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Pt/Ga₂O₃ catalysts of selective hydrogenation of crotonaldehyde

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Abstract

Hydrogenation of crotonaldehyde in a gas phase at atmospheric pressure over Pt/Ga₂O₃ catalysts was studied. Two types of platinum precursors [Pt(acac)₂ and H₂PtCl₆] and two gallia supports (α -Ga₂O₃ [60.7 m²/g] and β -Ga₂O₃ [2.2 m²/g]) were used for catalyst preparation. The catalyst 5 wt% Pt/ α -Ga₂O₃ prepared from Pt(acac)₂ precursor showed very high and stable selectivity to crotyl alcohol (91% and 63% at 10% and 70% crotonaldehyde conversion, respectively). Because Pt-supported catalysts, showing a high selectivity, usually have relatively low activity, the most interesting finding of this study is that the use of gallium oxide as a support for platinum makes it possible to obtain catalysts with significantly increased C=O bond hydrogenation selectivity while maintaining high activity.

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1. Introduction

Selective hydrogenation of α , β -unsaturated aldehydes to unsaturated alcohols has been a subject of many investigations because of its great interest as an important step in the preparation of various fine chemicals and applications of unsaturated alcohols in the flavor and fragrance industries and in pharmaceutical manufacturing [1]. The challenge lies in the selective hydrogenation of the carbonyl bond while keeping the olefinic bond unaffected. This can be achieved using stoichiometric amounts of reducing agents, such as hydrides (e.g., AlLiH₄, NaBH₄); however, such methods are useful only for a smallscale production because they involve costly chemicals and are hazardous to the environment.

The development of specific catalytic hydrogenation processes can replace the reduction using metal hydrides, which is in agreement with one of the 12 principles of green chemistry: "Catalytic reagents (as selective as possible) are superior to stoichiometric reagents." Catalysis offers advantages over stoichiometric reactions in terms of both increased selectivity and energy minimization. The specificity of catalysts favors the

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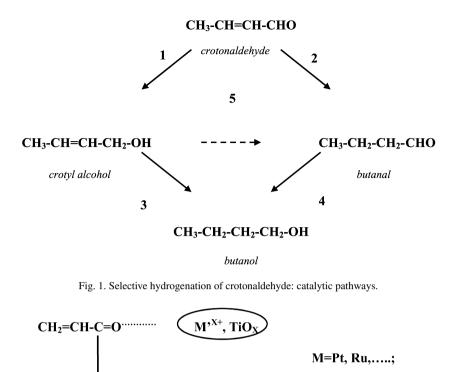
reaction to a preferred product, whereas the amount of undesired products is decreased. The amount of energy required for a given transformation is also reduced as the catalysts decrease the activation energy of the reaction [2]. Consequently, hydrogenation processes based on heterogeneous catalysis have been developed [3]. Hydrogenation of α , β -unsaturated aldehydes to unsaturated alcohols is difficult to realize, especially under heterogeneous catalysis conditions, due to the much greater susceptibility to hydrogenation of the C=C double bond (578.8 kJ/mol) compared with the C=O double bond (705.8 kJ/mol) for both thermodynamic and kinetic reasons [4].

The reaction of hydrogenation of α , β -unsaturated aldehydes may occur in different ways, as shown in Fig. 1. α , β -Unsaturated aldehydes may be hydrogenated to the most desired product, unsaturated alcohols (step 1), as well as to other saturated products, butanal (steps 2 and 5) and butanol (steps 3 and 4).

The selectivity to unsaturated alcohols depends on various factors, such as the structure of aldehydes, the nature of catalysts, and the presence of additives, as well as the reaction conditions [5]. Previous studies have shown that unpromoted metals have specific selectivities to unsaturated alcohols. For example, iridium and osmium are rather selective; palladium, rhodium, and nickel are unselective or slightly selective; and

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Fig. 2. Reaction sites for hydrogenation of α,β -unsaturated aldehydes on metallic-promoted catalysts [24].

platinum, ruthenium and cobalt are moderately selective. These trends were confirmed by Cordier for cinnamaldehyde hydrogenation (Os > Ir > Pt > Ru > Rh > Pd) [6]. Different geometric and electronic properties of metals can affect hydrogenation activities and selectivities by influencing not only adsorption, but also surface reactions. The adsorption phenomenon itself is limited by many factors, such as the mode of reactant adsorption on a specific metal surface. Different crystal phases of metals have different geometrical constraints, which explains the need to study the performance of distinct crystallographic faces. Platinum has been used most intensively as an active metal in chemoselective hydrogenations. Among the nonnoble metals, special attention has been given to the supported cobalt catalysts. This approach, which was initiated by Japanese scientists [7-10], was developed in the works of Hutchings et al. [11-13], Rodrigues and Bueno [14-16], and in our previous paper [17]. Recently, interesting properties of bimetallic Pt-Co/SiO₂ were reported by Borgna et al. [18]. Nonetheless, systems based on platinum are still the most frequently explored catalysts of crotonaldehyde hydrogenation. Pt is a very active metal in the hydrogenation of the C=C double bond but is not intrinsically selective to unsaturated alcohols. The selectivity to the desired product greatly depends on the steric and electronic structure of the active phase and reactant [19].

Enhanced selectivity can be obtained by an increase in C=O bond activity, with a simultaneous decrease in C=C bond activity. This can be achieved by using various promoters, which were divided into three groups: (a) alkali metal (Na, K, La,

Ca, Cd) ionic compounds, (b) transition metal (Ti, V, Cr, Mn, Fe) compounds, and (c) nontransition element (Ge, Ga, Sn) compounds, with an increased promoting effect in the order (a) < (b) < (c) [20].

M'=Sn, Ga, Ge, Fe

Earlier work [21,22] has shown the role and effects of promoters and metal–support interaction in the reaction of hydrogenation of α,β -unsaturated aldehydes. As a general rule, activity and selectivity to unsaturated alcohols are improved when adding Sn, Ge, Ga, Fe, and others to active transitional metals (e.g., Pt, Ru, Ni) and when a partially reducible support like TiO₂ is used [23]. The promoting effect is seen as a strong interaction between the carbonyl group and a positively charged center (e.g., Fe^{$\delta+$}, Sn^{$\delta+$}, TiO^{$\kappa+$}) (Fig. 2) [24].

Gallium has been mentioned as an effective promoter in the reduction of carbonyl group in Pt-based catalysts [5]. Englisch et al. [22] showed that transitional metals like Ga can be used as promoters in catalysis for selective hydrogenation of α , β -unsaturated aldehydes. Transition metals used in catalysts have partially filled *d*-orbitals. When the platinum *d*-orbital is filled, the metal is relatively catalytically inactive, as in the cases of silver, gold, and copper. The interstitial electron densities in metals filling *d*-orbitals are low, and these metals are not eager to form bonds. However, the electronic structure of metal can be changed by adding a second metal, leading to, for instance, the formation of an alloy, by changing the metal particle size and enhancing the interaction with the support. This interaction decreases electron density at the carbonyl bond of α , β -unsaturated aldehyde and increases its reactivity. The re-

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