

Bifunctional Catalyst for the One-step Continuous Synthesis of exo-tetrahydrodicyclopentadiene from Dicyclopentadiene

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Introduction

The exo-tetrahydrodicyclopentadiene (exo-THDCPD; IUPAC name: exotricyclo[5.2.1.0^{2,6}]decane) is characterized in low toxicity, low freezing point (-79 °C), low viscosity, satisfactory long-term storage stability, and a large volumetric energy content or heating value [1-2]. It can be widely used as rolling oils, resin powders, lubricating oils, and solvents for paints, diluents for surfactants, waxes and washing agents for semiconductor [2, 3]. Moreover, exo-THDCPD is the main component of the high-energy-density fuel referred to as JP-10, which is a commonly used fuel for small missiles [1]. Presently, exo-THDCPD is commercially produced in a two-step process as shown in Scheme 1. In the first step, dicyclopentadiene (DCPD) is hydrogenated into endo-THDCPD either in a batch or continuously-flow reactor. In the second step, endo-THDCPD is isomerized into exo-THDCPD in a batch reactor catalyzed by acids. As a result of the obvious drawbacks of liquid acids and aluminum chloride, recent works are focused on zeolites and heteropoly acids for the second-step reaction [3, 4]. In this work, a one-step process for converting DCPD into exo-THDCPD in a continuously-flow fixed-bed reactor was developed for the first time based on the development of a high-performance bifunctional catalyst.

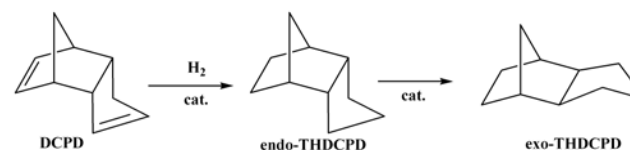
Materials and Methods

The catalysts were prepared by impregnating the supports of γ -Al₂O₃ and β zeolite with nickel nitride. The reaction was carried out in a fixed-bed reactor under the conditions of $T = 120$ - 180 °C, $P = 0.5$ - 4 MPa. Before reaction, the catalyst was activated in a hydrogen flow, and the DCPD dissolved in petroleum ether was pumped into the reactor via a gasifier kept at 80 °C. The products were analyzed on a GC equipped with an FID detector and an HP-5 capillary column.

Results and Discussion

Firstly, the hydrogenation of DCPD was investigated over Ni/ γ -Al₂O₃ catalyst. It was found that DCPD can be easily hydrogenated to endo-THDCPD with a good stability when the nickel loading was above 15 wt.%. The activity of the catalyst for the hydrogenation of DCPD was clearly increased with the increase of pressure until 1.0 MPa, and there was only a slight influence when the pressure was further increased. To achieve the one-step hydroisomerization of DCPD to exo-THDCPD, we investigated a series of Ni/ β zeolite bifunctional catalysts with various nickel loadings. Results indicate that there was a maximum selectivity to exo-THDCPD with the increase of nickel loading over β zeolite. Moreover, the bifunctional catalyst was easily deactivated within 50 h test. After characterizing the fresh, reduced and used catalysts by using XRD, XPS, TG-DSC, NH₃-TPD, it can be concluded that the balance of the acidic function of β zeolite for isomerization and the hydrogen function of

the metallic nickel is a key factor to determine the activity and stability of the catalyst for the titled reaction.



Scheme 1. Reactions for the synthesis of exo-THDCPD from DCPD.

Based on this finding, 25 wt.% Ni/ γ -Al₂O₃ and 15 wt.% Ni/ β zeolite catalysts loaded separately in two-consecutive fixed-bed reactors were investigated for the one-step synthesis of exo-THDCPD, and the results are given in Fig. 1. With this catalyst modification, the selectivity of exo-THDCPD was kept around 65% for over 200 h while the DCPD was fully converted to the hydrogenated products. Moreover, based on the characterization of the used catalysts, the fast decrease for the selectivity of exo-THDCPD at the end of the test can be reasonably ascribed to the obvious loss of the acidic sites over β zeolite by coke formation, leading to the unbalanced acidic and metallic catalytic functions.

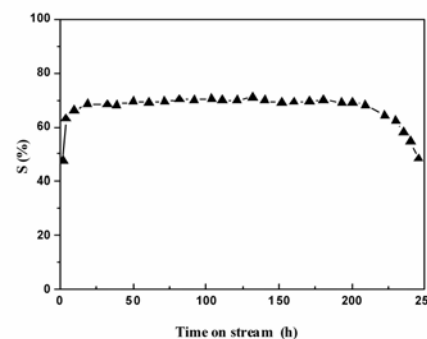


Figure 1. The time-on-stream selectivity of exo-THDCPD for the one-step hydroisomerization of DCPD over 25 wt.% Ni/ γ -Al₂O₃ and 15 wt.% Ni/ β zeolite catalysts in a dual fixed-bed reaction system under the conditions of $P = 1.0$ MPa and average $T = 150$ °C.

Significance

Based on the development of a high-performance bifunctional catalyst, the one-step continuous synthesis of exo-THDCPD was investigated for the first time, which is characterized in high efficiency and low environmental impact.

References

1. Chung, H.S., Chen, C.S.H., Kremer, R.A., Boulton, J.R. *Energy Fuels* 13, 641 (1999).
2. Xing, E., Mi, Z., Xin, C., Wang, L., Zhang, X. *J. Mol. Catal. A: Chemical* 231, 161 (2005).
3. Jeong, B., Han, J., Ko, S., Lee, J., Lee, B. *J. Ind. Eng. Chem.* 13, 310 (2007).
4. Xing, E., Zhang, X., Wang, L., Mi, Z. *Green Chem.* 9, 589 (2007).