Contents lists available at SciVerse ScienceDirect





journal homepage: www.elsevier.com/locate/apcata

Applied Catalysis A: General

Effect of reduction temperature on selective hydrogenation of crotonal dehyde over Ir/TiO_2 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

ARTICLE INFO

Article history: Received 1 October 2011 Received in revised form 15 May 2012 Accepted 17 May 2012 Available online 26 May 2012

Keyword: Ir/TiO₂ catalyst Crotonaldehyde hydrogenation Crotyl alcohol Lewis acid

ABSTRACT

Vapor-phase selective hydrogenation of crotonaldehyde was conducted over Ir/TiO_2 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).

© 2012 Elsevier B.V. All rights reserved.

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/TiO_2 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/TiO_2 –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).

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.apcata.2012.05.024

support such as TiO_2 and the use of chlorine-containing metal precursors such as H_2PtCl_6 , which are crucial for the selectivity, as it was reported that the surface Lewis acid sites could enhance the adsorption strength of the C=O bond, thus resulting in the promotion of selectivity to crotyl alcohol [15,36]. As for the influence of presence of chlorine ions, they also have an important impact on the catalytic behaviors of Ir catalysts, for the remained Cl⁻ can not only directly influence the support acidic properties, but also probably influence the surface electronic properties of the Ir catalysts, however, such vital effect of remained Cl⁻ is still not be carefully identified until now.

In this work, a series of Ir/TiO_2 catalysts were prepared and tested for selective hydrogenation of crotonaldehyde. The effect of reduction pretreatment on the catalyst properties and consequently catalytic behaviors was investigated in detail. More attentions were paid to three essential factors that could influence the catalytic behaviors of Ir/TiO_2 catalysts: (1) the morphologies and electronic properties of Ir catalysts, (2) the acidic properties of the TiO₂ support, (3) the amount of remaining Cl⁻. In the end, the relationship between the catalyst property and catalytic behavior was discussed.

2. Experimental

2.1. Catalyst preparation

Degussa P25 (90% anatase and 10% rutile) with a surface area of $62.9 \text{ m}^2 \text{ g}^{-1}$ was dried at 100 °C for 12 h under vacuum before use. Supported Ir/TiO₂ catalysts with a nominal Ir content of 3 wt% were prepared by impregnating the TiO₂ support with an aqueous solution of H₂IrCl₆. In a typical preparation, 1.358 g of the TiO₂ support was impregnated with 6 ml of H₂IrCl₆ (Ir content = 7 g L⁻¹) aqueous solution for 12 h, and the mixture was dried overnight at 90 °C. The catalysts were reduced at different temperature before reaction (see section 2.3). For comparison, a supported Ir/SiO₂ catalyst was also prepared in a similar manner. The catalysts were denoted as Ir/TiO₂-X and Ir/SiO₂-X (X = 100, 200, 300, 400 and 500), where X refers to the reduction temperature.

2.2. Catalyst characterizations

As the catalysts were reduced before the reaction, all the characterizations were carried out following the reduction procedure in order to obtain intrinsic information of the catalyst. The catalysts were reduced in H₂ at different temperatures (100, 200, 300, 400 and 500 °C) for 1 h prior to characterization, except for the hydrogen temperature-programmed reduction (H₂-TPR) experiment.

X-ray diffraction (XRD) patterns were recorded using a PANalytic X'Pert PW3040 diffractiometer with Cu K α radiation operating at 40 kV and 40 mA. The patterns were collected in a 2 θ range from 20° to 80°.

Elemental compositions of the reduced catalysts were determined by X-ray fluorescence (XRF) analysis, on an ARLADVANT'X Intelli Power 4200 scanning X-ray fluorescence spectrometer. The results were analyzed using UniQuant non-standard sample quantitative analysis software.

Surface areas of the catalysts were determined by the modified BET method from the N₂ sorption isotherms at liquid nitrogen temperature (-195.7°C) on an Autosorb-1 apparatus. The samples were heated at 100°C for 4 h under vacuum before measurement.

High-resolution transmission electron microscopy (HRTEM) was performed on a JEM-2100F microscopy with a field emissive gun, operated at 200 kV and with a point resolution of 0.24 nm. The samples were prepared by dispersing a few milligrams of powder in ethanol. The dispersion was then immersed for 10 min in an

ultrasonic bath in order to disagglomerate the powder particles. Finally, one drop was deposited on a Formvar/carbon copper grid. Various regions of the grid were observed and the particle sizes were measured from the observation of 250–500 particles.

The redox properties of the catalysts were measured by hydrogen temperature-programmed reduction (H₂-TPR) experiments. 50 mg of sample was placed in a quartz tubular reactor (i.d. = 6 mm) and pretreated in a flow of N₂ (30 ml min⁻¹) at 100 °C for 1 h, and then cooled to room temperature. After that the sample was heated from room temperature to 700 °C at a rate of 10 °C min⁻¹ in a H₂-N₂ gas mixture (5 vol% H₂, 30 ml min⁻¹). The hydrogen consumption during the reduction was determined by a gas chromatograph with a thermal conductivity detector.

Ammonia temperature-programmed desorption (NH₃-TPD) was conducted on a home-made apparatus. 50 mg of catalyst was loaded in a quartz tubular reactor (i.d. = 6 mm) prior to the measurement, and was in situ reduced in a H₂-Ar mixture at different temperatures for 1 h. Then it was cooled down to 50 °C. A flow of NH₃ was introduced for 30 min. The gaseous or physisorbed NH₃ was removed by purging Ar flow at 100 °C for 90 min. Then the sample was heated to 700 °C with a ramp of 10 °C min⁻¹. The desorbed NH₃ was monitored continuously via a TCD detector. The total amount of NH₃ desorbed was determined by reaction with an excess of dilute hydrochloric acid and back titration with sodium hydroxide solution. The sensitive indicator contains a mixture of 0.1% brom-cresol green ethanol solution and 0.2% methyl red ethanol solution with a volume ratio of 3:1.

X-ray photoelectron spectra (XPS) were recorded using a VG ESCALAB MK-2 spectrometer with Al K α radiation (1486.6 eV). The voltage and power for the measurements were 12.5 kV and 250 W, respectively. The vacuum in the test chamber during the collection of spectra was kept 2×10^{-8} Pa. The samples were reduced in situ in H₂ in the chamber of this equipment at different temperatures (100, 200, 300, 400, 500 °C) and once the solid was outgassed, it was transported to the analysis chamber.

The spectra obtained, once the background was removed, were fitted to Lorentzian and Gaussian lines to obtain the number of components, peak position, and their areas. The adventitious C 1s line at 284.6 eV was used as an internal standard.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra of the samples were recorded using a Nicolet 6700 spectrometer equipped with a MCT detector and a DRIFTS (Harrick, CHC-CHA-3). Prior to the measurement, the sample was in situ reduced in a H_2 -Ar mixture (20 ml min⁻¹, 10 vol% H_2) at different reaction temperatures (100, 200, 300, 400, 500 °C) for 1 h. After that, the sample was cooled down to 30 °C and a flow of Ar (30 ml min⁻¹) was fed to remove the residual H_2 . Then the sample was exposed to CO-Ar mixture (30 ml min⁻¹, 1 vol% CO) for 30 min. Finally, the sample was purged by Ar for another 30 min and the spectra were recorded. In all cases the spectra were taken at 30 °C, with a resolution of 4 cm⁻¹ and cumulative 32 scans.

2.3. Activity testing

Gas phase hydrogenation of crotonaldehyde was performed in a fixed bed reaction system at atmospheric pressure, using a quartz tube (8 mm i.d.) reactor. About 100 mg of the catalyst was loaded in the reactor with a thermal couple placed in the middle of the catalyst bed to monitor the reaction temperature. Before running the catalyst test, the catalyst was reduced at different temperatures (100, 200, 300, 400, 500 °C) for 1 h in ultra-pure H₂ flow (99.999%, 20 ml min⁻¹) and then it was cooled down to 80 °C. Crotonaldehyde was introduced in a trap set maintained at 0 °C before to achieve a constant crotonaldehyde partial pressure (1.06 kPa), then aldehyde at constant partial pressure was carried over the catalyst by hydrogen flow (26 ml min⁻¹). The gas line was kept at about

Table 1	
BET surface areas and the element of	contents of Ir/TiO ₂ catalysts.

Catalyst	Specific surface area (m² g ⁻¹)	Element content (wt%)		
		Ir	Cl	
Ir/TiO2-100	53.6	2.85	2.25	
Ir/TiO ₂ -200	64.6	2.89	1.26	
Ir/TiO ₂ -300	64.1	2.94	0.98	
Ir/TiO2-400	60.9	2.92	0.49	
Ir/TiO ₂ -500	61.2	2.93	0.24	
Ir/SiO ₂ -300	390	3.04	0	

50 °C to avoid any condensation. The reaction products and reactant were analyzed on line using a gas chromatography (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and a DB-Wax column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu \text{m}$) capillary column.

3. Results and discussion

3.1. Compositions and textures of Ir/TiO₂ catalysts

XRD patterns of the Ir/TiO₂ catalysts (not shown) show that the diffraction peaks of all the catalysts are similar to that of the TiO_2 support and no diffraction peaks due to Ir, IrCl₃ or IrO_x are observed, indicating that the Ir species are highly dispersed on the catalysts. Table 1 lists specific surface areas of the catalysts, as well as Ir and Cl contents, as analyzed by XRF. It is found that the Ir contents

in all catalysts are close to the nominal Ir values. Also, Cl element is detected in the Ir/TiO_2 catalysts, but its content declines with increasing reduction temperature. In contrast, there is no Cl element detected in the Ir/SiO_2 catalysts. This indicates that Cl species could stably exist in the Ir/TiO_2 catalysts but be completed removed in the Ir/SiO_2 catalyst. The BET surface areas of the catalysts hardly change for the Ir/TiO_2 catalysts, ranging from about 54 to 65 m² g⁻¹. Fig. 1 shows representative HRTEM images of the Ir/TiO_2 catalysts reduced at different temperatures. Based on these images, distribution of Ir particles is estimated. It is found that the Ir particle sizes in the catalysts slightly increase with reduction temperature, mainly in the range of 1–2 nm. These findings are in good agreement with the XRD results, suggesting that the Ir particles are highly dispersed in the catalyst.

3.2. Redox properties of Ir/TiO₂ catalysts

Fig. 2 shows the H₂-TPR profiles of TiO₂, Ir/TiO₂ and Ir/SiO₂ catalysts. It is found that no reduction peak is observed in the temperature range of 50–700 °C for the TiO₂ support, indicating that single component TiO₂ cannot be reduced by H₂. For the Ir/SiO₂ catalyst, two peaks with maxima at about 190 °C (β) and 405 °C (γ) are observed, which could be assigned to the consecutive reduction of IrCl_x species to Ir⁰. For the Ir/TiO₂ catalyst, three peaks centered at about 115 °C (α), 175 °C (β) and 350 °C (γ) are observed [37]. The α peak could be assigned to the reduction of Ir cations that are not in close contact with the TiO₂ support. Compared with the Ir/SiO₂



Fig. 1. TEM images and particle size distribution histograms of Ir/TiO₂ catalysts reduced at different temperatures: (a) Ir/TiO₂-100, (b) Ir/TiO₂-200, (c) Ir/TiO₂-300, and (d) Ir/TiO₂-500.



Fig. 2. H₂-TPR profiles of TiO₂, as-prepared Ir/TiO₂ and as-prepared Ir/SiO₂ catalysts: (a) TiO₂, (b) Ir/TiO₂, and (c) Ir/SiO₂.

catalyst, the β and γ peaks shift to lower temperatures on the Ir/TiO₂ catalyst (175 and 350 °C, respectively). The lowtemperature shift of the β and γ peaks suggests an easier reduction of the Ir/TiO₂ catalyst compared to the Ir/SiO₂. Moreover, the peak area of the Ir/TiO₂ catalyst (1083 a.u.) is larger than that of the Ir/SiO₂ (860 a.u.), implying the co-reduction of TiO₂ during the process, due to a typical spillover effect [37,38]. This indicates a strong interaction between Ir species and the TiO₂ support [37]. Thus, the β and γ peaks of the Ir/TiO₂ catalyst could be assigned to the reduction of IrCl_x species with different interaction strength with the TiO₂ support and partially the contacting TiO₂ with these IrCl_x species.

3.3. Surface acidity of Ir/TiO₂ catalysts

Fig. 3 shows the NH₃-TPD profiles and the amounts of acid sites of the Ir/TiO₂ catalysts reduced at the different temperatures. It can be seen that the TiO₂ support reduced at 300 °C shows no obvious desorption peak, suggesting that the TiO₂ support has rare surface acidic sites. For the Ir/TiO₂ catalysts, desorption peaks of NH₃ are detected, indicating the Lewis acid sites generated by the residual chlorine ions on the catalyst surface [15,39]. The



Fig. 3. NH₃-TPD profiles of Ir/TiO_2 catalysts reduced at different temperatures: (a) TiO_2 , (b) Ir/TiO_2 -100, (c) Ir/TiO_2 -200, (d) Ir/TiO_2 -300, (e) Ir/TiO_2 -400, and (f) Ir/TiO_2 -500.



Fig. 4. XPS spectra of Ir 4f core level of Ir/TiO₂ catalysts reduced at different temperatures: (a) Ir/TiO₂-100, (b) Ir/TiO₂-200, (c) Ir/TiO₂-300, (d) r/TiO₂-400, and (e) Ir/TiO₂-500.

Ir/TiO₂-100 catalyst has two NH₃ desorption peaks at around 300 °C (α) and 460 °C (β), assigning to the weak and strong surface acid sites, respectively. With increasing reduction temperature, the intensities of the α and β peaks decline and the peak positions shift to lower temperature. This indicates that both the strength and the amount of surface acid sites decrease as reduction temperature increases. This phenomenon could be interpreted by the decreasing chlorine content with increasing reduction temperature. These results indicate that catalysts with high acidity in the range of strong acid sites (400–550 °C) are obtained by the reduction temperature.

3.4. XPS analysis of Ir/TiO₂ catalysts

Fig. 4 shows the XPS spectra of Ir_{4f} core level of Ir/TiO_2 catalysts after in situ reduction treatment at different temperatures. The detailed Ir^0 and $Ir^{\delta+}$ surface atomic content determined by XPS are also listed in Fig. 4. In the same region appears a peak due to Ti_{3s} , and therefore the spectra are complex. It is found that the peaks may be deconvoluted in two components, one corresponding to Ir^0 at about 60.7–61.0 eV and the other assigned to a partially oxidized $Ir^{\delta+}$ at about 62.3–62.7 [40].

As can be seen in Fig. 4, A shift toward lower binding energies of the Ir⁰ peaks accompanied by a simultaneous decline in the binding energy of the Ir^{δ^+} species is observed with increasing reduction temperature, which can be attributed to the increase in the electron density of Ir due to gradual formation of Ir⁰ at elevated reduction temperature. This is evidenced by the surface analysis as the Ir⁰/Ir^{δ^+} ratio increases with the reduction temperature.

3.5. In situ DRIFTS of CO chemisorption on Ir/SiO_2 -300 and Ir/TiO_2 catalysts

Fig. 5 shows the in situ DRIFT spectra of CO adsorbed at $30 \circ C$ on the Ir/TiO₂ catalysts reduced at different temperatures as well as the Ir/SiO₂-300 catalyst. For the Ir/SiO₂ catalyst, one band at



Fig. 5. In situ DRIFTS spectra of CO adsorbed on Ir/SiO₂-300 and Ir/TiO₂ catalysts reduced at different temperatures: (a) Ir/SiO_2 -300, (b) Ir/TiO_2 -100, (c) Ir/TiO_2 -200, (d) Ir/TiO_2 -300, (e) Ir/TiO_2 -400, and (f) Ir/TiO_2 -500.

ca. 2060 cm⁻¹ is observed, which could be assigned to linearly adsorbed CO species (LCO) on Ir⁰ sites [41,42]. For the Ir/TiO₂ catalysts, two types of adsorbed CO species have been reported in literature: linear CO (LCO) and gem dicarbonyls (GCO). Bourane et al. observed a strong peak at 2044 cm⁻¹ that was assigned to LCO species on fully reduced Ir sites [43]. Also, GCO species can accommodate the simultaneous adsorption of two CO molecules [43,44], with a band at around 2080 cm^{-1} due to the symmetric dicarbonyl vibration and a band at ca. 2010 cm⁻¹ band due to the antisymmetric carbonyl vibration [44-46]. In our experiment, the peak at ca. 2045 cm⁻¹ is assigned to LCO species adsorbed on Ir⁰ sites. The peak position of this band shifts to lower wavenumbers (from 2045 to 2037 cm^{-1}) with increasing reduction temperature, which is due to the higher reduction temperature brings an increase in the electron density of Ir [43,47]. A pair of peaks at ca. 2089 and 2008 cm⁻¹ are could be assigned to GCO species on $Ir^{\delta+}$ sites [44,48]. The band at around 2089 cm⁻¹ is due to the symmetric dicarbonyl vibration and the ca. 2008 cm⁻¹ band is due to the antisymmetric carbonyl vibration [44]. Furthermore, it is found that with increasing reduction temperature, the adsorption of CO on the Ir^{δ^+} surface species decreases but the adsorption of CO on the Ir⁰ surface species increases, indicating a lowered surface $Ir^{\delta+}/Ir^0$ ratio with reduction temperature. As the $Ir^{\delta+}$ species are in form of $IrCl_x$, the decreasing content of $Ir^{\delta+}$ species is accompanied with a declined content of Cl, which is consistent with the element composition analysis (Table 1).

The small band just above ca. 2109 cm^{-1} is assigned to linear CO adsorbed on Ir cations [44,49,50]. For the Ir/TiO₂-200 and Ir/TiO₂-300 catalysts, the peak at ca.1966 cm⁻¹ was observed which can be assigned to bridge CO (BCO) adsorbed on supported Ir⁰ sites [45]. The presence of these bands on the Ir/TiO₂ catalysts shows that Ir sites strongly chemisorb CO at room temperature, which may explain the enhanced activity over the Ir/TiO₂ catalysts as they provide more active sites for the reaction compared to the Ir/SiO₂ catalyst.



Fig. 6. Crotonaldehyde conversion and selectivities to hydrogenation products as a function of time on stream over the Ir/TiO₂ catalysts reduced at different temperatures: (a) Ir/TiO₂-100, (b) Ir/TiO₂-200, (c) Ir/TiO₂-300, (d) Ir/TiO₂-400, and (e) Ir/TiO₂-500. *Reaction conditions*: reduction temperature = 30°C, reaction temperature = 1.06 kPa.

3.6. Ir/TiO₂ catalysts for selective hydrogenation of crotonaldehyde

Fig. 6 shows the crotonaldehyde conversion and selectivity to hydrogenation products as a function of reaction time over the Ir/TiO₂ catalysts reduced at different temperatures. The products are crotyl alcohol (hydrogenation of the carbonyl C=O bond), butanal (hydrogenation of the C=C bond), butanol (hydrogenation of the C=O and C=C bands) and others (mainly C3 compounds formed by decarbonylation and C8 compounds formed by polymerization). It can be seen that the catalysts reduced at 200, 300 and 400 °C have very high initial reactivities (>80%) while those reduced at 100 and 500 °C have relatively low initial reactivities (<45%). However, all the catalysts deactivate during the reaction, but a guasi-state is obtained after 500 min, with the Ir/TiO₂-300 possessing the highest activity (26.9%) after 500 min. As for the selectivity to crotyl alcohol, it increases rapidly during the first 60 min reaction and then reaches a stable level. The catalysts reduced at temperature higher than 200 °C have similar selectivities to crotyl alcohol (about 70%), but the selectivity first increases with reduction temperature and then slightly decreases. On the other hand, only less than 30% selectivity to crotyl alcohol is obtained on the Ir/TiO₂-100.

Table 2 lists crotonaldehyde conversions, TOFs and product selectivities over the Ir/TiO_2 catalysts reduced at different temperatures. As can be seen in Table 2, with increasing reduction temperature, the conversion of crotonaldehyde, TOF and selectivity to crotyl alcohol and butanol first increase and then decrease, with an optimal reduction temperature of 300 °C. However, the selectivities to butanal and others follow an opposite trend. Moreover, it is found that Ir/TiO_2 catalyst has better catalytic performance compared to the Ir/SiO_2 catalyst.

3.7. Reaction model

In the current work, a series of Ir/TiO₂ catalysts are tested for selective hydrogenation of crotonaldehyde and it is found that the

Catalyst	Conversion (%)	$TOF^{b} (\times 10^{-3} s^{-1})$	Selectivity (%)				
			Crotyl alcohol	Butanal	Butanol	C3	C8
Ir/TiO2-100	2.4	0.33	28.9	56.6	2.7	7.1	4.7
Ir/TiO2-200	16.6	2.2	69.7	20.3	3.8	2.4	3.8
Ir/TiO2-300	26.9	3.8	74.6	14.6	5.4	2.3	3.1
Ir/TiO ₂ -400	9.8	1.6	70.4	21.5	2.4	2.0	3.7
Ir/TiO ₂ -500	6.2	1.3	66.9	24.8	2.2	1.9	4.2
Ir/SiO ₂ -300	3.4	1.9	23.7	67.5	1.7	3.6	3.5

TOFs, dispersion of Ir, conversions and product selectivities for selective hydrogenation of crotonaldehyde over the Ir/TiO₂ catalysts reduced at different temperatures.^a

^a Reaction conditions are the same as in Fig. 6 (data obtained after 500 min reaction).

^b Calculated based on Ir particle sizes by TEM results.

Table 2

reduction pretreatment has great influence on the catalytic behaviors of these catalysts. Therefore, an interpretation is needed in order to illustrate the catalytic behaviors of these catalysts. It is commonly agreed that the catalytic behavior of the catalyst for the selective hydrogenation of crotonaldehyde depends on the adsorption model of the reactant, which is remarkably affected by the surface properties of the catalysts.

The results in the current work indicate that the reduced catalyst contains Ir⁰ and Ir^{δ +} species, and the Ir⁰/Ir^{δ +} ratio increases with reduction temperature. Therefore, according to the results reported in literature [30,36,51–53] and the feature of the catalysts employed in the current work, an adsorption model of crotonaldehyde on Ir/TiO₂ catalyst is proposed, as shown in Scheme 1. The carbonyl oxygen is suggested to interact with Lewis acid sites (σ_2) and the metallic Ir⁰ particles are the adsorption centers of C=C (π) and carbonyl carbon (σ_1). This model is also similar to the proposals of Reyes et al. [30] that the reaction takes place at the metal–support interface, and the activity and selectivity of the catalyst depends on the nature of these bonds (σ_1 , σ_2 and π).

Concerning the activity, it is found that all the catalysts suffered severe deactivation during the reaction. Deactivation is commonly observed in various catalysts for this reaction, mainly due to the high surface acidity of the catalyst which would cause a rapid coke formation and consequently block of active sites [54]. In the case of Ir/TiO₂ catalyst, Reves et al. attributed the deactivation to the formation of strongly chemisorbed asymmetric carboxylate and the formation of productions with conjugated C=O and C=C bonds, by using in situ DRIFT method [30]. This is supported by the findings in this work that C8 by-products are detected during the reaction (Table 2). Also, according to the NH₃-TPD results (Fig. 3), the acidity of the catalysts decreases with increasing reduction temperature, due to the gradual removal of chlorine species at elevated temperature. For the Ir/TiO₂-100 catalyst, note that it has a high $Ir^{\delta+}/Ir^0$ ratio, which results in strong surface Lewis acid sites due to the high amount of residual chlorine species in the catalyst. These strong surface Lewis acid sites would interact with the carbonyl oxygen through the σ_2 bond, and thus makes the chemisorbed crotonaldehyde molecules difficult to desorb and thus block the active sites and suppress the activity. On the contrary, for the catalyst reduced at high temperature (e.g. 500 $^\circ$ C), although the σ_2 bond is less intense due to the weak acidity, a strong interaction between the Ir⁰ sites and the carbonyl carbon (σ_1) may form. This strong σ_1 bond also makes the desorption of crotonaldehyde difficult, which



Scheme 1. Proposed adsorption model of crotonaldehyde on Ir/TiO₂ catalyst.

may be responsible for the deactivation of the catalyst. Meanwhile, the high temperature (e.g. 500 °C) reduction may result in partial coverage of Ir particles by the TiO₂ support due to a strong metal support interaction (SMSI), which was observed in Pt/TiO₂ and PtSn/TiO₂ systems by Huidobro et al. [55].

Therefore, appropriate strengths of the σ_1 and σ_2 bondings are necessary for the chemisorption and activation of crotonaldehyde molecules. In this case, the Ir/TiO₂-300 catalyst with medium surface acidity and electron density on Ir⁰ due to a proper Ir⁰/Ir^{δ_+} </sup> may be suitable for the chemisorption and activation of the crotonaldehyde molecule, and thus leading to a high activity.

On the other hand, small amounts of C3 by-products are formed, indicating a decarbonylation reaction [3]. It was reported that decarbonylation and the irreversible adsorption of CO on the metal surface (such as Pt) is the reason for the loss of activity [3,4,36,56] due to a poisoning effect. Thus, the strong adsorption of CO molecules on the Ir species as revealed by DRIFTS results (Fig. 5) may also responsible for the deactivation, because it could block the active Ir sites.

As for the selectivity to crotyl alcohol, it is found that it first increases and then decreases with reduction temperature. The average selectivities (about 70%) obtained on the catalysts (except for the Ir/TiO₂-100 catalyst) are higher than those reported in literature [30,57]. The main difference between the catalysts in the current work and those in literature [30,57] is that the former are not calcined during the preparation while the latter were calcined at 400 °C for 4 h. Although little information about the element composition of the catalyst was given in the literature, it is reasonable to assume that these catalysts reported in literature contained very small amount of chlorine species as they could be almost completely removed by high temperature calcination, which would result in weak surface Lewis acidity. It is well known that the surface Lewis acidity plays an important role in the selectivity because these acid sites provide centers for carbonyl oxygen chemisorption, which is crucial for the formation of the desirable crotyl alcohol (although it may cause the catalyst deactivation as mentioned above). However, according to the adsorption model presented in Scheme 1, too strong Lewis acid sites may not beneficial for the selectivity because it could also result in a strong interaction between C=C bond and the Ir⁰ sites (π bond in Scheme 1). Also, it was reported that in fact, a too large amount of chlorine at the catalyst surface leads to a detrimental additional reaction, chlorinated products can be formed and then decrease the crotyl alcohol selectivity [58]. Another essential factor that promotes the selectivity of the catalyst is the electronic property of the Ir⁰ species, because it may alter the interaction between the Ir⁰ and carbonyl carbon through the σ_1 bond. The XPS results clearly show that the binding energy of the Ir⁰ species shifts to lower values with increasing reduction temperature, suggesting an increasing electron density over the Ir⁰ species with reduction temperature, due to the gradual reduction of cationic Ir species. The high electron density over the Ir⁰ species is also evidenced by in situ DRIFTS results (Fig. 5), as the band assigning to Ir⁰–CO has a distinct red shift with increasing reduction temperature, implying a higher electron density over the catalyst reduced at higher temperature. This high electron density over the Ir⁰ species is believed to be beneficial to the selectivity of crotyl alcohol, since it would enhance the interaction between the charge-enriched Ir⁰ sites and the charge-deficient carbonyl carbon (the σ_1 bond), and meanwhile, weaken the interaction between the Ir⁰ sites and the charge-enriched C=C bond (π). Meanwhile, the roles of Ir particle size on the selectivity should also be concerned. According to the adsorption model of crotonaldehyde presented in Scheme 1, the C=C bond (π) and the C=O bond (σ_1) are more likely to be formed simultaneously on the large Ir particles compared to the small Ir particles, which may lead to a competitive formation of these bonds, consequently enhancing the selectivity to butanal and suppressing the selectivity to the desired crotyl alcohol, as shown in Table 2.

4. Conclusions

In this work, the effect of reduction temperature on the reactivities and selectivities of the Ir/TiO₂ catalysts are studied. Catalyst deactivation is observed in all the catalysts, due to the strong adsorption of crotonaldehyde on the catalyst surface and decarbonylation reaction. However, high selectivity to crotyl alcohol could be obtained by the reduction of the uncalcined $IrCl_x/TiO_2$ catalysts. Both activity and selectivity depend on the electronic properties of the Ir species and the surface Lewis acid in the catalyst. The catalyst reduced at low temperature (100 °C) contains large content of $Ir^{\delta+}$ (a high $Ir^{\delta+}/Ir^0$ ratio) and Cl^- species, which results in large amount of strong surface Lewis acid sites and thus suppresses the activity and selectivity. Meanwhile, the catalyst reduced at 300 °C (Ir/TiO₂-300) has the highest activity and selectivity after 500 min reaction. It seems that the enhanced activity and selectivity obtained on the Ir/TiO₂-300 catalyst are due to the moderate interaction between the C=O bond and the Ir species, and weakened surface Lewis acid sites.

Acknowledgments

This work was supported by the National Science Foundation of China (Grant no. 21173194) and the Natural Science Foundation of Zhejiang Provincial of China (Grant no. Y4100300).

References

- [1] P. Gallezot, D. Richard, Catal. Rev. Sci. Eng. 40 (1998) 81-126.
- [2] P. Mäki-Arvela, J. Hájek, T. Salmi, D.Yu. Murzin, Appl. Catal. A: Gen. 292 (2005) 1-49.
- [3] M.E. Grass, R.M. Rioux, G.A. Somorjai, Catal. Lett. 128 (2009) 1-8.
- [4] M. Englisch, V.S. Ranade, J.A. Lercher, Appl. Catal. A: Gen. 163 (1997) 111-122.
- [5] P. Claus, Top. Catal. 5 (1998) 51-62.
- [6] M.A. Vannice, B. Sen, J. Catal. 115 (1989) 65-78.
- [7] M.A. Vannice, J. Mol. Catal. 59 (1990) 165-177.
- [8] J. Jenck, J.E. Germain, J. Catal. 65 (1980) 133-140.
- [9] P. Kluson, L. Cerveny, Appl. Catal. A: Gen. 128 (1995) 13-31.
- [10] V. Ponec, Appl. Catal. A: Gen. 149 (1997) 27-48.

- [11] U.K. Singh, M.A. Vannice, Appl. Catal. A: Gen. 213 (2001) 1-24.
- [12] L. Červený, V. Růžička, Catal. Rev. Sci. Eng. 24 (1982) 503-566.
- [13] E. Gebauer-Henke, J. Grams, E. Szubiakiewicz, J. Farbotko, R. Touroude, J. Rynkowski, J. Catal. 250 (2007) 195–208.
- [14] A.M. Ruppert, T. Paryjczak, Appl. Catal. A: Gen. 320 (2007) 80–90.
- [15] F. Ammari, J. Lamotte, R. Touroude, J. Catal. 221 (2004) 32–42.
- [16] K. Liberková, R. Touroude, J. Mol. Catal. A: Chem. 180 (2002) 221–230.
- [17] M. Abid, V. Paul-Boncour, R. Touroude, Appl. Catal. A: Gen. 297 (2006) 48–59.
 [18] R. Zanella, C. Louis, S. Giorgio, R. Touroude, J. Catal. 223 (2004) 328–339.
- [19] P. Claus, Appl. Catal. A: Gen. 291 (2005) 222–229.
- [20] J.E. Bailie, H.A. Abdullah, J.A. Anderson, C.H. Rochester, N.V. Richardson, N. Hodge, J.-G. Zhang, A. Burrows, C.J. Kiely, G.J. Hutchings, Phys. Chem. Chem. Phys. 3 (2001) 4113–4121.
- [21] B. Campo, M. Volpe, S. Ivanova, R. Touroude, J. Catal. 242 (2006) 162-171.
- [22] J.E. Bailie, G.J. Hutchings, Chem. Commun. (1999) 2151–2152.
- [23] H. Rojas, G. Borda, J. Murcia, P. Reyes, N. Rojas, Dyna 157 (2009) 173-180.
- [24] H. Rojas, J. Murcia, G. Borda, P. Reyes, N. Rojas, Dyna 159 (2009) 125–134.
 [25] M. Abid, R. Touroude, D.Y. Murzin, in: D.G. Morrell (Ed.), Chemical Indus-
- tries (Catalysis of Organic Reactions), Marcel Dekker Inc., New York, 2003, pp. 577–585.
- [26] P. Reyes, H. Rojas, G. Pecchi, J.L.G. Fierro, J. Mol. Catal. A: Chem. 179 (2002) 293–299.
- [27] P. Reyes, H. Rojas, J.L.G. Fierro, J. Mol. Catal. A: Chem. 203 (2003) 203–211.
- [28] P. Reyes, H. Rojas, J.L.G. Fierro, Appl. Catal. A: Gen. 248 (2003) 59-65.
- [29] H. Rojas, G. Borda, P. Reyes, J.J. Martínez, J. Valencia, J.L.G. Fierro, Catal. Today 133–135 (2008) 699–705.
- [30] P. Reyes, M.C. Aguirre, I. Melián-Cabrera, M. López Granados, J.L.G. Fierro, J. Catal. 208 (2002) 229–237.
- [31] C.G. Raab, J.A. Lercher, J. Mol. Catal. 75 (1992) 71–79.
- [32] J.M. Bonnier, J.P. Damon, J. Masson, Appl. Catal. 42 (1988) 285-297.
- [33] T.B.L.W. Marinelli, S. Nabuurs, V. Ponec, J. Catal. 151 (1995) 431–438.
- [34] A. Sepúlveda-Escribano, F. Coloma, F. Rodríguez-Reinoso, J. Catal. 178 (1998) 649–657.
 [35] B.A. Riguetto, C.E.C. Rodrigues, M.A. Morales, E. Baggio-Saitovitch, L. Gengem-
- bre, E. Payen, C.M.P. Marques, J.M.C. Bueno, Appl. Catal. A: Gen. 318 (2007) 70–78.
- [36] M. Englisch, A. Jentys, J.A. Lercher, J. Catal. 166 (1997) 25–35.
- [37] P. Reyes, D. Salinas, C. Campos, M. Oportus, J. Murcia, H. Rojas, G. Borda, J.L.G. Fierro, Quim. Nova 33 (2010) 777-780.
- [38] X. Zhang, W. Chu, X. Wang, W. Yang, S. Sheng, T. Zhang, Chin. J. Catal. 27 (2006) 863–867.
- [39] F. Ammari, C. Milone, R. Touroude, J. Catal. 235 (2005) 1-9.
- [40] D. Briggs, M.P. Seah (Eds.), Practical Surface Analysis: Auger and X-ray Photoelectron Spectroscopy, 2nd ed., Wiley, Chichester, 1990.
- [41] K. Tanaka, K.L. Watters, R.F. Howe, J. Catal. 75 (1982) 23-38.
- [42] F. Solymosi, J. Raskó, J. Catal. 62 (1980) 253–263.
- [43] A. Bourane, M. Nawdali, D. Bianchi, J. Phys. Chem. B 106 (2002) 2665-2671.
- [44] Y.M. López-De Jesús, A. Vicente, G. Lafaye, P. Marécot, C.T. Williams, J. Phys. Chem. C 112 (2008) 13837–13845.
- [45] C.R. Guerra, J.H. Schulman, Surf. Sci. 7 (1967) 229–249.
- [46] A. Erdőhelyi, K. Fodor, G. Suru, Appl. Catal. A: Gen. 139 (1996) 131–147.
- [47] K. Liu, A.Q. Wang, W.S. Zhang, J.H. Wang, Y.Q. Huang, J.Y. Shen, T. Zhang, J. Phys. Chem. C 114 (2010) 8533–8541.
- [48] F. Solymosi, É. Novák, A. Molnár, J. Phys. Chem. 94 (1990) 7250–7255.
- [49] E. Iojoiu, P. Gélin, H. Praliaud, M. Primet, Appl. Catal. A: Gen. 263 (2004) 39-48.
- [50] P. Gelin, G. Coudurier, Y.B. Taarit, C. Naccache, J. Catal. 70 (1981) 32-40.
- [51] A. Dandekar, M.A. Vannice, J. Catal. 183 (1999) 344–354.
- [52] F. Delbeq, P. Sautet, J. Catal. 152 (1995) 217-236.
- [53] X.X. Wang, H.Y. Zheng, X.J. Liu, G.Q. Xie, J.Q. Lu, L.Y. Jin, M.F. Luo, Appl. Catal. A: Gen. 388 (2010) 134–140.
- [54] K.V. Narayana, A. Benhmid, J. Radnik, M.-M. Pohl, U. Bentrup, A. Martin, J. Catal. 246 (2007) 399–412.
- [55] A. Huidobro, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, J. Catal. 212 (2002) 94–103.
- [56] A.B. Merlo, G.F. Santori, J. Sambeth, G.J. Siri, M.L. Casella, O.A. Ferretti, Catal. Commun. 7 (2006) 204–208.
- [57] P. Reyes, M.C. Aguirre, G. Pecchi, J.L.G. Fierro, J. Mol. Catal. A: Chem. 164 (2000) 245–251.
- [58] M. Consonni, D. Jokic, D.Yu. Murzin, R. Touroude, J. Catal. 188 (1999) 165–175.