Deep Hydrogenation of C_9 Petroleum Resin over Skeletal Nickel Prepared from Ni-Al-Mo Alloys by Rapidly Quenching Technology

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Introduction

C_9 petroleum resins(C_9PR) are important raw material widely used in adhesives, rubbers, hot-melt coatings, printing inks, road marking etc. [1] Conventionally, C_9PR are manufactured by polymerization of C_9 fraction of cracked oil.[2]However, the heavy color, unpleasant odor and low thermal stability of the C_9PR seriously limit its application. Hydrogenation proved to be a valid method to upgrade its properties. Due to the structural characteristics, hydrogenated C_9PR(H-C_9PR) features excellent thermal stability, transparent and colorless, as well as high compatibility with other resins. Thus, H-C_9PR can be mixed with various plastics, rubbers and oil-soluble materials for application as tacky adhesives, paints, inks, polyolefin films, plastic moldings and the like. [3]So far, there have been few reports on the hydrogenation of C_9PR using novel metal or Ni as catalyst. The hydrogenation efficiency is not satisfied and urgently need to be improved. It has already been known that Skeletal Ni activated from its mother alloy which was made by rapid quenching technique shows high hydrogenation activity[4,5,6]for various reactions like glucose hydrogenation to sorbitol, [7] selective hydrogenation of adiponitrile[8] and so on. Here, we report the efficient deep hydrogenation of C_9PR over modified Skeletal Ni catalysts prepared from rapidly quenched Ni-Al-Mo alloys. The reaction was conducted at 160ºC, and 7.0MPa H_2 pressure. The products are colorless (less than 1# by Fe-Co Colorimeter) with excellent thermal stability, light resistance and compatibility with other resins.

Materials and Methods

Ni-Al-Mo mother alloy was prepared by the following procedure: 46.4wt% Ni, 49.3wt% Al and 4.3wt% Mo was melted and rapid quenched on a fast-rotating copper roller to form alloy ribbon. After ball-milling and sieving, the powder fraction of 150-300 mesh was collected and then the Al was leached out by using excess amount of 17wt% NaOH aqueous solution at 100 ºC for 3hs. Catalytic testing was performed in a 75ml stainless steel autoclave. For each reaction, C_9PR, THF solvent and catalyst were quantitatively charged into the autoclave . After sealing, the autoclave was purged by N_2 and H_2. Then the autoclave was heated to a required temperature. The reaction started by turning on the agitation.

Results and Discussion

The particle size distribution of the Ni-Al-Mo mother-alloy powder was obtained and the result is illustrated in Fig.1. The alloy particles have a wide range of size distribution with 50-100μ m as main fraction. Surface morphologies of both Ni-Al-Mo mother alloy powder and activated skeletal Ni catalyst were studied by SEM. Fig.2 shows the SEM image of activated skeletal Ni catalyst . It was observed that after leaching aluminum the alloy surface becomes highly fractured with vividly round and angular topographies, which contributes partly to the high surface area and high hydrogenation activity. The XRD(Fig.3) diffraction peaks around 45°,52° and 77° are attributed to the Ni crystalline plane of (111), (200) and (222), respectively, indicating typical character of the Ni crystallite with face-centered cubic(fcc) structure. Fig.4 illustrates the FT-IR spectra of C_9 petroleum resin and hydrogenated product. Although the

peaks are complicated, we found distinct difference between the petroleum resin reactant and hydrogenated product including the aromatic C-H stretching peaks at wave numbers(v) of 3020 cm^{-1} , the aromatic C=C stretching peaks at v of 1600cm^{-1} and 1510cm^{-1} , the aromatic C-C out-of-bending peaks at v of 690 850 cm^{-1}. Typically, the aromatic C-stretching peaks at wave numbers(v) of 3020 cm^{-1} almost disappeared in the hydrogenation product, indicating the saturation of aromatic rings. Furthermore, the C=O stretching peaks at v of 1710cm^{-1} become weaker after hydrogenation, which support the conclusion of double bond reduction. The peaks at v of 550cm^{-1}, 475 cm^{-1}, 425 cm^{-1} are attributed to C-Br and C-I stretching libration. The halogens might be introduced during the polymerization process of making resin and the content obviously decreases after hydrogenation.

In conclusion, the hydrogenated C_9 petroleum resin were obtained over modified Skeletal Ni catalyst prepared from rapidly quenched Ni-Al-Mo alloys. The colorless hydrogenated product has high thermal stability, light resistance and remarkably low halogen contents.
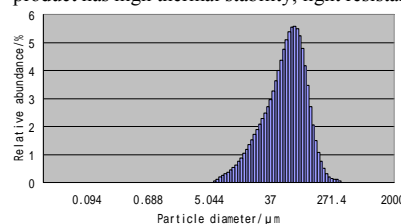

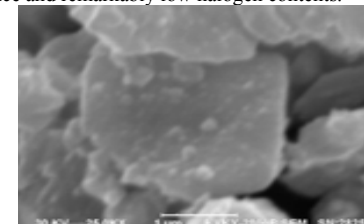**Fig.1** Histogram of particle size distribution of alloy powder

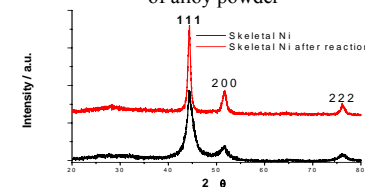**Fig.2** SEM image of skeletal Ni catalyst

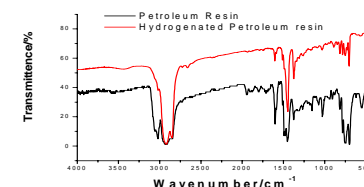**Fig.3** Comparison of XRD patterns of skeletal Ni before and after reaction

Fig.4 FT-IR spectra of petroleum resin before and after hydrogenation

Significance

References

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