C9 Petroleum Resin Hydrogenation over a PEG1000-Modified Nickel Catalyst Supported on a Recyclable Fluid Catalytic Cracking Catalyst Residue

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ABSTRACT: A PEG1000-modified nickel-based catalyst (Ni-PEG1000/FC3R) supported on an activated fluid catalytic cracking catalyst residue (FC3R) was synthesized and applied to C9 petroleum resin (C9PR) hydrogenation. The results of the Brunauer−Emmett−Teller method, X-ray diffraction, H2 temperature-programmed reduction, and scanning electron microscopy−energy-dispersive X-ray spectroscopy show that the Ni-PEG1000/FC3R catalyst had a smaller crystallite size and higher Ni dispersion than those of a Ni/FC3R catalyst. The prepared Ni-PEG1000/FC3R catalyst was applied in a hydrogenation of C9PR at 270 °C and 6 MPa H2 pressure for 3 h. Under these conditions, the bromine value of C9PR was decreased from 46.1 g Br/100 g (Gardner color grade no. 11) to 0.72 g Br/100 g (Gardner color grade no. 1), and the sulfur content was reduced from 25.7 to 1.66 mg kg⁻¹. Experimental results show that the Ni-PEG1000/FC3R catalyst exhibited high activity and stability for C9PR hydrogenation.

1. INTRODUCTION

C9 petroleum resin (C9PR) is a thermoplastic polymer obtained by polymerization of the C9 fraction, which is derived from ethylene cracking. C9PR without any post-treatment normally exhibits a glassy state at room temperature with a color of yellow to amber, and the molecular weights range from 300 to 3000 Da. The unsaturated bonds (mainly ethylene C=C bonds and aromatic rings) present in the C9PR are easily oxidized, which results in its dark color, low thermal stability, and poor compatibility. Various modification methods have been conducted to improve the performance of C9PR, among which hydrogenation is the most effective method for obtaining high-quality petroleum resins. Hydrogenated C9 petroleum resin (HC9PR) has a low bromine value, light color, high thermal stability, and good light resistance. This resin is commonly referred as “tackifying resin”, which is widely applied to the field of oil field chemicals, rubber tackifiers, coating agents, sizing agents, pressure-sensitive adhesive tapes, food packaging supplies, etc. Noble-metal catalysts (Ru, Pd, or Pt) loaded on various supports have been widely used in such kind of hydrogenation and showed significantly high activities. Sae-Ma et al. prepared a 2% Pd/γ-alumina catalyst for C9PR hydrogenation, and the prepared catalyst showed a significant hydrogenation activity under a pressure of 70 bar and a temperature of 250 °C. However, noble-metal catalysts are prone to be deactivated quickly, owing to the poisoning of the noble metal caused by [S] or [Cl] remaining in the petroleum resin. Furthermore, the high price of noble-metal catalysts limits their widespread application in an industrial scale. Nickel catalysts have been extensively used in hydrogenation reactions because of their low price, poisoning resistance, and high selectivity. Previous work reported a NiMoS catalyst for C9PR hydrogenation and obtained a maximum degree of hydrogenation under 290 °C, 7 h, and 30 bar H2 (100 and 78% for olefinic and aromatic moieties, respectively). Nevertheless, it is well-known that the conventional supported nickel-based catalysts show low activities due to the Ni²⁺ agglomeration on the support. In order to improve the activity and stability of the catalysts, some surfactants have been employed to improve the dispersion of the active component on the supported catalyst. Liaw et al. reported that the particle sizes of the Co−Ni−B catalyst could be effectively controlled by using poly(vinylpyrrolidone) (PVP) as a modifier. It was found that polyethylene glycol 1000 (PEG1000) could effectively prevent agglomeration of active components in catalysts, resulting in a higher dispersion and activity in catalytic hydrogenation.
The fluid catalytic cracking catalyst residue (FC3R) is the most popularly used catalyst in the heavy oil cracking process.\(^{20}\) The production of the FC3R catalyst reached about 370,000 t/a worldwide. Because of the heavy-metal deposition (such as Ni, Fe, and V), abrasion, and carbon deposition, catalyst deactivation is discarded.\(^{21}\) The main way to deal with the residue is to dump it into a landfill, but heavy metals in the residue can leach into groundwater and soil, causing environmental pollution. The FC3R residue mainly consists of SiO\(_2\) and Al\(_2\)O\(_3\) and can be considered as an agglomeration of zeolite crystals (mainly USY zeolite and ZSM-5 zeolite) held together by an aluminosilicate matrix.\(^{22}\) In recent years, the FC3R was extensively studied and applied for the catalytic cracking of C9PR. Furthermore, PEG1000 was used to modify the support and catalyst, and the e

2. RESULTS AND DISCUSSION

2.1. Characterization of the Support and Catalyst. The XRD patterns of FC3R, activated FC3R, NiO-PEG1000/FC3R, Ni-PEG1000/FC3R, NiO/FC3R, and Ni/FC3R are shown in Figure 1a–f. Figure 1a,b shows that the crystalline structure of the FC3R did not change before and after activation. The FC3R contained different crystalline zeolite phases (mainly Y zeolite and ZSM-5 zeolite) and Al\(_2\)O\(_3\), which were identified well through XRD.\(^{27}\) The diffraction peaks of the activated FC3R sample showed a higher intensity at 2\(\theta\) = 10.27, 12.07, 15.87, and 24.00°, which indicated the higher crystallinity of the Y zeolite present in the FC3R. This result was attributed to the residues on the surface of FC3R, which were removed (this result was consistent with SEM–EDS (Table 1)). The XRD patterns of the precursor NiO/FC3R (Figure 1e) and NiO-PEG1000/FC3R (Figure 1c) were similar. Both the patterns showed clear characteristic peaks of NiO at 2\(\theta\) = 37.31, 44.33, 62.90, 75.42, and 78.92°, which correspond to the (111), (200), (220), (311), and (222) planes, respectively.\(^{28,29}\) Figure 1d,f shows that the characteristic peaks of Ni of both the NiO-PEG1000/FC3R and NiO/FC3R could be identified after being reduced. The diffraction peaks of Ni/FC3R were intense and sharp, whereas the peaks of NiO-PEG1000/FC3R were weak and broad. The crystallite sizes of Ni were estimated using the Scherrer equation,\(^{30}\) which were approximately 22.5 and 12.3 nm for Ni/FC3R and NiO-PEG1000/FC3R, respectively. These results indicated that a high dispersion of Ni on the support and smaller crystallite size could be obtained after the treatment of PEG1000; the reason could be attributed to the adsorption of PEG1000 on the surface of FC3R, which inhibited the aggregation of crystallites.\(^{31}\)

The SEM images of FC3R and activated FC3R supports are shown in Figure 2. As shown in Figure 2a, the unactivated FC3R exhibited regular spherical particles with a very rough surface. Figure 2b,c shows a compact surface of unactivated FC3R, and no significant pore structure was observed. The reason is that the cracking residues were deposited on the surface of the FC3R, causing the blocking of channels. However, as shown in Figure 2d–f, the activated FC3R had a rich pore structure, which was beneficial for the dispersion of Ni species on the FC3R support surface. The elemental analysis of FC3R before and after being activated is presented in Table 1. After being activated, carbon deposition and heavy-metal ions were removed effectively, which resulted in a richer pore structure and greater surface area.

The morphology and size distributions of NiO/FC3R and NiO-PEG1000/FC3R are shown in Figure 3a–f. Figure 3a shows that a large amount of NiO crystallites accumulated on the surface of the NiO/FC3R catalyst and the NiO crystallites agglomerated after being calcined at 450 °C. In contrast, the NiO crystallites of the NiO-PEG1000/FC3R sample were homogeneously dispersed on the FC3R, as shown in Figure 3b. Figure 3c,d shows that the NiO crystallite size decreased after modifying using PEG1000. The particle size distribution histograms of NiO/FC3R and NiO-PEG1000/FC3R pasted in Figure 3e,f show that the mean NiO crystallite sizes were 31.05 and 13.21 nm, respectively, suggesting that NiO-PEG1000/FC3R achieved a higher surface dispersion than that of NiO/FC3R.

The BET results of FC3R, activated FC3R, Ni/FC3R, and NiO-PEG1000/FC3R are listed in Table 2. After being activated, the specific surface area of FC3R improved from 67.26 to 144.02 m\(^2\) g\(^{-1}\), and the total pore volume also increased from

![Figure 1](https://example.com/fig1.png)

**Figure 1.** XRD patterns of (a) FC3R, (b) activated FC3R, (c) NiO-PEG1000/FC3R, (d) Ni-PEG1000/FC3R, (e) NiO/FC3R, and (f) Ni/FC3R.

| sample          | C   | O   | Mg  | Al  | Si  | V   | Ca  | Fe  | Ni  |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| FC3R            | 5.08| 60.71| 0.87| 15.15| 15.4 | 0.37| 0.34| 0.62| 1.82|
| activated FC3R  | 0.25| 64.67| 0.81| 12.42| 18.79| 0.15| 1.09| 0.22| 1.60|

*Unit: %.*
0.11 to 0.15 cm$^3$ g$^{-1}$, which was attributed to the cracking residues on the surface of FC3R is removed by calcination; therefore, the pore structure of FC3R was restored. The specific surface area of Ni-PEG1000/FC3R was larger than that of Ni/FC3R. This finding may be explained by that PEG1000 inhibited the aggregation growth of Ni crystallites, which resulted in a smaller average crystallite size and the absence of blockages within the internal pores (such a result is also verified by the XRD results in Figure 1); meanwhile, these results could reasonably be explained by the smaller average pore size of Ni-PEG1000/FC3R than that of Ni/FC3R.

The H$_2$-TPR profiles of NiO/FC3R and NiO-PEG1000/FC3R catalysts are presented in Figure 4. The TPR traces of NiO/FC3R (Figure 4a) shows a high narrow hydrogen consumption peak centered at 400 °C and a high temperature hydrogen consumption peak at 780 °C, which were attributed to NiO particle reduction and the reduction of spinel NiAl$_2$O$_4$ or strongly interacting NiO/FC3R phases, respectively. The presence of such phases was confirmed by XPS characterization. The NiO-PEG1000/FC3R (Figure 4b) catalyst exhibited a broad reduction peak at around 300–600 °C and peaks centered at 400 °C and a shoulder peak at 517 °C. The lower-temperature peak at 400 °C was attributed to the reduction of pure NiO, and the shoulder peak at approximately 517 °C corresponded to the reduction of the NiO crystallites supported on FC3R. The reduction peaks shifted to a higher-temperature location after the NiO/FC3R.
catalyst was modified by PEG1000, illustrating that the interaction between NiO and the FC3R support was enhanced. The \( \text{H}_2 \) uptake and calculated Ni dispersion\(^3\) based on the \( \text{H}_2 \) uptake for the NiO/FC3R and NiO-PEG1000/FC3R are listed in Table 3. Ni loading was determined by ICP, and the crystallite size was estimated using the Scherrer equation according to the characteristic peaks toward the (200) plane of Ni (Figure 1). As can been seen in Table 3, the Ni loadings of the two catalysts were approximately the same, but the PEG1000-Ni/FC3R sample showed higher Ni dispersion (10.1\%) and smaller Ni crystallite size (12.3 nm) than those of Ni/FC3R (7.3\% and 22.5 nm, respectively), which is attributed to that the specific surface area of the Ni-PEG1000/FC3R was larger than that of Ni/FC3R. It should be noted that the Ni reduction degree was lower than 100\% due to the existing NiAl\(^2\)O\(_4\) in the reduced samples,\(^3\) which was consistent with XPS analysis.

**2.2. Catalytic Performance of Ni-PEG1000/FC3R and Ni/FC3R Catalysts in C9PR Hydrogenation.** The catalytic behaviors of Ni-PEG1000/FC3R and Ni/FC3R catalysts for C9PR hydrogenation were evaluated under a variety of conditions. Important variables including Ni loading, reaction temperature, reaction pressure, and reaction time were studied. Figure 6a shows the effects of various reaction conditions on the activity of Ni-PEG1000/FC3R and Ni/FC3R for C9PR hydrogenation. Reaction conditions: C9PR (300 g) was dissolved in 200\# oil (600 g); stirring speed, 500 r min\(^{-1}\); catalyst, 30 g. (a) Temperature, 270 °C; pressure, 6 MPa; time, 3 h. (b) Ni loading, 13 wt \%; pressure, 6 MPa; time, 3 h. (c) Ni loading, 13 wt \%; temperature, 270 °C; time, 3 h. (d) Ni loading, 13 wt \%; temperature, 270 °C; pressure, 6 MPa.

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**Table 3. Physicochemical Properties of the Ni-PEG1000/FC3R and Ni/FC3R Catalysts**

| samples            | Ni loading (wt \%) | \( \text{H}_2 \) uptake (mmol g\(^{-1}\)) | Ni dispersion (%) | Ni reduction degree (%) | Ni average crystallite size (nm) |
|--------------------|--------------------|--------------------------------------------|-------------------|-------------------------|----------------------------------|
| Ni-PEG1000/FC3R    | 12.5               | 1.72                                       | 10.1              | 80.8                    | 12.3                             |
| Ni/FC3R            | 12.3               | 1.24                                       | 7.3               | 58.4                    | 22.5                             |

\(^{a}\)Determined by ICP before \( \text{H}_2 \) reduction. \(^{b}\)Determined by \( \text{H}_2 \)-TPR. \(^{c}\)Calculated on the basis of ref 36. \(^{d}\)Calculated by the percentage of the actual \( \text{H}_2 \) uptake to the theoretical \( \text{H}_2 \) uptake for NiO being complete reduced. \(^{e}\)Calculated on the basis of XRD.

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**Table 4. XPS Analysis Results of the Ni-PEG1000/FC3R and Ni/FC3R Catalysts**

| samples            | Ni\(^0\) peak area (%) | Ni\(^2+\) peak area (%) |
|--------------------|-------------------------|-------------------------|
| Ni-PEG1000/FC3R    | 852.2 eV                 | 855.1 eV                 |
| Ni/FC3R            | 852.2 eV                 | 855.1 eV                 |

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**Figure 5. XPS spectra of the Ni 2p region of (a) Ni/FC3R and (b) Ni-PEG1000/FC3R.**

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**Figure 6. Effect of various reaction conditions on the activity of Ni-PEG1000/FC3R and Ni/FC3R for C9PR hydrogenation.** Reaction conditions: C9PR (300 g) was dissolved in 200\# oil (600 g); stirring speed, 500 r min\(^{-1}\); catalyst, 30 g. (a) Temperature, 270 °C; pressure, 6 MPa; time, 3 h. (b) Ni loading, 13 wt \%; pressure, 6 MPa; time, 3 h. (c) Ni loading, 13 wt \%; temperature, 270 °C; time, 3 h. (d) Ni loading, 13 wt \%; temperature, 270 °C; pressure, 6 MPa.

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species and more Ni active sites on the support surface after modifying. These results could be attributed to the addition of PEG1000 and ultrasonic interference during the preparation of the catalyst, which allowed the Ni crystallites to highly disperse on the FC3R support.
The effect of reaction temperature on hydrogenation of C9PR is shown in Figure 6b. When the reaction temperature was increased from 250 to 270 °C, the bromine value of Ni-PEG1000/FC3R decreased from 6.18 to 1.16 g Br/100 g. The bromine value only decreased to 1.02 g Br/100 g even when the reaction temperature was increased to 290 °C. However, the high temperature might accelerate the carbon deposition on the catalyst and reduce the activity of the catalyst. In comparison, the bromine value of Ni/FC3R decreased from 20.15 to 14.34 g Br/100 g when the temperature was increased to 290 °C. These results were attributed to that the Ni-PEG1000/FC3R catalyst possessed a smaller crystallite size and higher Ni dispersion than those of Ni/FC3R.

Figure 6c shows the effect of reaction pressure on hydrogenation of C9PR. When H2 pressure was increased from 4 to 6 MPa, the bromine value of C9PR of Ni-PEG1000/FC3R decreased from 7.09 to 0.96 g Br/100 g, but the bromine value slightly decreased to 0.88 g Br/100 g when the H2 pressure was further increased to 8 MPa. The decrease in the bromine value between 4 and 6 MPa could be attributed to that the increasing pressure could effectively enhance the adsorption of H2 in the Ni active sites and then increase the reaction rate. The slight decrease in the bromine value resulted from the pressure beyond 6 MPa was due to that the adsorption of H2 had already reached saturation with the occupation of most of the Ni active sites.18

The change in bromine value over time is shown in Figure 6d. The bromine value of Ni-PEG1000/FC3R quickly decreased from 46.1 g Br/100 g (initial bromine value from C9PR) to 20.7 g Br/100 g after 1 h of the reaction. After being reacted for 3 h, the bromine value decreased to 1.02 g Br/100 g, implying that the C9PR was almost saturated with hydrogen. When the reaction time was prolonged to 5 h, the bromine value only decreased from 1.02 to 0.88 g Br/100 g. Hence, a reaction time of 3 h was considered as the optimum reaction time for C9PR hydrogenation over Ni-PEG1000/FC3R. However, the bromine value of Ni/FC3R only decreased to 9.43 g Br/100 g even after being reacted for 5 h. Therefore, it could be concluded that Ni-PEG1000/FC3R exhibited higher catalytic activity than that of Ni/FC3R.

The contrast experiments of C9PR hydrogenation were carried out under the optimum reaction conditions of a temperature of 270 °C, a H2 pressure of 6 MPa, and a reaction time of 3 h, and the results are listed in Table 5. Activated FC3R exhibited extremely low performance, the bromine value decreased from 46.10 to 42.62 g Br/100 g, and the sulfur content decreased slightly. The results demonstrated that inherent Ni in the FC3R was favorable for the C9PR hydrogenation reaction. The bromine value and the Gardner color grade of Ni-PEG1000/FC3R decreased to 0.72 g Br/100 g and 1, respectively, and the sulfur content reduced from 25.70 to 1.66 mg kg−1. These results illustrated that the unsaturated functional groups in C9PR (mainly ethylenic C==C bonds and aromatic rings) were saturated by hydrogenation. However, the bromine value and Gardner color grade of Ni/FC3R decreased only to 10.83 g Br/100 g and 7, and the sulfur content decreased to 15.36 mg kg−1, indicating that the hydrogenation of C9PR was uncompleted. The softening points were slightly decreased by approximately 10 K, owing to the degradation of the resin. As expected, the Ni-PEG1000/FC3R catalyst exhibited a higher hydrogenation activity and sulfur removal capacity compared with the Ni/FC3R catalyst.

The FTIR results of C9PR and HC9PR are shown in Figure 7. The bands between 650 and 900 cm−1 in the spectrum of C9PR (Figure 7a) were associated with the different substituents on the benzene rings; the peak at 700 cm−1 corresponded to the aromatic C−C bending peak, the peaks at 745, 1480, and 1600 cm−1 belonged to the aromatic C==C stretching vibration absorption peak, and the peak at 3040 cm−1 corresponded to the C==C stretching peak. However, the absorption peaks of C==C bonds and aromatic rings in HC9PR (Figure 7b) almost disappeared, indicating that the unsaturated bonds in C9PR were hydrogenated. The result showed that the Ni-PEG1000/FC3R catalyst was effective for aromatic ring hydrogenation of C9PR.

### 2.3. The Reusability of the Catalyst

The stability tests of Ni-PEG1000/FC3R and Ni/FC3R were carried out under a lower initial conversion, and the experimental process is as follows. After the first cycle of hydrogenation was completed, the catalyst was allowed to settle down, and the supernatant product mixture was removed from the reactor; after adding new reactants, the next experiment was conducted. The results are shown in Figure 8. The Ni-PEG1000/FC3R catalyst showed a higher initial activity for C9PR hydrogenation than that of the Ni/FC3R catalyst. The activity of the Ni-PEG1000/FC3R catalyst had no significant change during the first 3-time recycle experiments, and the catalytic activity decreased slightly when the recycle experiment was beyond 3 times. In contrast, a clear deactivation occurred in the Ni/FC3R with the bromine value of C9PR increased from 20.15 to 32.74 g Br/100 g after a recycle experiment of 7 times. This decrease in the catalytic activity of Ni/FC3R can be attributed to the agglomeration of Ni active sites aggregated on the FC3R support.

### Table 5. The Contrast Experiments of C9PR Hydrogenation

| catalyst | bromine value (g Br/100 g) | Gardner color grade no. | softening point (K) | sulfur content (mg kg−1) |
|----------|--------------------------|-------------------------|---------------------|------------------------|
| blank    | 45.86                    | 11                      | 382                 | 25.65                  |
| FC3R (1.6% Ni) | 42.62                    | 11                      | 376                 | 24.43                  |
| Ni/FC3R (13% Ni) | 10.83                    | 7                       | 372                 | 15.36                  |
| Ni-PEG1000/FC3R (13% Ni) | 0.72                     | 1                       | 374                 | 1.66                   |

As determined by ICP-OES. Deposited Ni in FC3R.

![Figure 7. FTIR spectra of (a) C9PR and (b) HC9PR.](image-url)
activity might have resulted from the carbon deposition or the loss of nickel during the reaction. The XRD analysis of fresh and spent catalysts was carried out (Figure 9). The crystallite sizes of the spent catalysts were estimated using the Scherrer equation according to the characteristic peaks toward the (200) plane of Ni. The crystallite sizes of Ni in spent Ni/FC3R and Ni-PEG1000/FC3R catalysts were 25.5 and 13.6 nm, respectively. Compared with the fresh catalyst shown in Table 3, the crystallite sizes of Ni in both catalysts were increased, which indicated the presence of a sintering phenomenon during the reaction.39 However, compared to the spent Ni/FC3R, the spent Ni-PEG1000/FC3R catalyst showed slight sintering. For these results, the reasons could be explained as follows: as proven by the H2-TPR results, the reduction peak of the NiO-PEG1000/FC3R (Figure 4b) catalyst is higher than that of NiO/FC3R, which illustrated that the interaction between NiO and the FC3R support was enhanced after PEG1000 modifying. In addition, the BET results listed in Table 2 show that the specific surface area of the spent Ni/FC3R catalyst decreased obviously compared to that of fresh Ni/FC3R; meanwhile, the average pore diameter also increased, suggesting that the carbon deposition blocked the microchannels.40 Compared to the spent Ni/FC3R, the spent Ni-PEG1000/FC3R catalyst showed a slight change in the specific surface area and average pore diameter. The results conclude that the Ni-PEG1000/FC3R catalyst showed a better resistance to carbon deposition.

3. CONCLUSIONS

In this work, the Ni-PEG1000/FC3R was successfully prepared under ultrasonic conditions and was applied for the hydrogenation of C9PR. PEG1000 effectively inhibited the aggregation growth of Ni crystallites on FC3R and therefore resulted in the smaller size of Ni crystallites, allowing Ni crystallites to be highly dispersed on the surface and the pores of the FC3R support. The prepared Ni-PEG1000/FC3R catalyst showed excellent catalytic performance and stability for C9PR hydrogenation, the bromine value and sulfur content of C9PR were reduced significantly, and the color of C9PR changed from the original yellow to water white. In summary, this work not only reports a method on how to obtain a high value-added hydrogenated C9 petroleum resin but also may offer a new strategy for the treatment of a waste solid catalyst (FC3R), which is beneficial for the sustainable use of resources.

4. MATERIALS AND METHODS

4.1. Materials. FC3R with a particle size of 60–80 μm was supplied by PetroChina Guangxi Tiandong Petrochemical Co., Ltd. Analytical-reagent grade Ni(NO3)2·6H2O and PEG 1000 were purchased from Tianjin Kernel Chemical Reagent Co., Ltd. Activated clay was purchased from Tianjin Fine Chemical Research Institute. C9PR (Gardner color grade no. 11, bromine value of 46.1 g/100 g, softening point of 383.1 K, and sulfur content of 25.70 mg kg−1) was supplied by PetroChina Lanzhou Huifeng Petrochemical Co., Ltd. No. Industrial grade solvent oil (200# solvent oil) was purchased from Jiangsu Hualun Chemical Industry Co., Ltd., China, and the 200# solvent oil could be recycled and reused. Hydrogen and nitrogen (purity of 99.999%) were purchased from Nanning Air Separation Gas Co., Ltd., China.

4.2. Catalyst Preparation. First, the FC3R was activated by high-temperature oxidation and chemical methods. A certain amount of FC3R was calcined in air at 500 °C (heating rate of 20 °C min−1) for 4 h to remove the coke deposited on the surface. After screening with 200 sieves, the FC3R was added to a beaker with 10% H2SO4 solution. The beaker was subsequently placed in a water bath with a rotation speed of approximately 200 rpm at 90 °C for 3 h. After cooling to room temperature, the solid was recovered by filtration and then washed to pH = 7 with deionized water and dried at 100 °C to constant weight to obtain the activated FC3R supporter. Then, the Ni-PEG1000/FC3R catalyst was prepared by incipient wetness impregnation. Briefly, specified amounts of Ni(NO3)2·6H2O (Ni loading amounts of 5, 10, 13, 15, or 20 wt %) and PEG1000 (1.5 g) were dissolved in 9.8 mL of distilled water, and the resulting solution was then added to a beaker with 30.00 g of FC3R with stirring. After that, the beaker was transferred to an ultrasonic machine and continuously ultrasonicated for 30 min under a frequency of 40 kHz and a power of 300 W cm−2. Then, the sample was dried at 110 °C for 8 h to remove the water and was calcined at 500 °C (heating rate of 20 °C min−1) for 4 h in air to obtain the PEG1000-modified NiO/FC3R catalyst (the PEG1000 was decomposed into the gaseous form at high temperature). Finally, PEG1000-modified NiO/FC3R was reduced at 450 °C for 2.5 h in flowing H2 (40 mL min−1) prior to cooling to room temperature and shifted out for the hydrogenation reaction. The obtained catalyst sample was denoted as Ni-PEG1000/FC3R.
FC3R. Similarly, the Ni/FC3R catalyst was prepared through the above method only without adding PEG1000.

4.3. Analysis and Characterization. Powder XRD was performed on a Rigaku Smartlab X-ray diffraction instrument with a Cu Kα source (λ = 1.541 Å) at 40 kV and 200 mA in air. The sample was scanned over Bragg angles (2θ) ranging from 10 to 90°, with a scan speed of 10° min⁻¹. The BET specific surface areas were determined by N₂ adsorption in a Micromeritics Instrument ASAP 2460 surface area analyzer.

4.4. Catalytic Performance Tests. The hydrogenation of C9PR was performed in a 2 L stainless steel autoclave with a double-tiered paddle agitator (Dalian Jingyi Autoclave Co., Ltd., China). The reaction temperature was controlled by an external 1.5 kW electrically heating jacket and an internal water cooling coil. Before the reaction, the C9PR (300 g) was dissolved in 200# oil (600 g) and pretreated with 15 g of activated clay to adsorb the hydrogel in the C9PR. The C9/200# clarified solution and the catalyst (30 g, the amount of catalyst was obtained through experiments) were introduced into the autoclave, and the autoclave was closed and sealed. Then, air was pumped out of the autoclave to an absolute pressure of approximately 0.007 MPa. Prior to starting the reaction, the reactor was three times purged with 0.5 MPa H₂ to remove any residual air. The first-stage reaction was performed under low temperature and low pressure (220 °C, 2 MPa, and 1 h). Then, all gases in the autoclave were removed to eliminate the H₂S generated. The second-stage reaction was carried out at 250–290 °C and 4–8 MPa for 1–5 h. After the reaction, the reaction products were separated by vacuum distillation to obtain HC9PR products.

The color was determined through the Gardner color number method (50 wt % solution in toluene) with a Lovibond Gardner scale 3000 comparator. The softening point was measured according to ASTM D 6493-11. The sulfur contents were determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES, model IRIS Intrepid II XSP). The bromine value was measured by the coulometric method with a bromine valence and bromine index apparatus (denoted as BVBI, model BR-I, made in China GuoRui).

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Notes

The authors declare no competing ﬁnancial interest.

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