Naphthalene Hydrogenation Saturation over Ni$_2$P/Al$_2$O$_3$ Catalysts Synthesized by Thermal Decomposition of Hypophosphite

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**ABSTRACT:** A series of Ni$_2$P/Al$_2$O$_3$ catalysts with different Ni$_2$P loadings were synthesized via thermal decomposition of hypophosphate and employed for naphthalene hydrogenation saturation. Results showed that Ni$_2$P loading greatly affected Ni$_2$P particle size and the number of active sites of the as-synthesized catalysts, which was derived from the variable interaction between PO$_x$ and Al$_2$O$_3$. When the hydrogenation saturation reaction was performed at 300 °C, 4 MPa, a H$_2$/oil volume ratio of 600, and a liquid hourly space velocity (LHSV) of 3 h$^{-1}$, 98% naphthalene conversion and 98% selectivity to decalin were achieved over Ni$_2$P/Al$_2$O$_3$ catalysts with 10 wt % Ni$_2$P. The superior naphthalene hydrogenation saturation performance was ascribed to the large specific surface area (169 m$^2$·g$^{-1}$), small Ni$_2$P particle size (3.8 nm), and the high number of exposed active sites (CO sorption 30 μmol·g$^{-1}$), which were beneficial to the adsorption and diffusion of the reactant molecules on the catalyst.

1. INTRODUCTION

Direct coal liquefaction oil is rich in aromatic hydrocarbons. The similarity between the aromatic carbon number (C$_8$–C$_{15}$) of direct coal liquefaction oil and the carbon number of ideal jet fuel makes direct coal liquefaction oil a valuable feedstock. If the aromatics in direct coal liquefaction oil could be hydrogenated and transformed into hydroaromatics or cycloalkanes, they would be used as ideal components of jet fuel, which is due to their high volumetric calorific value, good combustion performance, and good thermal stability. The key point for realizing this chemical process is to develop a catalyst for aromatic hydrogenation saturation with high selectivity. Therefore, remarkable attention has been continuously given to design and prepare a hydrogenation catalyst.

Traditional hydrogenation catalysts generally include transition-metal sulﬁdes, noble metals, transition-metal carbides, and transition-metal nitrides. Nevertheless, a commercial transition-metal sulﬁde catalyst generally has problems such as insufficient hydrogenation capacity, severe operating conditions, etc. A noble metal catalyst possesses outstanding activity for aromatic saturation, but it is expensive, scarce, and unable to use widely. Transition-metal carbides and nitrides show great hydrogenation activity, but they have poor sulfur resistance and deactivate quickly. In recent years, transition-metal phosphide catalysts, especially Ni$_2$P catalysts, are found to present potential application in the field of catalytic hydrogenation such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodearomatics (HDA) due to their special crystal structure and electronic property. Ni$_2$P catalysts possess more edges and corner positions due to the spherical structure of stacked triangular prism structural units; furthermore, they could expose more coordinated unsaturated surface atoms and provide more reaction active sites for catalytic hydrogenation. For instance, Kim et al. compared the HDS of 4,6-dimethyldibenzothiophene and dibenzothiophene over NiMo sulﬁde, CoMo sulﬁde, Ni$_2$P/USY, and Ni$_2$P/SiO$_2$ catalyst and found that the Ni$_2$P catalyst (15.2–23.7 s$^{-1}$-active site$^{-1}$) possessed higher kinetic rate constants than NiMo and CoMo sulﬁdes (4.0–8.8 s$^{-1}$-active site$^{-1}$).

It was reported that Ni$_2$P with small particle size possessed higher hydrogenation activity. Oyama et al. reported that there were two types of sites in Ni$_2$P, Ni(1) sites with tetrahedral coordination and Ni(2) sites with square pyramidal coordination. Moreover, they found that Ni(2) sites were beneﬁcial to the hydrogenation reaction, and there were more Ni(2) sites as the Ni$_2$P particle size became smaller.
Bussell et al. investigated the difference in using phosphate and hypophosphite for Ni$_2$P/Al$_2$O$_3$ catalysts and found that hypophosphite-based Ni$_2$P/B-Al$_2$O$_3$ with smaller Ni$_2$P particle size exhibited higher HDS activities. As we all know, the particle size of Ni$_2$P is greatly related to the preparation methods. Normally, Ni$_2$P catalysts are prepared by a programmed temperature reduction method. However, the employed phosphate-based precursor in this method possesses a stable P−O bond (410 kJ·mol$^{-1}$) and it usually needs higher energy to break, which determines that this method requires a very high temperature (>600 °C) for the preparation of Ni$_2$P catalysts. High temperature not only increases the energy consumption in the preparation process but also accelerates the aggregation of Ni$_2$P to form large particles. Moreover, the phosphate in precursor could interact strongly with Al$_2$O$_3$ (widely used as a support of the hydrogenation catalyst in industry) to form low-activity AlPO$_4$, inhibiting the formation of the Ni$_2$P active phase. To overcome the above weakness, two ways are developed to improve the catalytic performance of Ni$_2$P/Al$_2$O$_3$. One is to modify Al$_2$O$_3$ with other oxides (such as CeO$_2$, TiO$_2$, etc.) to weaken the interaction between phosphate and Al$_2$O$_3$. The other is to prepare Ni$_2$P catalysts at low temperatures. For instance, d’Aquino et al. prepared Ni$_2$P/Al$_2$O$_3$ from nickel hypophosphite at lower reduction temperatures (<500 °C). They found that the as-prepared Ni$_2$P catalysts possessed superior HDN and HDS activities in comparison to Ni$_2$P catalysts synthesized by the programmed temperature reduction method. Liu et al. prepared Ni$_2$P/Al$_2$O$_3$ from NH$_4$H$_2$PO$_2$ and Ni$_9$S$_8$ at 300 °C and found that when the P/Ni molar ratio was 3, the catalyst showed the best activity in the hydrogenation of dibenzothiophene. Song et al. synthesized Ni$_2$P/MCM-41 at 210−390 °C by reducing ammonium hypophosphite and nickel chloride and found that the catalyst obtained the highest hydrodesulfurization activity when the P/Ni molar ratio was 2. Miles et al. prepared Ni$_2$P/B-Al$_2$O$_3$ using hypophosphite or phosphate as a P source and found that hypophosphite-based Ni$_2$P/B-Al$_2$O$_3$ catalysts exhibited higher HDS activities than phosphate-based Ni$_2$P/B-Al$_2$O$_3$ catalysts. Thus, it is obvious that preparing the Ni$_2$P catalyst at a low temperature is an effective way to avoid the formation of AlPO$_4$.

As we all know, the hydrogenation activity of the Ni$_2$P catalyst is greatly influenced by many factors, including the preparation method, the type and dosage of precursors, preparation parameters, and so on. Among them, the Ni$_2$P loading is an important factor affecting the structure and activity of the catalyst. Zhang et al. prepared the Ni$_2$P/SiO$_2$ catalyst by the programmed temperature reduction method. They found that the catalyst with a P/Ni molar ratio of 0.8 and a Ni$_2$P loading of 30 wt % presented 99% naphthalene conversion and its selectivity to decalin was 92%. In our previous work, we found that the optimal Ni$_2$P loading was 17 wt % for Ni$_2$P/Ce-Al$_2$O$_3$ prepared by the programmed temperature reduction method. It is obvious that even if the same active component is used, different preparation methods and supports would lead to different particle distributions, dispersions, and microstructures of the resultant catalysts. Furthermore, the optimal Ni$_2$P loading would also vary due to the difference in preparation methods and supports. Due to the difference in operation parameters and the Ni$_2$P formation mechanism among different preparation methods, it is not reasonable to directly adopt the optimal Ni$_2$P loading obtained from the temperature programmed reduction method to other preparation methods.

Considering thermal decomposition of the hypophosphite method was effective to avoid the formation of AlPO$_4$ herein, we prepared the Ni$_2$P/Al$_2$O$_3$ catalyst via thermal decomposition of the hypophosphite method. The effects of the Ni$_2$P loading on the structure, morphology, and hydrogenation performance were investigated to obtain superior hydrogenation saturation activity and stability.

2. RESULTS AND DISCUSSION

2.1. Properties of Ni$_2$P/Al$_2$O$_3$ Catalysts. 2.1.1. Crystallographic Structure. Figure 1 presents X-ray diffraction (XRD) patterns of Ni$_2$P/Al$_2$O$_3$ catalysts with different Ni$_2$P loadings. It was clear that when the Ni$_2$P loading was no more than 10 wt %, Cat-5 and Cat-10 only presented diffraction peaks at 37.6, 45.6, and 67.1°, which corresponded to the crystallographic planes (311), (400), and (440) of Al$_2$O$_3$ (JCPDS no. 10−0425). The absence of typical diffraction peaks of Ni$_2$P (2θ = 40.8, 44.6, 47.3, 54.2, and 74.7°) reported by Liu et al.42 when PH$_3$ was generated, it is obtained that the particle size of Cat-15 was 4.9 nm, while that of Cat-20 catalyst was 13.2 nm, indicating that higher Ni$_2$P loading would result in larger particle size of Ni$_2$P.

2.1.2. Reducibility. H$_2$-temperature programmed reduction (TPR) was used to monitor the reducibility of the as-prepared Ni$_2$P/Al$_2$O$_3$ precursors by determining their H$_2$ consumption amount. It has been reported that the involved phosphorus compounds and the preparation methods had a distinct influence on the reduction process. In this work, nickel acetate (Ni(CH$_3$COO)$_2$·4H$_2$O) and ammonium hypophosphite (NH$_4$H$_2$PO$_2$) were employed to synthesize Ni$_2$P catalysts. Figure 2a shows the thermal gravimetric (TG) curves of NH$_4$H$_2$PO$_2$. It was obvious that the decomposition temperature of NH$_4$H$_2$PO$_2$ to produce PH$_3$ was in the range of 230−320 °C, which was lower than that of NaH$_2$PO$_2$ (330−340 °C) reported by Liu et al. When PH$_3$ was generated, it would react with Ni to form Ni$_2$P at lower temperatures. Figure 2b presented H$_2$−TPR profiles of the Ni$_2$P/Al$_2$O$_3$ precursors with different Ni$_2$P loadings. As can be seen from...
Figure 2b, except the precursor of the Cat-5 catalyst (Cat-5-pre), Cat-10-pre, Cat-15-pre, and Cat-20-pre all mainly showed two H2 consumption peaks, which were attributed to Ni2+ reduction to Ni or the reduction of P species. It was consistent with the H2-TPR analysis of Ni2P/SBA-15 catalysts reported by Zhu et al.43 In our previous work,40 it was found that Ni2P reduction from a precursor synthesized by Ni(NO3)2·6H2O and (NH4)2·HPO4 did not occur until the temperature was higher than 600 °C, which was ascribed to the strong thermodynamic stability of the P–O bond. The remarkable decrease (at least 300 °C) in the reduction temperature of Ni2P/Al2O3 precursors was mainly attributed to the low valence of P species in NH4H2PO2, which was prone to be reduced at lower temperatures. Furthermore, it can be seen that the reduction peak position and area varied as the Ni2P loading increased. This indicated that the interaction between Ni species and P species was enhanced, which might be derived from the enhanced interaction between POx and Al2O3 with the increasing Ni2P loading.21 As for the reduction peak area, according to the principle of H2-TPR, it is known that the reduction peak area is proportional to the amount of the species being reduced under the same reduction condition. Thus, it is obvious that more P species were reduced as the Ni2P loading increased, while the reduced Ni species first increased then decreased and Cat-10-pre obtained more active Ni species. This indicated that Cat-10 might possess superior catalytic performance.

2.1.3. Morphology and Particle Size Analysis. Transmission electron microscopy (TEM) was employed to observe the morphology and particle size distribution of the Ni2P/Al2O3 catalysts with different loadings (Figure 3). It is obvious that unlike the typical stacked morphology of metal sulfides, Ni2P/Al2O3 catalysts were spherical particles, which could be better dispersed on the support and expose more active sites.38 As shown in Figure 3, Cat-5, Cat-10, and Cat-15 were all well dispersed, while Cat-20 showed obvious agglomeration, leading to poor dispersibility. Combined with Table 1, it was concluded that as the Ni2P loading increased, the Ni2P particle size became larger. Moreover, when the Ni2P loading increased from 15 to 20 wt %, the increase of Ni2P particle size (6.5 → 15 nm) was much larger than that of the Ni2P loading increasing from 5 to 15 wt % (3.5 → 6.5 nm). This phenomenon was due to the low dispersion degree of Cat-20, which further caused the aggregation of Ni2P particles and resulted in a large increase in the particle size.

2.1.4. Textural Property. Table 1 presents the textural and structural properties of Ni2P/Al2O3 catalysts with different Ni2P loadings. Compared to Al2O3, all of the Ni2P/Al2O3 catalysts possessed lower specific surface area, which indicated that Ni2P was successfully loaded on the support. As the Ni2P loading increased from 5 to 10 wt %, the specific surface area and pore size of the Ni2P/Al2O3 catalysts decreased, which may be due to the formation of more Ni2P in Cat-10. When the Ni2P loading further increased to 15 or 20 wt %, the specific surface area and pore size of Cat-15 and Cat-20 were

![Figure 2. (a) TG curves of NH4H2PO2 and (b) H2-TPR profiles of Ni2P/Al2O3 precursors with different Ni2P loadings.](image)

![Figure 3. TEM images and size distribution of Ni2P/Al2O3 catalysts with different Ni2P loadings.](image)

**Table 1. Textural and Structural Properties of Ni2P/Al2O3 Catalysts with Different Ni2P Loadings**

| sample  | BET surface area (m²·g⁻¹) | average pore size (nm) | crystallite size (nm)¹ | particle size (nm)² | CO uptake (μmol·g⁻¹) |
|---------|---------------------------|------------------------|------------------------|---------------------|----------------------|
| Al2O3   | 215                       | 7.8                    |                        |                     |                      |
| Cat-5   | 173                       | 6.8                    | 3.5                    | 12                  |
| Cat-10  | 169                       | 5.2                    | 3.8                    | 30                  |
| Cat-15  | 144                       | 3.8                    | 4.9                    | 6.5                 | 18                   |
| Cat-20  | 102                       | 3.4                    | 13.2                   | 15                  | 15                   |
| Ni2P    | 7                         | 10.7                   | 44.9                   | 0.5                 |

¹Calculated from the XRD results. ²Calculated from the TEM results.
greatly decreased, which may be related to the excessive loading of Ni2P. On one hand, when the Ni2P loading was higher, the generated Ni2P particles aggregated with each other to form larger Ni2P particles, which was consistent with the XRD results (Figure 2). On the other hand, as the Ni2P loading increased, the amount of hypophosphate (HPO32−) also increased. According to our previous investigation, some of the PH3 generated by their disproportionation decomposition were used to reduce Ni2+ to Ni2P, while some of the PH3 could flow out with carrier gas. In addition, some P species may be deposited in the catalyst as phosphate to block the pore channel of the catalysts. Thus, these two aspects work together and result in the loss of the specific surface area and pore size of the Ni2P/Al2O3 catalysts.

CO pulse adsorption was employed to determine the active site number in Ni2P/Al2O3 catalysts with different loadings. As can be seen from Table 1, the amount of CO adsorption increased first and then decreased as the Ni2P loading increased. For example, the CO adsorption of the Cat-10 catalyst was 30 μmol·g−1, which meant that most Ni2P active sites were on the catalyst surface. Combining with the results from XRD, H2-TPR, and TEM, it can be seen that when the Ni2P loading increased from 5 to 10 wt %, the amount of the reduced Ni2P active phase increased, thus the CO adsorption amount gradually increased. However, when the Ni2P loading further increased to 15 or 20 wt %, the CO adsorption amount began to decrease. This might be due to the agglomeration of Ni2P particles and the deposition of P species. It can also be observed that the specific surface area and pore size of Cat-15 and Cat-20 were greatly decreased, and the pore size of Ni2P/Al2O3 catalysts with different Ni2P loadings are presented in Figure 5. It was clear that Cat-10 possessed the highest naphthalene conversion of 98% and decalin selectivity of 98% within 8 h reaction, which were greatly higher than those of NiW/Al2O3 catalysts (75% naphthalene conversion and 50% decalin selectivity) commonly used in industry. Furthermore, its activity was also better than that of Ni2P/Ce-Al2O3 prepared by the programmed temperature reduction method (95% naphthalene conversion and 76% decalin selectivity). This superior hydrogenation saturation activity could be ascribed to the large specific surface area (169 m2·g−1) of Cat-10, which enabled good dispersion of the Ni2P active phase, resulting in small particle size (3.8 nm) and the largest number of exposed active sites (CO adsorption 30 μmol·g−1). Compared to Cat-10, Cat-5 had a higher specific surface area (173 m2·g−1) and smaller Ni2P particle size (3.5 nm), but its activity (90% for naphthalene conversion and 65% for decalin selectivity) was lower than that of Cat-10. This phenomenon was due to the low loading of Ni2P, which resulted in much lower active sites (CO adsorption 12 μmol·g−1) on the surface of Cat-5. As the Ni2P loading increased to 15 wt %, the naphthalene conversion increased, less Ni active sites were exposed (Table 1), while the amount of surplus P species became higher. Thus, the fewer Ni active sites and the excessively surplus P species contributed to the variation of the acid amount.

2.2. Naphthalene Hydrogenation Saturation Performance. 2.2.1. Effect of Ni2P Loadings. The naphthalene hydrogenation saturation activity evaluation over Ni2P/Al2O3 catalysts was conducted at 300 °C, 4 MPa, a H2/oil volume ratio of 600, and liquid hourly space velocity (LHSV) of 3 h−1, which was the optimal operation condition obtained in our previous work. The reactant feed was 0.1 mL·min−1 for 3 wt % naphthalene solution and 60 mL·min−1 for H2. All experiments were repeated three times to guarantee the calculated relative deviation within 3%. The naphthalene conversion and decalin selectivity over Ni2P/Al2O3 catalysts with different Ni2P loadings are presented in Figure 5. It was clear that Cat-10 possessed the highest naphthalene conversion of 98% and decalin selectivity of 98% within 8 h reaction, which were greatly higher than those of NiW/Al2O3 catalysts (75% naphthalene conversion and 50% decalin selectivity) commonly used in industry. Furthermore, its activity was also better than that of Ni2P/Ce-Al2O3 prepared by the programmed temperature reduction method (95% naphthalene conversion and 76% decalin selectivity). This superior hydrogenation saturation activity could be ascribed to the large specific surface area (169 m2·g−1) of Cat-10, which enabled good dispersion of the Ni2P active phase, resulting in small particle size (3.8 nm) and the largest number of exposed active sites (CO adsorption 30 μmol·g−1). Compared to Cat-10, Cat-5 had a higher specific surface area (173 m2·g−1) and smaller Ni2P particle size (3.5 nm), but its activity (90% for naphthalene conversion and 65% for decalin selectivity) was lower than that of Cat-10. This phenomenon was due to the low loading of Ni2P, which resulted in much lower active sites (CO adsorption 12 μmol·g−1) on the surface of Cat-5. As the Ni2P loading increased to 15 wt %, the naphthalene conversion

Figure 4. NH3-TPD profiles of Ni2P/Al2O3 catalysts with different Ni2P loadings.
maintained at 98% but the decalin selectivity decreased to 78%. When the Ni2P loading was 20 wt %, the naphthalene conversion became 96% and the decalin selectivity decreased to 40%, while the tetralin selectivity increased to 60%. Based on the data presented in Table 1, it was reasonable to conclude that higher Ni2P loading would greatly decrease the specific surface area of the catalysts and block the pore channel of the catalysts, which would further inhibit the adsorption and diffusion of the reactant molecules on the catalyst. Meanwhile, NiP particles with higher dosage were prone to agglomerate on a smaller specific surface; as a result, the Ni2P particle size increased significantly (3.8 → 15 nm). In addition, as the Ni2P particle size increased with the higher Ni2P loading, there were more unreduced P species deposited on the active sites of the catalyst. All of these contributed to the great loss of exposed active sites (CO adsorption 30 → 15 μmol·g⁻¹) on the catalysts, leading to the decrease of the decalin selectivity of Cat-15 and Cat-20.

Although the unsupported NiP catalyst possessed pure phase Ni2P, its naphthalene conversion was only 32%, and there was only tetralin in its hydrogenation product. Thus, its hydrogenation activity is not presented in Figure 6. The poor hydrogenation activity of unsupported NiP was ascribed to its small specific surface area (7 m²·g⁻¹), which affected the dispersion of NiP, resulting in larger Ni2P particle size (44.9 nm) and a small number of active sites (CO adsorption 0.5 μmol·g⁻¹).

2.2.2. Analysis of the Spent Catalyst. To further explore why the Cat-10 catalyst possessed a superior naphthalene hydrogenation reaction, XRD is used to analyze the crystallographic structure of the fresh and spent Cat-10 catalyst (Figure 6). It is clear that the diffraction peak intensity of the spent Cat-10 was enhanced compared to that of the fresh Cat-10 catalyst, and there is still no NiP peak, which indicated that after the reaction, NiP was also well dispersed on Al2O3. TEM images (Figure 7) further provide evidence about NiP dispersion and its particle size. After the 8 h hydrogenation reaction, the NiP particle size of the Cat-10 catalyst increased from 3.8 to 5.4 nm, but it is still small enough to endow the Cat-10 catalyst with a superior naphthalene hydrogenation performance.

Moreover, X-ray photoelectron spectroscopy (XPS) was employed to monitor the electronic properties and elemental state of the Cat-10 catalyst surface before and after the reaction, and the results are shown in Figure 8. It is reported that the peak with a binding energy between 853.0 and 853.5 eV can be assigned to Ni2+ interacting with PO₄³⁻ as a consequence of superficial passivation. The Ni 2p binding energy has a low-intensity peak at 129.0–129.5 eV, which belongs to P⁶⁻ in the Ni2P phase and the peak at 133–135 eV can be ascribed to PO₄³⁻. From Figure 8, it is found that both Ni2⁺ and P⁶⁻ existed on the Cat-10 catalyst surface before and after the reaction, indicating that the type of active phase NiP unchanged during the naphthalene hydrogenation reaction. Interestingly, according to the variation of Ni2⁺ peak area, it can be noted that there are more Ni2⁺ and P⁶⁻ species in the spent Cat-10 catalyst than in the fresh Cat-10 catalyst, which means that new Ni2P produced during the naphthalene hydrogenation reaction. This phenomenon might be related to the pressure difference between the preparation condition (0.1 MPa, H₂) and the actual reaction condition (4 MPa, H₂). Under high pressure, H₂ could further reduce the phosphate deposited on the surface of the Cat-10 catalyst to active phase NiP. A similar phenomenon was observed in the hydrodeoxgenation reaction over NiP/TiO₂-Al₂O₃. In fact, further investigation about how to match the preparation and reaction condition is being conducted in our lab.

3. CONCLUSIONS
NiP/Al₂O₃ catalysts with different NiP loadings were successfully synthesized via thermal decomposition of hypophosphite. The NiP loading could greatly influence the naphthalene hydrogenation saturation activity. When the NiP loading is 10 wt %, a naphthalene conversion of 98% and decalin selectivity of 98% were obtained compared to 75% naphthalene conversion and 50% decalin selectivity for commercial NiW/Al₂O₃ catalysts. The higher naphthalene conversion and decalin selectivity were ascribed to the large specific surface area (169 m²·g⁻¹), small particle size (3.8 nm), and the large number of exposed active sites (CO adsorption 30 μmol·g⁻¹).

4. EXPERIMENTAL SECTION
4.1. Catalyst Preparation. A series of NiP/Al₂O₃ catalysts with a P/Ni molar ratio of 2 were prepared via the thermal decomposition of hypophosphite method. In a typical process, a mixture of nickel acetate (Ni(CH₃COOH)₂·4H₂O) and ammonium hypophosphite (NH₄H₂PO₃) with a P/Ni molar ratio of 2 were dissolved in a certain amount of deionized water to form a uniform solution at room temperature.
temperature. Then, 0.6 g of γ-Al₂O₃ was weighed and impregnated in the above solution. The obtained suspension was continually stirred for 12 h at room temperature and then dried at 60 °C for 12 h to obtain a catalyst precursor. The precursor was reduced in a tube furnace by heating to 400 °C (2 °C·min⁻¹) in the presence of 99.99% H₂ gas (100 mL·min⁻¹) and then reduced in a H₂ atmosphere (99.99%) at 400 °C for 2 h. In the following step, the obtained catalyst was first cooled down to room temperature under the H₂ atmosphere and then passivated with 30 mL·min⁻¹ O₂/N₂ (1 vol %) to prevent the catalyst from being oxidized by water vapor and oxygen in the air. The Ni₃P/Al₂O₃ catalyst synthesized with Ni amounts (weight percentage) of 5, 10, 15, and 20% were denoted as Cat-5, Cat-10, Cat-15, and Cat-20, respectively. Their precursors were labeled as Cat-5-pre, Cat-10-pre, Cat-15-pre, and Cat-20-pre, respectively. Moreover, considering that the precursor might decompose to produce PH₃ (a highly toxic substance) during the preparation procedure, sufficient acidic potassium permanganate solution was employed to absorb the PH₃. The following formula showed the reaction process.

\[
10\text{PH}_3 + 16\text{KMnO}_4 + 19\text{H}_2\text{SO}_4
= 16\text{MnSO}_4 + 10\text{K}_2\text{PO}_4 + 3\text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}
\]  

(1)

4.2. Catalyst Characterization. The crystal structure of the as-synthesized catalyst was analyzed by a Rigaku Ultima IV multifunctional X-ray diffractometer (Rigaku, Japan) in the range of 10–80° at a step size of 8 °·min⁻¹. The radiation was generated at 40 kV and 40 mA. The reducibility of the as-synthesized catalysts was monitored by the H₂-temperature programmed reduction (H₂-TPR) experiment over an AutoChemII 2920 chemisorption analyzer (Micromeritics). Typically, 0.05 g of catalyst precursor was placed in a quartz tube and pretreated by Ar gas (40 mL·min⁻¹) at 120 °C for 2 h to eliminate the water vapor and impurities from the catalyst precursor. Then, the sample was heated to 800 °C at 10 °C·min⁻¹ in the presence of 10 vol % H₂/Ar at a flow rate of 50 mL·min⁻¹. The H₂ consumption amount was recorded via a thermal conductivity detector.

The morphologies of the as-synthesized catalysts were monitored on a JEOL JEM2100F transmission electron microscope (TEM, Japan), which was operated at 200 kV. The particle size distribution of the samples was analyzed by Image Pro Plus 5.0.

The specific surface area of the as-synthesized catalysts was tested using a physical adsorption instrument (JW-BK122W). The samples were outgassed under vacuum at 300 °C for 3 h before proceeding with the analysis. The N₂ adsorption–desorption experiment was carried out at −196 °C. The specific surface area of the samples was obtained using the Brunauer–Emmett–Teller (BET) method, and Barrett–Joyner–Halenda (BJH) analysis was used to obtain pore distribution.

The acidic properties of the as-synthesized catalysts were evaluated by the temperature programmed desorption (NH₃-TPD) experiment over a Micromeritics AutoChemII 2920 chemisorption analyzer and a thermal conductivity detector (TCD). Typically, 0.06 g of catalyst precursor was placed in a quartz tube and purged by 99.999% Ar gas with the temperature increased to 400 °C at 20 °C·min⁻¹. The reduction of samples was then performed in the presence of 10 vol % H₂/Ar mixed gas (50 mL·min⁻¹) for 2 h. When the reactor temperature was decreased to 100 °C in a He atmosphere, 3 vol % NH₃/He mixed gas was employed to conduct NH₃ adsorption at 100 °C for 0.5 h, and then the temperature increased to 700 °C at 10 °C·min⁻¹ to desorb NH₃ under the He atmosphere.

The active site number of the as-synthesized catalysts was measured by CO pulsed chemisorption over an AutoChemII 2920 chemisorption analyzer (Micromeritics). Generally, 0.1g of catalysts were put in a quartz tube and purged with Ar gas (99.999%). The temperature was increased to 400 °C at 20 °C·min⁻¹, and then 10 vol % H₂/Ar mixture gas (50 mL·min⁻¹) was employed to reduce the samples at 400 °C for 2 h. When the reactor temperature was decreased to room temperature in an Ar atmosphere, 5 vol % CO/Ar mixed gas was pulsed into the reaction system until the adsorption was saturated (the sampling loop capacity was 0.1 mL).

4.3. Catalytic Activity Evaluation. The naphthalene hydrogenation activity evaluation was performed in a fixed-bed stainless steel reactor at 300 °C, 4 MPa. The flow rate of the feed solution (3 wt % naphthalene in decane) was 0.1 mL·min⁻¹ and the flow rate of H₂ was 60 mL·min⁻¹. The liquid hourly space velocity (LHSV) of the feed solution was 3 h⁻¹. Typically, 0.2 g of catalyst (0.25–0.42 mm) was diluted with quartz sand (0.25–0.42 mm) to reach 2 mL, and then the diluted catalyst was filled into the constant temperature area of the reaction tube. Before the reaction proceeded, the catalyst was reduced at 400 °C under a H₂ atmosphere (0.1 MPa, 100 mL·min⁻¹) for 2 h to expose the active phase. After the reduction is completed, the reaction temperature and pressure were adjusted to 300 °C and 4.0 MPa, respectively. The naphthalene solution (0.1 mL·min⁻¹) and H₂ (60 mL·min⁻¹) are then passed through the reactor. In this experiment, the internal standard method was used for the quantitative analysis.
of the products. Dodecane was used as the internal standard substance and ethanol was the solvent. Each naphthalene hydrogenation reaction proceeded for 8 h, and the hydrogenation product obtained at every interval of 1 h was mixed with the internal standard for sampling and analysis. Each reaction was performed three times, and the experimental data were considered reliable only if the calculated relative deviation was within 3%. The naphthalene conversion and the product selectivity were calculated as follows

$$X_{C_{10}H_8} = \frac{N_{C_{10}H_8,in} - N_{C_{10}H_8,out}}{N_{C_{10}H_8,in}} \times 100\%$$

(2)

$$S_j = \frac{N_j}{\sum N_j} \times 100\%$$

(3)

where $X_{C_{10}H_8}$ is the conversion of naphthalene, $S_j$ is the selectivity of the product, $N_{C_{10}H_8,in}$ and $N_{C_{10}H_8,out}$ represent the molar weight of $C_{10}H_8$ at the reactor inlet and outlet, respectively. $N_j$ and $\sum N_j$ are the molar weight of each product and the total molar weight of all products, respectively.

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Notes

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