



Mild Hydrogenation of α-Pinene Catalyzed by Ru Nanoparticles Loaded on Boron-doped Amphiphilic Core-Shell Mesoporous Molecular Sieves

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Highly dispersed and stable catalysts comprising Ru nanoparticles supported on boron-doped amphiphilic core-shell mesoporous molecular sieves (MMS–C@MMS–NH₂/B/Ru) with alkyl-modified hydrophobic silica core and NH₂-functionalized hydrophilic silica shell are successfully prepared for use in hydrogenation of α -pinene for the first time. Dodecyl-modified MMS–C₁₂@MMS–NH₂/B/Ru exhibits the best catalytic activity under mild hydrogenation conditions. The abundant –NH₂ functional groups on the molecular sieve surface and their amphipathy allow the sieves to facilitate attachment of more

Introduction

Biomass utilization has been attracting increased attention because it can ensure energy security, protect the environment, and promote sustainable development of the eco-society.^[1] Turpentine obtained from pine trees is one of the naturally rich resources that contains more than 80% of α -pinene.^[2] Pinane, obtained by the hydrogenation of α -pinene, is an important chemical intermediate for the synthesis of valuable spices, medicines, and other fine chemicals.^[3] Two species, including *cis*pinane and *trans*-pinane, can be obtained during the hydrogenation of α -pinene, but *cis*-pinane exhibits higher reactivity relative to *trans*-pinane.^[4] Therefore, it is essential to obtain a high yield of *cis*-pinane during the hydrogenation of α -pinene processes.

Metal nanoparticles possess an excellent catalytic activity for the hydrogenation reaction owing to their quantum sizes and surface effects.^[5] For example, Ni nanoparticles exhibited an excellent selectivity for *cis*-pinane which was better than those of

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Ru nanoparticles, and to simplify their dispersion in the waterorganic reaction medium. Moreover, B-doped molecular sieves may adjust their acidity to meet the needs of α -pinene hydrogenation. Under mild reaction conditions (25 °C, 1 MPa H₂, and 1 h), α -pinene can be completely converted with 99% selectivity to *cis*-pinane, because every nanocomposite is equivalent to a microreactor. The catalytic activity does not change much over 5 cycles, indicating that Ru nanoparticles are stably loaded on the molecular sieves.

Raney-Ni and Pd/C.^[6] However, the catalytic activity decayed quickly owing to the aggregation of the nanoparticles. To prevent the aggregation of metal nanoparticles, some stabilizers, such as nonionic surfactants and polymers are usually added to the catalytic system.^[7] Our research group has also made progress in the stabilization of metal nanoparticles with the use of some polymers, such as PVA, F127, P123, and TPGS-1000.^[8] However, the addition of stabilizers may lead to the formation of emulsions, thus resulting in difficulties in product separation.^[9] Currently, the developed alternative approach is to ensure the attachment of nanoparticles on solid support materials, including amorphous silica, activated carbon, and molecular sieves. These materials play a significant role since they prevent the aggregation of metal nanoparticles.^[10] Among the developed supporting materials, mesoporous molecular sieves (MMSs) have become a research hotspot in catalysis, because their high-specific surface area could allow the attachment of additional metal nanoparticles, while the large, uniform pore structure, can achieve molecular shapeselective catalysis.^[11]

However, pure silica MMS cannot be adequately dispersed in the organic phase owing to its inherent hydrophilicity. This drawback can be resolved via the surface modification or functionalization of MMS through the binding of the organic functional groups with the massive Si–OH on its surface.^[12] A more important strategy is the doping of heteroatoms in molecular sieves to improve their acidities or oxidizabilities.^[13] Modified MMSs, owing to their specific hydrophilic/hydrophobic properties, acidity, or oxidizability, have been extensively used in the adsorption-separation, catalysis, drug delivery, and sensors.^[14]

To-this-date, no prior report has investigated metal nanoparticles which have been loaded on an amphiphilic and doped periodic mesoporous molecular sieve (PMMS) with a core-shell structure. The present work first reports the synthesis of ruthenium



Scheme 1. Preparation of the catalyst MMS-C@MMS-NH₂/B/Ru.



Figure 1. STEM of MMS-C12@MMS-NH2/B/Ru and STEM-EDS mappings showing the elemental distribution of Si, Bi, and Ru.

(Ru) nanoparticles loaded on boron atoms-doped PMMS with amphipathy and a core-shell structure. PMMS is composed of an alkyl-modified hydrophobic mesoporous silica core and an aminofunctionalized hydrophilic mesoporous silica shell (MMS-C@MMS-NH2). The catalyst of MMS-C@MMS-NH2/B/Ru used for hydrogenation of α -pinene has several superior advantages. The abundant -NH₂ in the prepared PMMS allows the attachment of additional Ru nanoparticles, while the amphipathy of the molecular sieve ensures its proper and adequate dispersion in the water-organic reaction medium. The doping of boron atoms into the molecular sieve may adjust both the acidity and selectivity of the catalyst to meet the need of the reaction. Accordingly, Ru nanoparticles are well dispersed on the obtained PMMS with excellent stabilization. Therefore, the prepared catalyst of MMS-C@MMS-NH₂/B/Ru exhibits an excellent catalytic activity, high selectivity, and good recyclability in the hydrogenation of α pinene. In particular, the catalyst MMS-C12@MMS-NH2/B/Ru can effectively catalyze α -pinene to *cis*-pinane in very mild hydrogenation conditions because of the formation of the three-phase interface microreaction environments.

Results and Discussion

Preparation and Characterization of the Catalyst

Scheme 1 illustrates the overall preparation procedure of the target catalyst. Firstly, by using hexadecyl trimethyl ammonium

chloride (CTAC) as the template in a methanol aqueous solution, and tetramethoxysilane (TMOS) and alkyl trimethoxysilane (R-TriMOS) as the co-precursors, alkyl-functionalized hydrophobic silica core (MMS–C) was synthesized in alkaline conditions. Secondly, NH₂-functionalized hydrophilic silica shell (MMS–NH₂) was formed subsequently in the presence of the same template, i.e., TMOS and 3-aminopropyl trimethoxysilane (NH₂-TriMOS). Thirdly, boric acid was added in the amphiphilic MMS–C@MMS–NH₂ prepared above to prepare the doped PMMS (MMS–C@MMS–NH₂/B). Finally, the in situ reduction of the Ru precursor by NaBH₄ resulted in the target catalyst of MMS–C@MMS–NH₂/B/Ru. In consideration of the modification of catalyst with organic functional groups, the reduction by H₂ with strict conditions is not used.

In combination with the catalytic activity experiments, the structure of the prepared dodecyl (C_{12}) modified catalyst of MMS– $C_{12}@MMS-NH_2/B/Ru$ was fully characterized. Accordingly, high-angle annular dark field scanning TEM (STEM), and corresponding energy dispersive X-ray (EDX) elemental mapping images were acquired (Figure 1). The EDX images clearly displayed the distribution of the Si, B, and Ru elements. The results confirmed that the B atoms were well doped in the skeleton of the molecular sieves, and the Ru atoms were uniformly immobilized on the surface of the molecular sieves, thus indicating that Ru existed in the nanoparticles rather than in aggregated (nanocluster) forms.

The prepared silica core $MMS-C_{12}$ has an average diameter of 235.5 nm (Figure S1, Supporting Information). After the outer



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Figure 2. SEM and TEM images of $MMS-C_{12} @MMS-NH_2$ (a and c – left) and $MMS-C_{12} @MMS-NH_2/B$ (b and d - right).

silica shell was formed, the average diameter of the prepared MMS-C₁₂@MMS-NH₂ was found to 386 nm (Figure S2). According to the SEM images of MMS--C12@MMS--NH2 and MMS–C₁₂@MMS–NH₂/B shown in Figure 2 (a and b), the doping of the boron atom in the molecular sieves gave rise to increased surface roughness but maintained a uniform spherical structure. Comparison of the TEM images of MMS-C₁₂@MMS-NH₂ and MMS-C₁₂@MMS-NH₂/B in Figure 2 (c and d) indicates that the pore channels of the doped molecular sieves are still intact and not damaged. The high-resolution SEM image of MMS-C12@MMS-NH2/B/Ru shows an average diameter of 2.5 nm for the loaded Ru nanoparticles.

XRD patterns of various molecular sieves are shown in Figure 3. The small-angle diffraction peak near $2\theta = 2.3^{\circ}$ was characteristic for the mesoporous structure, and existed in all



Figure 3. XRD patterns of (a) MMS– $C_{12}@MMS–NH_{2\prime}$ (b) MMS– $C_{12}@MMS–NH_2/$ B, and (c) MMS– $C_{12}@MMS–NH_2/B/Ru.$

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modified molecular sieves. It was demonstrated that the doping of boron atoms still maintained the primary pore structure and its integrity.^[15] However, after the doping of B atoms and the loading of Ru nanoparticles, the peak intensity gradually declined. This indicated the incorporation of B and Ru made the pores less regular.

Zeta potential is an important index of colloidal dispersion stability. When the absolute value of zeta potential is higher than 30, the colloid is generally considered stable. The zeta potential of the formed MMS– $C_{12}@MMS-NH_2/B/Ru$ in aqueous solution was examined and yielded a value of -36.7 mV (Figure S3) that confirmed a good stability of the prepared catalyst. The unique hydrophilicity/hydrophobicity of the catalyst was also examined by the quantification of the water droplet contact angle (Figure S4). Elicited results indicated that the water droplet contact angle was approximately 91° for MMS– $C_{12}@MMS-NH_2/B/Ru$, thus revealing the fact that the catalyst was amphiphilic.

FT-IR spectra of various molecular sieves are shown in Figure S5. The characteristic absorption peaks at 2960, 2920, and 1138 cm⁻¹ in the IR spectrum of MMS– $C_{12}@MMS-NH_2$ showed that the organic group C_{12} was successfully introduced in the molecular sieves. The new absorption peak near 1310 cm⁻¹ for MMS– $C_{12}@MMS-NH_2/B$ corresponded to the B–O bond, which showed that B atoms were successfully doped in the skeletons of the molecular sieves. After the loading of Ru nanoparticles, the structure of MMS– $C_{12}@MMS-NH_2/B$.

Moreover, the spectrum of ²⁹Si MAS-NMR in Figure S6a showed there were three types of Si in the B-doped molecular sieves. The chemical shifts near -106.134 corresponded to Si (OSi)₃-OH and Si(OSi)₄. The other peak at -71.677 was ascribed to Si-C. This also demonstrated that the organic group C₁₂ was successfully introduced to the molecular sieves. The ¹¹B MAS-NMR spectrum in Figure S6b shows that there are two types of B in the B-doped molecular sieves. The chemical shift of -1.430 corresponding to BO₄ indicated that most of the B atoms were doped in molecular sieves. Otherwise, a few B atoms existed in the form of BO₃ with three coordinations at the chemical shift of 12.400.

TG-DTG curves of MMS– $C_{12}@MMS-NH_2/B/Ru$ are shown in Figure S7a. There were four parts of weightlessness for the B-doped molecular sieves. The removal of the adsorbed moisture mainly occurred at approximately 187 °C, and the decomposition of residual organic template agents was in the range of 187–400 °C. With increasing temperature, organic functional groups grafted in molecular sieves became cracking and shedding in the range of 400–610 °C. When the temperature became higher than 610 °C, the removal of B atoms began. However, the loss of B atoms was not found for nondoped molecular sieves based on the comparison of the TG curves of MMS– $C_{12}@MMS-NH_2$ and MMS– $C_{12}@MMS-NH_2/B/Ru$ (Figure S7b). Therefore, the B-doped molecular sieves exhibit good stability at temperatures under 400 °C.

 N_2 adsorption-desorption isotherms of $MMS-C_{12}@MMS-NH_2/B$ in Figure S8a show a typical type IV adsorption-desorption isotherm characteristics with a specific



surface area of 13 m²/g and a specific pore volume of 0.06 cm³/ g. The BJH pore size distribution curve of MMS-C₁₂@MMS-NH₂/ B in Figure S8b shows that the molecular sieves doped with B atoms had two types of different pore structures with different sizes. However, the vast majority of the pore structures were uniform with sizes in the range of 2–2.5 nm.

According to the NH₃-TPD spectra of the molecular sieves depicted in Figure S9, the peak indicating the desorption of the molecular sieves doped with B atoms was enhanced dramatically, and the area of the desorption peak increased considerably relative to SiO₂ and MMS-C₁₂@MMS-NH₂, thus indicating that the B-doping led to a significant increase of the acid amount. In addition, a strong acidic center was produced owing to the B-doping according to the temperature desorption curve achieved at temperatures above 400 °C.

XPS spectra were afforded in Figure 4. The binding energy changes of the C, O, and N atoms in the molecular sieves before and after the loading of Ru nanoparticles were also detected by XPS. The binding energy of the C atoms elicited no any changes (Figure S10). However, $\Delta E = 0.45$ and 0.60 eV are observed for the O and N atoms, respectively (Figures S11 and S12), which demonstrate that Ru nanoparticles are mainly bonded to -OH and -NH₂ on the surface of the molecular sieves. Moreover, the possibility that --NH₂ could adsorb more Ru nanoparticles was higher.



Figure 4. XPS spectra of MMS-C₁₂@MMS-NH₂/B/Ru including a) full spectrum scanning (top) and b) local amplification (bottom).

Table 1. Catalytic activity of different modified catalysts. ^[a]				
Catalyst	Ru content [wt%]	Conversion [%]	Selectivity [%]	
MMS/Ru	1.62	35.72	98.50	
MMS-C ₁₂ /Ru	1.99	34.26	98.23	
MMS–NH ₂ /Ru	2.25	44.35	99.21	

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MMS-C12@MMS-NH2/Ru 3.76 63.56 99.80 MMS-C₈@MMS-NH₂/B/Ru 3.47 73.59 99.01 99.00 MMS-C12@MMS-NH2/B/Ru 3.65 99.71 MMS-C₁₈@MMS-NH₂/B/Ru 3.74 97.15 98.82 [a] Reaction conditions: 40 °C, 1 MPa, 2 h.

Catalytic Hydrogenation of α -Pinene

The prepared Ru nanoparticles loaded on different MMSs were used to catalyze the hydrogenation of α -pinene. As shown in Table 1, nonmodified MMS/Ru showed low-catalytic activity owing to the inherent hydrophilicity of the Si material and low Ru loading. However, alkyl-modified MMS-C12/Ru did not improve the conversion but yielded a lower conversion rate. The reason was that the bulky alkyl impeded the contact of Ru nanoparticles with the substrate. NH2-modified MMS-NH2/Ru improved the conversion process in spite of its very low lipophilicity. This was because -NH₂ adsorbed more Ru nanoparticles compared to -OH. Amphiphilic MMS-C₁₂@MMS-NH₂/ Ru with a high Ru loading yielded a higher conversion. However, B-doped amphiphilic MMS-C@MMS-NH₂/B/Ru comparatively displayed the best catalytic activity, and the modification of different carbon chains on MMS-C@MMS-NH₂/ B/Ru had a considerable influence on the catalytic hydrogenation. The length of the carbon chain determined the hydrophobic ability of the amphiphilic molecular sieves. Longer carbon chains with a larger steric hindrance were unfavorable to the establishment of contacts with the substrate. Shorter carbon chains with relatively poor hydrophobicities were not conducive to the dispersion of the catalyst in the water-organic system. According to Table 1, MMS-C₁₂@MMS-NH₂/B/Ru modified with dodecyl trimethoxysilane (C_{12}) elicited the best catalytic activity. For the hydrophilic group of amphiphilic molecular sieves, the commonly used aminopropyl (3-aminopropyl trimethoxysilane) possessed excellent hydrophilicity and good coordination properties that enhanced the stability of the metal nanoparticles.

It has been reported that Pd and Ni nanoparticles exhibited good catalytic activity in the hydrogenation of α -pinene with harsh reaction conditions. However, when Pd and Ni nanoparticles were loaded on amphiphilic molecular sieves doped with B atoms, the corresponding catalysts exhibited very low catalytic activity in the hydrogenation of α -pinene (Table S1). Interestingly, Pd and Ni nanoparticles were replaced by Ru nanoparticles that resulted in very high α -pinene conversion and in increased cis-pinane selectivity. The most important reason for this finding is attributed to the severe hydrogenation conditions of Pd and Ni.

In addition, the different precursors of Ru nanoparticles, including ruthenium nitrosyl nitrate, tri-ruthenium dodecacarChemPubSoc

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Figure 5. Optimization of hydrogenation conditions.

bonyl, and ruthenium trichloride, were also investigated. The results showed that the prepared catalysts using the first two precursors had almost no catalytic activity, and the catalyst prepared by the ruthenium trichloride precursor exhibited a very high catalytic activity. Owing to the large sizes of the molecules of ruthenium nitrosyl nitrate and *tri*-ruthenium dodecacarbonyl, they could not easily enter the pore channels of the molecular sieves. Therefore, the formed Ru nanoparticles only were on the surface of the molecular sieves, which led to their easy removal.

For the hydrogenation of α -pinene catalyzed by MMS–C₁₂@MMS–NH₂/B/Ru, the reaction conditions included the Si/B molar ratio, catalyst dosage, water volume, H₂ pressure, reaction temperature, and the reaction time, which were all optimized. The results are shown in Figure 5 (a–f).

The doping of the molecular sieves with B atoms may adjust its acidity to meet the needs of the hydrogenation process of α pinene. The catalysis results of B-doped catalysts with different Si/B molar ratios are shown in Figure 5a. It is observed that the lower and the higher Si/B molar ratios were unfavorable to the hydrogenation of α -pinene. When the Si/B molar ratio was





Figure 6. Recyclability of the catalyst (25 °C, 1 MPa, 1 h).

between 30 and 100, the corresponding catalysts yielded a better catalytic activity both in terms of a higher conversion rate and a higher selectivity. In other words, the hydrogenation of α -pinene required a catalytic acidity within a certain range. To minimize the number of B atoms used, the selected Si/B molar ratio was set to 100.

Figure 5e shows the effects of the reaction temperature on hydrogenation. The conversion of α -pinene could reach 96% even at 15 °C, which indicates that the catalyst exhibited high catalytic activity. For an α -pinene mass of 0.3 g, the best hydrogenation conditions were as follows: a catalyst mass equal to 7 mg, water volume equal to 1 mL, a H₂ pressure of 1 MPa, a reaction temperature equal to 25 °C, and a reaction time of 1 h. The α -pinene was completely converted with a *cis*-pinane selectivity of 99%.

With the use of the same experimental conditions, the industrial catalysts used for the hydrogenation of α -pinene included Ru/C, Pd/C, and Raney Ni were compared with the novel Ru catalyst loaded on the molecular sieves (Table S2). The novel Ru catalyst obviously exhibited the best catalytic activity compared to the currently used industrial catalysts.

After the reaction, the catalyst was centrifuged, washed, dried, and was then applied to the subsequent reaction. The

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Figure 8. Depiction of the hydrogenation reaction process of α -pinene.

recyclability of the catalyst for the hydrogenation of α -pinene was investigated, and the results are shown in Figure 6. The conversion and selectivity did not change during the five recycling times. However, when the catalyst was reused six times, the conversion of α -pinene significantly decreased. The Ru content in the catalyst was determined by ICP-AES detection. The freshly prepared catalyst contained 3.649 wt% Ru, but 3.585 wt% Ru was still detected after the catalyst was reused six times, thus indicating that Ru nanoparticles could be loaded in a stable manner on the modified molecular sieves. The decrease of the catalytic activity is attributed to the carbon deposition in the holes of the molecular sieves.

Mechanism of Catalysis

The greatest advantage of the new catalytic system was attributed to the increased reactivity at very mild hydrogenation conditions. Figure 7 shows the microscopic image changes of the oil-water biphasic interface during the reaction process. It can be clearly observed that the bubbles gradually migrate into the oil phase from the water phase, and gradually break. The released hydrogen reacts with α -pinene in the oil phase on the surface of the solid catalyst. In simpler terms, the catalytic reaction progressed at the gas-liquid-solid interface. Therefore, every nanocomposite was equivalent to a microreactor as shown in Figure 8. There were numerous micro-



Figure 7. Microscopic images of the oil-water biphasic interface during the process of the reaction.

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reactors in the catalytic system, which resulted in increased hydrogenation efficiency. Moreover, because of the sp³ hybridization of the B atom, there was an unoccupied orbital that led to an easier access to the π -orbital of α -pinene. That was to say, the double bond of α -pinene was activated by the catalyst. Thus, H atoms were more easily added to the double bond of α -pinene. Therefore, the hydrogenation reaction had lower activation energy, and the hydrogenation condition was very mild.^[16] Additionally, the steric hindrance of the molecular sieves allowed only the endo-surface of the α -pinene to contact with the Ru nanoparticle catalyst, as shown in Figure 9. Therefore, the new catalytic system also exhibited a high selectivity for *cis*-pinane.

Conclusions

B-doped amphiphilic core-shell mesoporous molecular sieves MMS-C@MMS-NH₂/B were successfully prepared with the use of an alkyl-functionalized hydrophobic silica core and a NH₂functionalized hydrophilic silica shell. The doping of B atoms to the molecular sieves still maintained the primary pore channel and the integrity of the structure. Ru nanoparticles were loaded in a stable manner on MMS-C@MMS-NH2/B to form the hydrogenation catalyst of MMS-C@MMS-NH₂/B/Ru. The existence of abundant –NH₂ on the surface of the molecular sieves could achieve the attachment of an increased number of Ru nanoparticles. The catalyst MMS-C@MMS-NH₂/B/Ru was firstly used to catalyze the hydrogenation of α -pinene to *cis*-pinane. It exhibited an excellent catalytic activity, high selectivity, and good recyclability under mild conditions. When B atoms were doped in the skeletons of the molecular sieves, the acidity values of the sieves were adjusted, and the catalyst was



Figure 9. Proposed hydrogenation mechanism of $\alpha\mbox{-pinene}.$

spatially closer to the double bond of the α -pinene from the endo-surface. The amphipathy of the molecular sieves ensured that the catalyst was well dispersed in the water-organic reaction medium. The catalytic hydrogenation reaction progressed in the gas-liquid-solid interface. Every nanocomposite was equivalent to a microreactor, and resulted in an increased hydrogenation efficiency in mild reaction conditions. This study provided a potential new method for mild and highly efficient hydrogenation.

Experimental Section

Materials: Hexadecyl trimethyl ammonium chloride (CTAC), tetramethoxysilane (TMOS), octyl trimethoxysilane, dodecyl trimethoxysilane, octadecyl trimethoxysilane, 3-aminopropyl trimethoxysilane (APTS), and RuCl₃·3H₂O were purchased from the Aladdin Industrial Corporation or the Shanghai Siyu Chemical Technology Co., Ltd. Sodium hydroxide (NaOH), boric acid (H₃BO₃) and sodium borohydride (NaBH₄) were obtained from the Sinopharm Chemical Reagent Co., Ltd. Additionally, α -pinene (98%) was supplied by Jiangxi Hessence Chemicals Co., Ltd., and hydrogen (99.99 wt%) was obtained from Qingdao Airichem Specialty Gases & Chemicals Co., Ltd. All solvents were purified before use. Doubly deionized water was used in all experiments.

Compound characterizations: The structure of the catalyst was characterized using a Nicolet 510P Fourier transform infrared spectrometer (FT-IR) using the KBr method (frequency range from 4000 to 400 cm^{-1}), and with an Agilent V NMRS 600 magic angle spinning nuclear magnetic resonance spectrometer (²⁹Si MAS-NMR and ¹¹B MAS-NMR). The morphology of the catalyst was investigated with a JEOL JEM-2100 transmission electron microscope (TEM) and a JSM-6010LV scanning electron microscope (SEM). The high-angle, annular dark field scanning TEM (STEM), and the corresponding energy dispersive X-ray (EDX) elemental mapping images were recorded on TALOS F200X. The zeta potential was examined by a Malvern particle size analyzer (Nano S90). The water droplet contact angle was quantified using a JC2000 contact angle meter. Rigaku D/max-2500PC X-ray diffractometer (XRD) was used to study the crystal structure of Ru. Thermal gravity (TG) and differential thermal gravity (DTG) curves were recorded on a Netzsch-TG209 thermogravimetric analyzer. A NH₃ temperature programmed desorption curve (NH₃-TPD) was used to determine the acidity of the catalyst with the use of a BET-3000 adsorption instrument. The N₂ adsorption-desorption isotherm was used to determine the porous structure of the catalyst by a micromeritics ASAP 2020 adsorption instrument. The content of Ru in the catalyst was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). The valence state of Ru was determined by a Kratos Axis Ultra DLD X-ray photoelectron spectroscopy (XPS). Laser scanning confocal microscopy (Leica SP8) was used to study the bubble images during the hydrogenation reaction. The hydrogenation product was analyzed by a GC-9790 gas chromatography instrument with an FID detector.

Preparation of amphiphilic MMS–C@MMS–NH₂: CTAC (0.88 g) was dissolved in 225 mL of an aqueous solution of methanol with a weight fraction of 55.56%. NaOH solution (625 mL, 1 mol/L) was then added. The mixture was put in a 45 °C water bath and stirred at 600 r/min for 1 h. Subsequently, 160 mL of TMOS and 81 mL of the corresponding alkyl trimethoxysilane (octyl trimethoxysilane, dodecyl trimethoxysilane, or octadecyl trimethoxysilane) were dropped under stirring. After 2 h of stirring, an alkyl-functionalized hydrophobic core (MMS–C) was formed. A volume of 179 mL of TMOS and a volume of 11 mL of APTS were added to the MMS–C

solution during stirring and placed in a 35 °C water bath. After stirring for 12 h, the mixture was aged for another 12 h. The formed precipitate was separated, desiccated, and then extracted by 30 mL of anhydrous ethanol to remove the organic template agent in an oil bath at 80 °C during stirring at 500 r/min. The anhydrous ethanol was replaced by the fresh anhydrous ethanol every 12 h. After three extractions, the precipitate was centrifuged and dried under vacuum at 50 °C to obtain the target mesoporous molecular sieve with an amphiphilic and core-shell structure, which was abbreviated as MMS–C@MMS–NH₂.

Preparation of MMS–C@MMS–NH₂/B/Ru: Ruthenium nanoparticle catalysts loaded on the boron-doped amphiphilic mesoporous molecular sieves were prepared by using the impregnation method. A mass of 0.0500 g MMS–C₁₂@MMS–NH₂, 0.0020 g H₃BO₃, and 0.0150 g RuCl₃·3H₂O were dissolved in 4 mL of ethyl acetate. After supersonic dispersion for 30 min, the mixture was put in a water bath at 40 °C and stirred at 500 r/min for 12 h. Subsequently, the mixture was centrifuged, and the supernatant was removed. Another 4 mL of ethyl acetate was added. Sodium borohydride (0.0300 g) was added slowly in a dropwise manner in 1 mL of an anhydrous ethanol solution, and the reaction was allowed to occur for 2 h. After three centrifugation separations with the use of anhydrous ethanol as a detergent, the collected precipitates were dried under vacuum at 50 °C for 4 h to obtain the catalyst MMS–C₁₂@MMS–NH₂/B/Ru.

Hydrogenation of α -pinene: A typical hydrogenation procedure was executed based on which 0.30 g α -pinene, 7 mg MMS-C₁₂@MMS-NH₂/B/Ru catalyst, and 1 mL H₂O, were added to a 75 mL autoclave with a polytetrafluoroethylene liner. After sealing the autoclave, the atmosphere in the autoclave was replaced by H₂ for four times at 2.5 MPa, and H₂ was then subsequently filled at 1.0 MPa. The mixture in the autoclave was stirred for 1 h at 25 °C. Subsequently, the reaction mixture was centrifuged, and the upper product phase was separated for GC analysis. The catalyst MMS-C₁₂@MMS-NH₂/B/Ru was removed and washed with ethyl alcohol. After drying, the catalyst was reused.

Supporting Information

Supporting information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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Mild Hydrogenation of α-Pinene Catalyzed by Ru Nanoparticles Loaded on Boron-doped Amphiphilic Core-Shell Mesoporous Molecular Sieves