Hydrogenation of Citral to Citronellal Catalyzed by Waste Fluid Catalytic Cracking Catalyst Supported Nickel

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ABSTRACT: In this paper, a waste fluid catalytic cracking (FCC) catalyst is used as a carrier to prepare a supported non-noble metal nickel catalyst (Ni/wFCC), which is applied to the selective hydrogenation of citral to citronellal. X-ray powder diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy were used to analyze the structural characteristics of the Ni-loaded sample. The catalyst after loading Ni still maintained a good zeolite structure, and the surface impurities were reduced. The effect of reaction conditions on the Ni/wFCC-catalyzed hydrogenation of citral to citronellal was investigated, and the optimal reaction conditions were obtained as follows: a Ni loading of 20 wt%, a catalyst amount of 5.6%, a hydrogenation temperature of 180 °C, a hydrogenation time of 90 min, and a hydrogen pressure of 3.0 MPa. Under these conditions, the conversion of citral and selectivity of citronellal were 98.5 and 86.6%, respectively, indicating that the Ni/wFCC catalyst had strong catalytic activity and selectivity. This research provided new ideas for the recycling of waste FCC catalysts and industrial synthesis of citronellal.

1. INTRODUCTION

Natural citral exists in plant essential oils, such as lemon wormwood oil, lemongrass oil, and *Litsea cubeba* oil. Citral can be used in cosmetics, flavors, food, and other industries and is a key raw material for the synthesis of ionone and vitamin A, and other pharmaceutical intermediates. The citral molecule has three hydrogenated double bonds: C=C double bond, C=O double bond, and C≡C double bond conjugated with the carbonyl group. Therefore, the common citral hydrogenation products are geraniol, citronellol, and citronellal. From a thermodynamic point of view, the C=C double bond of citral is more likely to be hydrogenated to generate citronellal. Citronellal has a unique fragrance and is often used as a food flavor additive or intermediate for further synthesis of isopulegol, menthol, citronellol, and hydroxylidrocitronellol and has high economic value.

Salminen et al. fixed ionic liquid-dispersed Pd nanoparticles on an activated carbon cloth and used them for the selective catalytic hydrogenation of citral. At a reaction temperature of 100 °C and a hydrogen pressure of 0.5 MPa, the citral conversion rate was 100% and citronellal selectivity was 70%. Syunbayev et al. studied the activity of group VIII metal (Pd, Ni, Pt, Os, Rh, Ru, Ir-black, and NiR) catalysts in the liquid phase hydrogenation of citral to produce citronellal and the effect of reaction conditions. The results showed that Ru, Ni, and Pd showed high selectivity, which were 93.7, 87.0 and 75.3%, respectively, under the conditions of 2.0 MPa, 30 °C, and 96% ethanol solvent. Zhao et al. loaded Pd onto graphite oxide and catalyzed the selective hydrogenation of citral to citronellal under the action of an alkali accelerator (NaOH/NaCO₃). The selectivity of citronellal was 89.6%. The adsorption of molecules on the catalyst surface and the ability to activate the C≡C and carbonyl groups can directly affect the conversion and selectivity of citral. If the reaction occurs in the macroporous and mesoporous network of the catalyst, then its wide pore size will not affect the product and the main product of the diffusion will be citronellal. The commonly used catalysts for selective hydrogenation of citral to produce citronellal are precious metal catalysts, which are expensive and require the participation of alkaline additives or a large amount of solvents (96% ethanol, etc.). Besides, the process is complicated, and the industrial production cost is high.

Fluid catalytic cracking (FCC) is an important unit operation in the petroleum refining industry, and the waste FCC catalysts account for 700,000–900,000 metric tons per year in the world. Because of the precipitation of heavy metals (Fe, Al, Ni, V, Sb, Co, etc.), waste FCC catalysts are highly hazardous and are listed as hazardous solid waste by the National Hazardous Waste List in China. Waste FCC catalysts are not only a huge quantity but also difficult to handle. In recent years, the resource utilization of waste FCC catalysts has become a hot research issue in the oil refining industry, and the recycling of waste FCC catalysts and industrial synthesis of citronellal are highly promising areas of research.
industry. FCC catalysts use zeolites as the main active ingredient, in which activity is reduced after being discarded, but they still maintain the basic porous structure of zeolites. Therefore, waste FCC catalysts have stable porous structures and good adsorption performances, which make them potential carriers for catalyst preparation. According to the different properties of the supported active components, the new catalyst prepared from the waste FCC catalysts can be used for different catalytic reactions. Vasireddy et al. used the waste FCC catalyst as the carrier of the iron-based catalyst to prepare the FT catalyst with high abrasion resistance. Liu et al. loaded MgO onto the waste FCC catalyst, and the obtained new catalyst had good catalytic ozone oxidation degradation performance of phenol-containing wastewater. Ding et al. used the sol–gel method to prepare waste FCC catalyst supported nano-zinc oxide, which was applied to the catalytic esterification reaction of rosin. A nickel-based catalyst supported on a waste FCC catalyst also shows high catalytic activity and stability on catalytic hydrogenation reactions.

In this paper, the waste FCC catalyst is used as a carrier, and the non-noble metal Ni is the active component. A supported nickel-based catalyst is prepared for selective catalytic hydrogenation of citral to citronellal. X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy were used to analyze the structural characteristics of the Ni-loaded sample. The conversion of citral and selectivity of citronellal under different hydrogenation conditions were studied. The optimization conditions of citral hydrogenation were obtained, and the mechanism of the reaction process of citral hydrogenation catalyzed by Ni/wFCC was proposed, providing new ideas for studying the industrialized production of citral and recycling of waste FCC catalysts.

2. RESULTS AND DISCUSSION

2.1. Physical and Chemical Properties of the Catalyst.

XRD was performed on the wFCC, NiO/wFCC, and Ni/wFCC samples after reduction activation, and the results are shown in Figure 1. As shown in Figure 1, the wFCC sample presents strong Y-type zeolite and Al2O3 diffraction peaks, and a small amount of ZSM-5 is also found. The overall peak shape is chaotic, and the peak intensity is low, indicating the amorphous structure of wFCC. Evident characteristic peaks of NiO appear in the spectrum of the precursor NiO/wFCC, corresponding to the 111, 200, 220, and 311 crystal planes. After reduction, the oxidation state of Ni on wFCC is fully reduced to a metal with catalytic hydrogenation activity of state Ni (111, 200, and 220 crystal planes). The Al2O3, ZSM-5, and Y-type zeolite components in the wFCC sample are all good carriers for the catalyst. After the active components are successfully loaded, all the samples have no evident structural changes, indicating that the obtained catalyst has a certain structural stability.

The wFCC, precursor NiO/wFCC, and Ni/wFCC samples after reduction activation were subjected to FT-IR, and the results are shown in Figure 2. The FCC catalyst is composed of a Y-type zeolite and matrix. The main components of the matrix are Al2O3 and SiO2. Therefore, the infrared spectra of the three samples all reflect the structural characteristics of Al2O3 and SiO2. As shown in Figure 2, given the zeolite structure, the vibration peaks of the samples are primarily concentrated in the mid–far-infrared region. The characteristic peak at 811 cm⁻¹ is the symmetrical stretching vibration absorption peak of Si−O−Si, and the strong absorption peak at 1080 cm⁻¹ is the antisymmetric stretching vibration peak of Si−O−Si. Moreover, the weak absorption peak at 1631 cm⁻¹ is the bending vibration peak of the zeolite adsorbing water−OH. In the infrared spectrum of the wFCC sample, the weak absorption peak at 1385 cm⁻¹ is considered to be the −N=C=O phase in-plane stretching vibration because the coke produced in the FCC process is derived from the aromatic hydrocarbons and N-containing materials in the cracking raw materials. The absorption peak of NiO/wFCC and Ni/wFCC samples loaded with Ni at 1385 cm⁻¹ is enhanced because of the presence of nitrate, which is a common phenomenon when the supported Ni catalyst is prepared by the equal volume impregnation method. The broad absorption peak near 3453 cm⁻¹ is caused by the stretching vibration of the zeolite adsorbing molecular water and hydroxyl OH.

TPR was adopted to investigate the reduction behavior of NiO/wFCC with different Ni loadings, and the profiles are presented in Figure 3. As can be seen, all samples show a narrow hydrogen consumption peak centered at 386.5 °C, which corresponds to the reduction of the NiO particle interacting weakly with the wFCC support. The high-temperature hydrogen consumption peaks at 678.8 and 835.0 °C were attributed to spinel NiAl2O4 or strongly interacting...
metal–support phases. The reduction peaks at high temperature were gradually decreased with increasing Ni loading, indicating that Ni/wFCC with low Ni loading is difficult to completely reduce.

H₂ pulse chemisorption was performed to determine the metal dispersion, metallic surface area, and cubic crystallite size of the Ni/wFCC samples. As shown in Table 1, when the Ni loading increases from 10 to 20 wt %, the Ni dispersion increases from 0.67 to 0.74% and the metallic surface area increases from 4.49 m²/gcat. to 4.96 m²/gcat., respectively. The reason is that Ni/wFCC with 20 wt % is easier to completely reduce than the first two catalysts, which corroborated with the results obtained using H₂-TPR.

Furthermore, as the amount of Ni increases to 25 wt %, the corresponding metal dispersion and metallic surface area decrease to 0.47% and 2.77 m²/gsample, respectively. It may be attributed to the migration and agglomeration of excess Ni particles. It was generally considered that catalysts presenting high metal dispersion and large metallic surface area have good catalytical activities.

The structures of the wFCC and NiO/wFCC samples were analyzed by SEM, and the results are shown in Figure 4. Considering that the FCC process produces high-temperature coking and carbon deposits, the surface of the wFCC sample is uneven. After the load roasting treatment, the surface roughness of the NiO/wFCC particles is reduced. The reason may be that some impurities are eliminated at high temperature during the preparation of the catalysts.

Table 1. Hydrogen Chemisorption Results for Ni/wFCC with Different Ni Loadings

| Ni loading /wt % | metal dispersion/% | metallic surface area /m²/gcat. | cubic crystallite size/nm |
|------------------|--------------------|-------------------------------|--------------------------|
| 10               | 0.67               | 4.49                          | 125.14                   |
| 15               | 0.70               | 4.87                          | 119.56                   |
| 20               | 0.74               | 4.96                          | 113.32                   |
| 25               | 0.47               | 2.77                          | 216.66                   |

Figure 3. H₂-TPR profiles of NiO/wFCC with different Ni loadings.

2.2. Ni/wFCC-Catalyzed Citral Hydrogenation Process. After analyzing the components of the samples before and after the reaction by GC–MS, the citral hydrogenation process catalyzed by Ni/wFCC was explored (Figure 5). The main components of citral are neral (cis-citral) and geranial (trans-citral). In Ni/wFCC-catalyzed hydrogenation of citral, the main reaction is the hydrogenation of neral and geranial to produce citronellal. The side reactions are as follows: (1) citronellal is isomerized to isopulegol, which is further hydrogenated to form menthol; (2) citronellal is further hydrogenated to form tetrahydrocitronellol; (3) citral is isomerized into cis-oxylimonene and α-terpineol. The by-products of Ni/wFCC-catalyzed citral hydrogenation are isopulegol and menthol, and the contents of tetrahydrocitronellol, oxylimonene, and α-terpineol are small. The reaction mechanism of the selective hydrogenation of citral on the Ni/wFCC catalyst is shown in Figure 6. Hydrogen molecules are adsorbed on the active center of the catalyst and decompose to form free radicals H· under the action of heat. The molecules of neral and geranial are combined with carbon and oxygen. The conjugated C=C bond of the double bond is polarized by Ni in the active center. After polarization, the C=C bond becomes unstable, and producing citronellal instead of unsaturated alcohols is easy (nerol and geraniol are not found on GC–MS).

In this paper, the waste FCC catalyst supported Ni is used as the catalyst to determine the effects of Ni loading, catalyst
amount, hydrogenation temperature, reaction time, and hydrogen pressure on Ni/wFCC catalytic citral hydrogenation.

The effect of the Ni/wFCC catalyst with Ni loadings of 10, 15, 20, and 25 wt % on citral hydrogenation over Ni/wFCC was studied under the following conditions: an amount of catalyst of 5.6%, a hydrogen pressure of 4 MPa, a hydrogenation temperature of 180 °C, and a hydrogenation time of 90 min. The results are shown in Figure 7. With the increase of Ni loading, the citral conversion rate and citronellal selectivity show similar trends, and both gradually increase to the maximum when the Ni loading is 20 wt %, which are 98.4 and 83.8%, respectively (Figure 7). The reason is that the metal dispersion and large metallic surface area increase when Ni loading increases from 10 to 20 wt % (Table 1). The decrease occurs when the Ni loading exceeds 20 wt % because excessive Ni loading will block the pores of the Ni/wFCC catalyst, and migration and agglomeration are prone to occurring during calcination reduction, resulting in insufficient reduction activation and reducing the catalyst’s activity and selectivity. This decrease is in line with the decreasing metallic surface area determined by H₂ pulse chemisorption. Therefore, 20 wt % Ni loading is more appropriate.

Figure 5. Hydrogenation of citral over the Ni/wFCC catalyst.

Figure 6. Mechanism of citral hydrogenation over the Ni/wFCC catalyst.

Figure 7. Influence of Ni loading on citral hydrogenation.
The effect of the amount of Ni/wFCC catalyst on the catalytic hydrogenation of citral is investigated when the Ni loading, hydrogen pressure, reaction temperature, and reaction time was 20 wt %, 4 MPa, 180 °C, and 90 min, respectively. The results are shown in Figure 8. When the amount of catalyst is less than 2.8%, the citral conversion rate is less than 61.4% (Figure 8). Simultaneously, the reaction control step is the adsorption of hydrogen molecules on the active sites of the catalyst. The amount of catalyst and the corresponding active sites are small, leading to the low conversion and selectivity. As the amount of catalyst increases, the number of active sites increases and the conversion and selectivity also increase. When the amount of catalyst is greater than 5.6%, the conversion of citral is close to 100% and the selectivity of citronellal does not change. Therefore, the appropriate amount of catalyst is 5.6%.

The Ni loading, catalyst amount, reaction time, and hydrogen pressure are 20 wt %, 5.6%, 90 min, and 4 MPa, respectively. The hydrogenation reaction of citral at a reaction temperature of 160 to 200 °C is studied. The results are shown in Figure 9. Figure 9 shows that with the increase of the reaction temperature, the surface reaction rate increases rapidly and the citral conversion rate gradually increases. After 180 °C, the citral conversion rate basically remains constant. The selectivity of citronellal is the highest at 170 °C, reaching 88.7%, but with the increase of temperature, the side reaction intensifies and the selectivity of citronellal decreases significantly. Therefore, the suitable reaction temperature was 180 °C.

The Ni loading, amount of catalyst, reaction temperature, and hydrogen pressure are 20 wt %, 5.6%, 180 °C, and MPa, respectively. The changes in the catalytic hydrogenation of citral with reaction time are studied. The results are shown in Figure 10. As shown in Figure 10, as the reaction time increases, the conversion gradually increases from 60 to 90 min. After 90 min, the citral conversion stabilizes and the citronellal selectivity shows a slow downward trend. The experimental results indicate that the conversion of citral has been completed when the reaction time is 90 min. As time increases, citronellal continues to react to form other substances. After GC–MS analysis, citronellal further reacts to form isopulegol. Therefore, the optimal reaction time is 90 min.

The Ni loading, catalyst amount, reaction temperature, and reaction time are 20 wt %, 5.6%, 180 °C, and 90 min, respectively. The effect of hydrogen pressure on the catalytic hydrogenation of citral is studied when the hydrogen pressure is 2−4 MPa. The results are shown in Figure 11. As shown in Figure 11, the hydrogen pressure increases from 2 to 3 MPa and the citral conversion rate increases significantly to 97.0% because increasing the hydrogen pressure is equivalent to increasing the hydrogen concentration, which accelerates the reaction rate and further increases the citral conversion. After the hydrogen pressure is increased to 3 MPa, the citral conversion rate reaches 97.0%.
conversion slowly increases by 98.4%, whereas the citronellal selectivity decreases from 87.7% at 2.5 MPa to 83.8%. When the hydrogen pressure is greater than 3 MPa, the hydrogen concentration in the reaction solution tends to be saturated. Simultaneously increasing the amount of hydrogen has little effect on the citral conversion rate, but the supersaturated hydrogen molecules promote the hydrogenation of other double bonds of citral, thereby reducing the selectivity of citronellal. Therefore, the optimal hydrogen pressure is 3.0 MPa.

2.3. The Reusability of the Catalyst. After studying the selective hydrogenation of citral catalyzed by Ni/wFCC, the optimal reaction conditions were obtained: a Ni loading of 20 wt%, a catalyst amount of 5.6%, a reaction temperature of 180 °C, a reaction time of 90 min, and a hydrogen pressure of 3.0 MPa. Moreover, the stability test of Ni/wFCC was carried out under these conditions. The experimental results are shown in Table 2. The activity of the Ni/wFCC catalyst had no significant change during the first three-times recycle experiments, and the slight difference between the values may be due to the analysis and calculation process.

3. CONCLUSIONS

The characterization results show that the wFCC sample is in an amorphous state and consists of Al2O3, ZSM-5, and Y-type zeolites. After loading the Ni metal, the surface impurities of the particles are reduced and the zeolite framework structure does not change significantly. The optimal conditions for the selective hydrogenation of citral catalyzed by Ni/wFCC are as follows: a Ni loading of 20 wt%, a catalyst dosage of 5.6%, a reaction temperature of 180 °C, a reaction time of 90 min, and a hydrogen pressure of 3.0 MPa. Under the optimal reaction conditions, the conversion of citral is 98.5% and the selectivity of citronellal is 86.6%.

Table 2. Results of Parallel Experiments

| running time | citral conversion/% | citronellal selectivity/% |
|--------------|----------------------|---------------------------|
| 1#           | 97.9                 | 85.9                      |
| 2#           | 98.3                 | 86.5                      |
| 3#           | 98.5                 | 86.6                      |

4. EXPERIMENTAL MATERIALS AND METHODS

4.1. Materials. Citral, C10H16O (99.13%, neral 50.92% + geraniol 48.21%), with AR was purchased from Xilong Chemical Co., Ltd. Waste FCC catalysts were provided by CNPC Guangxi Tiandong Petrochemical Complex Co., Ltd. Nickel nitrate (NiNO2·6H2O) with AR was purchased from Shanghai Haiqiu Chemical Co., Ltd. Canned hydrogen with 99.9% H2 and H2/N2 mixed gas at 200 mA in the air, and the sample was scanned at the Bragg angle (2θ) ranging from 5 to 80°, with a scanning speed of 3°/min. FT-IR was analyzed using a PerkinElmer-65 spectrometer with a Boiling point of 140 °C, a reaction time of 90 min, and a hydrogen pressure of 3.0 MPa. Under the optimal reaction conditions, the conversion of citral is 98.5% and the selectivity of citronellal is 86.6%.

4.2. Preparation of Waste FCC Catalyst Supported Ni.

The equal volume impregnation method assisted by ultrasound was adopted to prepare the waste FCC catalyst (wFCC) supported Ni catalyst (Ni/wFCC), and the steps are as follows: a certain amount of wFCC was roasted at 500 °C for 4 h, and after cooling, wFCC was removed through a 160 mesh sieve before use. The required mass of NiNO2·6H2O and volume of H2O were calculated on the required Ni loading of the experiment (the water absorption rate of wFCC was 0.7 mL/g). wFCC, NiNO2·6H2O, and H2O were mixed and stirred ultrasonically for 15 min and then immersed for 12 h; the impregnated catalyst was dried at 110 °C for 8 h and calcined at 500 °C for 8 h to obtain the oxidized wFCC-supported Ni precursor (NiO/wFCC), which was reduced by H2/N2 mixed gas at 550 °C for 2.5 h to prepare the wFCC-supported Ni catalyst (Ni/wFCC).

4.3. Citral Catalytic Hydrogenation Reaction. The reaction was carried out with a magnetically stirred high-pressure microreactor (Hotong Instrument/HT-50FJ). The effective volume of the reactor was 50 mL. The design temperature was under 300 °C, and the design pressure was 20.7 MPa. The reactor was equipped with a magnetic coupling mechanical stirrer, charge and discharge gas valve, safety valve, and temperature controller. A certain amount of citral (1:1 ratio to solvent oil) and Ni/wFCC catalyst were poured into the reactor; the reactor was sealed and replaced with N2 gas three times. The pressure was maintained, and the reactor was checked for leaks. When no leak was found, the reactor was emptied and filled with a small amount of hydrogen, and the pressure was maintained for 10 min. Then, the experiment temperature and speed were set, and the temperature increased. When the temperature increased to the required temperature, H2 was charged at a certain pressure. The reaction began, and the reaction time was recorded. After the reaction was completed, it was cooled to room temperature. After the pressure was released, the reaction sample was removed, filtered, and analyzed by gas chromatography−mass spectrometry (GC−MS).

4.4. Catalyst Characterization. The morphology of the sample was analyzed using a Zeiss EVO 80 scanning electron microscope (Germany). Structural analysis was performed using a Bruker D8 Advance X-ray diffractometer (Germany), with a Cu Kα source (λ = 1.541 Å) at 40 and 200 kV, and 200 mA in the air, and the sample was scanned at the Bragg angle (2θ) ranging from 5 to 80°, with a scanning speed of 2°/min.

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Notes
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