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Synthesis and Performance of Nano Silver Coated ZSM-5/SBA-15

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A new synthetic approach were chosen to prepare the desired small Ag nanoparticles on a mesoand microporous ZSM-5/SBA-15 system. By the functionalization of ZSM-5/SBA-15 surface with the amine groups, it was possible to obtain small coated silver nanoparticles (in the range of 2 to 5 nm) formed both inside and outside the mesoporous system. The size and distribution of AgNPs can be shown by transmission Electron Microscopy and by the decrease of mesoporous volume of Ag/ZSM-5/SBA-15 sample. The catalytic activity of AgNPs and the effect of mesopore system were proved by antibacterial and benzene oxidation applications. AgNPs inside the mesoporous system of Ag/ZSM-5/SBA-15 limited its antibacterial performance. The improved performance of this catalytic system could be shown in the benzene oxidation, for which a total benzene oxidation temperature of 300 °C could be observed.: Wed, 07 Dec 2016 04:03:13

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1. INTRODUCTION

ZSM-5 zeolite has been well known as a benzene and its derivatives adsorbate. A Benzene molecule is roughly around 6 Å in size. It can be adsorbed on the 5.5 Å micropore in the zeolite pore framework by porous adsorption. In addition, benzene and its derivatives can be adsorbed on the bronsted sites of ZSM-5 by an interaction between benzene molecule and proton and/or Na⁺ cation of bronsted site.^{1,2}

Silver particles at nanosize (AgNPs) have been well known as an excellent catalyst for oxidation because of the subsurface oxygen species formation at low temperature.³ By coating AgNPs on ZSM-5, it showed that AgNPs were formed with very small size (2-3 nm).⁴ Ag/ZSM-5 could be a effective catalyst for benzene and its derivatives oxidation. However, the activity of AgNPs mainly depends not only on their size but also on their content. Because the bronsted sites number is limited, ZSM-5 could not load high Ag content by ion exchange method. In addition, benzene molecules (6 Å) could not diffuse into the micropore system of ZSM-5 (5.5 Å). Therefore, its catalytic activity could be limited.

The synthesis and application of ZSM-5/SBA-15 composite material (Z5S15) have been much interested in recent times.⁵⁻¹¹ Z5S15 material has similar micropore system and bronsted sites to ZSM-5 zeolite, so it can well absorb benzene and its derivatives. AgNPs also can be loaded at bronsted site positions of Z5S15 material. In addition, this composite material also has SBA-15 structure which has a lots of silanol groups (–OH) on the surface. Therefore, it is the same as SBA-15, Z5S15 material can be functionalized to produce surface functional groups which can help it loading higher AgNPs content than ZSM-5 zeolite.

Furthermore, Z5S15 material has a multiporous structure of micro- and mesopores which has a beneficial influence on the catalytic performance.^{10, 11} Benzene molecules could diffuse through the mesopore system of Z5S15. Therefore, it may help AgNPs coated Z5S15 (Ag/Z5S15) material having high catalytic activity in benzene or its derivatives oxidation.

In this study, the Ag/Z5S15 preparation was investigated to optimize the content and size of the formed

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AgNPs. The presence, content, size, and valence state of AgNPs were characterized by X-ray diffraction (XRD), atomic absorption spectroscopy (AAS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) methods. Before the coating process, Z5S15 material was functionalized via two steps:

(1) P123 template removal using H_2O_2 oxidation agent to remain silanol groups and

(2) functionalization with (3-Aminopropyl)triethoxysilane (APTES) to produce functional amine groups on the surface of Z5S15.

The obtained materials were characterized by infrared spectroscopy (IR), XRD, and thermo gravimetric analysis (TGA) methods.

2. EXPERIMENTAL DETAILS

2.1. Chemicals

The chemicals used for the preparation of Ag/Z5S15 are AgNO₃ (>99%, Sigma-Aldrich); H_2O_2 solution (30% w/w, Sigma-Aldrich); ethanol (>99.8%, china); APTES (99%, Sigma-Aldrich); Toluene (anhydrous, 99.8%, Sigma-Aldrich); Distilled water.

2.2. Modification of the Z5S15 Composite Material

The Z5S15 composite material (Si/Al molar ration of 50) was successfully synthesized and characterized according to our previous report.⁸ The modification of Z5S15 was performed by using the as-synthesized Z5S15 (signed as Z5S15-AS). Z5S15-AS sample was the Z5S15 sample that was received after the hydrothermal treatment. It had not undergone templates removal. Z5S15-AS sample was modified by two stages. In the first stage, Z5S15-AS sample was P123 copolymer removed to remain the silanol (–OH) groups by H_2O_2 oxidizing agent. After that, sample was functionalized with amine groups by using APTES linker in the second step. These amine groups enabled the coating of Ag⁺ ion onto Z5S15 sample via proton exchange reaction.

2.3. P123 Co-Poplyme Removal from Z5S15-AS Material

The procedure of P123 removal from Z5S15-AS sample was performed as follows: 1 g Z5S15-AS composite material and 150 ml H_2O_2 solution (30% v/v) were put into an autoclave with stirring and being heated at 100 °C for 24 h. The solid was filtered and washed with distilled water and ethanol. Then, it was dried at 100 °C in vacuum. The solid product was signed as Z5S15-PR.

2.4. Functionalization of Z5S15-PR Material

1 g Z5S15-PR sample was dispersed in a mixture of 2.5 ml APTES and 100 ml anhydrous toluene. The mixture was homogenized in a ultrasonic bath for 30 min at room temperature. Then, the mixture was stirred and refluxed at

90 °C for 24 h in Argon flow (2 ml/min) to avoid water moisture absorption from the air. The solid was filtered and washed with 100 ml anhydrous toluene. After that, it was dried at 100 °C in vacuum for 12 h. The solid product was signed as Z5S15-APTES.

2.5. Synthesis of Ag/Z5S15 Material

The nominal loading Ag content was fixed at 8 wt%. Ag/Z5S15 sample was synthesized by dispersing Z5S15-APTES sample in 10^{-3} M AgNO₃ solution. The exchange reaction was performed by stirring mixture in the dark for 24 h. Ag⁺ ion was reduced by adding a sufficient amount of 0.05 M NaBH₄ solution into resulting mixture. This mixture was further stirred for 24 h. The solid was filtered and washed by distilled water. Then, the solid was dried at 60 °C for 24 h in vacuum. The solid product was signed as Ag/Z5S15 sample.

2.6. Performance Tests

In order to evaluate the effect of mesopore system of Ag/Z5S15 on its activity, Ag/Z5S15 sample was evaluated in two applications, including *E. coli* bacterial elimination and benzene oxidation. The activity of Ag/Z5S15 sample was compared to that of Ag/ZSM-5 material that was synthesized and characterized in our previous article.⁴

2.7. E. coli Bacterial Elimination

The procedures of antibacterial experiment include mediums preparation, initial cells suspension preparation, antibacterial assay by contact time between *E. coli* bacteria and sample, and the analysis of the *E. coli* concentration by colony counter method. All these procedures are the same as one reported in our previous article.⁴ The initial concentration of *E. coli* was 10^7 cfu/ml. The experimental contact time was varied at 10 min, 20 min, 30 min, and 60 min.

2.8. Benzene Oxidation

Benzene oxidation measurements were performed in a fixed-bed microreactor under atmospheric pressure. An amount of 100 mg catalyst was used for each experiment. The feed gas rate was 50 ml/min with oxy-gen/benzene molar ratio of 15 and space velocity (WHSV) of 30,000 ml \cdot h⁻¹ \cdot g⁻¹. Reaction temperature was controlled by a *k*-type thermocouple that directly contacted with the catalyst bed. Before reaction, catalyst was calcined at 550 °C for 5 h in air flow. Then, catalyst was reduced at 450 °C in a 5% H₂ gas flow. The feed and product compositions were analyzed by a gas chromatography (GC) equipped with a TCD detector to determine CO₂, and a FID detector to determine hydrocarbon.

The CO₂ product yield (Y_{CO_2} , %) was calculated via amount of CO₂ actual which was analyzed by GC-TCD of product ($S_{CO_2 \text{ actual}}$), and amount of CO₂ which was received in the case of oxidation reaction of benzene

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Figure 1. IR spectra of samples: (A) Z5S15-AS; (B) Z5S15-CA; (C) Z5S15-PR; and (D) Z5S15-APTES.

reaches fully conversion ($S_{CO_2 100\%}$). At that time, there was not any benzene or hydrocarbon signals could be detected by GC-FID. Y_{CO_2} value was calculated by the equation as follows: IP: 5.8.37.237 On: We

$$Y_{\rm CO_2} = (S_{\rm CO_2 \ actual} / S_{\rm CO_2 \ 100\%}) * 100\%$$

2.9. Characterization Method

Characterization of samples was performed by using the following methods: FT-IR spectra were recorded using an IMPACT-410 (Germany) Infrared Spectrophotometer at room temperature in the range 400–1300 cm⁻¹ on thin wafer of KBr in which 1% (w/w) of sample was dispersed. Powder X-ray diffraction patterns were recorded on a HUT-PCM-Bruker D8 Advance instrument diffractometer system equipped with Ni-filtered Cu K α



Figure 2. XRD patterns of samples: (A) Z5S15-CA; (B) Z5S15-PR; (C) Z5S15-APTES.

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Figure 3. High-angle XRD patterns of Ag/Z5S15 sample (A) before and (B) after AgNPs coating.

radiation (operating at 40 kV, 40 mA, wavelength $\lambda =$ 0.154 nm). The patterns were recorded at room temperature (298 K); 2θ values ranged from 0.1° to 5° and 5° to 50°, and the scanning speeds were 1° min⁻¹ and 2° min⁻¹. Transmission electron microscopy (TEM) was performed using a Philips Tecnai-10 microscope at 100 kV. AAS method was performed with an ICE 3300 AA Spectrometer. XPS investigation was performed with a ESCALAB 220iXL (ThermoFisher) using monochro-237 On: Wed matic Al K α radiation (E = 1486.e eV). For charge comcan Spensation a flood gun was used. The binding energy was referenced to the C1s peak of adventitious carbon at 284.8 eV. The binding energy of the peaks and the surface composition were obtained after Shirley background subtraction and fitting the peaks with a mixed Gaussian-Lorenttzian function. The BET surface area and pore volume were measured by using nitrogen adsorption/desorption isotherms by using ASAP2010 equipment (Micrometrics-USA). The sample was treated in vacuum of 10^{-6} mmHg, at 120 °C for 4 h and at 350 °C for 9 h.



Figure 4. Low-angle XRD patterns of Ag/Z5S15 sample (A) before and (B) after AgNPs coating.

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Figure 5. XPS spectrum of Ag/Z5S15 sample.

The samples were calcined at 550 °C for 5 h before the TEM and BET analysis.

3. RESULTS AND DISCUSSION

3.1. Result of Z5S15 Functionalization

The as-synthesized Z5S15 (Z5S15-AS) sample consists of P123 and TPABr templates. The conventional method of removing these templates is calcination in an air atmosphere. However, the calcination can cause the disappearance of silanol groups of Z5S15-AS material during the condensation.¹² So as to prevent these problems, P123 oxidation method using H_2O_2 oxidation agent is a good alternative. TPABr template also can be partially extracted by this method.

The result of template removal by H_2O_2 from Z5S15-AS sample is demonstrated in IR spectra (Fig. 1). The IR spectrum of Z5S15-AS sample shows the peaks attributed to the bonding vibration of P123 and TPABr templates. They are C–H (CH₂ and CH₃) stretching vibrations in the Nam et al.

range of 2900–3000 cm⁻¹ as well as C–H (CH₂ and CH₃) bending vibrations in the range of 1370–1470 cm⁻¹.¹³ The C–N stretching vibration, a typical bond of TPABr, is normally observed in the range of 1000–1200 cm⁻¹.¹⁴ However, this peak is not resolved due to the overlay with the IR absorptions of Si–O–Si asymmetric stretching and Si–CH₂-R deformation in the ranges of 1130–1000 cm⁻¹ and 1250–1200 cm⁻¹, respectively.

The disappearance of the typical peaks of templates (P123 and TPABr) in the Z5S15-PR infrared spectrum, and the agreement of IR spectra between Z5S15-PR and Z5S15-CA samples (Z5S15-CA sample is the Z5S15 sample that is undergone templates removal by calcination at 550 °C for 5 h in our previous report⁸) indicate that P123 and even TPABr templates have been completely removed from Z5S15-AS sample. IR spectrum of Z5S15-PR sample shows the appearance of silanol groups in term of the higher intensity of the O–H (silanol groups) stretching vibrations in the range 3200–3700 cm⁻¹ compared with IR spectra of Z5S15-CA and Z5S15-AS.

The success of the functionalization can be proven by the IR spectrum of Z5S15-APTES sample (Fig. 1(d)) that shows the appearance of C–H (CH₂ and CH₃) bending and stretching vibrations because of APTES presence. The incorporation of amine groups in the silicate framework can be confirmed. At the wavenumber of 693 cm⁻¹, a weak peak can be seen due to the bending vibrations of N–H bonds, and the symmetrical NH₃⁺ bending vibrations at 1560 cm⁻¹. That weak peak indicates the existence of amine groups.¹³ In addition, the IR spectrum of Z5S15-APTES sample also shows the dramatically decrease of the O–H stretching vibrations in the range of 3200–3700 cm⁻¹. This may be due to the loading of amine groups that take the place of surface silanol groups.

A comparison between the small angle XRD patterns of Z5S15-APTES sample and Z5S15-CA samples (Fig. 2) indicates that the functionalization has an effect on the



Ag-Zs7.6_015 Print Mag: 125000x @ 51 mm 10:34:11 a 03/27/14 TEM Mode: Imaging

100 nm HV=80.0kV Direct Mag: 60000x EMLab-NIHE



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100 nm HV=80.0kV Direct Mag: 80000x EMLab-NIHE

Figure 6. TEM images of Ag/Z5S15 sample.

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long range ordering of the mesostructure of Z5S15 material. The slight shift to lower angle and the decrease in reflection intensity of the peak around 2-theta value of 1° may be explained by the presence of grafted APTES molecules. This presence may cause a change of XRD pattern of Z5S15-APTES sample due to the phase cancellation between X-rays scattered from the walls and pores regions.

3.2. The Characterization of Ag/Z5S15 Sample

Ag/Z5S15 sample are characterized by XRD, TEM, XPS and BET methods. XRD patterns in Figures 3 and 4 show that the microporous and mesoporous structure of Z5S15 substrate are strongly affected by too much of AgNPs formed both inside and outside the mesoporous system of Ag/Z5S15 sample. The peaks at around 2-theta values of 38°, 44°, and 65° (Fig. 3) correspond respectively to (111), (200), (220) reflections of pure silver metal with face centered cubic symmetry (a = b = c = 4.08570).¹⁵

The valence state of AgNPs on the Ag/Z5S15 samples is further characterized by XPS method. The XPS spectrum of Ag/Z5S15 sample in Figure 5 shows the binding energies of 368.0 eV for the Ag $3d_{5/2}$ peak and 374.0 eV for the Ag $3d_{3/2}$ peak that correlate to zerovalent Ag.^{16,17} The binding energies of 366 eV for the Ag $3d_{5/2}$ peak and 372 eV for the Ag $3d_{3/2}$ peak could be correlated to the Ag(np)-APTES bonds.¹⁸

The size of AgNPs on Ag/Z5S15 sample are characterized by TEM images that are shown in Figure 6. TEM images of Ag/Z5S15 sample show very small AgNPs with average nanosize of 2–5 nm. There are only few AgNPs with size of 6–17 nm. AgNPs are distributed both inside and outside the mesoporous channels of Ag/Z5S15 sample. The nanosize range formation of AgNPs in Ag/Z5S15



Figure 7. N_2 adsorption/desorption isotherms of Z5S15-CA sample.

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Figure 8. Pore distribution of Z5S15-CA sample.

sample may be due to the exchange reaction of Ag^+ ions with both amine groups and bronsted sites of Z5S15-APTES sample. This result also indicate that the bronsted sites may be existed inside the mesoporous channels of Z5S15-APTES.

The N₂ adsorption–desorption isotherms, pore distribution of Z5S15-CA sample in Figures 7 and 8 were compared with that of Ag/Z5S15 sample in Figures 9 and 10. The results show that the mesoporous system of Z5S15 substrate was considerably changed. This may be because of the entering of AgNPs into it.

Properties of samples in Table I show a high AgNPs loading content of Ag/Z5S15 sample (3.734 wt%).



Figure 9. N₂ adsorption/desorption isotherms of Ag/Z5S15 sample.

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Figure 10. Pore distribution of Ag/Z5S15 sample.

The loading of AgNPs causes the low specific surface area of Ag/Z5S15 (267 m^2/g) in comparison to that of Z5S15-CA sample (541 m^2/g). In addition, the mesopore size of Ag/Z5S15 sample is 10–25 nm with very low intensity (dV/dlog(w) pore volume value) (Fig. 10). Z5S15-CA sample has the mesopore size of 7–8 nm with high intensity (Fig. 8). These results may prove the pore fillng effect of AgNPs on the porous system of Ag/Z5S15sample.

3.3. Performance Evaluation

Performance of Ag/Z5S15 sample was measured in comparison to that of Ag/ZSM-5 material. These materials have near similar size of AgNPs (around 2–3 nm). However, Ag/Z5S15 sample has much higher AgNPs content (3.734 wt%) than Ag/ZSM-5 sample (only 0.253 wt%).⁴

3.4. Antibacterial Performance of Samples

The *E. coli* antibacterial performance of samples are presented in Table II. A very interesting result can be seen that Ag/ZSM-5 sample (0.253 wt% AgNPs) has better antibacterial performance than Ag/Z5S15 sample (3.734 wt% AgNPs) after all experimental contact times. The *E. coli* concentration after the contact time of 60 min is decreased from 2.7×10^7 cfu/ml (initial concentration) to 4.45×10^5 cfu/ml in the case of Ag/Z5S15.

Table I. Physico-chemical properties of samples.

Sample	Ag content by AAS, wt%	S _{BET} , m²/g	Pore volume, cm ³ /g		Average pore
			V _{meso}	$V_{ m micro}$	width, nm
Z5S15-CA	0	541	0.43	0.11	5.3
Ag/Z5S15	3.734	267	0.35	0.07	10.1

Table II. Antibacterial performance of samples.

	E. coli concentration, cfu/ml							
Samples	0 min	10 min	20 min	30 min	60 min			
Ag/Z5S15 Ag/ZSM-5	$\begin{array}{c} 2.7\times10^7\\ 2.7\times10^7\end{array}$	$\begin{array}{c} 2.85\times10^6\\ 1.10\times10^6 \end{array}$	$\begin{array}{c} 2.70 \times 10^{6} \\ 6.10 \times 10^{5} \end{array}$	$\begin{array}{c} 2.65\times10^6\\ 2.50\times10^5\end{array}$	$\begin{array}{c} 4.45\times10^5\\ 2.90\times10^4\end{array}$			

But in the case of Ag/ZSM-5, the *E. coli* concentration after 60 min is 2.90×10^4 cfu/ml with the same initial concentration. This is due to the fact that the AgNPs (2–5 nm) may be formed inside the mesoporous system of Z5S15 substrate (7–8 nm). These AgNPs can not contact with *E. coli* bacteria which have much bigger size (0.5 × 5 μ m). This limits the antibacterial performance of Ag/Z5S15.

3.5. Catalytic Performance of Samples in Benzene Oxidation

The size of one benzene is around 6 Å. So benzene molecules may easily diffuse through the mesopore system of Ag/Z5S15 sample. Benzene oxidation reaction over catalysts are performed by temperature ranging from 100 °C to 500 °C. CO_2 product yield of reaction by temperature over Ag/Z5S15 sample is compared with that over Ag/ZSM-5 sample. The results are demonstrated in Figure 11 ersity Libraries

System of $Ag/Z5S15_{cd}$ 07 The catalytic result of samples show that the con-Copyright: American Stent of PAgNPs decides the oxidation performance of samples. Because of the considerable increase of AgNPs content from 0.253 wt% (Ag/ZSM-5 sample) to 3.734 wt% (Ag/Z5S15 sample), and the increase of contact ability between benzene, oxygen and AgNPs inside the mesoporous system of Ag/Z5S15 sample, the CO₂ product yield (Y value) is strongly increased



Figure 11. Product efficiency of benzene oxidation by temperature over catalysts.

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from 37.55 % (over Ag/ZSM-5 sample) to 100% (over Ag/Z5S15 sample). In addition, the temperature that benzene molecules are started to be totally oxidized is only 300 °C. This result may prove that in this application, the AgNPs inside the mesoporous system work. Benzene and oxygen molecules can diffuse into mesoporous system of Ag/Z5S15 to contact with AgNPs. This result also shows the effective support ability of mesoporous system in term of increasing the contact ability between the feed gas (benzene and oxygen molecules) with AgNPs.

4. CONCLUSIONS

Ag/Z5S15 material based on a Z5S15 composite material was successfully prepared. In comparison to Ag/ZSM-5 material (AgNPs content was only 0.253 wt%), the AgNPs content of Ag/Z5S15 is considerably increased to 3.734 wt%. The small AgNPs 2-5 nm were formed both inside and outside the mesoporous system of Z5S15 substrate.

The performance test results showed that the combination of high content, small size of AgNPs and the mesoporous system of Z5S15 substrate helped improving catalytic activity of Ag/Z5S15 material in benzene oxidation. It showed very good catalytic activity in term of totally oxidizing benzene at low temperature (300 °C).

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