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# New advances in catalysts for C9 petroleum resin hydrogenation

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**Abstract.** C9 petroleum resin is a thermoplastic polymer produced by polymerization of C9 fraction obtaining from the steam cracking unit, and could be catalytic hydrogenated to remove the ethylenic C=C bond, aromatic ring with improved physical properties. The research progress in the efficiency supported nickel or/and palladium catalysts for C9 petroleum resin hydrogenation was illustrated and reviewed, further development was discussed.

## 1. Introduction

C9 petroleum resin is a thermoplastic polymer made from the polymerization of the C9 fraction (mainly vinyl toluene and indene, which are by-products from the catalytic cracking of petroleum hydrocarbons at high temperature during the preparation of ethylene) and has a molecular weight of 200 to 3000 and a softening point of 50-150 °C. It has a very wide range of applications in adhesives, paints, printing inks, coatings, rubber and other industries for its excellent water resistance, acid and alkali corrosion resistance, weather resistance, light aging resistance, miscibility and adhesion. The C9 petroleum resin without any post-treatment normally has yellow or amber color, along with a foul odor, poor thermal stability, poor oxidation resistance, poor adhesion, poor compatibility and other defects, mainly because of its high content of unsaturated bonds, which limiting its applications. Studies showed that C9 petroleum resin with dark brown color might come from aromatic rings, alkene structure, a small amount of heavy metal ions, sulfur, bromine and other impurities. When the unsaturated bond of in C9 petroleum resin is catalysed and hydrogenated, the obtained hydrogenated C9 petroleum resin was usually colorless, transparent and stable with better physical properties[1].

Catalytic hydrogenation was commonly used to modify C9 petroleum resin for wider industrial applications. The purpose of catalytic hydrogenation of C9 petroleum resin is to remove the ethylenic



C=C bond, aromatic, and residual halides formed during the polymerization process. Over the past decades, scholars have made a series of explorations and experiments in improving hydrogenation catalyst and optimizing hydrogenation process conditions, which was well illustrated in the previous literature[2,3]. The hydrogenation of C9 petroleum resin has witnessed a rapid development in recent years, the milestone achievements and recent results of the catalytic reaction in the fixed-bed or batch reactor are demonstrated in this paper.

## 2. Catalysts for C9 petroleum resin hydrogenation

### 2.1 Fluid catalytic cracking catalyst residue supported nickel catalyst

A Ni-based catalyst was synthesized with polyvinyl pyrrolidone as a dispersant supported in a pretreated fluid catalytic cracking catalyst residue. The results indicated that polyvinyl pyrrolidone prevented agglomeration and crystallization of nickel, and pretreated fluid catalytic cracking catalyst residue provided significant economic and environmental benefits. The bromine number could be reduced to 1.25 under the ideal conditions[4].

Another spent fluid catalytic cracking supported nickel catalyst was prepared by improved solution vacuum-impregnation reduction method with citric acid as chelating agent. The carbon from citric acid decomposition was preferentially filled on spent fluid catalytic cracking, which made the surface of the catalyst being smooth. The active component of nickel was highly dispersed in the support surface with smaller grain. The Gardner color of the hydrogenated C9 petroleum resin was reduced from 11 to 4, and the sulfur mass fraction was reduced from 0.016% to 0.00024%[5].

### 2.2 SiO<sub>2</sub> supported nickel catalyst

The Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst was prepared by the temperature-programmed reduction method with Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, nitric acid and SiO<sub>2</sub>. The special globe-like structure, high sulfur resistance, anti-sintering anti-coking and carbon-resistance of Ni<sub>2</sub>P were accountable for the high activity and stability of the catalyst, which was also ascribed to the special Ni-P-S surface phase, high thermal stability of Ni<sub>2</sub>P nanoparticles and weak surface acidity for the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst. The bromine numbers of hydrogenated C9 petroleum resin was maintained at low values within 300 h at the optimum reaction conditions in a fixed-bed reactor[6].

### 2.3 γ-Alumina supported nickel or/and palladium catalyst

Ni/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was chose and synthesized for evaluation in the hydrogenation of C9 petroleum resin. The univariate analysis was studied in lab scale high-pressure fixed-bed reactor. Catalyst with narrow pore size distribution of 5-12 nm exhibited excellent catalytic performance at the optimal reaction conditions. The resins color became very light-colored or water-white, and the bromine value was declined to ca. 1. The ratio of new hydrogen and cycle hydrogen gas, new hydrogen gas and those sent to stripping tower, and reaction temperature in each stage were optimized. The followed pilot-scale experiment indicated that 3-4% of hydrogen consumption and more than 95% of C9 petroleum resin yield could be obtained[7].

NiO/Al<sub>2</sub>O<sub>3</sub>-LDO catalyst with layered double hydroxides structures from hydrotalcite was prepared with co-precipitation and in-situ crystallization method. The results showed that precipitation and Ni ion concentration was the most significant factor in the catalyst preparation process. The bromine number and Gardner color of the hydrogenated C9 petroleum resin was reduced to 1 and 1.8, respectively, at the ideal reaction conditions[8].

NiWS/γ-Al<sub>2</sub>O<sub>3</sub> and PdRu/γ-Al<sub>2</sub>O<sub>3</sub> were prepared by co-impregnation method, respectively. The NiWS/γ-Al<sub>2</sub>O<sub>3</sub> catalyst exhibited excellent C9 petroleum resin desulfurization performance, and could prevent PdRu/γ-Al<sub>2</sub>O<sub>3</sub> catalyst at the second stage from being poisoned by sulfur or other impurities, resulting in remarkable extension of the catalyst life. The two-stage hydrogenation process could reduce the Gardner color of C9 petroleum resin from 11 to 0[9].

Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was synthesis by incipient wetness impregnation method. Hydrogenation of aromatic rings to alicyclic rings with degree of aromatic rings hydrogenation about 94% reduced the color of C9 petroleum resin from Gardner color 17.1 to 5.7. The hydrogenated resin showed high color stability and a unchanged softening point under various hydrogenation conditions and catalyst used[10].

#### 2.4 Conditions of C9 petroleum resin hydrogenation experiments

The name of nickel or palladium catalysts, reaction pressure and temperature, solvent and reactor used in the hydrogenation experiments were summarized in Table 1. As shown in Table 1, solvent oil or cyclohexane were used as solvent for C9 petroleum resin hydrogenation. The hydrogenation pressure and temperature for batch hydrogenation were raged from 4.0 to 8.0 MPa, and 230 to 270 °C, respectively. The hydrogenation pressure and temperature for fixed-bed hydrogenation were raged from 6.0 to 18.0 MPa, and 245 to 300 °C, respectively. 200# solvent oil, dearomatized solvent oil D40 or cyclohexane were used as solvent in the hydrogenation.

Table 1. Comparison of hydrogenation experiments over different catalysts.

Catalyst	Pressure	Temperature	LHSV	H <sub>2</sub> /oil	Solvent	Reactor	Reference
Ni-PVP/PFC3R	8.0 MPa	270 °C	/	/	200# solvent oil	batch	[4]
Ni/CA-SFCC	4/8 MPa	230/270 °C	/	/	200# solvent oil	batch	[5]
Ni <sub>2</sub> P/SiO <sub>2</sub>	6.0 MPa	250 °C	1.0 h <sup>-1</sup>	600:1	cyclohexane	fixed-bed	[6]
Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	18 MPa	260 °C	0.8 h <sup>-1</sup>	600-800:1	dearomatized solvent oil D40	fixed-bed	[7]
NiO/Al <sub>2</sub> O <sub>3</sub> -LDO	8.0 MPa	300 °C	1.5 h <sup>-1</sup>	300:1	/	fixed-bed	[8]
NiWS/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	6.0 MPa	245/275 °C	1.0 h <sup>-1</sup>	600:1	cyclohexane	fixed-bed	[9]
PdRu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>							
Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	7.0 MPa	250 °C	/	/	cyclohexane	batch	[10]

### 3. Conclusions

Over the past years, scholars managed to develop series of efficiency nickel or/and palladium catalysts for C9 petroleum resin hydrogenation. Improvements in the performance of the nickel or/and palladium catalyst were based on the recognition of the importance of C9 petroleum resin-support, metal-support synergy. It is believed that further development of a molecular understanding of catalytic action would create a basis for a rational design of new and improved C9 petroleum resin hydrogenation catalysts.

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