A novel nickel catalyst derived from layered double hydroxides (LDHs) supported on fluid catalytic cracking catalyst residue (FC3R) for rosin hydrogenation

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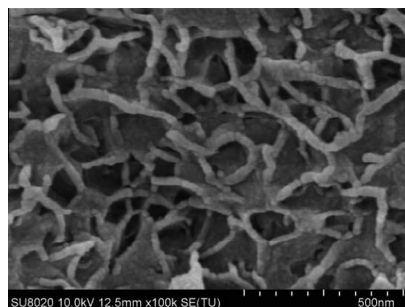[a] School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, PR China
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HIGHLIGHTS

- A novel layered nickel catalyst using spent FCC catalyst as support was prepared.
- Spent FCC catalyst was used as Al^{3+} source for the synthesis of NiAl-layered precursor.
- The confinement effect in the LDHs main layer lead to small nickel particles and high Ni dispersion.
- The catalyst was more active and stable than the catalyst prepared by impregnation method.
- The conversion of abietic-type resin acid reached 99.02% under relatively mild condition (5 MPa, 190 °C).

GRAPHICAL ABSTRACT

A Ni-based catalyst derived from LDHs precursor supported over FC3R is proved to be a highly efficient heterogeneous, reusable catalyst for hydrogenation of rosin under relatively mild conditions.

ABSTRACT

A novel Ni-based catalyst (LP-Ni/FC3R) derived from a layered double hydroxides (LDHs) precursor was synthesized in situ and applied to rosin hydrogenation. Fluid catalytic cracking catalyst residue (FC3R) was used as a support material and sole Al^{3+} source. The effects of nickel loading, H_2 pressure, temperature, and reaction time on catalytic performance were extensively investigated in a 2 m^3 stainless steel autoclave. Maximum conversion of abietic-type resin acids reached 99.29% under relatively mild conditions with a nickel content of 8 wt.% and reaction time of 100 min. For comparison, a nickel catalyst (IM-Ni/FC3R) was prepared via incipient wetness impregnation. The textural, structural, and morphological properties of the two catalyst precursors were characterized by XRD, SEM, XPS, FT-IR, and H_2-TPR/TPD. Results showed that $Ni^{2+}Al^{3+}$-containing LDHs (NiAl-LDHs) in the novel catalyst grow in situ at the surface and in the pores of FC3R. Compared with IM-Ni/FC3R, LP-Ni/FC3R shows a smaller crystallite size, higher Ni dispersion, and stronger interactions between Ni species and the FC3R support. LP-Ni/FC3R exhibited higher activity and better stability, which may be mainly ascribed to its unique NiAl-LDHs structures.

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1. Introduction

Rosin is a clear or semi-transparent solid obtained from coniferous trees. The substance is composed primarily of rosin acids and minor neutral components. Rosin acids are monocarboxylic acids

that are isomeric with abietic acid. The unsaturated conjugated double bond of rosin molecules increases rosin susceptibility to oxygen, which causes a decline in rosin quality. Rosin stability can be improved by various modification methods, such as hydrogenation, disproportionation, and polymerization. Hydrogenated rosin is the largest modified rosin product that is conventionally used in the adhesive industry to increase adhesion of hot-melting, pressure-sensitive, and other types of adhesives. Hydrogenated rosin is also used in the food, solder, and pharmaceutical industries [1]. Newly developed applications of hydrogenated rosin include the synthesis of anionic surfactants [2] and viscous cosmetics [3] and manufacture of coatings [4]. Hydrogenated rosin is conventionally obtained by hydrogenation of rosin at pressures of 12–35 MPa and temperatures of 220–270 °C in the presence of a noble metal catalyst such as Pd/C or Rh/C [1,5]. However, noble metal catalysts present certain disadvantages, such as high price, limited availability, and high reaction pressures and temperatures. Nickel catalysts, which are inexpensive and possess lower toxicity, have been widely used in hydrogenation reactions [6–8], despite the lower activity of nickel metal compared with that of noble metals. Thus, developing an efficient method to improve the reactivity and recoverability of nickel catalysts used in rosin hydrogenation presents considerable challenges, as evidenced by the scarcity of reports on the subject.

Supported nickel catalysts combine the advantages of inorganic heterogeneous catalysts and metal complex homogeneous catalysts, including considerable activity, selectivity, stability, and easy recovery. Supported nickel catalysts are conventionally prepared by incipient wetness impregnation, which results in nonhomogenous Ni^{2+} distribution over the support, because of surface tension of the impregnating solution and other solvent effects. Layered double hydroxides (LDHs) comprise an unusual class of layered materials made up of positively charged layers and charge compensating anions located in the interlayer regions. After calcination, the mixed metal oxides, which possess porous structures, large specific surface areas, and good thermal stability, are formed from LDHs precursor with the loss of interlayer water and decomposition of interlayer anions [9]. By reducing mixed metal oxides, well-dispersed supported catalysts can be obtained. Supported metal catalysts derived from LDHs usually exhibit peculiar metal–support interaction or metal–support cooperation [10]. Supported Ni-based catalysts with highly dispersed of nickel derived from LDHs precursors have recently been reported [11–14]. In the literature, carbon nanotubes and Al_2O_3 are commonly used as catalyst supports. NiAl-LDHs precursors can in situ grow in pores or on the surface of Al_2O_3, which acts as the sole Al^{3+} source. However, other porous materials used as supports and Al sources of LDHs-derived catalysts have yet to be reported.

Fluid catalytic cracking catalyst residue (FC3R, also called spent FCC catalyst) is a large-scale solid waste with porous structure that is often discharged from petroleum refineries. Approximately 300,000 tons of FC3R from 350 FCC units worldwide are produced annually, and 500 tons/day of this residue are disposed after use [15]. Disposal of this residue requires compliance with stringent environmental regulations. Considering that heavy metals, such as Ni and V, in the spent catalyst can leach into the ground water and soil, disposal in landfills is unsatisfactory [16]. Studies [17,18] on the utilization of spent FCC catalysts were conducted through chemical and magnetic separation to remove heavy metals, such as Ni, for regeneration. However, in this process, strict reaction conditions are implemented. The process is complex because it entails the use of toxic gases, corrosive gases, and liquid acids, which also cause secondary pollution to the environment. In recent years, utilization of FC3R as a raw material to produce other valuable products (e.g., cement [19], zeolite [20], and brick [21]) has received considerable attention. FC3R mainly contains SiO_2 and Al_2O_3, as well as certain minor impurities [22], and possesses a well-developed specific surface and excellent physical strength. Vasireddy et al. [23] claimed that FC3R can be used as a support for Fe- and Co-based catalysts to improve the attrition resistance of F-T catalysts despite the presence of heavy metals.

In this paper, we present the catalytic hydrogenation of rosin using a FC3R-supported Ni catalyst (LP-Ni/FC3R) derived from LDHs precursors under relatively mild conditions. FC3R was used as a support and sole Al^{3+} source to synthesize NiAl-layered precursors without requiring removal of heavy metal ions. For comparison, a catalyst (IM-Ni/FC3R) with uniform Ni distribution was prepared by an incipient wetness impregnation method under identical treatment conditions of calcination and reduction. The structures and properties of the supported Ni catalysts were characterized by XRD, SEM, XPS, FT-IR, H_2-TPR/TPD, and their catalytic performance in the rosin hydrogenation was investigated.

2. Experimental section

2.1. Materials

Analytical-reagent grade $Ni(NO_3)_2 \cdot 6H_2O$, NH_4NO, ammonia, and aqueous tetramethylammonium hydroxide (TMAH) were purchased from Shanghai Xingao Chemical Reagent Co., Ltd. (China), and used without further purification. FC3R with a particles size of 50–100 μm was supplied by PetroChina Guangxi Tiandong Petrochemical Co., Ltd. and received in powder form. FC3R is a coarse, porous, and spherical material with a large BET surface area. The chemical composition of FC3R as determined by SEM-EDX is listed in Table 1. To combust deposited coke, FC3R was calcined at 500 °C for 4 h prior to use as a support. Gum rosin (acid value, 160 mg KOH/g) from *Pinus massoniana* pine tree was obtained from Guangxi Wuzhou Pine Chemicals Ltd., China. No. 200 solvent oil was obtained from Jiangsu Hualun Chemical Industry Co., Ltd., China; this oil is transparent, clear and virtually insoluble liquid composed of C7–C12 hydrocarbons. The solvent has an initial boiling point of 158 °C, a flash point of 40 °C, and a density of 0.76 g mL^{-1}. The use of No. 200$^{\#}$ oil in rosin hydrogenation serves two functions: dissolution of reactants and dissipation of the heat generated during the hydrogenation reaction.

2.2. Preparation of catalyst samples

FC3R-supported nickel catalysts with different Ni loading amounts of 6, 7, 8, 9, and 10 wt% were in situ synthesized as follows. First, specific amounts of $Ni(NO_3)_2 \cdot 6H_2O$ and NH_4NO_3 (molar ratio was 1:1) were dissolved in 300 mL of deionized water to obtain a mixture with Ni concentration of 0.10, 0.12, 0.15, 0.17, and 0.20 mol L^{-1}. The resulting solution was then added to a three-necked flask with 30.00 g of FC3R after which 4 wt.% of aqueous ammonia solution was added drop-wise to the mixed salt solution with stirring until the pH of the mixed solution reached 7.5. The flask was subsequently placed in a water bath with a rotation speed of about 200 r min^{-1} at 40 °C for 12 h. After filtration and washing with a solution containing 0.1 mol L^{-1} ammonium nitrate with the same pH as the final pH of the reaction solution, the wet sample was kept in air for 1 h; this time is referred to the aging time. The sample was then washed for three to four times with deionized water. This sample, which was denoted NiAl-LDHs/FC3R, was dried at 70 °C for 6 h and calcined in air at 500 °C for

Table 1
Element analysis of waste catalyst using SEM–EDS (unit: %).

Element	O	Na	Mg	Al	Si	Ca	V	Fe	Ni
Content (%)	48.28	0.56	0.39	26.03	18.88	0.49	0.20	1.80	3.37