



Highly Efficient Isomerization of Allylic Esters over Supported Platinum Catalysts with Residual Chloride

Qi-An Huang,¹ Asahi Haruta,¹ Yuhya Kumamoto,¹ Haruno Murayama,¹ Eiji Yamamoto,¹
Tetsuo Honma,² Mitsutaka Okumura,³ Hiroki Nobutou,³ Makoto Tokunaga¹
(¹Kyushu Univ.; ²JASRI; ³Osaka Univ.)

Sustainable production of C4 chemicals is significant in the industry. During the series of catalytic reactions for C4 compounds, there are still several intermediate byproducts, such as but-3-ene-1,2-diyl diacetate (3,4-DABE) (Fig. 1). The minor product, 3,4-DABE, is an isomer of but-2-ene-1,4-diyl diacetate (1,4-DABE), which is an important intermediate for the synthesis of tetrahydrofuran (THF). THF is produced million tons/year for polyesters and polyethers but several thousand tons/year of 3,4-DABE is incinerated. Therefore, the sustainable transformation of 3,4-DABE into 1,4-DABE will be valuable in the industry and environmental protection and will be conducive to moving toward a low-carbon society. Recently, we developed a direct transformation of but-1,3-diene into but-2-ene-1,4-diol with O₂ and H₂O using supported Pd catalysts.¹ This is an alternative route to THF, but the selectivity needs to be improved. Several kinds of metal complex catalysts were developed for this reaction via the π -allyl intermediate or soft Lewis acid mechanism.² Only low catalytic activity (TON \leq 33) was obtained when testing current catalysts. hence, we focus on developing highly efficient catalysts and thus choose the isomerization of 3,4-DABE as a model reaction.

In this research, supported Pt catalysts with soft Lewis acid functionality were successfully developed. We for the first time unraveled that Pt/CeO₂ with residual chloride can act as soft Lewis acids and can facilitate the efficient isomerization of allylic esters. The reaction can be realized under solvent-free conditions, and the TON of the catalyst reaches 5400 (Fig. 2). The active species in this reaction are demonstrated as highly dispersed Pt clusters consisting of Pt–Cl and Pt–O bonds (Fig. 3).

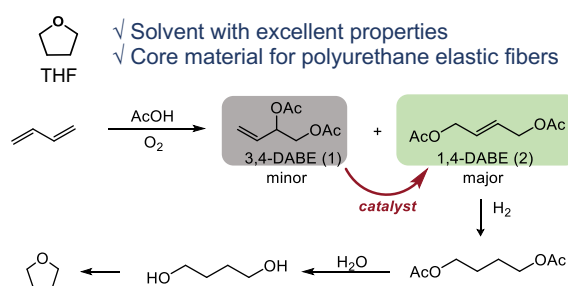


Fig.1 A C4 synthesis route from buta-1,3-diene.

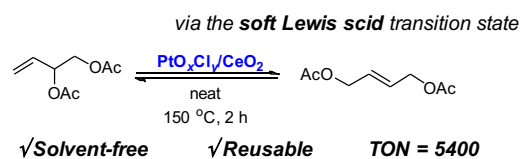


Fig.2 Isomerization of 3,4-DABE with supported Pt catalysts.

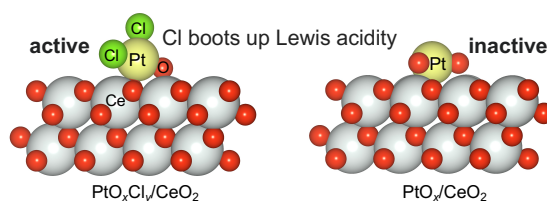


Fig.3 Efficient soft Lewis acid catalyst PtO_xCl_x/CeO₂

<参考文献>

- 1) Z. Zhang, M. Tokunaga, *et al.*, *Appl. Catal. B Environ.* **2019**, 246, 100.
- 2) N. Marion, S. P. Nolan, *et al.*, *Org. Lett.* **2007**, 9, 2653.

発表者紹介

氏名 黄 啓安 (コウ ケイアン)
所属 九州大学大学院理学府
 化学専攻
学年 博士課程 2 年
研究室 触媒有機化学研究室

