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Short Communication

# Effects of Ir content on selective hydrogenation of crotonaldehyde over $Ir/ZrO_2$ catalysts

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## ABSTRACT

A series of  $Ir/ZrO_2$  catalysts with different Ir contents were tested for gas phase selective hydrogenation of crotonaldehyde. It was found that the reactivity of the catalyst increased with increasing Ir content, but rapid deactivation was observed on all the catalysts during the reaction, which might be due to CO poisoning generated by decarbonylation reaction. The highest selectivity (82.2%) to crotyl alcohol was obtained over a catalyst with 3% Ir content, which was attributed to the proper Ir particle size and the highest amount of surface acid sites in the catalyst.

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### 1. Introduction

Crotonaldehyde (CH<sub>3</sub>CH=CHCHO) is a typical  $\alpha$ ,  $\beta$ -unsaturated aldehyde, and its main hydrogenation products are crotyl alcohol (hydrogenation of C=O bond), butanal (hydrogenation of C=C bond) and butanol (hydrogenation C=C and C=O bonds). Crotyl alcohol (CH<sub>3</sub>CH=CHCH<sub>2</sub>OH), the product of C=O hydrogenation is highly desired because it has wide applications in the synthesis of fine chemicals, such as pharmaceutical, agrochemical, and fragrance compounds [1–3]. However, chemoselective hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes to unsaturated alcohols is more difficult, because the hydrogenation prefers to C=C bond compared with C=O bond for both thermodynamic and kinetic factors [4].

Noble metal catalysts show good performance for crotonaldehyde hydrogenation. Pt catalysts have been intensively studied, such as Pt/ Ga<sub>2</sub>O<sub>3</sub> [5], Pt/TiO<sub>2</sub> [6], Pt/Ta<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> [7], Pt/ZnO [8], and Pt/SnO<sub>2</sub> [9]. Although most attention has been devoted to Pt catalysts, recently, another noble metal Ir catalysts are also found to be quite high selectivity to crotyl alcohol for gas-phase hydrogenation of crotonaldehyde. Abid et al. [10] reported the catalytic performance of 5%Ir/ TiO<sub>2</sub> catalysts after high temperature calcination for gas phase hydrogenation of crotonaldehyde with selectivity to crotyl alcohol of 70% at 20–80% conversion. Reyes et al. [11] found that Ir/TiO<sub>2</sub> catalysts reduced at high temperature showed high activity due to a strong metal support interaction (SMSI) effect. Moreover, the same authors

also found that the presence of partially reducible supports such as  $ZrO_2$  and  $TiO_2$  could enhance the selectivity to crotyl alcohol [12].

It appears that the Ir systems are promising for selective hydrogenation of crotonaldehyde, therefore, these Ir catalysts deserve a systematic investigation because it is well known that catalytic reactivity of the catalyst for this reaction depends on various parameters such as preparation method, metal precursor, support type, particle size of active metal, and pretreatment conditions [13]. However, the correlationship between the Ir catalysts and catalytic behaviors has been rarely reported. More importantly, catalyst deactivation is commonly observed for this reaction [14,15], and thus the mechanism of deactivation is also worthy for investigations in order to design catalyst systems with better performance.

Therefore, in this work, a series of  $Ir/ZrO_2$  catalysts with different Ir contents were prepared and tested for selective hydrogenation of crotonaldehyde. The relationship between the catalyst features and catalytic behaviors was established and the deactivation of the catalysts was discussed.

#### 2. Experimental

#### 2.1. Catalyst preparation

 $ZrO_2$  was prepared from  $ZrOCl_2$  by a precipitation method. An NH<sub>3</sub> aqueous solution was added to a  $ZrOCl_2$  solution under constant stirring. The final pH value of the resulting mixture was controlled at  $10\pm0.5$ . The mixture was kept stirring at room temperature for 24 h and aged at 90 °C for 5 days. Then it was filtered and washed with deionized water. The achieved white powder was dried at 60 °C for 8 h under vacuum, followed by calcination at 400 °C for

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4 h, and the final  $ZrO_2$  support with a specific surface area of 313 m<sup>2</sup> g<sup>-1</sup> was obtained.

The  $Ir/ZrO_2$  catalyst was prepared by impregnating the  $ZrO_2$  support with an aqueous solution of  $H_2IrCl_6$ . After impregnation for 12 h, the mixture was dried overnight at 90 °C for 8 h. The catalysts were denoted as  $xIr/ZrO_2$ , where x refers to the Ir content in the catalyst (wt.%).

#### 2.2. Catalyst characterizations

All the catalysts were reduced in  $H_2$  at 500 °C for 1 h prior to characterizations.

X-ray diffraction (XRD) patterns were recorded using a PANalytic X'Pert PW3040 diffractiometer. Elemental compositions were determined by X-ray fluorescence (XRF) analysis, using an ARLADVANT'X Intelli Power 4200 scanning X-ray fluorescence spectrometer. Surface areas of the catalysts were determined by the modified BET method from the N<sub>2</sub> sorption isotherms at -196 °C on an Autosorb-1 apparatus. All the samples were degassed at 100 °C prior to measurements. CO chemisorption experiments were carried out on a Quantachrame CHEMBET-3000 instrument in order to determine the dispersion of Ir and the particle size. Ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) was conducted on a home-made apparatus, and the total amount of NH<sub>3</sub> desorbed was determined by reaction with an excess of dilute hydrochloric acid and back titration with sodium hydroxide solution.

#### 2.3. Catalytic testing

The gas phase hydrogenation of crotonaldehyde was performed in a fixed bed reaction system at atmospheric pressure, using a quartz tubular (8 mm i.d.) reactor. Before running the test, the catalyst was reduced at 500 °C for 1 h in ultra-pure H<sub>2</sub> (20 ml min<sup>-1</sup>) and then it was cooled down to 60 °C. Crotonaldehyde was introduced to the reactor by a H<sub>2</sub> flow (26 ml min<sup>-1</sup>) passing through a crotonaldehyde saturator maintained at 0 °C to achieve a constant crotonaldehyde partial pressure (1.06 kPa). The reaction products were analyzed using an on-line gas chromatography (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and a DB-Wax column (30 m×0.25 mm×0.25 µm) capillary column.

## 3. Results and discussion

#### 3.1. Composition and texture of Ir/ZrO<sub>2</sub> catalysts

Fig. 1 shows the XRD patterns of the  $Ir/ZrO_2$  catalysts. It can be seen that the diffraction peaks of the catalysts are similar to that of the  $ZrO_2$  support, and no peaks related to Ir species are observed, implying that the Ir species are highly dispersed. Table 1 lists the Ir, Cl contents, and specific surface areas of the catalysts. It is found that the Ir contents in all catalysts are close to the nominal Ir values. Also, Cl species are still present in the catalysts even after reduction at 500 °C, and the Cl content increases with increasing Ir content. In addition, the surface area of the catalyst decreases with Ir content in the catalyst which could be attributed to the factor that the pores of  $ZrO_2$  may be partially blocked by Ir species [16]. In addition, the dispersion of Ir particles decreases with increasing Ir content, and the average particle size of Ir grows from 1.5 to 6.8 nm.

#### 3.2. Surface acidity of Ir/ZrO<sub>2</sub> catalysts

Fig. 2 shows the NH<sub>3</sub>-TPD profiles of the Ir/ZrO<sub>2</sub> catalysts. It can be seen that the Ir/ZrO<sub>2</sub> catalysts and the ZrO<sub>2</sub> support have two NH<sub>3</sub> desorption peaks at around 210 ( $\alpha$ ) and 415 °C ( $\beta$ ). With increasing Ir content, both the  $\alpha$  and  $\beta$  peaks shift to higher temperature and reach maxima (456 °C) when the Ir content is 3%. This indicates



Fig. 1. XRD patterns of Ir/ZrO<sub>2</sub> catalysts.

that the  $3Ir/ZrO_2$  catalyst has the strongest surface acidity. Also, the amount of surface acid sites increases with Ir content, and reaches a maximum (3.68 mmol/g) when the Ir content is 3% ( $3Ir/ZrO_2$ ). Further increase of Ir content results in a decline in surface acid sites. This is because the surface acid sites might be covered by excess Cl species. Therefore, the  $3Ir/ZrO_2$  catalyst has the strongest surface acidity and the largest amount of surface acid sites.

#### 3.3. Ir/ZrO<sub>2</sub> catalysts for selective hydrogenation of crotonaldehyde

Fig. 3 shows the selective hydrogenation of crotonaldehyde over the  $3Ir/ZrO_2$  catalyst reduced at 500 °C. It is found that the catalyst is quite active at the initial stage, with a crotonaldehyde conversion of 46%. However, the catalyst gradually deactivates with time on stream and reaches a quasi-steady state after 400 min. Such deactivation is commonly observed for the hydrogenation of crotonaldehyde [17,18]. Concerning the selectivity to crotyl alcohol, it shows a rapid growth during the first 100 min of reaction, and then reaches a stable level (82.2%) after 350 min.

Also seen in Fig. 3, small amount of C3 hydrocarbons are produced during the reaction, indicating the occurrence of decarbonylation reaction and the simultaneous formation of CO [19]. It was reported that CO molecules could be strongly adsorbed on the Ir surface and the active sites are blocked, which leads to a partial loss of active sites [20]. In order to further confirm whether the deactivation is caused by CO poisoning, 1 ml CO was injected into reactor before the reaction. Fig. 4 shows the effect of CO poisoning on the catalytic behavior of the 3Ir/ZrO<sub>2</sub> catalyst. It can be seen that the crotonalde-hyde conversion has a dramatic decline (from 51 to 19%) at the initial stage after CO adsorption, and the reactivity is obviously suppressed by the poisoning during the whole reaction. Therefore, it can be concluded that the strong CO adsorption on the surface of Ir atoms is

Table 1			
Physical	properties	of Ir/ZrO <sub>2</sub>	catalysts.

Catalyst	BET specific surface area (m <sup>2</sup> /g)	Dispersion of Ir <sup>a</sup> (%)	Particle size of Ir <sup>a</sup> (nm)	Conten Ir	t(wt.%) Cl
ZrO <sub>2</sub>	313	-	-	-	-
1lr/ZrO <sub>2</sub>	289	65.8	1.5	1.23	1.21
2lr/ZrO <sub>2</sub>	282	33.3	2.9	2.29	2.04
3lr/ZrO <sub>2</sub>	274	25.2	3.9	3.26	2.55
4lr/ZrO <sub>2</sub>	262	21.1	4.7	4.43	2.81
5lr/ZrO <sub>2</sub>	253	14 6	6.8	5.54	2.92

<sup>a</sup> Measured by CO chemisorption, assuming that CO: Ir = 1.



Fig. 2. NH<sub>3</sub>-TPD profiles of Ir/ZrO<sub>2</sub> catalysts.

responsible for the dramatic and irreversible deactivation of the Ir/ ZrO<sub>2</sub> catalyst. Similar deactivation was also observed over Pt catalysts and attributed to the strong CO chemisorption over surface Pt atoms [13,21].

Table 2 lists the catalytic activities of the  $Ir/ZrO_2$  catalysts obtained at 60 and 300 min of reaction. All the catalysts suffer deactivation during the reaction. With increasing Ir content, the quasi-steady state conversion of crotonaldehyde and TOF increases gradually. When the Ir content is 5%, the conversion of crotonaldehyde is 31.6% after 300 min of reaction.



Fig. 3. Crotonaldehyde conversion and the selectivities to hydrogenation products as a function of time on stream over  $3Ir/ZrO_2$  catalyst.



**Fig. 4.** Effect of CO poisoning on the crotonaldehyde hydrogenation over  $3Ir/ZrO_2$  catalyst ( $\bigcirc$ ,  $\bullet$ -fresh catalyst;  $\diamondsuit$  +-catalyst pretreated with CO).

Concerning the selectivity, it is noticed in Table 2 that the selectivity to crotyl alcohol is much higher (75-82%) on the catalysts with high Ir contents (> 1%) than that with a Ir content of 1% (58%), which reflects the influence of Ir particle size on the selectivity. Englisch et al. [20] suggested that extended low index planes (e.g. {111}) on large Pt particles provided the sites that favored crotyl alcohol formation. In the case of Ir/ZrO<sub>2</sub> catalysts, similar effect of Ir particle size may also exist since the Ir particles grow up with increasing contents (Table 1), although detailed studies of the exposing planes of Ir particles in these catalysts (such as HRTEM) are very necessary to obtain solid evidence. However, it is found that the selectivity slightly decreases with further increasing Ir content (e.g. 4 and 5%), implying factors that influence the selectivity other than Ir particle size. It has been reported that the surface Lewis acid sites in the catalyst are beneficial to the adsorption of crotonaldehyde via carbonyl group, and thus improve the selectivity of crotyl alcohol [22,23]. In the present work, it is found that the surface acidity of ZrO<sub>2</sub> was even enhanced by the addition of Ir because of the acidic precursor  $H_2IrCl_6$  (Fig. 2). Therefore, based on the results reported in literature [24,25] and our current work, an adsorption model of crotonaldehyde on Ir/ZrO<sub>2</sub> catalyst is proposed, as shown in Scheme 1. The carbonyl oxygen is suggested to strongly interact with Lewis acid sites ( $\sigma$ 2) and the Ir particle is the adsorption center of C=C band  $(\pi)$  and carbonyl carbon ( $\sigma$ 1). According to the NH<sub>3</sub>-TPD results (Fig. 2), for the Ir/ZrO<sub>2</sub> catalyst, the numbers and strength of surface acid sites are relevant to Ir content, and the highest amount of acid sites is observed on the 3Ir/ ZrO<sub>2</sub> catalyst. In this case, the terminal oxygen of crotonaldehyde could strongly interact with the Lewis acid sites and this interaction leads to high selectivity to crotyl alcohol.

When the Ir content is higher than 3% (e.g. 5%), although the  $\sigma$ 1 bond is less intense due to the weak acidity, the Ir particles grow from 3.9 to 6.8 nm, so that C=C bond and the carbonyl carbon could be easily chemisorbed on Ir<sup>0</sup> sites, and thus leads to a high reactivity. Additionally, according to the crotonaldehyde adsorption model (Scheme 1), the formation of crotyl alcohol takes place on the interfacial region and involves both Ir and Lewis acid sites. The growth of Ir particle results in a decline in the amount of interfacial sites of Ir contacting with Lewis acid sites, while the sites for C=C

## Table 2

LIEU UI UIU II CUITUITIS UII UIU DUITUITIAITUU UI II/LIUS CALAIVST	Effect of th	Ir contents	on the	performance	of Ir	$/ZrO_{2}$	cataly	sts <sup>a</sup>
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Catalyst	Conversion	TOF <sup>b</sup>	Selectivity (%)			
(%)	$(\times 10^{-5}  \mathrm{s}^{-1})$	Crotyl alcohol	Butanal	Butanol	Others <sup>c</sup>	
1Ir/ZrO <sub>2</sub>	6.0(12.7)	2.9(6.1)	58.2(55.7)	21.6(17.6)	4.6(10.0)	15.6(16.7)
2Ir/ZrO <sub>2</sub>	12.2(34.9)	6.2(17.8)	77.0(66.5)	13.2(8.5)	6.1(19.5)	3.7(5.5)
3Ir/ZrO <sub>2</sub>	16.0(40.8)	7.6(19.3)	82.2(70.5)	8.1(5.4)	7.1(20.0)	2.7(4.1)
$4Ir/ZrO_2$	25.2(59.1)	10.5(24.6)	76.2(56.6)	10.1(6.9)	9.5(31.8)	4.2(4.6)
$5Ir/ZrO_2$	31.6(59.4)	15.2(70.6)	75.5(54.1)	9.8(7.0)	10.8(33.4)	3.9(5.5)

<sup>a</sup> Experimental data were taken at 300 min or (60 min).

<sup>b</sup> Calculated based on Ir dispersion by CO chemisorption results.

<sup>c</sup> Others include C3 and C8.



Scheme 1. Proposed adsorption model of crotonaldehyde on Ir/ZrO<sub>2</sub> catalyst.

bond adsorption increase. Moreover, the weakened Lewis acidity on the catalyst may suppress the adsorption of C=O bond, which would result in a lower selectivity to crotyl alcohol. Therefore, the suppressed selectivity to crotyl alcohol could be attributed to the pronounced adsorption of C=C bond with increasing Ir particle size.

#### 4. Conclusion

In summary, Ir/ZrO<sub>2</sub> catalysts showed high activities for crotonaldehyde hydrogenation and high selectivities to crotyl alcohol. With increasing Ir content in the catalyst, the crotonaldehyde conversion gradually increased. However, all the catalysts suffered deactivation during the reaction, which may be due to the CO poisoning caused by decarbonylation reaction. Also, it is found that both the Ir particle size and surface Lewis acidity play important roles in the selectivity to the desired crtoyl alcohol. The highest selectivity (82.2%) is obtained on the 3Ir/ZrO<sub>2</sub> catalyst, due to its proper Ir particle size and the highest amount of surface acid sites in the catalyst.

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