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Journal Name

ARTICLE

CO₂-in-PEG emulsion-templating synthesis of poly(acrylamide) with controllable porosity and their use as efficient catalyst supports

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The CO₂-in-PEG emulsions were made with Pluronic 104 at different CO₂ pressure. In these emulsions, porous poly(acrylamide)s (PAM) nanoparticles around 250 nm were prepared. The nano-sized metal Ru particles were loaded on the porous PAM, which have much higher catalytic activity for benzene hydrogenation reaction compared to commercial Ru/C catalyst. More importantly, the drop size of internal phase CO₂ and the pore diameter of as-prepared PAMs can be simply tuned by changing the pressure of CO₂.

1. Introduction

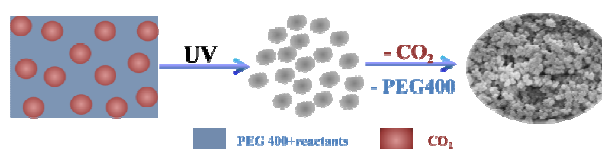
Porous polymers have attracted much attention owing to their diverse fascinating topologies, pore size tunability, and extensive usage in gas storage and separation,¹⁻³ drugs release,^{4,5} catalysts,⁶⁻⁸ membranes,⁹ electrode materials,¹⁰ phase separation,¹¹ etc. Several reliable methods, such as direct templating,¹²⁻¹⁵ block copolymer self-assembly,¹⁶⁻¹⁸ direct synthesis methodology¹⁹⁻²¹ and interfacial polymerization,²²⁻²⁴ could be used for preparation of porous polymers. Particularly, emulsion polymerization is an excellent method for preparation of porous polymers, and emulsion-templating techniques (high internal phase emulsion in-particular) are usually used to prepare porous polymers and other materials, wherein the internal phase (nonpolymerizable phase) usually act as a porogen.²⁵⁻²⁹ However, in some cases, both the internal phase and the continuous of emulsion might play a role as porogen that template porosity.³⁰ Traditional oil-in-water (O/W) emulsions provide a direct template to a variety of porous hydrophilic polymers. The use of organic solvents suffers from economic and environmental costs and post-treatment complexity.

CO₂ is cheap, non-toxic, and non-flammable. Compressed (liquid or supercritical) CO₂ could be used to form emulsion as the internal phase.^{30,31} The properties of compressed CO₂ can be tuned continuously by changing pressure and temperature.³² So far, some works on the formation of CO₂ emulsions, include CO₂-in-water emulsions and CO₂-in-ILs emulsions have been reported.^{30,33,34} These emulsion systems have been used for preparation of porous

polymers.

In the preparation processes, CO₂ can be easily removed by reducing pressure and no contamination on the porous structure could happen. Besides compressed CO₂, liquid poly(ethylene glycol)s (PEGs) are regarded as another green solvent. They are cheap, easily available, and have good solvation powers. More importantly, their properties are tunable by simply changing the molecular weight of PEG.³⁵ Therefore, liquid PEGs have been used as solvent in various fields.³⁶ To form microemulsions or emulsions of PEG and CO₂ can expand the utility of these two green solvents. Recently, we have found that the PEG-in-CO₂ microemulsion could be formed with the aid of surfactant N-EtFOSA (C₂H₅NHSO₂C₈F₁₇).³⁷ However, the emulsion consisted by PEG and CO₂ has not been explored.

Herein, we prepared CO₂-in-PEG emulsion used non-fluorous Pluronic 104 as surfactant. Porous poly(acrylamide) (PAM), which is widely used in stimuli responsive materials as polymer matrix^{38,39} and membrane science,⁴⁰ was synthesized in the formed PEG emulsion under UV irradiation ($\lambda = 254$ nm) through a CO₂-in-PEG emulsion templating route (Scheme 1). Furthermore, the PAM was used as a support to load Ru nanoparticle and Ru/PAM composites were synthesized under tip sonication. The as-synthesized Ru/PAM composites have high catalytic efficient for hydrogenation of benzene. The CO₂-in-PEG emulsion could be used to replace the CO₂-in-water emulsion in case the reactant is susceptible to water.



Scheme 1. Schematic illustration for the formation of porous polymers by a CO₂-in-PEG emulsion templating route.

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2. Experimental

2.1 Materials

The surfactant Pluronic104 (P104, EO₂₇PO₆₁EO₂₇) was obtained from BASF Corporation. The PEG-400 (poly(ethylene glycol)), N,N'-methylenebisacrylamide (laboratory grade), and benzophenone (97% purity) were purchased from Alfa Aesar. Acrylamide (AR) was produced by Beijing Chemical Reagent Company. Ruthenium (III) Chloride Hydrate (RuCl₃·3H₂O) was purchased from Shenyang Jinke Reagent Plant. Benzene (AR) was obtained from Beijing Chemical Reagent Company. Commercial Ru/C catalyst was purchased from Baoji Ruike Corporation, China. Double-distilled water was used. CO₂ (> 99.99% purity) and H₂ (99.99% purity) were provided by Beijing Analytical Instrument Factory. PEG-400 was dried at 60 °C under vacuum for 48 h before use. All other materials were used directly without further purification.

2.2 Preparation of emulsions

The solution of surfactant in PEG was prepared by mixing P104 with PEG-400 together and the solution was transparent after dissolution. The apparatus for preparation of the emulsions consisted of a gas cylinder, a high-pressure sample cell with two quartz view windows and the cell volume was 9.5 ml, a high-pressure pump, a pressure gauge, and a YKKY A2 digital temperature controller. The apparatus and procedures were similar to those used previously.³⁰ In a typical experiment, 0.48 g of P104 was added in 4.8 g PEG-400 at room temperature and stirred until they were totally miscible with the concentration of 9.1 wt%. Then, the solution was transferred into a steel cell, which is immersed in a water bath, with a constant temperature. After that, liquid CO₂ was charged into the solution and stirred at desired pressure until the emulsion formed. At last the emulsions were stored at and the phase behavior at different pressure was observed.

2.3 Synthesis and Characterization of PAM

9.1 wt% P104/PEG-400 (5.28 g) solutions were loaded in the view cell (9.5 mL). The monomer acrylamide (0.8g), cross linker N,N'-methylenebisacrylamide (0.04 g) and initiator benzophenone (0.04 g) were added into the solution at 30 °C. CO₂ was flowed into the cell with stirring until the desired pressure was reached. The two quartz view windows of the cell was radiated by two high-pressure mercury vapor lamps at wavelength of $\lambda = 254$ nm for 1 hour. Then CO₂ was released slowly. The white product was washed with acetone for several times and dried at 60°C under vacuum for 48 h.

The morphologies of PAMs were characterized by a HITACHI S-4800 scanning electron microscope and JEOL-1010 transmission electron microscope at 100 kV. The macroporosities were recorded by mercury intrusion porosimetry using a Micromeritics Autopore IV 9500 porosimeter. The samples were subjected to a pressure cycle starting at 5 psia, increasing to 44500 psia in predefined steps

to give pore size/pore volume information. The porosity properties were determined by N₂ adsorption/desorption isotherms using a Quadrasorb SI-MP system. FT-IR spectra were obtained by a Bruker Tensor 27 spectrometer. The TGA measurement was carried out on a TA Q50 with N₂ flow of 40 mL·min⁻¹.

2.4 Synthesis of Ru/PAM composites

Typically, 0.05 g RuCl₃·3H₂O and 0.5 g PAM were initially dispersed in 50 mL of methanol solution to form a uniform suspension with the aid of tip sonication (Vibra Cell CVX, 500 W, 20 kHz) for 10 min. Then, 30 mL of a NaBF₄ (1g) methanol solution was added drop-wise into the dispersion containing metal precursor under tip sonication within 20 min. After the NaBF₄ methanol solution was completely added, the mixture was continually subjected to tip sonication for 30 min. Finally, the obtained mixture was centrifuged, and the collected precipitate (Ru/PAM) was washed repeatedly with ethanol. Afterwards, the Ru/PAM catalyst was vacuum-dried at 60 °C for 12 h.

2.5 Hydrogenation of benzene catalyzed by Ru/PAM

The hydrogenation reaction was carried out in a stainless reactor of 15 mL. In a typical experiment, benzene (1.1 mL) and desired amounts of catalysts (benzene/Ru (mol/mol) = 5000) were added into the reactor. After being sealed, the reactor was put into a constant-temperature reacting furnace at a known temperature. H₂ was then charged into the reactor until the desired pressure was reached, and the stirrer was started. After a desired reaction time, the excess H₂ was released slowly. Then, the mixture was diluted by ethyl acetate. After that, the mixture was analyzed by gas chromatography (GC, Agilent 7890B), and identification of the products was done by GC-MS (Shimadzu QP2010).

3. Results and discussion

3.1 Formation of CO₂-in-PEG emulsions

In the process for the formation of CO₂-in-PEG emulsions, P104 was utilized as the surfactant to emulsify PEG-400 and CO₂. It was found that the CO₂-in-PEG emulsions were formed when the volume ratio of PEG to total volume of the cell (V_{PEG}) was 0.6. The phase behaviors of the P104/PEG/CO₂ systems were observed at 30 °C and 8.0 MPa, 10.0 MPa, 12.0 MPa and 14.0 MPa, respectively. The surfactant concentration with respect to the amount of PEG is 9.1 wt%. When the pressure of the CO₂ is higher than 7.0 MPa, which is the saturated vapor pressure of CO₂ at 30 °C, the CO₂-in-PEG emulsions can be formed. Fig. 1 shows the photograph of the CO₂-in-PEG before (a) and after phase separation (b) at 14.0 MPa. A system where a creaming front is formed (rising CO₂ droplets) followed by the appearance of an upper clear phase (coalescence of CO₂ droplets) is due to the creaming of dispersed CO₂ droplets (CO₂-in-PEG emulsion) rather than to

the coalescence of dispersed PEG droplets (PEG-in-CO₂ emulsion). The surfactant P104 favors the bottom PEG phase. It is identified as a CO₂-in-PEG emulsions.⁴¹ After stopping the stirring, the system separated into two phases, an upper CO₂-rich phase and a lower PEG-rich phase.

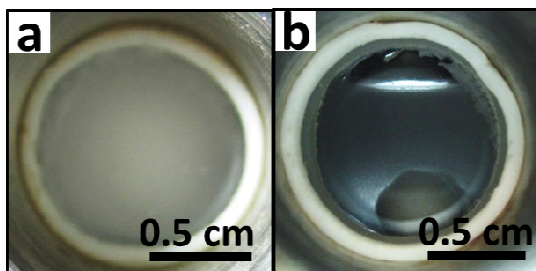


Fig. 1. Photograph of the CO₂-in-PEG emulsion before (a) and after phase separation (b) in 14.0 MPa.

3.2 Morphologies of PAMs

Fig. 2 shows the SEM and TEM images of the PAM synthesized within the emulsion at 14.0 MPa as an example. The macropores were about 200-500 nm. It is observed that the macropores were made of several particles, which is about 200 nm and dispersed uniformly. We also studied the properties of the polymer in the pressure of 8.0 MPa, 10.0 MPa and 12.0 MPa (Fig. S1). As shown in Fig. S1, it was found that the effect of the CO₂ is more obvious at higher pressure. The particles of PAMs synthesized became more uniform with the increase of CO₂ pressure. In addition, the particles of the polymer under different CO₂ pressure were non-sticky. Furthermore, in order to prove the templating effect of the CO₂-in-PEG emulsion, some control experiments were conducted. When the polymerization was conducted in PEG alone or the system of PEG and P104 in the absence of CO₂, the synthesized PAM had no uniform shape and no obvious pores could be observed (Fig. S2). These results indicated that the both the internal phase and continuous phase of CO₂-in-PEG emulsion was the template for the growing of the polymers and the distribution of the particles could be tuned by the CO₂ pressure. However, we can not exclude the possibility of P104 as porogen when CO₂ is charged into the mixture.

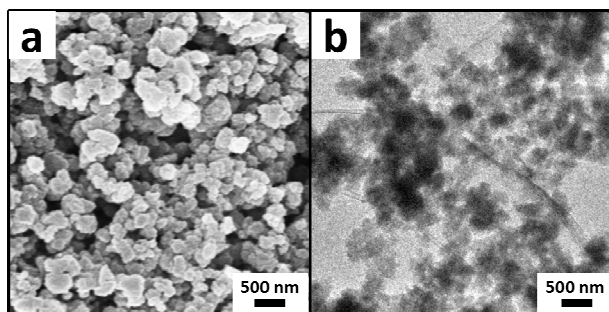


Fig. 2. SEM (a) and TEM (b) images of the PAM synthesized in CO₂-in-PEG emulsion at 14.0 MPa.

3.3 Porosities of PAMs

The mercury porosimetry method was utilized to determine the macroporosity of the as-synthesized PAM materials.³⁰ Fig. 3 presents the macropore size distribution of the PAM at different pressure. It was found that the distribution of the macropores was wide. More importantly, Fig. 3 indicated that the pore size distribution of the PAM was narrowed and moved to the small pore diameter with the increase of the pressure, which is consistent with that observed from the SEM and TEM images (Fig. 2 and Fig. S1). Furthermore, if the structure of the CO₂-in-PEG emulsion could be retained during polymerization, i.e., CO₂ was act as porogen, the degree of porosity of the PAM in as-formed emulsion could reach up to 40%, which is equal to the volume ratio of the internal phase. However, porosity degree (> 69%) of the as-synthesized PAM formed in the emulsions at different CO₂ pressure was higher than the volume fraction of CO₂, which might be caused by the templating effect of the PEG-400 during polymerization.¹⁶ This is a proof that both the internal CO₂ and the continuum phase PEG could play a role as porogen, which is similar to Peng and Zhang's report.³⁰ The excess macropores with sizes in the hundreds of nanometers range as shown in Fig. 2 might originate from the release of the CO₂ after polymerization. In addition, the effect of the CO₂ was also more obvious on the distribution of the macropores (Fig. S1) and the macropores were dispersed more uniformly along with the rising CO₂ pressure. In addition, the synthesized PAM prepared in PEG alone or the system of PEG and P104 in the absence of CO₂ showed no macropores, which was consistent with the results obtained from the SEM examinations (Fig. S2), further indicating the templating role of both the internal phase and continuous phase of CO₂-in-PEG emulsion. However, it should noted that again that P104 might act as porogen too in the emulsion. These results further indicated that the CO₂-in-PEG emulsion was the template to induce the growing of the polymers.

The porosity properties of the PAM were also investigated by N₂ adsorption-desorption method after the sample was degassed at 100 °C overnight (Fig. S3 and Table S1). It was found that the mesopore size increased with the increasing CO₂ pressure (Table S1), which could be caused by the enlarged P104 micelles at higher pressures due to the templating effects of micelles on the mesopore formation.⁴² Meanwhile, the BET surface area and mesopore volume also increased with the increasing CO₂ pressure (Table S1). This could be resulted from that CO₂ could be solubilized in bulk PEG-400 except for dissolving inside micelles and the amount of CO₂ solubilized in the bulk phase increased with CO₂ pressure, a phenomenon which had been reported for CO₂-in-water micelles,^{43,44} and thus caused the PAM synthesized at higher pressure was more porous after releasing CO₂. Therefore, the BET surface area and mesopore volume increased with the increasing of the CO₂ pressure. In addition, the total macropore volume increased with CO₂ pressure because of the increasing CO₂ droplet size as the template of macropore (Table S1). However, the increase in macropore volume was less than mesopore volume because the PEG-400 became more CO₂ soluble at higher pressures.³⁷ Therefore, the volume of mesopores compared to the volume of macropores changed with the CO₂ pressure.

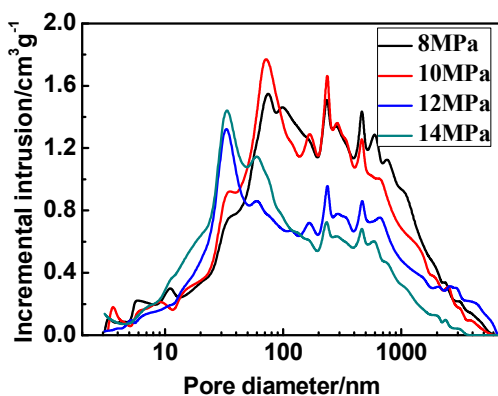


Fig. 3. Macropore size distribution of the PAM synthesized at 8.0 MPa, 10.0 MPa, 12.0 MPa, and 14.0 MPa.

3.4 FT-IR spectra and TG of PAMs

The IR spectra of the PAMs synthesized in the emulsions and the pure acrylamide were also examined and the results were shown in Fig. 4. The acrylamide absorption peak of $=\text{CH}_2$ in 960 cm^{-1} was vanished in the spectrum of PAMs (curve a-d), confirming that monomers have polymerized completely.⁴⁵ Meanwhile, in Fig. 4, there was a strong absorption at about 1663 cm^{-1} , which could be attributed to the C=O stretching in the $-\text{CONH}_2$ group, and the shoulder around 1610 cm^{-1} was corresponding to the NH_2 bending.⁴⁵ TGA curves (Fig.5) show that the polymer can stable at about $250\text{ }^\circ\text{C}$. In addition, it was also indicated that the PAMs synthesized in CO_2 -in-PEG emulsions at different pressures had similar stability.

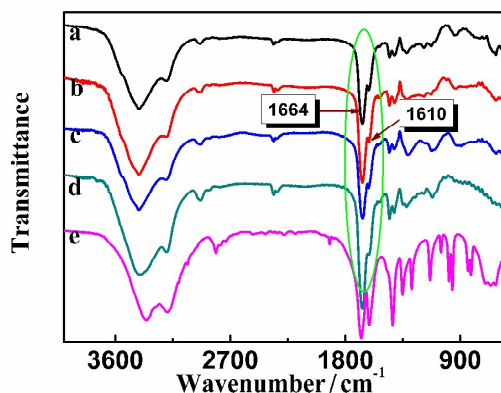


Fig. 4. FT-IR spectra of PAMs synthesized in CO_2 -in-PEG emulsions at CO_2 pressure of 8.0 MPa (a), 10.0 MPa (b), 12.0 MPa (c), 14.0 MPa (d) and the acrylamide monomer (e).

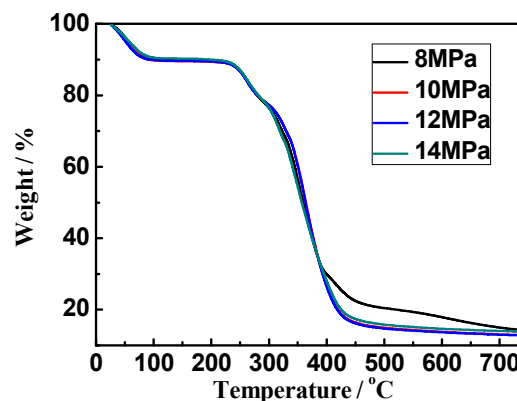


Fig. 5. Thermogravimetric curves of the PAMs synthesized in CO_2 -in-PEG emulsions at different pressures.

3.5 Formation mechanism

The mechanism for the formation of macroporous PAM polymers in the as-formed CO_2 -in-PEG emulsion was presented in Scheme 1. At first, the reactants were dissolved in PEG phase. Then polymerization could occur stimulated by UV light, where the emulsion might act as template for the macropore formation. After the removal of CO_2 , PEG, and surfactant, a highly porous polymer could be formed (Scheme 1). Since more P104 can be dissolved in CO_2 at higher pressure, the interface between the external phase PEG and internal phase CO_2 is less curved, and furthermore the CO_2 droplet size is increased. Therefore, the as-synthesized PAMs have larger macropores due to the templating effect of the CO_2 internal phase at higher CO_2 pressure.

3.6 Ru/PAM composite

As discussed above, the as-synthesized highly porous polymers had both macropores and mesopores. They have been used in catalysis as an efficient support. Herein, we utilized the as-prepared PAM as a support for a Ru catalyst. The Ru/PAM nanocomposites were prepared under tip sonication. The morphology of the Ru/PAM composites was examined by TEM. As shown in Fig. 6a, the PAM was loaded dispersedly with Ru nanoparticles with a mean diameter of about 2 nm. The high-resolution TEM (HR-TEM) examination (Fig. 6b) and the energy dispersive X-ray spectroscopy (EDS) analysis (Fig. 6c) confirm the existence of Ru element. The loading content of the Ru on PAM was 2.24 wt%, as determined by ICP-AES method.

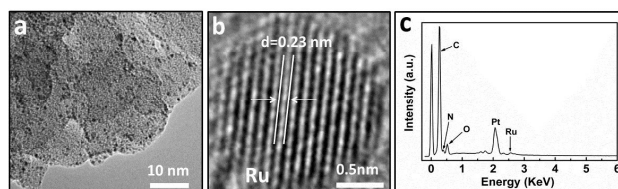


Fig. 6. TEM image (a), HR-TEM image (b) and EDS (c), of Ru/PAM particles obtained at CO_2 pressure of 14.0 MPa.

The catalytic performance of the as-synthesized Ru/PAM for hydrogenation of benzene was examined using molecular H_2 as the

hydrogen resource under solvent-free conditions, and the results were presented in Table 1. Control experiments showed that the reaction could not happen without catalyst (Table 1, entry 1) or with PAM as the catalyst (Table 1, entry 2), indicating the catalytic effect of Ru nanoparticles. The catalytic activity was affected by the reaction temperature significantly from 30 °C to 60 °C with the same reaction time of 2.5 h (Fig. S4). Benzene was almost completely converted into cyclohexane within 2.5 h at 60 °C and at H₂ pressure of 6.0 MPa when using a substrate/Ru molar ratio of 5000 (Table 1, entry 5) and the turnover frequency (TOF) was about 2460 h⁻¹. In contrast, the conversion of benzene was only 23% at 30 °C under the same reaction conditions with 60 °C with a TOF of 577 h⁻¹. To our delight, the conversion of benzene could reach 93% with a TOF of 486 h⁻¹ when the reaction time was prolonged to 12 h at 30 °C (Table 1, entry 6). In addition, it was found that the H₂ pressure could also affect the reaction activity. When the H₂ pressure was decreased from 6.0 MPa to 2.0 MPa with a reaction time of 2.5 h at 60 °C, the conversion of benzene decreased from >99% to 46% (Table 1, entry 8). Furthermore, the Ru/PAM could be reused at least four times without considerable decrease in the benzene conversion (Table 1, entries 5 and 8-11), indicating the catalyst was stable under the reaction conditions in our reaction system. For comparison, the benzene hydrogenation was performed using a commercial Ru/C catalyst under the same conditions (Table 1, entry 12). The TOFs of the Ru/PAM are much higher than commercial Ru/C catalyst. These results indicate that the as-synthesized Ru/PAM catalyst has a much higher activity.

Table 1. Catalytic activity test for the hydrogenation of benzene.^a

Entry	Catalyst	P _{H2}	T (°C) ^b	t (h) ^b	C (%) ^c	TOF ^d
1	--	6	60	2.5	0	--
2	PAM	6	60	2.5	0	--
3	Ru/PAM	6	60	1 h	42	2634
4	Ru/PAM	6	60	2 h	96	2460
5	Ru/PAM	6	60	2.5 h	>99	>2483
6	Ru/PAM	6	30	12 h	93	486
7	Ru/PAM	4	60	2.5 h	72	2258
8	Ru/PAM	2	60	2.5 h	46	1154
9	Ru/PAM (2 nd)	6	60	2.5 h	>99	>2483
10	Ru/PAM (3 rd)	6	60	2.5 h	>99	>2483
11	Ru/PAM (4 th)	6	60	2.5 h	>99	>2483
12	Ru/C	6	60	7 h	93	664

^aReaction conditions: benzene 1.1 mL; benzene/Ru (mol/mol) = 5000.
^bT=Temperature, t=Time. ^cYield of cyclohexane by the hydrogenation of benzene. ^dTurnover number (TON) = mol of product (cyclohexane) per mole of Ru, turnover frequency (TOF) = TON·h⁻¹.

Conclusions

In this study, CO₂-in-PEG emulsion was first formed by non-fluorous surfactant P-104. Then porous PAMs, which could be used as support for metal catalysts, were synthesized in the emulsion at different CO₂ pressure. Furthermore, we synthesized the porous Ru/PAM nanocomposites, which were found to be high efficient for catalyzing hydrogenation of benzene. Moreover, the drop size of internal phase CO₂ and the pore diameter of as-prepared PAMs can be simply tuned by changing the pressure of CO₂. This work presents a novelty method for preparation of porous metal/polymer nanocomposites with highly dispersion, which could be used as catalysts in various catalytic reactions.

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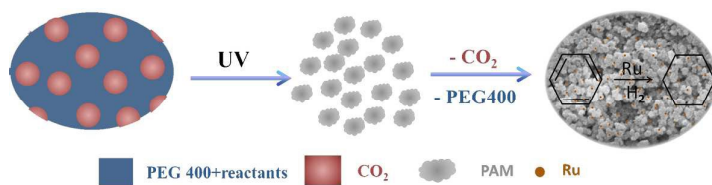
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