doublet has a Pt 4f$_{7/2}$ peak at 71.4 eV which was assigned to Pt$^{0}$. Consequently, all Pt particles in the as-prepared beads were in the elemental state and there were no measurable amounts of Pt oxides produced during the treatment process.

### 3.3 Microstructure

Span 80 and cyclohexanol were added as coporogens in the comonomer. Cyclohexanol is known as an efficient conventional porogen for building up the porosity in the SDB copolymer [17]. Span 80 was applied as a coporogen due to its poor
solubility and high viscosity [18]. After removing the coporogens, a macroporous structure was formed in the Pt/(SDB-TPGDA) catalyst beads.

The SEM image of the inner part of an as-prepared catalyst bead is shown in Fig. 6. The observation is that the porous structure of catalyst beads is comprised of many voids which exist between the interior microspheres and their agglomerates. Thus, the macropores of the as-prepared beads are considered to be the interstices between these microspheres and agglomerates, which were formed due to the phase separation occurring early between the polymer and the Span 80 phase during the UV-induced polymerization [19]. After finishing polymerization and extracting the coporogens with a Soxhlet apparatus, this macroporous microstructure was formed, which provided enough space for active Pt metal.

The high viscosity of Span 80 assisted the dispersion of Pt nanoparticles in the comonomer. As shown in Fig. 7, a few Pt particles are located together just between copolymer microspheres in the as-prepared catalyst beads. The Pt particles modified by ODA tended to be dispersed in the Span 80 phase while phase separation occurred between the Span 80 phase and polymer phase during polymerization. During the extracting process, in which coporogens were removed, Pt particles were agglomerated and adhered to the surface of the copolymer microspheres to reduce their surface energy. Also, the conjugated system formed by the unsaturated bonds in poly(SDB-TPGDA) and Pt d-orbital enhances the Pt particles’ affinity to attach onto the polymer.

The specific surface areas of the as-prepared catalyst beads were estimated using the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) method. Fig. 8 shows the isotherms and pore characteristics of the catalyst samples measured by N2-physisorption. The BET surface area is 20.30 m²/g, and the BJH mean pore diameter and volume are 29.56 nm and 0.15 m³/g, respectively. As Fig. 8A shows, the isotherm of the as-prepared catalyst beads was a type II isotherm, which in this case is characteristic of macroporous materials. As Fig. 8B shows, the BJH pore diameter distribution curve illustrates that the most widely distributed pore size occurs in the macropore region of the as-prepared catalyst beads which included the pore sizes of ~100 nm and ~65 nm. In agreement with the SEM results, the macropores were formed by early phase separation between the polymer and Span 80 phases. These macropores were favorable for the transport of the reactant or product molecules to and from the active centers. Fig. 8B also shows that there were a few micropores and mesopores relating to cyclohexanol and DVB content which contributed to the relatively low specific surface area of the as-prepared catalyst beads. The synergy of Span 80 and cyclohexanol induced this type of pore diameter distribution.

The high specific surface area of catalyst beads usually raises the catalytic efficiency of gas phase catalysis. However, as a catalyst used for liquid phase exchange reaction, the catalytic efficiency cannot be improved by increasing micropores when the size of the micropores is too small to allow the liquid reagent to infiltrate. Thus, it was worth sacrificing some surface area to get more macropores. Although more macropores were favorable for the improvement of the catalytic efficiency of the as-prepared catalyst beads and can be obtained by increasing Span 80 content in comonomer solution, the excess macropores contained in the catalyst beads induced a decrease in the compression strength of the catalyst beads, which may not satisfy the requirements of engineering applications requiring higher bead compression strengths. Therefore, it is necessary to control the porosity of the Pt/poly(SBD-TPGDA) catalyst beads for unique applications.

Fig. 6 – SEM image of microstructure in Pt/poly(SDB-TPGDA) beads with scale bars of 5 μm and 10 μm. SDB-TPGDA, styrene-divinylbenzene-tri(propylene glycol) diacrylate; SEM, scanning electron microscope.

Fig. 7 – TEM image of Pt in poly(SDB-TPGDA) catalyst beads with a scale bar of 40 nm. SDB-TPGDA, styrene-divinylbenzene-tri(propylene glycol) diacrylate; TEM, transmission electron microscopy.
4. Conclusion

This work demonstrated that the use of simple capillary-based microfluidic devices allows for the synthesis of size-controlled porous Pt/poly(SDB-TPGDA) hydrophobic catalyst beads in the size range of 200–1,000 μm. An excellent Pt nanoparticle distribution in the hydrophobic matrix was achieved thanks to the use of alkylamine as a surface modifier for changing the surface characteristic of Pt nanoparticles from hydrophilic to hydrophobic. Rapid UV-initiated polymerization of SDB-based comonomer droplets was obtained by adding TPGDA monomer with its photoinitiator in the comonomer, which is beneficial to synthesize Pt/poly(SDB-TPGDA) hydrophobic catalyst beads with a high sphericity. The porous structure of as-prepared hydrophobic catalyst beads were formed by employing Span 80 and cyclohexanol as coporogens.

Conflicts of interest

The authors declare no conflict of interest.

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REFERENCES


Fig. 8 – Hydrophobic catalyst beads. (A) N2 adsorption–desorption isotherms and (B) the BJH pore diameter distribution curve of the hydrophobic catalyst beads. BJH, Barrett–Joyner–Halenda; STP, Standard Temperature and Pressure.


