



Effect of reduction temperature on selective hydrogenation of crotonaldehyde over Ir/TiO₂ catalysts

Ping Chen^a, Ji-Qing Lu^a, Guan-Qun Xie^a, Geng-Shen Hu^a, Lin Zhu^a, Liang-Feng Luo^b, Wei-Xin Huang^b, Meng-Fei Luo^{a,*}

^a Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China

^b Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

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ABSTRACT

Vapor-phase selective hydrogenation of crotonaldehyde was conducted over Ir/TiO₂ catalysts to investigate the effect of reduction temperature on the catalytic behaviors. The catalyst reduced at 100 °C contained large amount of strong Lewis acid sites, which was detrimental to the activity because of the strong adsorption of crotonaldehyde molecules on the active sites. Also, the selectivity to crotyl alcohol was suppressed due to the interaction between C=C bond and the charge-deficient Ir species, which favored the formation of butanal. When the catalyst was reduced at high temperature, it was found that 300 °C was appropriate for high activity and selectivity, due to the moderate interaction between the C=O bond and the Ir species, as well as the weakened surface Lewis acid sites. However, higher reduction temperature (500 °C) led to a strong bonding of carbonyl carbon and the charge-rich Ir species and suppresses the activity, which may be related to a strong metal–support interaction (SMSI).

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1. Introduction

Selective hydrogenation of crotonaldehyde into crotyl alcohol is an important process in fine chemicals, pharmaceutical and fragrance industries [1,2]. However, hydrogenation of crotonaldehyde usually goes through various pathways [3–5]. More importantly, the hydrogenation tends to take place at the C=C bond instead of the C=O bond due to thermodynamic and kinetic factors [6–8], and thus leading to the formation of saturated aldehyde (butanal). Thus, development of catalysts that are highly active and selective remains challenging in the catalysis field [9–12].

Great efforts have been made to develop catalyst systems for the selective hydrogenation of crotonaldehyde. Noble metal catalysts are usually employed in this reaction. For example, Pt catalysts have been intensively studied, such as Pt/TiO₂ [6], Pt/α-Ga₂O₃ [13], Pt/ZrO₂/TiO₂ [14], Pt/ZnO [15], Pt/SnO₂ [16], Pt/CeO₂ [17]. In addition, gold catalysts also have been widely used in this reaction, such as Au/TiO₂ [18], Au/SiO₂ [19], Au/ZnO [20], Au/CeO₂ [21], Au/ZrO₂ [22]. Although most attention has been devoted to Pt and Au catalysts, Ir catalysts have been studied in selective hydrogenation of α, β-unsaturated aldehydes in recent years, such as crotonaldehyde [23–25] and citral [26–29]. For example, gas phase hydrogenation of crotonaldehyde on 5% Ir/TiO₂ resulted in selectivity to crotyl

alcohol of 70% at 20–80% conversion [25]. Reyes et al. [30] studied in detail the interfacial properties of an Ir/TiO₂ catalyst and concluded that the interfacial metal–TiO_x moieties created upon reduction treatment was responsible for the increase in activity and in selectivity to crotyl alcohol. Rojas et al. [23,24] reported the catalytic performance of Ir/TiO₂–SiO₂ catalysts for the crotonaldehyde hydrogenation, and pointed out that the reduction temperature (500 °C) induced the strong metal support interaction effect (SMSI), which improved the Ir catalyst activity and selectivity towards crotyl alcohols.

According to the published literatures, it can be seen that high reduction temperature is beneficial to the catalytic performance of Ir catalysts, and the reason is usually attributed to the surface decoration of the metal component from its reducible oxide supports, i.e. the strong metal support interaction (SMSI). However, there are still some contradictions in the results of the activity of Ir catalysts and selectivity to crotyl alcohol, especially the essential effects of some key factors on the crotonaldehyde hydrogenation are not clear, such as the morphologies and electronic properties of the active metals, the surface Lewis acid sites, and the residual chlorine ions in the catalyst.

Enhanced activity and selectivity to the desired crotyl alcohol could be achieved by modification of the active metals when varying the reduction temperature, by which the morphologies and electronic properties of the active metals could be properly adjusted for the hydrogenation of the C=O bond [31–35]. Surface Lewis acid sites could be generated from the reducible oxide

* Corresponding author. Fax: +86 579 2282595.

E-mail address: mengfeiluo@zjnu.cn (M.-F. Luo).