Synergistic Effect of Ethylene Glycol and Active Surface Group of SBA-15 under Ultrasound to Improve Catalytic Properties of Pd/SBA-15

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Abstract. Using ultrasonic methods in preparation of noble metal nanocatalysts is a hot spot in catalysis. In this paper, the synthesis of mesoporous material SBA-15 supported palladium catalyst Pd/SBA-15 was done by ultrasound assisted reduction and the synergistic effect between reductant and SBA-15 under ultrasound was discussed. The interaction of reductant ethylene glycol and active surface groups of SBA-15 under ultrasound led to the change in structure and surface properties of SBA-15, so that oxygen element in the structure of SBA-15 could chelate with palladium ions during impregnation, leading to the in-situ reduction of palladium nanoparticles (PdNPs) inside SBA-15. The obtained PdNPs in Pd/SBA-15 had a narrow size distribution and an average diameter of 2.98 nm. The yield of Suzuki coupling reaction between 4-bromotoluene and phenylboronic acid catalyzed by the prepared Pd/SBA-15 catalyst was 98.01%. And the results of recycle test proved the strong stability of Pd/SBA-15.

1. Introduction
Palladium catalyst attracts much attention as the most efficient catalyst for Suzuki coupling reaction, a carbon-carbon coupling reaction widely used in the field of chemical industry such as preparation for pharmaceutical intermediates and liquid crystal materials[1,2]. Considering practical problems such as stability and recyclability of the catalysts, supported Pd nanocatalysts are used in the actual production[3-6].

Mesoporous material SBA-15 possesses highly ordered mesoporous structures with adjustable pore diameter ranging from 5 to 30 nm varies from preparation process, making it an ideal carrier for supported Pd particles with controlled size[7-9].

Synthesis of noble metal nanocatalyst by ultrasonic assisted method is one of the hot spots in research of nanocatalysts[10,11]. In the preparation of supported nanocatalysts, the shock wave of ultrasound can effectively promote liquid circulation and thus accelerate the mass exchange, making it easier for metal ions in precursor solution to immerge in the pore structure of support material[12,13]. Acoustic cavitation effect of ultrasound provides extreme reaction conditions of transient high temperature and pressure, meanwhile, the high energy shockwaves of ultrasound serving as shear forces prevents the particle agglomeration of metal nanoparticles[14-16].

In this work, ultrasound assisted reduction was used in replacement of the conventional impregnation-chemical reduction procedure to prepare supported Pd/SBA-15 catalyst. By emphasizing the change of structure and surface properties for SBA-15 during the preparation, the reaction...
mechanism was discussed. The catalytic property of as-prepared catalyst was tested by Suzuki coupling reaction.

2. Experimental

2.1. Preparation of Pd/SBA-15

The support SBA-15 was pretreated at the heat of 200°C for 4 h, then 0.01 mol/L Na₂PdCl₄ solution was added in the hot powder quickly. The mixture was disposed with ultrasound at the power of 200 W under 30°C water bath for 30 min. After filtering and drying at 140°C for 2 h, the prepared mixture was mixed with 30 mL of ethylene glycol (EG) and treated under ultrasound of 600 W at 30°C water bath for 30 min. The final product of Pd/SBA-15 was acquired by removing the upper layer solution after centrifugation and dried at 140°C for 2 h.

2.2. The Synergistic Effect between EG and SBA-15 under Ultrasound

To understand the interaction between EG and SBA-15, control experiments was operated by mixing SBA-15 30 mL of EG and treated under ultrasound of 600 W at 30°C water bath for 30 min. The prepared sample was named as SBA-15EG.

2.3. Catalytic Performance

Suzuki coupling reaction was used as probe reaction to assess the catalytic property of the prepared Pd/SBA-15. Aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (2.0 mmol) and Pd/SBA-15 (1.0 mmol% of Pd content) was added in 12 mL of mixed solvent of EtOH/H₂O (1:1) and magnetic stirred under water bath of 60°C for 30 min. The final product was obtained by drying the upper layer of solution after extracting the mixture with ethyl acetate.

2.4. Recycle Test

The stability of Pd/SBA-15 catalyst was operated by the reuse of catalyst in Suzuki reaction between 4-bromonitrobenzene and phenylboronic acid. The catalyst was collected after the completion of each reaction and reused in a new round. The procedures were repeated until catalysts were obviously deactivated.

3. Result and Discussion

3.1. The Synergistic Effect between EG and SBA-15 Under Ultrasound

N₂ adsorption-desorption isotherms of the untreated SBA-15 and SBA-15EG were displayed in Figure 1 and detailed structural properties were collected in Table 1. SBA-15EG exhibited slight change in mesoporous structure Smeso of SBA-15, but there was a dramatic decrease in microporous surface SMicro down to 127.34 m²/g compared with untreated SBA-15, indicating that under ultrasonic effect, EG could be transferred into micropores of SBA-15 and change the structure of SBA-15.

![Figure 1. N₂ adsorption-desorption isotherms of untreated SBA-15 and SBA-15EG](image-url)
### Table 1. Structure properties of untreated SBA-15 and SBA-15$_{EG}$

| Sample      | Surface area (m$^2$/g) | Pore volume (cm$^3$/g) | Pore Diameter (nm) |
|-------------|------------------------|------------------------|--------------------|
| SBA-15      | 796.06                 | 515.89                 | 280.17             | 0.91 | 0.77 | 0.14 | 5.55 |
| SBA-15$_{EG}$ | 639.36                | 512.12                 | 127.34             | 0.91 | 0.84 | 0.07 | 5.55 |

Further discussion of structural properties was performed by FTIR spectrum and presented in Figure 2. The main resonance peaks of the untreated SBA-15 included Si-O-Si antisymmetric stretching vibration at 1072 cm$^{-1}$, Si-O-Si symmetrical stretching vibration at 804 cm$^{-1}$, stretching vibration of Si-OH at 975 cm$^{-1}$ and the stretching vibrations of O-H in water at 3428 cm$^{-1}$ and 1634 cm$^{-1}$[17]. Beside all peaks mentioned above, SBA-15$_{EG}$ contained the bending vibration of CH$_2$ in 1460 cm$^{-1}$ and 1409 cm$^{-1}$, the stretching vibrations of C-H at 2940 cm$^{-1}$ and 2871 cm$^{-1}$, the stretching vibrations of Si-C at 877 cm$^{-1}$[18]. The emerging of Si-C indicated the reaction between active surface group of SBA-15 and EG under ultrasonic effect. Also, it couldn’t be ignored that the stretching vibrations of O-H in SBA-15$_{EG}$ was higher than in SBA-15 and slightly shifted to lower wave number. It could be explained that by combining with EG, the hydrophilia of SBA-15 was improved, therefore the water peak was amplified, but the forming of intermolecular hydrogen bonds equalized the electron cloud density and reduced the stretching vibration frequency to 3380 cm$^{-1}$.

#### 3.2. Characterization of Pd/SBA-15

![Figure 3. XRD pattern of Pd/SBA-15](image-url)
The XRD patterns of the prepared Pd/SBA-15 was shown in Figure 3. The broad peak at 21.7° belonged to amorphous SiO$_2$ in SBA-15. The diffraction peaks at 39.7°, 45.9°, 67.2° and 81.1° were attributed to (111), (200), (220) and (311) Bragg reflections of the face-centered cubic Pd lattice\cite{19}, respectively.

Pore structure properties of SBA-15EG and Pd/SBA-15 were presented in Table 2. The specific surface area ($S_{\text{BET}}$) of Pd/SBA-15 was lower than SBA-15 EG, descending from 639.36 m$^2$/g to 579.28 m$^2$/g, proving that Pd was successfully loaded on SBA-15. Meanwhile, the descending in surface area were 6% in $S_{\text{Meso}}$ and 24% in $S_{\text{Micro}}$, respectively, indicating Pd NPs occupied both microporous and mesoporous structure of SBA-15 under ultrasound assisted reduction.

| Sample      | Surface area (m$^2$/g) | Pore volume (cm$^3$/g) | Pore Diameter(nm) |
|-------------|------------------------|------------------------|-------------------|
|             | $S_{\text{BET}}$ | $S_{\text{Meso}}$ | $S_{\text{Micro}}$ | $V_T$ | $V_{\text{Meso}}$ | $V_{\text{Micro}}$ |             |
| SBA-15EG    | 639.36                | 512.12                | 127.34            | 0.91  | 0.84               | 0.07               | 5.55          |
| Pd/SBA-15   | 579.28                | 479.45                | 99.84             | 0.82  | 0.76               | 0.06               | 5.55          |

Figure 4 displayed TEM image of Pd/SBA-15 and size distribution of PdNPs. As clearly presented in the pictures, PdNPs were loaded inside the pores of SBA-15 and had a uniform distribution without destroying the ordered channel structure of SBA-15. Size distribution of showed that Pd NPs had a narrow size distribution with an average diameter of 2.98 nm.

![Figure 4. TEM picture(A,B) of Pd/SBA-15 and size distribution of Pd in Pd/SBA-15(C)](image)

The catalytic performance of Pd/SBA-15 towards Suzuki coupling reaction were listed in table 3. Owing to the small diameter of PdNPs and its narrow size distribution in SBA-15, the catalytic activity of Pd/SBA-15 catalyst was strong, with the yield of Suzuki coupling reaction between 4-bromotoluene and phenylboronic acid reached 98.01%.
Table 3. Results of Suzuki coupling reaction of different substrates catalyzed by Pd/SBA-15

| Entry | -R     | Yield/% |
|-------|--------|---------|
| 1     | 4-CH₃  | 98.01   |
| 2     | 4-NO₂  | 92.26   |
| 3     | 4-COCH₃| 95.39   |
| 4     | 4-CN   | 94.29   |
| 5     | 4-OCH₃ | 97.15   |
| 6     | 2-CH₃  | 74.39   |
| 7     | 2-OCH₃ | 76.09   |
| 8     | 3-NO₂  | 76.81   |

The results of recycle test of Pd/SBA-15 were presented in Figure 5. As clearly displayed in bar graph, the prepared Pd/SBA-15 catalyst exhibited well stability, with its catalytic performance remained high after recycled for six times. This result further confirmed that by loading palladium inside tunnels of SBA-15, it became harder for particles to be washed off from the support, resulting in good reusability of catalyst.

Figure 5. The recycling of Pd/SBA-15 for the Suzuki coupling reaction

4. Conclusion

Pd/SBA-15-u was produced by ultrasound assisted reduction without chemical protective agents and strong reductant. The prepared Pd/SBA-15-u bifunctional catalyst was formed of SBA-15 with ordered channel and small Pd nanoparticles distributed inside the pore structure. Due to the synergistic effect between EG and SBA-15, PdNPs loaded in SBA-15 had a limited size distribution with the mean diameter of 2.98 nm. The small size and uniform distribution of Pd were beneficial for the catalytic performance of Pd/SBA-15-u in Suzuki reaction. The prepared Pd/SBA-15-u also had good stability, the yield of Suzuki coupling reaction maintained 80% after 5 cycles of reuse, confirming that Pd nanoparticles were firmly sticked to the support in the prepared Pd/SBA-15.
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