

# Ultrasmall Particle Sizes of Walnut-Like Mesoporous Silica Nanospheres with Unique Large Pores and Tunable Acidity for Hydrogenating Reaction

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The large particle sizes, inert frameworks, and small pore sizes of mesoporous silica nanoparticles greatly restrict their application in the acidic catalysis. The research reports a simple and versatile approach to synthesize walnut-like mesoporous silica nanospheres (WMSNs) with large tunable pores and small particle sizes by assembling with Beta seeds. The as-synthesized Beta-WMSNs composite materials possess ultrasmall particulate sizes (70 nm), large radial mesopores ( $\approx$ 30 nm), and excellent acidities (221.6 mmol g<sup>-1</sup>). Ni<sub>2</sub>P active phase is supported on the surface of Beta-WMSNs composite materials, and it is found that the obtained composite spherical materials can reduce the Ni<sub>2</sub>P particle sizes from 8.4 to 4.8 nm with the increasing amount of Beta seeds, which can provide high accessibilities of reactants to the active sites. Furthermore, the unique large pores and ultrasmall particle sizes of Beta-WMSNs samples facilitate the reduction of the diffusion resistance of reactants due to the short transporting length, thus the corresponding Ni<sub>2</sub>P/Beta-WMSNs composite catalysts show the excellent hydrogenating activity compared to the pure Ni<sub>2</sub>P/WMSNs catalyst.

# **1. Introduction**

With the continual increase of energy consumption, more stringent environmental protection laws and regulations require the petroleum industry to produce more environmental-friendly transportation fuels for the economic development. Aromatics in diesel are prone to produce hydrocarbon (HC) emission and particle matter (PM).<sup>[1]</sup> In order to protect the environment, hydrogenation of aromatic hydrocarbon in fuel would be one of the main approaches to decrease the toxic contents of aromatics. As a typical bicyclic aromatic species, naphthalene is usually taken as a probe molecule in the study of deep hydrogenation of aromatic hydrocarbons.<sup>[2,3]</sup>

It is reported that transition metal phosphides, such as MoP,<sup>[4]</sup> FeP,<sup>[5,6]</sup> CoP,<sup>[7]</sup> and  $Ni_2P$ ,<sup>[8–10]</sup> displayed higher catalytic activities

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and stabilities due to their low cost, nontoxicity, and like noble metal structures.<sup>[11-13]</sup> Oyama<sup>[14]</sup> found that Ni<sub>2</sub>P/SiO<sub>2</sub>-based catalyst showed higher activity than other tradition metal phosphides catalysts for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). The superior activity of Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst was attributed to the higher electron density in Ni<sub>2</sub>P, which could facilitate the dissociation of H<sub>2</sub>.<sup>[15,16]</sup> Ni<sub>2</sub>P supported catalysts have shown high hydrogenating activity in the application of HDS,<sup>[8,17,18]</sup> HDN,<sup>[19,20]</sup> and HDO.<sup>[21-23]</sup> The hydrogenation of aromatic compound is in urgent need of this highly active catalysts to produce deep hydrogenation products and further ring-opening products. And the higher electron density in Ni<sub>2</sub>P can enhance the adsorption of the aromatic hydrocarbons on the Ni<sub>2</sub>P active sites. Therefore, we choose Ni<sub>2</sub>P as the active species to prepare

the supported catalysts for aromatic hydrogenation.

Mesoporous silica nanoparticles (MSNs) have received considerable attraction owing to their advantageous structural properties.<sup>[24]</sup> It is well-known that the uniform mesopores and various morphologies of MSNs have great influence on their physical properties.<sup>[25-27]</sup> Compared to the conventional mesoporous silica supports (e.g., mesoporous crystalline material and Santa Barbara amorphous material series mesoporous materials), MSNs with hierarchically pore channels exhibit good biocompatibilities and high loading capacities as carriers for biomedicine and catalysis.<sup>[28-30]</sup> Especially, MSNs possess adjustable external and internal textural properties, such as relatively high specific surface areas and pore volumes, which contribute to the high accessibility of active sites.<sup>[31,32]</sup> Moreover, the multiple combination of micropore-mesopore-macropore in hierarchical channels facilitates the diffusion of reactants in various molecular sizes.<sup>[31,33]</sup> However, most of the reported particle sizes of MSNs are still in very large sizes (regularly >100 nm),<sup>[34-36]</sup> resulting in the low utilization efficiency of the active sites and in the high diffusion resistance to large aromatic hydrocarbons, which might restrict the relative applications significantly. Moreover, the acidity of catalysts plays an important role in hydrogenation, isomerization (ISO) and ring opening activity of naphthalene.<sup>[37]</sup> The intrinsic defects of weak acidity, low metal-support interaction, and poor hydrothermal stability





Figure 1. Wide angle XRD patterns of A) Beta seeds obtained at different crystallization times and B) BW series composite supports with different  $SiO_2/Al_2O_3$  molar ratios.

from pure mesoporous silicas should be avoided to benefit their extensive usages in different processes.<sup>[38]</sup> Previous studies<sup>[38–40]</sup> proved that in situ assembling of zeolites (Beta, ZSM-5, and Y-zeolites) into the framework of mesoporous silicas could not only improve the acidity and hydrothermal stability of MSNs materials, but also enhance the metal–support interaction, which would be conducive to the formation of high-dispersive Ni<sub>2</sub>P active phases. Compared with the commercial zeolites of Y and ZSM-5, Beta type zeolite has good structural selectivity, modulated acidity, and hydrothermal stability due to its unique 3D 12-ring pore system and the wide range of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio from tens to hundreds, which make it widely used in catalytic hydrogenation process.<sup>[41–43]</sup>

Nowadays, the synthesis of spherical mesoporous materials with ultrasmall particle sizes, uniform morphology, and large tunable pores, especially with the pore diameter larger than 20 nm, is significant in scientific research.<sup>[13]</sup> Moreover, it is a great challenge for coordinating the pore structure and acid property of spherical silica nanoparticles to achieve a good balance. In this research, we report an effective simple approach to fabricate walnut-like mesoporous silica nanospheres (WMSNs) with large tunable pores by combining with Beta zeolites. And, the Beta microcrystallines were added before TEOS to synthesize the Beta-WMSNs composites. This method can not only guarantee the complete combination of Beta and WMSNs materials, but also easily control the structure and morphology of the synthesized samples. Nickel phosphide is used as active species to evaluate the catalytic performance of naphthalene hydrogenation. Meanwhile, the acidity of Beta-WMSNs supported catalysts could be easily controlled by adjusting the amount of Beta addition. The influence of synthesis parameters on the typical physicochemical properties of walnut-like mesoporous silicas and the corresponding catalytic activity is investigated.

# 2. Results

# 2.1. Characterization Results of Supports

# 2.1.1. X-Ray Diffraction (XRD) Characterization

Crystallization time has a very important impact on the crystallinity and the growth of Beta zeolites. In order to explore the relationship between the growth of Beta zeolites and crystallization time, the growth of Beta zeolites at different crystallization times was investigated at the temperature of 120 °C. It can be seen from Figure 1A that there is no characteristic diffraction peak of Beta phase within 0-18 h, indicating solid phase is mainly amorphous during this period. When the crystallization time extends to 20 h, the characteristic peaks of Beta at  $2\theta = 7.7^{\circ}$  and  $22.3^{\circ}$  are detected.<sup>[44]</sup> During this period, Beta zeolites undergo a short nucleation induction period and a relatively rapid crystal growth period. After 20 h crystallization, there is no obvious change in crystallinity, indicating that the growth of the crystallization of Beta zeolites was relatively complete. Therefore, Beta zeolite obtained in 20 h crystallization time are chosen to be the optimal seeds to compound with WMSNs. Figure 1B shows the XRD patterns of BW series composite supports. All the BW composite supports display the characteristic peaks of Beta seeds compared with single WMSNs samples and the peak intensities increase with more amount of Beta, indicating that as-synthesized BW composite materials possess both Beta and WMSNs structures.

# 2.1.2. N<sub>2</sub> Adsorption–Desorption Characterization

Figure 2A,B displays the N<sub>2</sub> adsorption-desorption isotherms and the pore size distributions of BW series supports, respectively. The N<sub>2</sub> adsorption-desorption isotherms reveal that all the supports possess the type-IV isotherms. The step of the near-saturation adsorption at a high relative pressure of  $P/P_0 > 0.8$  become more sharper, and the H4 type of hysteresis loop gradually transforms to H3 type as adding more amount of Beta seeds, indicating the appearances of large mesoporous structures. When the ratios of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> decrease to 100, the corresponding specific surface areas increase from 340.2 to 542.5  $\,\mathrm{m^2}$  g^{-1}\!, and the pore volumes enlarge from 0.47 to 1.47 cm<sup>3</sup> g<sup>-1</sup> (Table 1). It can be found from Figure 2B that a narrow peak at 3.5 nm is shown on all the series supports, which belongs to pure WMSNs sample. Moreover, a wide peak appears as Beta seeds are added, which indicates that the pore sizes of corresponding samples are enlarged as the Beta seeds penetrate into the WMSNs framework.







Figure 2. A) N<sub>2</sub> adsorption-desorption patterns and B) pore diameter distribution patterns of BW series supports.

### 2.1.3. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) Characterizations

The changes of particle sizes of BW supports can be clearly observed from SEM images in **Figure 3**. After adding Beta seeds, the particle sizes of spherical silica materials directly decrease from 200 nm of pure WMSNs support to 120 nm of BW-120 composite support, and continue to shrink down to 70 nm of BW-100 as the addition of Beta increases. As seen from TEM images in **Figure 4**, the pore sizes of BW materials can also be gradually enlarged at the same time. The largest diameters of the opening pores on the surface almost reach 30 nm as the ratios of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> reach 100, which is beneficial for the mass transportation of reactants by reducing the diffusion barriers.

In order to trace the location of Beta seeds, the energydispersive X-ray spectroscopy (EDS) elemental mapping was performed and the results of Al, Si, and O species on BW-160 support are shown in **Figure 5**. It can be found that when only a small amount of Beta seeds is added, the Al species are already uniformly distributed in the silica pore channels, which confirms that the Beta seeds have been successfully assembled into the WMSNs framework.

#### 2.1.4. FT-IR Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra of the series BW composites are shown in **Figure 6**. The characteristic peaks at 803, 964, and 1094 cm<sup>-1</sup> are attributed to the Si–O–Si bond of pure mesoporous silica nanoparticles.<sup>[45]</sup> The distinct absorption peak of BW composite at 570 cm<sup>-1</sup> is appeared compared to the pure WMSNs, which is attributed to six- or five-

 Table 1. Textural properties of the supports.

Samples	S <sub>BET</sub> <sup>a)</sup> [m <sup>2</sup> g <sup>-1</sup> ]	V <sub>t</sub> <sup>b)</sup> [cm <sup>3</sup> g <sup>-1</sup> ]	D <sub>BJH</sub> <sup>c)</sup> [nm]
WMSNs	340.2	0.47	5.1
BW-160	400.7	0.54	6.0
BW-140	413.9	0.60	7.3
BW-120	528.0	1.15	11.2
BW-100	542.5	1.47	13.7

<sup>a)</sup>Surface area obtained by BET method; <sup>b)</sup>Total pore volume obtained by BET method; <sup>c)</sup>Pore diameter collected from the adsorption isotherm by BJH method.

membered rings of Si–O–Al bond due to the addition of zeolite Beta.<sup>[39,40]</sup> Moreover, the peak intensity of Si–O–Al bond in BW series composite becomes stronger when more amount of Beta seeds is added into the WMSNs, manifesting that WMSNs and Beta seeds are composited via Si–O–Al bonds.

#### 2.1.5. Synthesis Mechanism of the BW Supports

In order to investigate the formation mechanism of BW composite support, the ratio of Al<sub>2</sub>O<sub>3</sub>:TEAOH has changed in the formation of Beta seeds. The SEM images in Figure S2 in the Supporting Information show that the pore sizes of BF composite supports continue to enlarge when increasing the ratio of Al<sub>2</sub>O<sub>3</sub>:TEAOH amount, which confirms that Beta framework with more aluminum species can penetrate into the as-formed CTAB micelles easily via Si-O-Al bonds, as seen in Figure 7A. Moreover, the addition amount of TEOS at the final step has also been investigated. As seen in Figure 7B and Figure S3a in the Supporting Information, both WMSNs support and BW composite material cannot be synthesized without the addition of TEOS. As the amount of TEOS increasing to 10 mL, part of Beta seeds can insert into the CTAB micelles to form the BW composite materials successfully, whereas singe Beta seeds can still be seen in Figure 7B and Figure S3b in the Supporting Information. It can be seen from Figure 7B and Figure S3c in the Supporting Information and that all the Beta seeds are embedded within the framework of WMSNs when 20 mL TEOS are dropped into the final solution, and the as-synthesized BW composite nanoparticles are evenly dispersed. Therefore, it can be found that Beta seeds can penetrate into CTAB micelles through bonding with the surface silicon source. As the increasing amount of Beta combining with the TEOS through Si-O-Al bonds, the large pore sizes of BW composites tend to form small-sized nanoparticles in order to maintain the stability of spherical particles.<sup>[46]</sup>

#### 2.2. Characterization Results of Catalysts

# 2.2.1. XRD Characterization

**Figure 8** exhibits the XRD pattern of the synthesized series catalysts, which show the typical peaks at 40.7°, 44.8°, and 47.5° of Ni<sub>2</sub>P phase over all the Ni<sub>2</sub>P supported catalysts.<sup>[10]</sup> Furthermore, it is apparent that the corresponding peaks of







Figure 3. SEM images of the series supports. A) WMSNs; B) BW-160; C) BW-140; D) BW-120; E) BW-100; F) Beta zeolites.

 $Ni_2P$  over BW catalysts are weakened and broadened compared to those over  $Ni_2P/WMSNs$  pure siliceous catalysts without the addition of Beta. According to Scherrer equation, the sizes of  $Ni_2P$  crystallites decrease from 10.7 to 3.5 nm as the addition of Beta seeds (Table 2).<sup>[47]</sup>

**Figure 9.** It can be found that some Ni<sub>2</sub>P particles are aggregated over Ni<sub>2</sub>P supported pure WMSNs catalyst, due to its low surface areas and small pore sizes. The size distributions of Ni<sub>2</sub>P particles calculated by statistic method are displayed in Figure S4 in the Supporting Information. The size distribution of Ni<sub>2</sub>P particles over the Ni<sub>2</sub>P/WMSNs pure catalyst is much wider compared to the Ni<sub>2</sub>P/BW composite catalysts, ranging from 2 to 20 nm. As the addition amount of Beta increases, the size distribution of Ni<sub>2</sub>P become more concentrated and the corresponding average sizes of Ni<sub>2</sub>P particles calculated from TEM images decrease from 8.4 to 4.8 nm (Table 2), which agrees with the XRD analysis.

# 2.2.2. TEM Characterization

In order to further investigate the size change of  $Ni_2P$  particles, TEM images of  $Ni_2P$  supported series catalysts are shown in



Figure 4. TEM images of the series supports. A) WMSNs; B) BW-160; C) BW-140; D) BW-120; E) BW-100.





Figure 5. A) TEM, B) STEM images, and C-E) EDS patterns of BW-160 sample.

#### 2.2.3. Py-IR Characterization

The acidity of the series Ni<sub>2</sub>P/BW catalysts are measured by Py-IR at 200 and 350 °C, respectively (Figure S5, Supporting Information), and the corresponding quantifications are summarized in **Table 3**. According to Table 3, the total acid amounts of BW supports are increased due to the introduction of Beta seeds into the silica skeleton structures, from 37.8 mmol g<sup>-1</sup> for pure Ni<sub>2</sub>P/WMSNs catalyst to 221.6 mmol g<sup>-1</sup> for Ni<sub>2</sub>P/BW-100 catalyst. Moreover, the Lewis acid sites increase greatly as the amount of Beta addition changes, indicating that the addition of Beta seeds can adjust the ratio of Lewis acid and Bronsted acid in the supported Ni<sub>2</sub>P catalysts.

# 2.2.4. $H_2$ -Temperature-Programmed Reduction ( $H_2$ -TPR) Characterization

 $\rm H_2\text{-}TPR\,$  patterns of  $\rm Ni_2P/BW$  series catalysts, as shown in Figure 10, exhibit two major reduction peaks at around 420



**Figure 6.** FT-IR spectra of series supports. A) WMSNs; B) BW-160; C) BW-140; D) BW-120; E) BW-100.



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**Figure 7.** A) Schematic of the formation mechanism of BW materials by incorporating Beta seeds into CTAB micelles. B) The key role of silicon source TEOS in the synthesis process of BW composite materials.

and 800 °C, which belong to the reductions of Ni and P species, respectively. Since the P–O bond energy is extremely high, the reduction of P precursor is the key step in the formation of Ni<sub>2</sub>P. It can be seen from the H<sub>2</sub>-TPR patterns that the reduction peaks of Ni and P species over the series catalysts all move to the high temperature region, among which the reduction peak of the P species shifts to a higher temperature from 800 to 820 °C. These



Figure 8. The XRD patterns of Ni<sub>2</sub>P/BW series catalysts. A) Ni<sub>2</sub>P/WMSNs; B) Ni<sub>2</sub>P/BW-160; C) Ni<sub>2</sub>P/BW-140; D) Ni<sub>2</sub>P/BW-120; E) Ni<sub>2</sub>P/BW-100.

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Tab	le 2.	Textural	properties	of t	he	series	cata	ysts
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Samples	D <sub>c</sub> [nm] <sup>a)</sup>	D <sub>aver</sub> [nm] <sup>b)</sup>
Ni <sub>2</sub> P WMSNs	10.7	8.4
Ni <sub>2</sub> P/BW-160	7.9	6.5
Ni <sub>2</sub> P/BW-140	5.0	6.2
Ni <sub>2</sub> P/BW-120	4.1	5.5
Ni <sub>2</sub> P/BW-100	3.5	4.8

<sup>a)</sup>The particle size of Ni<sub>2</sub>P determined by Scherrer equation:  $D_c = K\lambda/\beta\cos(\theta)$ , where K is a constant taken as 0.9,  $\lambda$  is the wavelength of the X-ray radiation,  $\beta$  is the width of the peak at half maximum, and  $2\theta$  is the Bragg angle<sup>[52]</sup>; <sup>b)</sup>The average size of Ni<sub>2</sub>P obtained by statistical analyses based on TEM images from 200 to 300 Ni<sub>2</sub>P particles.

results confirm that the interaction between  $Ni_2P$  precursor and BW support become stronger as the increase amount of Beta addition, which can reduce the aggregation of  $Ni_2P$  particles and be conducive to the formation of high-dispersive  $Ni_2P$  active phases.

#### 2.2.5. XPS Characterization

For further investigating the states of Ni and P species over the series Ni<sub>2</sub>P supported catalysts, X-ray photoelectron spectroscopy (XPS) spectra of different catalysts were exhibited in Figures S6 and S7 in the Supporting Information. As seen from Figure S6 in the Supporting Information, two main Ni 2p peaks with the bonding energy of around 857 and 853 eV are shown on all the catalysts, which are assigned to Ni<sup>2+</sup> and Ni<sub>2</sub>P phase, respectively. Moreover, a small signal with the corresponding peak at about 861 eV corresponds to the divalent species.<sup>[48]</sup> According to Figure S7 in the Supporting Information, the binding energy of p2p at around 134 and 133 eV are assigned to the PO<sub>4</sub><sup>3-</sup> and H<sub>2</sub>PO<sub>3</sub><sup>-</sup>, respectively.<sup>[49]</sup> In addition, the broad peak detected at ~129 eV corresponds to the Ni<sub>2</sub>P phase.

The atom percentages over different Ni<sub>2</sub>P supported catalysts are calculated in **Table 4**. The atom percentages of Ni<sup> $\delta$ +</sup> and P<sup> $\delta$ -</sup> species in the Ni<sub>2</sub>P phase increase after adding Beta seeds,



Figure 9. TEM patterns of Ni<sub>2</sub>P/BW series catalysts. A) Ni<sub>2</sub>P/WMSNs; B) Ni<sub>2</sub>P/BW-160; C) Ni<sub>2</sub>P/BW-140; D) Ni<sub>2</sub>P/BW-120; E) Ni<sub>2</sub>P/BW-100.

indicating that a higher addition of Beta in our research scope can contributes to the formation of  $Ni_2P$  active phases.

#### 2.3. The Results of Naphthalene Selective Hydrogenation

Naphthalene is a kind of representative aromatic compound, which is widely used to evaluate the performance of aromatic hydrogenation catalysis. The results of naphthalene hydrogenating conversion are presented in **Figure 11**A. During the temperature range from 300 to 380 °C, the hydrogenating conversion rate of naphthalene over Ni<sub>2</sub>P/BW catalysts are all higher than that over pure WMSNs supported Ni<sub>2</sub>P catalyst. When the temperature continues to increase, the naphthalene conversions over Ni<sub>2</sub>P/WMSNs, Ni<sub>2</sub>P/BW-160, and Ni<sub>2</sub>P/BW-140 decrease to some extent, especially for the pure Ni<sub>2</sub>P/WMSNs catalyst, which can be ascribed to the exothermic reaction controlled by kinetical constrain at high temperature.

In order to investigate the reaction route of naphthalene hydrogenation, the products distribution is illustrated in Figure 11B. As can be seen from Figure 11B, the tetralin selectivity gradually decreases from 56.69% over Ni<sub>2</sub>P/WMSNs to 2.84% over Ni<sub>2</sub>P/ BW-100, while the contents of decalin increased from 33.62% to 65.78%. These trends indicate that more tetralin hydrogenates further to produce decalin and a higher hydrogenating conversion is achieved over BW composite catalysts compared to the pure WMSNSs supported catalyst. Moreover, besides the hydrogenation products, the ISO products of both tetralin and decalin are also detected over Ni<sub>2</sub>P/BW-120 and Ni<sub>2</sub>P/BW-100 catalysts. Those isomerization products are prepared for further ring opening reactions, which can be seen that some ring opening (OP) products are detected over Ni<sub>2</sub>P/BW-100 catalyst. Among all the catalysts, the Ni<sub>2</sub>P/BW-100 catalyst exhibit higher hydrogenation conversion as well as ISO and OP activities. The reaction route of naphthalene hydrogenation can be proposed based on the product distribution. As shown in Figure 12, naphthalene first undergoes hydrogenation reaction to produce tetralin and decalin, followed by isomerization and ring opening reactions. Thus, the hydrogenation products of tetralin and decalin have a significant effect on the ISO and OP products.

# 3. Discussion

Combined with the systematical characterization and assessment results, the series Ni<sub>2</sub>P/BW composite samples exhibit outstanding hydrogenating activity than the pure Ni<sub>2</sub>P/WMSNs silica materials. The superiorities of BW materials are closely related to its unique nanostructure and chemical properties, which could be described from the following aspects:

First, the unique structure properties of BW composite materials contribute a lot to the diffusion of large aromatic molecules. Through incorporating Beta seeds into WMSNs frameworks, the pore sizes of series BW supports enlarged from 5 nm of pure WMSNs to 30 nm of BW-100 composite. Moreover, the particle sizes of spherical silica supports directly decrease from 200 nm of pure WMSNs support to 70 nm of BW-100 support, which are beneficial to Ni<sub>2</sub>P loading due to its high specific surface areas. In addition, the short diffusion

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#### Table 3. Acid site amounts calculated from Py-IR.

		Acid amount (200 °C) [mmol g <sup>-1</sup> ]				Acid amount (350 °C) [mmol g–1]		
Catalysts	В	L	L+B	B/L	В	L	L+B	B/L
Ni <sub>2</sub> P/WMSNs	3.1	34.7	37.8	0.09	5.3	6.6	11.9	0.79
Ni <sub>2</sub> P/BW-160	3.0	44.7	47.7	0.06	3.2	26.4	29.6	0.12
Ni <sub>2</sub> P/BW-140	2.7	87.8	90.5	0.03	4.3	32.1	36.4	0.13
Ni <sub>2</sub> P/BW-120	2.1	167.6	169.7	0.01	3.6	49.0	52.6	0.07
Ni <sub>2</sub> P/BW-100	7.3	214.3	221.6	0.03	3.5	103.7	107.2	0.03

paths of ultrasmall particle sizes are also better for adsorption and desorption of reactants inside the hierarchical pore channels, which can largely reduce the diffusion resistance of large reactants.

Secondly, the acidity exerts a positive effect upon the ISO and OP activities for naphthalene. According to the Py-IR results, the amount of total (B+L) acids and medium-strong acids increase from 37.8 and 11.9 mmol g<sup>-1</sup> of Ni<sub>2</sub>P/WMSNs to 221.6 and 107.2 mmol g<sup>-1</sup> of Ni<sub>2</sub>P/BW-100, confirming that the addition of Beta seeds contributes to the optimal acidity. Moreover, Ni<sub>2</sub>P/BW-100 catalyst with the largest acidity exhibits high hydrogenating conversion as well as some isomerization products and ring opening products, while the pure Ni<sub>2</sub>P/WMSNs with the minimal acidity produces only hydrogenating products. Thus, the increased acidity plays a significant role in promoting the isomerization and ring opening reaction of naphthalene hydrogenation.

Thirdly, the Ni<sub>2</sub>P active sites have profound consequence for high hydrogenation activity. According to the statistical analysis from TEM images, the size distributions of Ni<sub>2</sub>P particles over BW composite supports are much concentrated than those over pure silica WMSNs support, which can attribute to the high specific surface areas and big pore volumes of BW supports. Among all the synthesized catalysts, Ni<sub>2</sub>P/BW-100 catalyst has smaller Ni<sub>2</sub>P average particle sizes, leading to high accessibility of active sites in the pore channel. It is achieved from the product distribution in Figure 11B, more hydrogenation products of decalin are produced over Ni<sub>2</sub>P/BW-100 catalysts due to its improved utilization rate of Ni<sub>2</sub>P active sites.



**Figure 10.** H<sub>2</sub>-TPR patterns of Ni<sub>2</sub>P/BW series catalysts. A) Ni<sub>2</sub>P/WMSNs; B) Ni<sub>2</sub>P/BW-160; C) Ni<sub>2</sub>P/BW-140; D) Ni<sub>2</sub>P/BW-120; E) Ni<sub>2</sub>P/BW-100.

The above analysis show that by adjusting the addition amount of Beta seeds, the acidity and pore structure of BW supports can be collaborative optimization, which contributes to the well-dispersion of  $Ni_2P$  active sites. The evaluation results show that the high hydrogenation activity is correlated with the acidity of BW support and the particle sizes of  $Ni_2P$  active sites, among which the isomerization reaction is closely related to the acidity.

# 4. Conclusions

In this research, walnut-like mesoporous silica nanoparticles with ultrasmall particle sizes and large radial pores were successful synthesized through the introduction of Beta seeds. The obtained BW composite materials exhibited high loading capacity, which enhanced the dispersity of Ni<sub>2</sub>P active phases. Meanwhile, the acidities of Ni<sub>2</sub>P/BW series materials could be easily adjusted through tuning the amounts of Beta addition, which consequently achieved the superior hydrogenation ability and isomerization activity. The results showed that the series Ni<sub>2</sub>P/BW catalysts exhibit higher hydrogenation activity than pure Ni<sub>2</sub>P/WMSNs catalysts. We believed that this combined synthesis of mesoporous silica nanoparticles provides a new insight into the catalytic materials for the widely potential application in the industry processes.

#### 5. Experimental Section

Synthesis of Beta Precursor Seeds: First, NaAlO<sub>2</sub>, TEOS, TEAOH, NaOH, and deionized water were mixed with the Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub>:TEAOH:NAOH:H<sub>2</sub>O molar ratio of 1:45:100:2:50. After stirring for 18 h, the precursor powders of Beta seeds were collected by filtration and desiccation.

Support Preparation: The pure WMSNs support was synthesized by the same method as mentioned in the previous papers.<sup>[50,51]</sup> Typically, 5 g CTAB, 3 g urea, 7.5 mL *n*-butyl alcohol, 150 mL deionized water, and 150 mL cyclohexane were agitated together. Then, TEOS was added dropwise to the above solution. After stirring for 30 min, the solution temperature was adjusted to 70 °C and stirring was continued for 24 h. Finally, the WMSNs product was obtained after filtering, dried, and calcinated at 550 °C for 6 h.

Beta-WMSNs support was prepared using the similar method by dissolving Beta precursor powder in the mixture solution of 5 g CTAB, 3 g urea, 7.5 mL *n*-butyl alcohol, 150 mL deionized water, and 150 mL cyclohexane. Then, TEOS was added dropwise into the above solution. The following steps were the same as the above synthetic method of pure WMSNs support. Through adjusting the amount of Beta precursor powders, Beta-WMSNs composites with different  $SiO_2/Al_2O_3$  molar

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Catalysts	Ni 2p <sub>3/2</sub> (bind	ding energy) <sup>a)</sup>	P 2p <sub>3/2</sub> (binding energy) <sup>a)</sup>			
	Ni <sup>2+</sup>	Ni <sub>2</sub> P	PO43-	H <sub>2</sub> PO <sub>3</sub> <sup>-</sup>	Ni <sub>2</sub> P	
Ni <sub>2</sub> P/WMSNs	857.0 (56.9)	853.6 (43.1)	134.1 (84.8)	133.0 (4.4)	129.7 (10.8)	
Ni <sub>2</sub> P/BW-160	857.0 (54.6)	853.6 (45.4)	134.1 (64.4)	133.3 (16.5)	129.8 (19.1)	
Ni <sub>2</sub> P/BW-140	856.8 (53.2)	853.5 (46.8)	134.1 (74.2)	133.3 (3.5)	129.9 (22.3)	
Ni <sub>2</sub> P/BW-120	856.9 (50.0)	853.5 (50.0)	134.3 (49.3)	133.4 (24.9)	129.9 (25.8)	
Ni <sub>2</sub> P/BW-100	857.0 (48.3)	853.6 (51.7)	134.2 (61.0)	133.4 (11.6)	129.8 (27.4)	

Table 4. The XPS analysis results of  $Ni_2P$  supported catalysts.

<sup>a)</sup>The data in parentheses are atom percentages.



Figure 11. A) Naphthalene conversion over  $Ni_2P$  supported catalysts and B) products distribution for  $Ni_2P$  supported catalysts under the temperature of 360 °C.

ratios (100/120/140/160) were synthesized and denoted as BW-X, where X represents the mass ratios of  $SiO_2/Al_2O_3$  molar ratios.

*Catalyst Preparation*: The Ni<sub>2</sub>P/BW catalysts were obtained after temperature-programmed reduction. The supported Ni<sub>2</sub>P catalyst precursors were prepared by impregnating with nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and ammonium hypophosphite (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) with an initial Ni/P molar ratio of 1/1. After drying and calcinating at 550 °C for 3 h, the oxidic precursors were placed in a fixed bed reactor at continued H<sub>2</sub> flow rate of 150 mL min<sup>-1</sup> and temperature of 120 °C. Then, the temperature was gradually heated to 440 °C and kept for 1 h, and then rising to 550 °C at a rate of 1 °C min<sup>-1</sup> was kept for another 3 h. The nickel phosphides were collected after cooling down to the room temperature.



**Figure 12.** Proposed reaction routes for the main products of naphthalene over Ni<sub>2</sub>P/BW catalysts. ISO: isomerization; RO: ring opening.

Measurement and Characterization: Wide-angle XRD patterns of supports and catalysts were measured on a Japan Shimadzu X-6000 diffractometer with Cu K $\alpha$  radiation (40 kV, 30 mA,  $\lambda$  = 0.1540598 nm). Nitrogen adsorption-desorption isotherms were collected using Micromeritics Tristar 3020 at 77 K. The specific surface areas were calculated by Brunauer-Emmett-Teller (BET) method. The acidity of the series catalysts was tested by Pyridine adsorption infrared spectroscopy (Py-FTIR) using a Digilab FT-IR infrared spectrometer from Bole Pacific Company. TEM was utilized through a JEM 2100 transmission electron microscope from Japan JEOL Corporation at the operating voltage of 200 kV. SEM measurements were conducted on a Hitachi SU-8010 instrument operating at 5.0 kV. The morphologies of the series supports and the dispersion of Ni<sub>2</sub>P phases were obtained by TEM images using a microscope grid in a Philips Tecnai G2 F20 S-TWIN microscope at an accelerating voltage of 300 kV. The size distributions of Ni<sub>2</sub>P phases were counted by more than 300 Ni<sub>2</sub>P particles from different regions in TEM images. The average Ni<sub>2</sub>P particles were calculated according to Equation (1)

$$D_{\text{aver}} = \frac{\sum_{i=1}^{n} d_i}{n_i} \tag{1}$$

where  $d_i$  represents the size of each Ni<sub>2</sub>P particle and  $n_i$  is the total number of Ni<sub>2</sub>P particles.

*Catalytic Activity Measurements*: After temperature-programmed reduction, 1.0 g samples of Ni<sub>2</sub>P supported catalysts were loaded in the middle of a fixed bed reactor, with both ends filled with mesh quartz sands. The hydrogenation activity of aromatic hydrocarbons was assessed by using 5% naphthalene in cyclohexane as a model compound. The naphthalene hydrogenation reaction was carried out under the condition of 4 MPa, H<sub>2</sub>/oil volumetric ratio of 500 (v/v), liquid hourly space velocity (WHSV) of 10 h<sup>-1</sup>, and temperature in the range of 300–380 °C. The reaction products were analyzed using gas chromatography-mass spectrometry (GC-MS).

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The conversion of naphthalene can be expressed by Equation (2)

Naphthalene (%) = 
$$\frac{N_{\rm f} - N_{\rm p}}{N_{\rm p}}$$
 (2)

where  $N_{\rm f}$  is the mass fraction of naphthalene in the feedstock and  $N_{\rm p}$  is the mass fraction of naphthalene in the products.

# **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.

# Keywords

beta, hydrogenating reaction, mesoporous silica nanospheres

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- Z. Wang, S. Pokhrel', M. Chen, M. Hunger, L. M\u00e4dler, J. Huang, J. Catal. 2013, 302, 10.
- [2] P. Gong, B. Li, X. Kong, J. Liu, S. Zuo, Appl. Surf. Sci. 2017, 423, 433.
- [3] C. Yan, H. Fan, S. Wu, W. Qian, G. Jin, G. Liang, B. Zong, B. Han, Green Chem. 2009, 11, 1061.
- [4] J. Bai, X. Li, A. Wang, R. Prins, Y. Wang, J. Catal. 2012, 287, 161.
- [5] X. F. Lu, L. Yu, X. W. D. Lou, Sci. Adv. 2019, 5, eaav6009.
- [6] H. Zhang, W. Zhou, J. Dong, X. F. Lu, X. W. D. Lou, Energy Environ. Sci. 2019, 12, 3348.
- [7] A. Infantes-Molina, J. Cecilia, B. Pawelec, J. Fierro, E. Rodríguez-Castellón, A. Jiménez-López, *Appl. Catal.*, A 2010, 390, 253.
- [8] J.-G. Jang, Y.-K. Lee, Appl. Catal., B 2019, 250, 181.
- [9] H. Song, M. Dai, H. Song, X. Wan, X. Xu, C. Zhang, H. Wang, Catal. Commun. 2014, 43, 151.
- [10] B. You, N. Jiang, M. Sheng, M. W. Bhushan, Y. Sun, ACS Catal. 2016, 6, 714.
- [11] K. Li, R. Wang, J. Chen, Energy Fuels 2011, 25, 854.
- [12] G. H. L. Savithra, E. Muthuswamy, R. H. Bowker, A. C. Bo, M. E. Bussel, S. L. Brock, *Chem. Mater.* 2013, 25, 825.
- [13] H. Wang, X.-K. Gu, X. Zheng, H. Pan, J. Zhu, S. Chen, L. Cao, W.-X. Li, J. Lu, Sci. Adv. 2019, 5, eaat6413.
- [14] S. T. Oyama, J. Catal. 2003, 216, 343.
- [15] J. A. Rodriguez, J.-Y. Kim, J. C. Hanson, S. J. Sawhill, M. E. Bussell, J. Phys. Chem. B 2003, 107, 6276.
- [16] S. T. Oyama, Y.-K. Lee, J. Catal. 2008, 258, 393.
- [17] L. Zhang, W. Fu, Q. Yu, T. Tang, Y. Zhao, H. Zhao, Y. Li, J. Catal. 2016, 338, 210.

- [18] S. Tian, X. Li, A. Wang, R. Prins, Y. Chen, Y. Hu, Angew. Chem., Int. Ed. 2016, 55, 4030.
- [19] C. A. Badari, F. Lónyi, E. Drotár, A. Kaszonyi, J. Valyon, Appl. Catal., B 2015, 164, 48.
- [20] P. S. Krishnan, R. Ramya, S. Umasankar, K. Shanthi, Microporous Mesoporous Mater. 2017, 242, 208.
- [21] Y. Yang, C. Ochoa-Hernández, V. C. A. de la Peña O'Shea, J. M. Coronado, D. P. Serrano, ACS Catal. 2012, 2, 592.
- [22] W. Zhen, X. Ning, B. Yang, Y. Wu, Z. Li, G. Lu, Appl. Catal., B 2018, 221, 243.
- [23] V. O. Gonçalves, P. M. de Souza, V. T. da Silva, F. B. Noronha, F. Richard, Appl. Catal., B 2017, 205, 357.
- [24] A. Bernardos, E. Piacenza, F. Sancenón, M. Hamidi, A. Maleki, R. J. Turner, R. Martínez-Máñez, Small 2019, 15, 1900669.
- [25] J. L. Vivero-Escoto, I. I. Slowing, B. G. Trewyn, V. S. Y. Lin, Small 2010, 6, 1952.
- [26] D. Desai, D. S. Karaman, N. Prabhakar, S. Tadayon, A. Duchanoy, D. M. Toivola, S. Rajput, T. Näreoja, J. M. Rosenholm, *Open Mater. Sci.* 2014, *1*, 16.
- [27] P. Qiu, B. Ma, C.-T. Hung, W. Li, D. Zhao, Acc. Chem. Res. 2019, 52, 2928.
- [28] Y. Wan, D. Zhao, Chem. Rev. 2007, 107, 2821.
- [29] X. Du, B. Shi, J. Liang, J. Bi, S. Dai, S. Z. Qiao, Adv. Mater. 2013, 25, 5981.
- [30] V. Polshettiwar, D. Cha, X. Zhang, J. M. Basset, Angew. Chem., Int. Ed. 2010, 49, 9652.
- [31] B. Y. Guan, S. L. Zhang, X. W. Lou, Angew. Chem., Int. Ed. 2018, 57, 6176.
- [32] L. Peng, C.-T. Hung, S. Wang, X. Zhang, X. Zhu, Z. Zhao, C. Wang, Y. Tang, W. Li, D. Zhao, J. Mater. Chem. 2019, 141, 7073.
- [33] K. Zhang, L.-L. Xu, J.-G. Jiang, N. Calin, K.-F. Lam, S.-J. Zhang, H.-H. Wu, G.-D. Wu, B. I. Albela, L. Bonneviot, *J. Mater. Chem.* 2013, 135, 2427.
- [34] X. Du, X. Li, H. Huang, J. He, X. Zhang, Nanoscale 2015, 7, 6173.
- [35] D. Shen, J. Yang, X. Li, L. Zhou, R. Zhang, W. Li, L. Chen, R. Wang, F. Zhang, D. Zhao, *Nano Lett.* **2014**, *14*, 923.
- [36] Y. Chen, H. Chen, J. Shi, Adv. Mater. 2013, 25, 3144.
- [37] S. Cui, G. Wang, Y. Yang, B. Liu, Fuel 2018, 225, 10.
- [38] X. Wang, J. Mei, Z. Zhao, P. Zheng, Z. Chen, D. Gao, J. Fu, J. Fan, A. Duan, C. J. A. C. Xu, ACS Catal. 2018, 8, 1891.
- [39] D. Zhang, A. Duan, Z. Zhao, C. Xu, J. Catal. 2010, 274, 273.
- [40] D. Gao, A. Duan, X. Zhang, K. Chi, Z. Zhao, J. Li, Y. Qin, X. Wang, C. Xu, J. Mater Chem. A 2015, 3, 16501.
- [41] R. L. Wadlinger, G. T. Kerr, E. J. Rosinski, U.S. Patent 3,308,069[P], 1967.
- [42] M. Treacy, J. Newsam, Nature 1988, 332, 249.
- [43] J. Higgins, R. B. LaPierre, J. Schlenker, A. Rohrman, J. Wood, G. Kerr, W. Rohrbaugh, Am. Chem. Soc., Div. Pet. Chem., Prepr. 1988, 33, 880939.
- [44] Q. Zhang, W. Ming, J. Ma, J. Zhang, P. Wang, R. Li, J. Mater. Chem. A 2014, 2, 8712.
- [45] L. Gao, Z. Shi, U. J. Etim, P. Wu, W. Xing, Y. Zhang, P. Bai, Z. Yan, Fuel 2019, 252, 653.
- [46] M. Wu, Q. Meng, Y. Chen, Y. Du, L. Zhang, Y. Li, L. Zhang, J. Shi, Adv. Mater. 2015, 27, 215.
- [47] H. Song, Q. Yu, N. Jiang, Z. Yan, T. Hao, Z. Wang, Res. Chem. Intermed. 2018, 44, 3629.
- [48] H. Song, J. Wang, Z. Wang, H. Song, F. Li, Z. Jin, J. Catal. 2014, 311, 257.
- [49] J. Cecilia, A. Infantes-Molina, E. Rodríguez-Castellón, A. Jiménez-López, J. Catal. 2009, 263, 4.
- [50] D.-S. Moon, J.-K. Lee, Langmuir 2012, 28, 12341.
- [51] D.-S. Moon, J.-K. Lee, Langmuir 2014, 30, 15574.
- [52] A. I. d'Aquino, S. J. Danforth, T. R. Clinkingbeard, B. Ilic, L. Pullan, M. A. Reynolds, B. D. Murray, M. E. Bussell, *J. Catal.* **2016**, *335*, 204.