



Thesis

Noble metal nanoparticles supported on amino-functionalized mesoporous silica as catalyst for tandem reaction

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06.06.2017

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Abstract

Mesoporous materials are a type of porous materials with ordered pores on the range of 2-50 nanometers, which have attracted great attention because of wide applications in adsorption, separation, catalysis, electrode materials, chemical sensors and optoelectronic devices, and so on, due to their high surface area, ordered mesopores and tunable pore distribution. The pore size of mesoporous silica is large enough to accommodate a variety of large molecules, and the high density of silanol groups on the pore wall is beneficial to the introduction of functional groups with a high coverage. Recently, many researches have focused on the catalytic action of amino-functionalized mesoporous silica. Here, the aim is to synthesize a bifunctional mesoporous silica Pd@NH₂-MSNSs, the process of synthesis is as follows. Using an anionic surfactant as the template and organosilane as co-structure directing agent, amino-functionalized mesoporous silica nano spheres (NH₂-MSNSs) were synthesized by self-assembly. After extraction of the anionic surfactant templates by solvent, silica nano-spheres with ordered and radially oriented amino-functionalized mesochannels were obtained. Then, we utilized the amine groups immobilized on the mesoporous surface as stabilizing and capturing agents to prepare Pd nanoparticle supported NH₂-MSNSs catalysts. The Pd-supported catalysts exhibited high and stable activity in aerobic oxidation of benzyl alcohol, which is benefit for the tandem reaction of alcohol oxidation to dehyde and Knoevenagel condensation reaction. The di-functional mesoporous silica Pd@NH₂-MSNSs exhibited better catalytic action than mono-functionalization mesoporous silica NH₂-MSNSs and Pd@MSNSs.

Key words: Mesoporous silica; amino-functionalized; aerobic oxidation; tandem reaction.

摘 要

介孔材料是指孔径介于 2-50nm 的一类多孔材料。由于其高比表面积,有序孔道和孔径分布连续可调等特点,在吸附、分离、催化、电极材料、化学传感器和光电器件等方面有广泛的应用价值。介孔二氧化硅的孔径足够大以容纳各种分子,硅醇基团的高密度孔壁有利于功能化得到最大体现。近年来,许多研究都集中在氨基功能化介孔二氧化硅的催化作用上。在这篇论文中,我的目的是合成双功能化的介孔二氧化硅催化剂 Pd@NH₂-MSNSs,合成过程如下:采用阴离子表面活性剂作为模板,以有机硅烷作为共结构导向剂,通过自组装方法合成氨基功能化的介孔二氧化硅纳米球。利用氨基功能化的介孔材料作为催化剂的基础。用溶剂萃取阴离子表面活性剂模板后,得到了径向有序的氨基功能化介孔二氧化硅纳米球。然后,我们利用固定在介孔表面上的胺基团作为稳定剂和捕获剂来使 Pd 纳米颗粒负载在 NH₂-MSNSs 催化剂上。这个负载型催化剂在苯甲醇的空气氧化过程中表现出较高的活性,这有利于醇氧化为醛的连串反应和 Knoevenagel 浓缩反应。双功能化的介孔二氧化硅催化剂 Pd@NH₂-MSNSs 比单功能化介孔二氧化硅催化剂 NH₂-MSNSs 和 Pd@MSNSs 表现出更好的催化作用。

关键词: 介孔二氧化硅 氨基功能化 空气氧化 连串反应

Chapter 1 Introduction

1.1 History and basic conception

People discovered the earliest natural zeolite in 1756. In the 19th century, people have a further understanding of natural zeolite, they known more about microporous properties of rock and the performance of adsorption, ion exchange, etc. However, until the 20th century zeolite chemist Barrer r. M. Led, successfully imitated formation environment natural of zeolite, Synthesized the first batch of low silica alumina ratio of zeolite molecular sieve under the water. Porous molecular sieves represented by porous silicon oxide are a large inorganic family. Which have attracted great interest due to their potential applications in catalysis, carrier, Ion exchanger because of open structure and a large specific surface area . According to naming rule of IUPAC, Porous materials can be divided into three categories according to the pore size: the pore size is less than 2.0 nm is known as the microporous material, bigger than 50nm is microporous material, between 2-50nm is known as mesoporous material.

Mesoporous materials are a kind of porous materials with ordered pores on the range of 2-50 nanometers, which have attracted great interest due to their potential applications in catalysis^[1], adsorption, separation, optoelectronic device, chemical sensors and nonlinear optical matter, and so on. Because of their high surface area, ordered mesoporous and tunable pore distribution.^[2] Hierarchically structured mesoporous silica has attract great attention due to their potential application and their relationship to the bio mineralization and biomimetic chemistry. In the past few years, on the basis of the interaction between the amphiphilic organic molecules and the inorganic species in the static hydrothermal system, only simply structure and morphology could be obtained, because it was difficult to control the mesosphere at

the different region and the morphology on the micrometer scale. The meso-structured silica were characterized by exploring the new synthetic system.^[3] The meso-structured silica were characterized by nitrogen absorption analyzer, power X-ray diffraction (XRD), small angle X-ray scattering(SAXS), transmission electron microscope (TEM) ect.

1.2 introduce of MCM-41 and SBA-15

We all know MCM-41 and SBA-15 are common mesoporous molecular sieves with two dimensional hexagonal structures; their basic structure is cylindrical channel with six closely packed sides. Since the discovery of MCM-41 by Mobil Company, the first mesoporous silica to be synthesized by a surfactant templated synthesis, a lot of research has been committed to the production of mesoporous membranes of this type. Their basic structure is cylindrical channel with six closely packed sides. The pore size is too large for size selective “molecular sieve” separation for all but the largest molecular so surface modification is needed to enhance the selectivity. MCM-41 is easily to synthesize, almost all the silicon source can become the material, such as sodium silicate, silicon dioxide and TEOS. The biggest advantage is pore size of MCM-41 can control as the result of chain length of surfactants. The longer is hydrophobic chain, the larger is pore size. Besides, add TMB also can increase the length of hydrophobic chain.

Triggered by the discovery of the so-called MCM-41 family of ordered mesoporous silica, a new research field about periodic mesoporous materials was developed. Among the extensive variety of silica mesophases, MCM-41 and SBA-15 have been the most widely investigated.^[4]

Though both of them exhibit two dimensional hexagonal structures (p6mm), they have some remarkable differences: (i) SBA-15 is possessed with larger pores and thicker pore walls than MCM-41; (ii) while the channels of MCM-41 are not connected to each other, those of SBA-15 are interconnected via secondary mesoporous; and (iii) MCM-41 is purely mesoporous in nature, whereas typical SBA-15 silica contains a significant amount of micropores within the pore walls. In

addition to the nature of the pore system, i.e. shape, pore size, and connectivity,^[5] depending on the targeted application, the morphology of the mesophase may be definitely important. Simple morphologies with unhindered, short path lengths such as small spheres and crystal-like particles as well as short, straight rods be in favor of applications limited by intraparticle diffusion processes such as catalysis,^[6] separation, guest molecule encapsulation^[7] and internal surface modification. However, extensive work was committed to the morphological control of mesoporous silica and organosilicates. Most methods were based on changes in synthesis conditions, including the silica source, surfactants, the nature of the surfactants, solvents, and additives, and the overall composition of the synthesis mixture.

1.3 Synthesis method of mesoporous silica nanoparticles (MSNS)

For the purpose of application, removal of surfactant and surface functionalization would be necessary. Generally, the mesoporous silica nanoparticles are synthesized using a sol-gel reaction. Nevertheless, like the silica gel, the MSNS are packed closely and shrink significantly when they are directly dried from a liquid. Because these nanoparticles come into contact with other nanoparticles and Si-O-Si bonds are consisted between them by dehydration of the surface silanol groups, the shrinkage is essential irreversible, and their characteristics are lost. Removal of surfactant by extraction is preferred over dry air calcination. It is demonstrated that Cauda et al. developed a method of “liquid-phase calcination” to remove surfactants at high temperatures in high boiling solvents, forestalling agglomeration of MSNS. Direct surface modification by refluxing the MSNS in a silane ethanol solution has been generally used for chemical removal of the reactive surface silanol groups. Because the surfactants can be dissolved very easy in the hot ethanol, silane-grafting and surfactant extraction from the nanopores are achieved simultaneously. During the direct surface modification in the silane ethanol solution, the reactive surface silanol group can be changed to non-reactive Si-R, and thus the irreversible aggregation between the mesoporous silica nanoparticles can be reduced significantly. Without high-temperature calcination, the extent of the silane modification can be relatively

high, and the surface properties can be easily adjusted. The colloidal MSNS functionalized with silanes are highly stable even after the removal of the organic templates. In the presence of the functional groups on the surface of MSNS, the irreversible aggregation between the MSNS can be reduced, which makes re-dispersion of the MSNS into the desired solution or matrixes relatively easy.

1.4 Preparation of amino-functionalized mesoporous silica.

In general, the functionalization of the surface of the mesopores has been achieved by direct co-condensation and post-synthesis grafting methods using organoalkoxysilane, $(R^2O)_{4-n}-Si-R^1_n$ ($n = 1 - 3$) (Fig. 1). A direct co-condensation method is based on the co-condensation of a tetraalkoxysilane and organoalkoxysilanes in the aqueous solution containing surfactant to produce inorganic - organic hybrid networks through sol - gel chemistry. On the other hand, a post-synthesis grafting method is based on the silylation of organoalkoxysilane with surface silanol groups on the mesopores of the pre-fabricated mesoporous silica. Organic - inorganic hybrid mesoporous materials have also been prepared by using the alkoxysilane monomer bridged by an organic group, e.g., 1,2-bis(trimethoxysilyl)ethane and 1,4-bis(triethoxysilyl)-benzene, as silica source. Although this method leads to a homogeneous distribution of organic fragments within the framework, the variation of functional groups introduced as well as mesostructure of the materials is limited. So, I selected direct co-condensation method in my experience, because the direct co-condensation would result in a homogeneous distribution of amino-organic moieties on the silica wall. But in the post-synthesis grafting method, most amino-organic moieties would concentrate near the openings of channels and/or on the external surface.

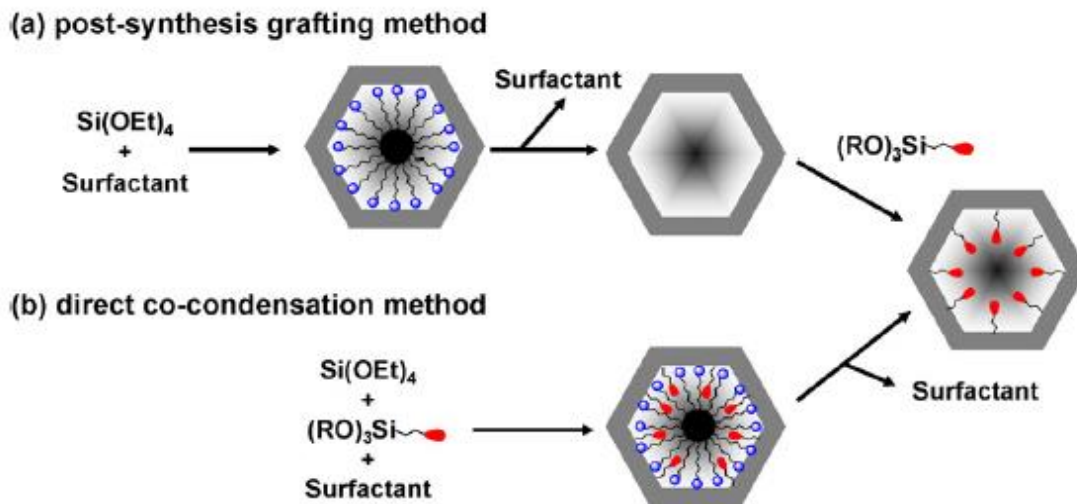


Fig 1. Functionalization of surface of mesopores by (a) post-synthesis grafting and (b) direct co-condensation method using organoalkoxysilane

Chapter 2 Experimental materials and methods

2.1 Preparation of monodispersed amino-functionalized mesoporous silica nanospheres

2.1.1 Chemicals

N-lauroylsarcosine sodium (Sar-Na) was purchased from SIGMA and 3-aminopropyltrithoxysilane (APES) was from MACKLIN. All the chemical agents were used without further purification.

2.1.2 Synthesis

In a typical synthesis of MSNSs, 1.0 mmol of N-lauroylsarcosine sodium (Sar-Na) was completely dissolved in 30.0 mL of deionized water under stirring, Next 4.0 mL of HCl (0.1 M) solution was added to the solution under vigorous stirring for 1

h, and then mix 1.50 mL TEOS and 0.12 mL APES in fuming cupboard, the mixture was added to the above solution. The final reactant molar ratio is $1890\text{H}_2\text{O}/1.0\text{Sar-Na}/0.4\text{HCl}/6.7\text{TEOS}/0.57\text{APES}$. The mixture was left in room temperature under vigorous stirring for 24 hours, and then put in an 80°C oven for another 6h. The products were centrifuged, dispersed with ultrasonic dispersion instrument, washed with deionized water for three times and dried at 80°C .

2.1.3 Characterization

Fourier transform infrared spectroscopy (FT-IR) were recorded on a Shimadzu Corporation IRPrestige-21 with resolution ratio 0.5cm^{-1} . Nitrogen adsorption experiments: the use of automatic surface and pore distributor (Tristar3020, Micrometrics Instrument Corporation), high purity nitrogen, 180°C degassing 6h, heating rate $1^\circ\text{C}/\text{min}$. Transmission electron microscopy (TEM) analysis: Transmission electron microscopy (TEM) of the samples was characterized by JEOL JEM-2011 transmission electron microscopy. The accelerating voltage was 120 kV. The samples were sieved through 80 mesh and then placed in anhydrous ethanol then characterize it. Thermogravimetry (TG) was performed with a SDT-Q600 thermogravimetry - differential thermal analysis (TG/DTA) analyzer in air with the heating rate of 20 K/min.

2.2 fabricate three kind of catalyst

① MSNS-NH₂ catalyst

To obtain the amino-functionalized mesoporous silica (denoted as MSNSs-NH₂), the surfactant was removed by an acid extraction. The detailed procedure was as followed: 1g as-synthesized sample was stirred in a mixture solution of 45 g acetonitrile and 5g 36-38 wt % HCl for 24 h at room temperature. The product was centrifuged, dispersed with ultrasonic dispersion instrument, washed with deionized water for three times. Then mesoporous silica product was added into 50ml 1wt% NH₃ · H₂O and stirred for half hours. The product was centrifuged, dispersed with ultrasonic dispersion instrument, washed with deionized water for three times and

dried at 50°C. [1.2 mmol NH₂ per gram MSNS-NH₂ catalyst]

② Pd@NH₂-MSNSs catalyst

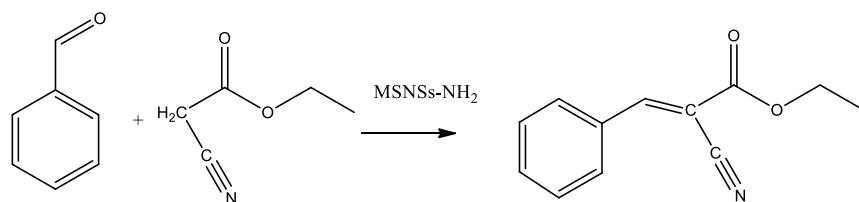
Typically, 1 g MSNS-NH₂ was suspended in 20 mL deionized water and dispersed with ultrasonic dispersion instrument, and then added 1ml 1 wt-Pd % aqueous H₂PdCl₄ solution and stirred at room temperature for 4 hours. The obtained light orange liquid was reduced with a freshly prepared solution of NaBH₄ (0.1 M) at room temperature. Added certain amounts of NaBH₄ until the no bubbles coming out of the liquid. The sample was centrifuged, washed extensively with distilled water, and dried at 80°C to obtain black power (denoted as Pd@NH₂-MSNSs). The theory amount is 1 wt. % Pd contents in Pd@NH₂-MSNSs catalyst

③ Pd@MSNSs catalyst.

The Pd@NH₂-MSNSs was calcined for one day to remove the -NH₂, we can get Pd@MSNSs .

2.3 Catalytic reaction tests

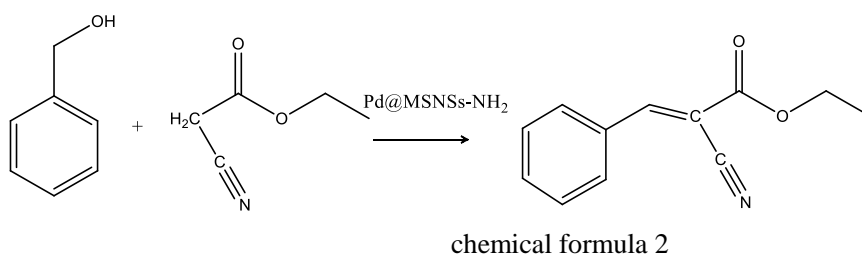
① MSNS-NH₂ catalyst



chemical formula 1

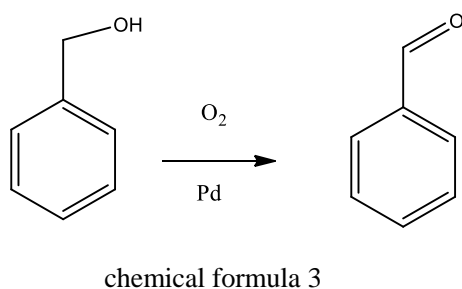
The Knoevenagel condensation reaction (formula 1) was performed in a round-bottom flask with a reflux condenser under magnetic stirring. 30mg MSNSs-NH₂ catalyst was added into the 10mmol (1.03ml) benzaldehyde and 10mmol (1.09ml) ethyl cyanoacetate, then added 10ml ethyl alcohol and heated the mixture by oil bath to reaction temperature 100°C for 4 h.

② Pd@NH₂-MSNSs catalyst



The liquid phase oxidation of benzyl alcohol and Knoevenagel condensation reaction. (formula 2) was performed in a three-necked flask with a reflux condenser under magnetic stirring. 50mg Pd@NH₂-MSNSs catalyst was added into the 5ml benzyl alcohol and 0.5ml ethyl cyanoacetate, and heated the mixture by oil bath to reaction temperature 100°C for 7 h, and O₂ flow (20 ml/min) was bubbled into the liquid by a instrument.

③ Pd@MSNSs catalyst.



The liquid phase oxidation of benzyl alcohol was performed in a three-necked flask with a reflux condenser under magnetic stirring. 50mg Pd@MSNSs catalyst was added into the 5ml benzyl alcohol, and heated the mixture by oil bath to reaction temperature 100 °C for 4 h, and O₂ flow (20 ml/min) was bubbled into the liquid by a instrument.

Chapter 3 Results and discussion

3.1 the principle of synthesize amino-functionalized mesoporous silica

The use of anionic surfactants as SDAs for the formation of the mesostructured silica-micelle composite has been designated as the “ $S^- N^+ \sim I^-$ pathway” that is promoted by utilization of an organoalkoxysilane containing amino groups such as 3-aminopropyl triethoxysilane (APES), where S^- , N^+ and I^- are negatively charged surfactants, positively charged amino groups and negatively charged silicates, respectively. Therefore, we named APES “co-structure-directing agent” (CSDA). The direct electrostatic interaction between the positively charged amino groups in APES and the negatively charged head groups in the anionic surfactant is a driving force in the “ $S^- N^+ \sim I^-$ pathway” for forming the silica-micelle composite.^{[3][11]} Amino-functionalized mesoporous silica nano spheres (NH_2 -MSNSs) were synthesized by self-assembly. After extraction of the anionic surfactant templates by solvent, silica nano-spheres with ordered and radially oriented amino-functionalized mesochannels were obtained. Then, we utilized the amine groups immobilized on the mesoporous surface as stabilizing and capturing agents to prepare Pd nanoparticle supported NH_2 -MSNSs catalysts.(Fig 2)

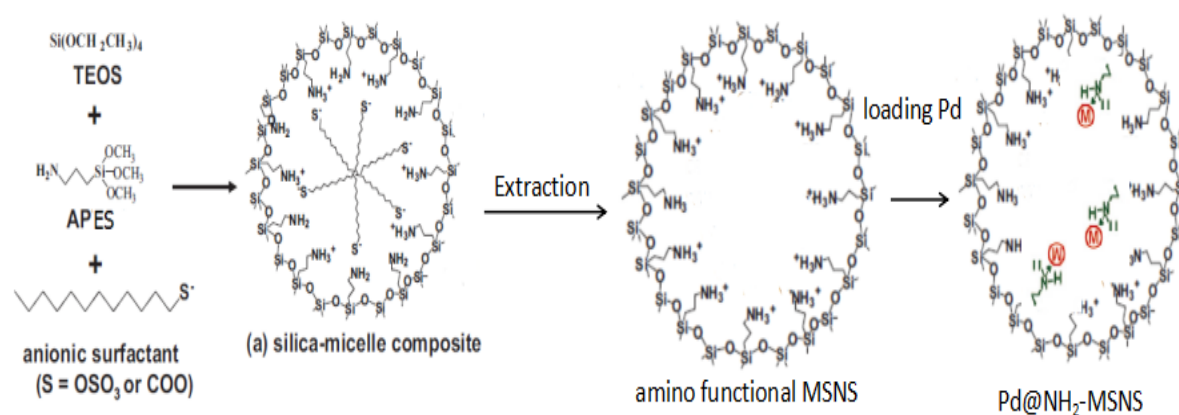


Fig2. Formation scheme of Pd@NH₂-MSNSs catalyst

The surfactants in the channels of as-MSNS adsorbed PbCl_2 -4 ions specifically and quickly from the aqueous solution of H_2PdCl_4 at room temperature. After reduction by NaBH_4 solution, well-dispersed Pd nanoparticles were formed and captured by the MSNSs- NH_2 . When the MSNSs- NH_2 was added into H_2PdCl_4 solution under stirring, the color of MSNSs- NH_2 changed from white to orange within several minutes. When above suspending liquid was reduced by NaBH_4 solution, the color changed from orange to grey and the gas bubble came out. Finally, after NaBH_4 reduction a homogenous black solution was obtained. As shown in Fig 3.

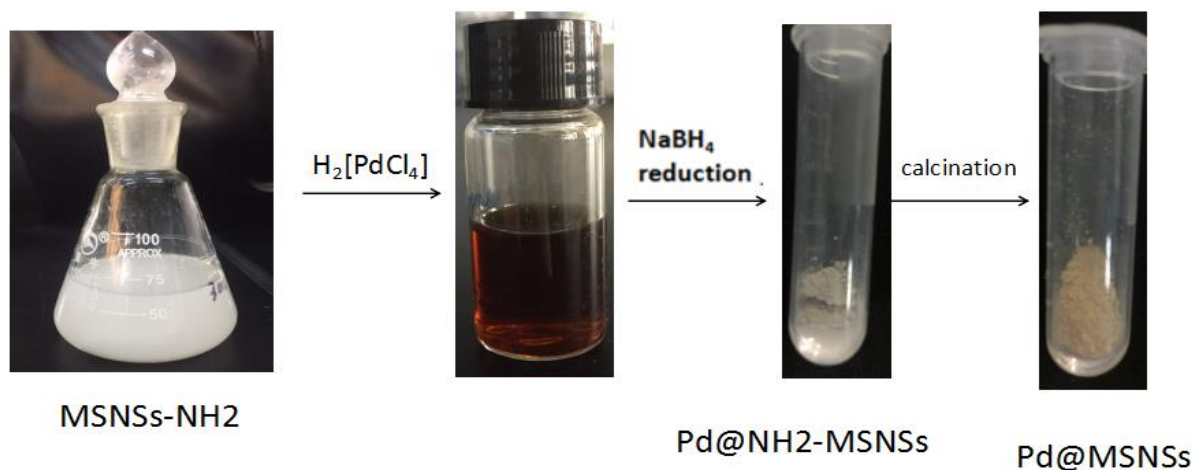


Fig 3. Photographs of preparation procedure of amino-functionalized mesoporous silica supported noble metal nanoparticle catalysts.

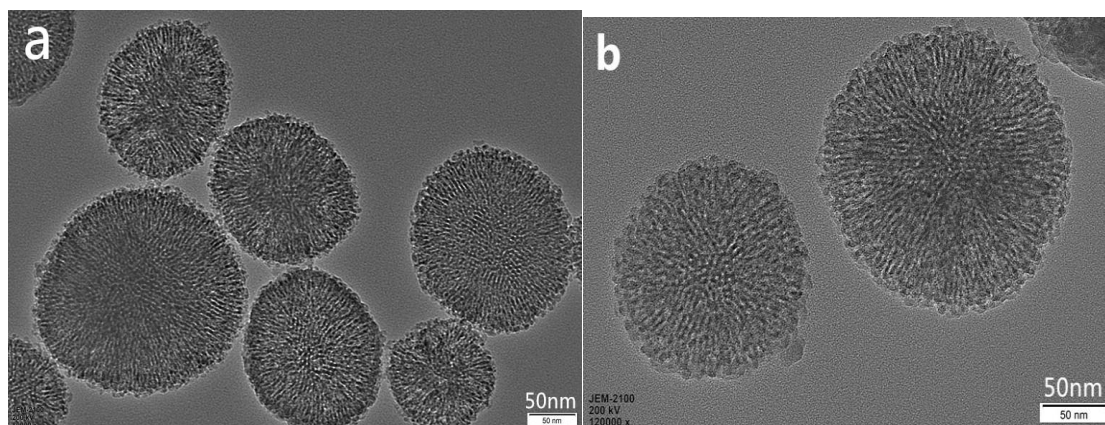
3.2 Characterization of four kinds of samples

The white products in solution showed stable suspension, and highly dispersed nano-spheres can be seen by TEM graphs. After a few days, the suspension did not generate precipitation. All the spheres exhibit uniform projections with the almost same pore arrangement patterns, indicating that the particles indeed have the spherical morphology and the pores are distributed in a spherically symmetric mode. (we can see in Fig 4)

The dispersion of the Pd nanoparticles in Pd@NH₂-MSNSs catalyst was analyzed by TEM analysis. All the particles were nano-spheres, which were intact

without aggregation. At low magnification (Fig. 4a and 4b) there were hardly any visible Pd nanoparticles, indicating that the Pd nanoparticles could be small. The small size of the Pd nanoparticles would result in the TEM images so this can prove the particles could be dispersed well in water to contain stable suspension for long time.

Lu et al also had reported this same phenomenon for supported Pd clusters in mesoporous carbon, and due to the small particle size no visible Pd clusters could be found in the framework by TEM analysis. When the TEM images with higher magnification, it is hard to find Pd nanoparticles inside the mesopores. Though there were no observable Pd nanoparticles in TEM images, Pd signal could be well detected in the spectra collected from different local areas. To further demonstrate the presence of Pd clusters in the catalyst, the Pd@NH₂-MSNSs was calcined and TEM revealed that many Pd nanoparticles appeared on the external surface of the MSNSs particles (Fig. 4c and 4d, indicated by white circle), due to the out transfer and aggregation of the dispersed Pd clusters during burn of the surfactants. Therefore, it is easy to infer that Pd nanoparticles could be identified which were located inside the mesopores. According to above results, in the Pd@NH₂-MSNSs catalyst the size of the Pd nanoparticles (or clusters) was small and well dispersed.



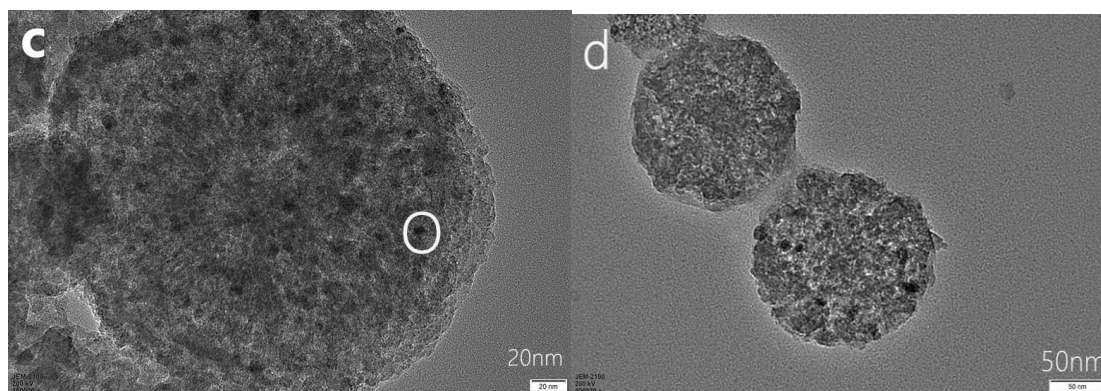


Fig. 4. TEM image of Pd@NH₂-MSNSs (a,b),Pd@MSNSs (c,d) . the white circle indicate a few observable Pd nanoparticles.

The N₂ adsorption-desorption isotherms of as-made MSNS (a) Pd@NH₂-MSNSs (b) and Pd@MSNSs (c) are both the type IV isotherm, the adsorption step of as-made MSNS (a) at partial pressure between 0.7-0.9 ,due to the capillary condensation of the filling nitrogen in the mesopores (Fig 5). The BET specific surface areas of the solvent-extracted MSNS,Pd@NH₂-MSNSs and Pd@MSNSs were 69.0264, 430.4874 and 162.1632 m²g⁻¹, respectively. The pore size distribution was very narrow with a peak centered at 4.0 nm for the Pd@NH₂-MSNSs sample The pore volumes of the as-made MSNS were 0.00318 cm³ g⁻¹. Both the samples exhibited hysteresis loops at higher partial pressures of about 0.5-0.8, which had also been observed for other meso-structures with mesoporous walls, and probably were due to the delay of nitrogen evaporation from the hollow voids blocked by the surrounding mesopores during the N₂ desorption process.

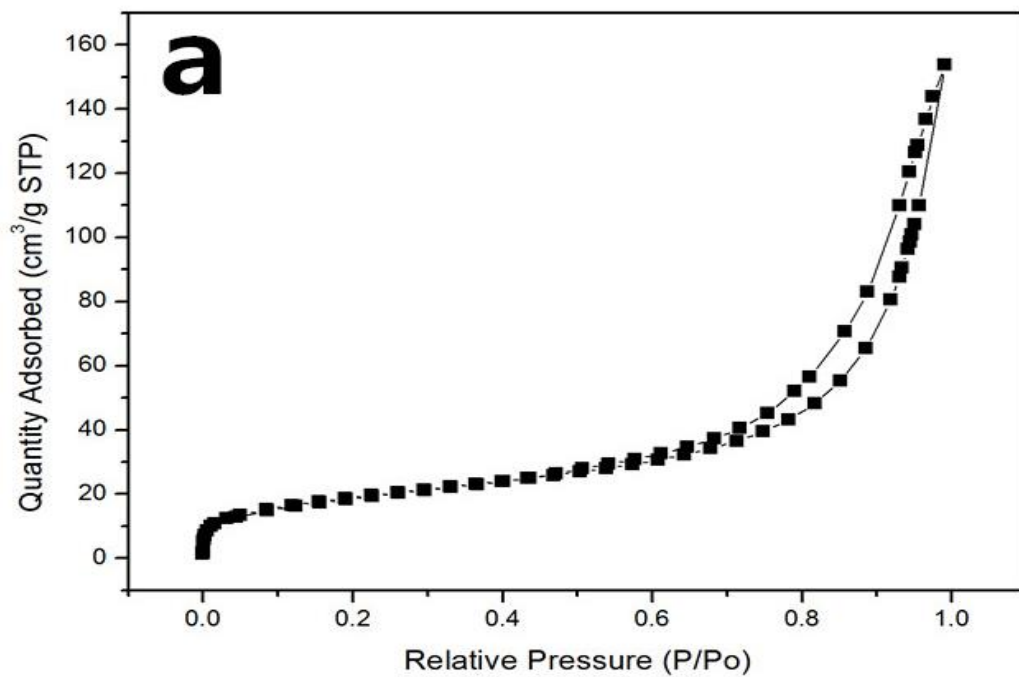
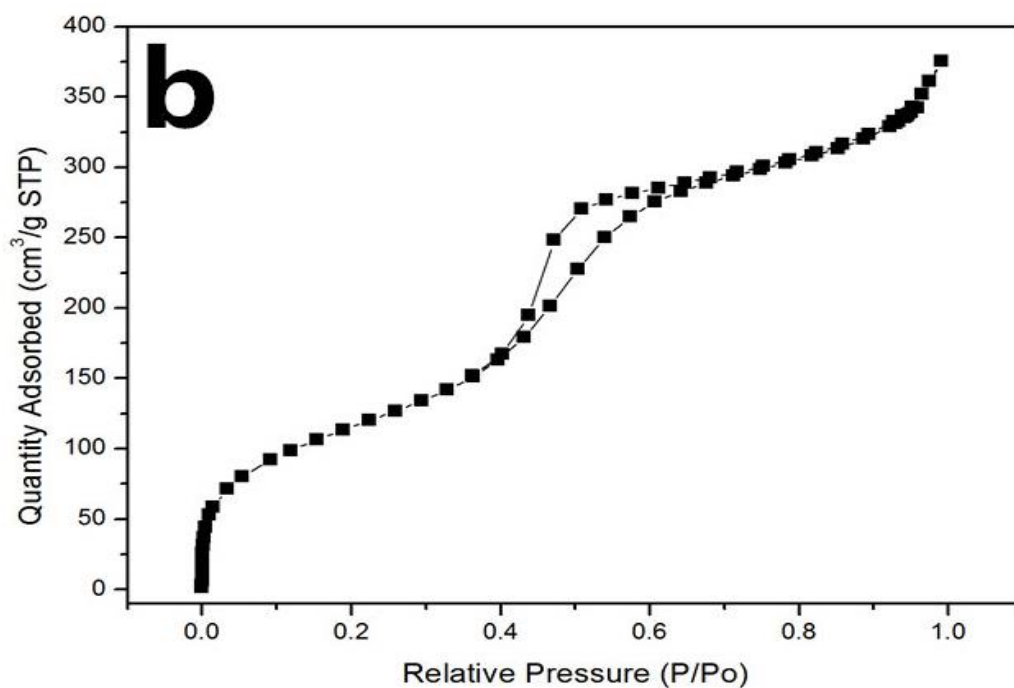


Fig 5a. The N₂ adsorption-desorption isotherms of as-made MSNS (a) BET surface=69 m²/g t-Plot=0.238cm³/g



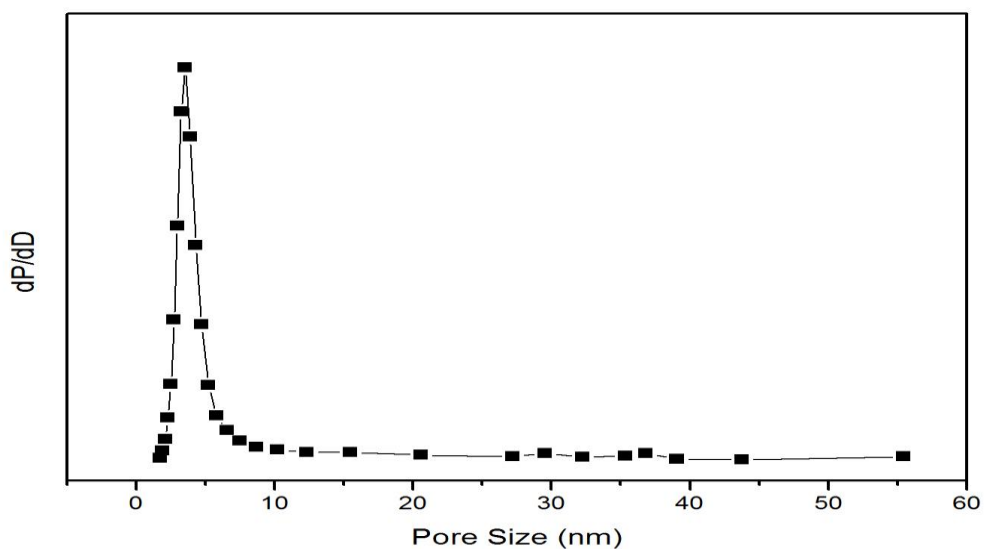


Fig 5b. The N_2 adsorption-desorption isotherms of Pd@NH₂-MSNSs (b) BET surface=430 m²/g Total volume= 1.88 cm³/g t-Plot=0.581cm³/g

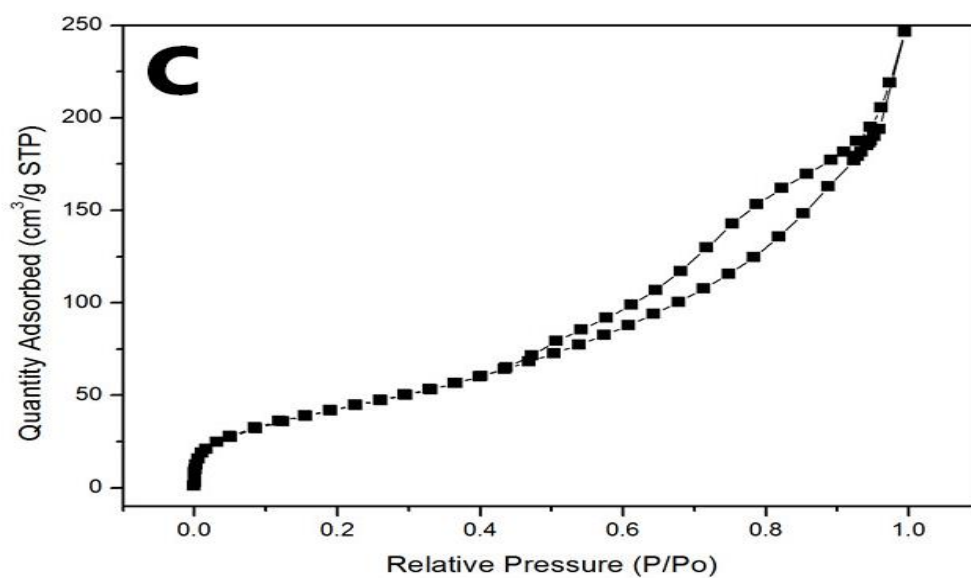


Fig 5c. The N_2 adsorption-desorption isotherms of Pd@MSNSs (c) BET surface=162 m²/g Total volume= 1.88 cm³/g t-Plot=0.381cm³/g

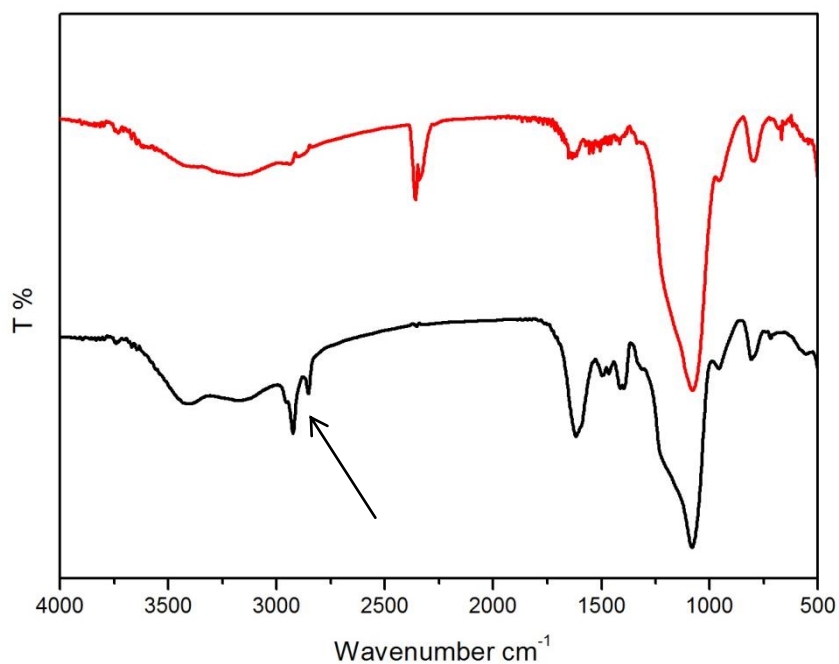


Fig 6. FT-IR spectra of as-synthesized (black line) and acetonitrile extracted MSNSs (red line)

Because our samples were synthesized through the $S^{-}N^{+} \sim I$ route and as reported previously, surface amino-functionalized products could be obtained after extraction the surfactants with a mixture of acetonitrile and HCl at room temperature. As for acetonitrile extracted product, first we need to confirm the complete removal of surfactant and then make sure the reservation of the amino-groups. Fourier Transform Infrared Spectroscopy (FT-IR) and Thermogravimetric Analysis (TG) of the as-synthesized MSNSs shows a strong resonance signal centered at about 2800cm^{-1} and 2900cm^{-1} wavenumber (indicated by the arrow), which corresponding to the C-H vibrations of the surfactant molecules in the mesoporous greatly decrease in the acetonitrile-extracted sample, which also indicates the efficient removal of the surfactant. These signals disappeared in the spectrum of the acetonitrile-extracted sample, indicating that the surfactant molecules had been completely removed.

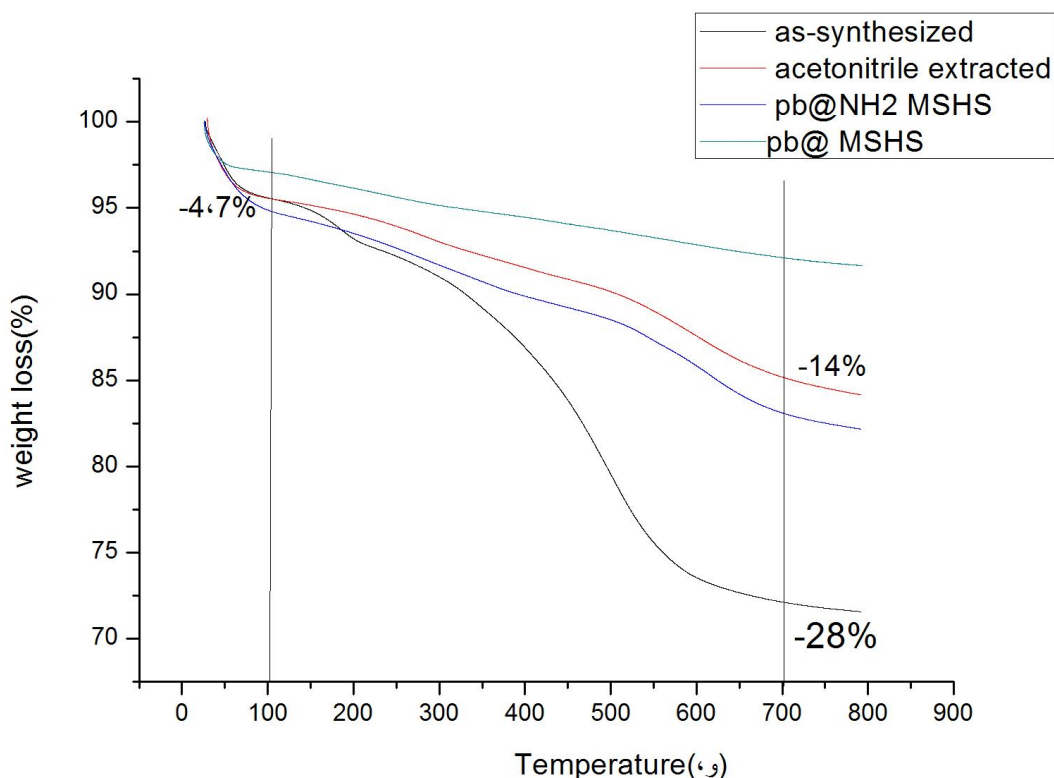


Fig 7. TG curves of the MSNSs.

TG measurement (see Fig7) shows that the weight loss was 23.3% for the as-synthesized sample and 9.3% for acetonitrile-extracted sample in the range of 100-700°C, confirming again the removal of the surfactant. The remaining Pb ion in the sample were also confirmed that the Pd@NH₂-MSNSs loss more weight than MSNSs-NH₂. It is worth noting that most of the amino groups would reside on the surface of the mesochannels because the formation of the mesostructured silica follows the S_N⁺~I pathway in our synthesis. All these results clearly indicate that after surfactant extraction, the surface amino functionalized MSHSs and Pd@NH₂-MSNSs were obtained.

3.3 catalytic experiments

Aerobic oxidation of alcohols has been widely studied in recent years because of its economic and environmental advantages,^[12] and different noble metal supported catalysts were tested on this reaction. Kaneda and coworkers reported that phenyl

ethanol and benzyl alcohol could be oxidized by hydroxyapatite supported Pd nanoparticles with high turnover frequencies. Prati and coworkers also investigated alloy effect of Au - Pd and Au - Pt catalysts in alcohol oxidation. Hutchings and coworkers showed that TiO₂-supported Au-Pd alloy nanocrystals give significantly enhanced activity for alcohol oxidation compared with monometallic Au or Pd catalysts. Corma and coworkers have demonstrated that gold nanoparticles transform nanocrystalline cerium oxide from a stoichiometric oxidant into a catalytic material for the oxidation of alcohols with high TOFs and selectivity. Here, I prepared three kind of catalytic to prove Pd@NH₂-MSNSs catalytic activity in Knoevenagel condensation reaction, the catalytic activities of the MSNSs-NH₂ catalysts were measured by aerobic oxidation of benzyl alcohol. In most cases, we can get 80%---100% reaction rate. The reaction rate is showed in Fig 8. It is concluded that MSNSs-NH₂ catalysts are benefit for reaction formula1. Whereas Pd@MSNSs catalyst are benefit the tandem reaction of alcohol oxidation to dehyde. Pd@NH₂-MSNSs catalyst congregated the virtues of above catalyst, which is benefit for Knoevenagel condensation reaction , we can get 30%-43% reaction rate in oxygen condition, which is higher than the reaction rate of the mixture of MSNSs-NH₂ and Pd@MSNSs.

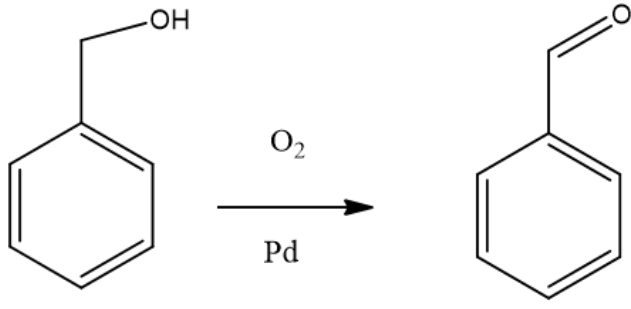
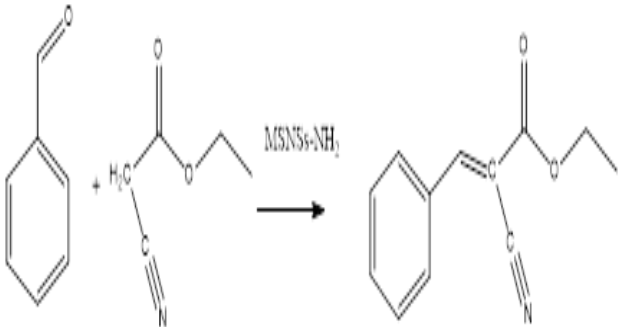
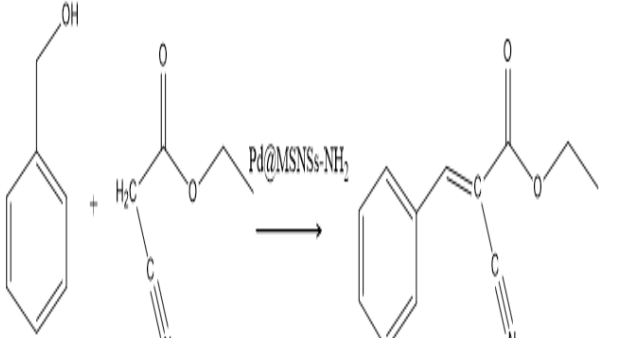
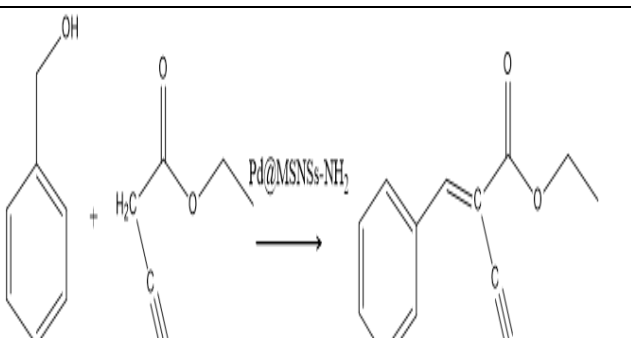
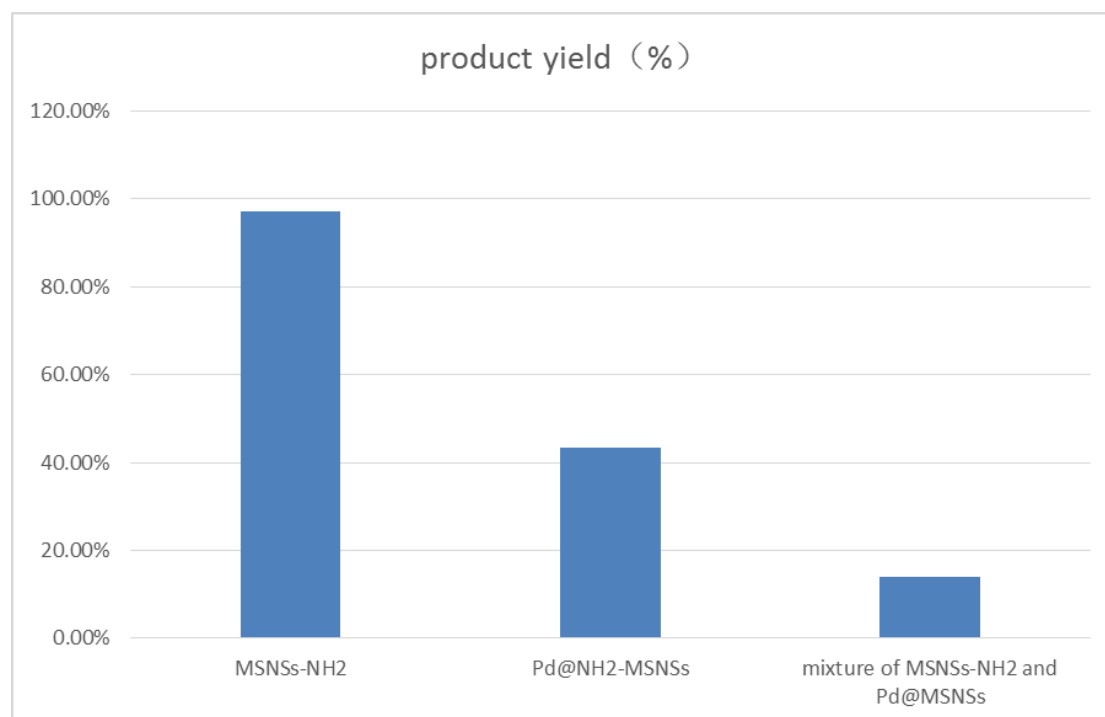
	reaction equation	reaction condition	Benzaldehyde yield	C ₁₂ NO ₂ H ₁₁ yield
Pd@MSNS		50mg catalyst +5ml benzyl alcohol	77.1%	
MSNSs-NH ₂		50mg catalyst +10mmol (1.03ml) benzaldehyde + 10mmol (1.09ml) ethyl cyanoacetate		97.3%
Pd@NH ₂ -MSNSs		50mg catalyst + 5ml benzyl alcohol + 0.5ml ethyl cyanoacetate		43.3%
mixture of MSNSs-NH ₂ and Pd@MSNSs		50mg catalyst + 5ml benzyl alcohol + 0.5ml ethyl cyanoacetate		14.1%

Fig8. The reaction of four kind of catalyst



Chapter 4 Conclusions

In the past twenty years, great progress has been made in the synthesis of mesoporous silica nanoparticles.^[13] Here, an easy method was presented to prepare supported noble metal catalysts by using as-synthesized mesostructured materials as the carrier. Using an anionic surfactant as the template and organosilane as co-structure directing agent, amino-functionalized mesoporous silica nano spheres (NH₂-MSNSs) were synthesized by self-assembly. After extraction of the anionic surfactant templates by solvent, silica nano-spheres with ordered and radially oriented amino-functionalized mesochannels were obtained. Then, we utilized the amine groups immobilized on the mesoporous surface as stabilizing and capturing agents to prepare Pd nanoparticle supported NH₂-MSNSs catalysts. The Pd@MSNSs-NH₂ catalyst showed higher catalytic activity in hydrogenation of allyl alcohol and aerobic oxidation of benzyl alcohol reactions than that of the mixture of amino-functionalized MSNSs and Pd@MSNSs catalyst. So it is easy to know MSNSs-NH₂ catalysts are benefit for reaction formula1. Whereas Pd@MSNSs catalyst are benefit the tandem reaction of alcohol oxidation to dehyde. Formula 2 is a total reaction of formula 1 and 3. Pd@NH₂-MSNSs catalyst congregated the virtues of above catalyst, which is benefit for Knoevenagel condensation reaction(formula2). For comparison, Pd@NH₂-MSNSs catalyst exhibit relatively good catalytic activity in tandem reaction.

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Acknowledgements

My study at the School of Chemistry and Pharmaceutical Engineering will soon come to an end, at the completion of my graduation thesis; I wish to express my sincere gratitude to all those who have support me and give me much help during the four years of my undergraduate study here at Qi Lu University of Technology.

Firstly, I would like to express my heartfelt appreciate to my supervisor, Professor Wang Jingui because of his constant guidance. He has walked me through all the stages of the experiment. When i failed in my first experiment, he encourage me to retry again. Without his strict requirements, my hand-working ability can not make progress and my experiment could not success in the short time..

Secondly, I should give my heartfelt thanks to all the other members of the CESS lab group for their patient instructions in various experimental instructions and their precious suggestions. I want to appreciate senior Fu Kairui and Wang Yichen, they taught me more about how to use a new instument.

Lastly, my thanks would go to my lovely family for their enough considerations and great confidence in me all through these years. I also want to express my sincere gratitude to my fellow classmates and my friends who gave me their help and time in supporing me and helping me solve my troubles during the difficult course of the thesis.