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Journal of Molecular Catalysis A: Chemical



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

A comparative study on Pt/CeO_2 and Pt/ZrO_2 catalysts for crotonal dehyde hydrogenation

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A R T I C L E I N F O

Article history: Received 23 December 2011 Received in revised form 22 March 2012 Accepted 3 May 2012 Available online 10 May 2012

Keywords: Pt/CeO₂ Pt/ZrO₂ Crotonaldehyde Hydrogenation Crotyl alcohol

ABSTRACT

Vapor-phase hydrogenation of crotonaldehyde was carried out over Pt/CeO₂ and Pt/ZrO₂ catalysts. It was found that both catalysts suffered deactivation, with the conversion of crotonaldehyde decreasing from 31 to 6% over the Pt/CeO₂ catalyst and 20 to 7% over the Pt/ZrO₂ catalyst, which was due to the formation of organic compounds on the catalyst surface as revealed by temperature programmed oxidation technique on the spent catalysts, and the poisoning effect of CO chemisorptions on Pt atoms via decarbonylation reaction. For the Pt/ZrO₂ catalyst, selectivity to crotyl alcohol reached 48% and kept stable during the reaction, while for the Pt/CeO₂ catalyst, the selectivity to crotyl alcohol decreased dramatically from 51 to 33%. The decrease of selectivity for the Pt/CeO₂ catalyst was attributed to carbon deposit formed on the catalyst surface by the reaction between CO and reduced Ce³⁺ ion in CeO₂. However, for the Pt/ZrO₂, no carbon deposit was formed on the catalyst surface, which could account for the stable selectivity during the reaction process.

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1. Introduction

Selective hydrogenation of α -, β -unsaturated aldehyde to α -, β -unsaturated alcohol is an important reaction in industrial production, because α -, β -unsaturated alcohols are vital intermediates in pharmaceutical, fragrance and fine chemicals [1–4]. As a typical type of α -, β -unsaturated aldehydes, crotonaldehyde (CH₃-CH=CH-CHO) is often used in model reaction of selective hydrogenation. Containing the conjugated C=O bond and C=C bond, the selective hydrogenation of crotonaldehyde usually produces three major products, namely, the partial hydrogenation as crotyl alcohol (C=O bond) and butanal (C=C bond), and the deep hydrogenation as butanol (C=C and C=O bond). Generally, hydrogenation of the C=C bond is much easier than that of the C=O bond in respect of thermodynamic and kinetic factors, so it is difficult for selective hydrogenation of the carbonyl bond while keeping the C=C double bond intact in the hydrogenation of crotonaldehyde.

Supported Pt [5–7] catalysts have been frequently used in the selective hydrogenation of crotonaldehyde to crotyl alcohol in recent years. The catalytic activity of Pt/SnO₂ catalyst deactivated quickly in the hydrogenation of crotonaldehyde, while an increasing selectivity to crotyl alcohol was observed due to the formation of PtSn alloys [8]. A Pt/ZnO catalyst also gave a rapid deactivation during the hydrogenation progress, but its selectivity to crotyl

alcohol could reach a value as high as 75–80% because of the alloying and chlorine effect [9]. In our recent work, it was suggested that Lewis acidic sites generated by chlorine species may be the key factor to the high crotyl alcohol selectivity [10]. For the Pt/Cr/ZnO catalyst, a high crotyl alcohol selectivity of 80% could be obtained and maintained during the hydrogenation reaction, due to the change of electronic structure of the active Pt metal [11]. For Pt/ZnCl₂/SiO₂ catalyst, the selectivity to crotyl alcohol was above 68%, but the catalytic activity did not change significantly with the change of reduction temperature [12].

It can be summarized from the above findings that the catalytic behaviors of the Pt catalysts are quite different during the reaction. For example, some supported Pt catalysts can give steady activity and selectivity, while some catalysts suffer severe deactivation and loss of selectivity. To better understand the causes of catalyst deactivation and the factors governing the selectivity, we designed two supported Pt catalysts, Pt/CeO₂ and Pt/ZrO₂, and applied them to the gas phase selective hydrogenation of crotonaldehyde. The different catalytic behaviors of these two catalysts relating to the catalyst property were compared and discussed.

2. Experimental

2.1. Catalyst preparation

CeO₂ and ZrO₂ supports were obtained by thermal decomposition of Ce(NO₃)₃.6H₂O and Zr(NO₃)₄.5H₂O in air at 400 °C for 4 h, with a specific surface area of $66 \, m^2/g$ and $73 \, m^2/g$,

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^{1381-1169/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.molcata.2012.05.002

respectively. Both the Pt/CeO₂ and Pt/ZrO₂ catalysts were prepared by an impregnation method. The support was impregnated with H₂PtCl₆ aqueous solution with a nominal Pt content of 3 wt%. Excess water solution was removed by a mild evaporation. Finally, the resulting solid was dried overnight at 120 °C, and was denoted as Pt/CeO₂ and Pt/ZrO₂ catalysts.

2.2. Catalyst characterizations

The specific surface areas of catalysts were determined by nitrogen adsorption at -196°C on a Quantachrome Autosorb-1 apparatus. 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 2θ range from 20° to 110°, with a scanning step of 0.15° s⁻¹. Particle sizes of Pt in the Pt/CeO₂ and Pt/ZrO₂ catalysts were measured by CO chemisorption on a Chembet 3000 instrument. The sample was reduced in a H₂-N₂ mixture gas (5 vol% H₂, 30 ml/min) at 500 °C for 1 h and cooled down to 30 °C under pure He flow (30 ml/min), then pulse of CO was injected. Pt dispersion was evaluated from the consumption of CO, assuming that CO: Pt = 1. The Pt particle size was estimated using the cubic Pt particle model with the calculated Pt metal dispersion. The reduction properties of the samples were measured by hydrogen temperature-programmed reduction (H₂-TPR) experiments. The sample was placed in a quartz reactor, and then heated from room temperature to 550 °C at a rate of 10 °C/min in a H_2 – N_2 gas (5 vol% H_2 ; 30 ml/min). The hydrogen consumption during the reduction was determined by a gas chromatograph with a thermal conductivity detector. Raman spectra were obtained on a Renishaw RM1000 confocal microscope with exciting wavelength of 514.5 nm and scanning range of 200–2000 cm⁻¹ under an ambient condition. In order to study the carbon deposit, in situ Raman spectroscopy of CO adsorption was carried in a Renishaw RM1000 confocal microscope with an excitation wavelength of 514.5 nm and a scanning range of 200–2000 cm⁻¹. The sample was reduced in a H₂-N₂ mixture (5 vol% H₂, 30 ml/min) stream at 500 °C for 1 h and cooled down to 25 °C in a He flow (30 ml/min). Then the sample was exposed CO–N₂ (1 vol% CO) 30 min at 50 $^{\circ}$ C. For the temperature-programmed oxidation (TPO) study, 50 mg of the used catalyst was placed in the middle of a quartz microreactor with a inner diameter of 6 mm. The outlet was analyzed on-line by mass spectrometry (Qic-20 Benchtop, Hiden Analytical). Then the sample was subsequently flushed by O₂ (20 ml/min) from room temperature to 600 °C at a rate of 10 °C/min. The mass numbers of 44 and 18 were selected to monitor the desorption of CO₂ and H₂O fragments, respectively.

2.3. Catalytic test

The gas phase crotonaldehyde hydrogenation was performed in a fixed bed reaction system at atmospheric pressure, using a quartz tube (8 mm i.d.) reactor. 100 mg of 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 catalytic test, the catalyst was reduced at 500 °C for 1 h in ultrapure H_2 (20 ml/min) and then it was cooled down to 50 °C. The crotonaldehyde was introduced in a trap set before the reactor tube and maintained at 0°C to achieve a constant crotonaldehyde partial pressure (1.06 kPa), therefore, aldehyde at constant partial pressure was carried over the catalyst by hydrogen flow (26 ml/min). The gas line was kept at about 50 °C to avoid any condensation. The reaction products and reactant were analyzed on line using a gas chromatography (Shimazu GC-2014) equipped with a flame ionization detector (FID) and a DB-Wax capillary column $(30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}).$

Table 1

Physical properties of Pt/CeO₂ and Pt/ZrO₂ catalysts.

Catalyst ^a	Pt content (wt%)	Particle size (nm) ^a	Surface area (m²/g)
Pt/CeO ₂	2.90	4.4	58
Pt/ZrO ₂	2.84	3.1	62

^a Sample reduced at 500 °C.

^bDetermined by CO adsorption.



Fig. 1. XRD patterns of Pt/CeO₂ and Pt/ZrO₂ catalysts reduced at 500 °C.

3. Results and discussion

3.1. Physical properties of catalysts

Table 1 lists the physical properties of the Pt/CeO₂ and Pt/ZrO₂ catalysts reduced at 500 °C. The actual Pt contents in the Pt/CeO₂ and Pt/ZrO₂ catalysts are 2.90 and 2.84 wt%, respectively, which are close to the nominal values. By CO chemisorption measurement, the Pt particle sizes in the Pt/CeO₂ and Pt/ZrO₂ are 4.4 and 3.1 nm, respectively. The specific surface areas of the Pt/ZrO₂ and Pt/CeO₂ catalysts are 62 and 58 m²/g, respectively. Fig. 1 shows the XRD patterns of Pt/CeO₂ and Pt/ZrO₂ catalysts reduced at 500 °C. For both catalysts, only diffraction peaks of the support (CeO₂ and ZrO₂) are observed. Diffraction peaks of PtO₂ or Pt are not detected, which indicates that the Pt species are highly dispersed on the catalyst surface.

Fig. 2 shows the H₂-TPR profiles of Pt/ZrO₂ and Pt/CeO₂ catalysts and their corresponding supports. The ZrO₂ support shows no reduction peak up to 550 °C [13], while the pure CeO₂ shows one reduction peak at around 470 °C, which can be assigned to the reduction of surface ceria [14]. As for the supported catalysts, a reduction peak at 200 °C is observed for the Pt/ZrO₂ catalyst, and two reduction peaks appear at 180 (α) and 410 °C (β) for the Pt/CeO₂ catalyst.

Assuming that the initial Pt oxidation state in the catalysts is Pt^{4+} (PtO₂), the nominal hydrogen consumptions of the Pt/ZrO₂ and Pt/CeO₂ catalysts are 291.2 and 297.3 μ mol_{H2} g_{cat}⁻¹, respectively. According to the TPR profiles in Fig. 2, the actual hydrogenation consumptions (α peak) calibrated by the known amount of CuO powder for the Pt/ZrO₂ and Pt/CeO₂ catalysts are 288.8 and 608.0 μ mol_{H2} g_{cat}⁻¹, respectively. For the Pt/ZrO₂ catalyst, it can be seen that the nominal hydrogen consumption is very close to the actual consumption, suggesting that the reduction peak at 200 °C



Fig. 2. $H_2\text{-}TPR$ profiles of Pt/CeO_2 and Pt/ZrO_2 catalysts and their corresponding supports.

is probably due to the reduction of PtO₂. On the contrary, for the Pt/CeO₂ catalyst, it is found that the actual hydrogen consumption (608.0 μ mol_{H2} g_{cat}⁻¹) is significantly higher than the nominal value (297.3 μ mol_{H2} g_{cat}⁻¹), which is due to the reduction of the CeO₂ support. This indicates that the presence of Pt promotes reduction of ceria via spillover of hydrogen from platinum to the support [15], which remarkably shifts the surface ceria reduction downwards in temperature. The H₂-TPR results also imply that the Pt species in

Table 2

The crotonal dehyde hydrogenation performance of \mbox{Pt}/\mbox{CeO}_2 and \mbox{Pt}/\mbox{ZrO}_2 catalysts.^a the catalysts after reduction 500 °C are metallic Pt⁰, together with partial reduction of Ce⁴⁺ to Ce³⁺.

3.2. Catalytic performance for the hydrogenation of crotonaldehyde

Fig. 3 shows the catalytic behaviors of the Pt/ZrO₂ and Pt/CeO₂ catalysts. It should be noted that the initial reactivity of the Pt/CeO₂ catalyst (about 31%) is much higher than that of the Pt/ZrO₂ (about 20.0%), indicating the vital role of support in the reaction. In addition, the conversion of crotonaldehyde decreases with reaction time for both catalysts. Concerning the selectivity, the main products are crotyl alcohol (hydrogenation of C=O bond), butanal (hydrogenation of C=C bond) and butanol (complete hydrogenation). Typical side reactions in the gas phase hydrogenation of crotonaldehyde are polymerization resulting in the formation of heavy compounds product and decarbonylation resulting in the formation of C3 (propane and propylene) hydrocarbons and carbon monoxide [16,17]. For the desired crotyl alcohol, the selectivity keeps a stable level around 48% on the Pt/ZrO₂ catalyst, while its selectivity decreases from 51.6 to 31.9% after 350 min on the Pt/CeO₂ catalyst. However, the selectivity to butanal increases with reaction time for both catalysts. Detailed catalytic results based on Fig. 3 are also listed in Table 2. It is found that the turnover frequencies (TOFs) are similar for the two catalysts after 300 min reaction, however, with the Pt/CeO₂ catalyst having higher TOF $(9.7 \times 10^{-3} \text{ s}^{-1})$ compared to the Pt/ZrO₂ $(6.1 \times 10^{-3} \text{ s}^{-1})$ at the initial stage. As for the bare supports, it is found that the pure CeO_2 or ZrO₂ is inactive for the reaction.

It is obviously that these two catalysts suffer deactivation during the reaction. The cause of deactivation over Pt catalysts has been extensively investigated and it was generally recognized that the

Catalyst	Conv. (%)	$TOF^{b} (\times 10^{-3} s^{-1})$	Selectivity (%)	Selectivity (%)		
			Crotyl alcohol	Butanal	Butanol	
Pt/CeO ₂	6.4 (18.4)	3.4 (9.7)	34.3 (55.4)	56.1 (26.6)	8.3 (17.1)	
Pt/ZrO_2	8.5 (15.8)	3.3 (6.1)	48.1 (50.3)	43.5 (35.5)	8.5 (13.5)	
CeO ₂	0	0	_	_	-	
ZrO ₂	0	0	-	-	-	

^a Experimental data were taken at 300 min or 60 min.

^b Calculated based on Pt dispersion by CO chemisorption results.



Fig. 3. Crotonaldehyde hydrogenation over Pt/CeO₂ and Pt/ZrO₂ catalysts.



Fig. 4. TPO spectra of used-Pt/CeO₂ and Pt/ZrO₂ catalysts at O₂ atmosphere.

formation of heavy organic compounds on catalyst surface via polymerization could block the active sites [10]. To further check the surface species on the catalysts, we performed TPO examinations of the used Pt/CeO₂ and Pt/ZrO₂ catalysts. As shown in Fig. 4, for the Pt/CeO₂ and Pt/ZrO₂ catalysts, there is one H₂O desorption peak around 70 °C, respectively, and no CO₂ were detected in this temperature range, indicating that this signal from the desorption of the adsorbed H₂O on the surface of the catalyst. With increasing temperature, simultaneous desorption of H₂O and CO₂ are detected, suggesting the oxidation of surface organic compounds at high temperature. This result indicates that organic compounds were deposited on the catalyst surface during the reaction, which may block the active sites and thus suppress the reactivity. Additionally, the ratio of desorption area of CO₂ between Pt/CeO₂ and Pt/ZrO₂ is 1.6/1, implying more deposition of the organic compounds on the Pt/CeO₂ compared to Pt/ZrO₂, which can be explained the rapid deactivation and lower activity at steady state.

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 [18]. It was reported that CO molecules could be strongly adsorbed on the Pt surface and the active sites are blocked, which led to a partial loss of active sites [19].



Fig. 6. Catalytic performance of Pt/ZrO_2 catalyst after N_2 purging and calcination in air atmosphere (A: purge with N_2 (24 ml/min) for 0.5 h at 100 °C; B: calcination at 400 °C in air for 1 h).

In order to further confirm whether the deactivation is caused by CO poisoning, 1 ml CO was injected into reactor before the reaction. Fig. 5 shows the effect of CO poisoning on the catalytic behavior of the Pt/CeO₂ and Pt/ZrO₂ catalysts. It can be seen that the crotonaldehyde conversion of both catalysts have a decline at the initial stage after CO adsorption, especially for the Pt/CeO₂ catalyst (from 31 to 8%), and the reactivity is obviously suppressed by the poisoning during the whole reaction. Therefore, it can be concluded that the CO chemisorption on the surface Pt atoms may also be responsible for the deactivation of the catalysts. Concerning the selectivity to the desired crotyl alcohol, no apparent changes are observed for both catalysts, indicating that the CO poisoning does not influence the selectivity of target product. Therefore, the deactivation of the catalysts during the reaction was caused by two factors. One is the deposition of organic compounds on the catalyst surface, as evidenced by TPO results (Fig. 4); the other is the strong CO adsorption on the Pt atoms via decarbonylation reaction, as evidenced by the CO poisoning experiments (Fig. 5).

In order to further verify the reasons of catalyst deactivation, a series of experiments were conducted, as shown in Fig. 6. It was



Fig. 5. Effect of CO on the crotonaldehyde hydrogenation performance of Pt/CeO2 and Pt/ZrO2 catalysts (O, •-fresh catalyst; ◊, •-catalyst pretreated with CO).

found that the fresh catalyst deactivated rapidly in 5 h reaction. When the spent catalyst was in situ purged with N_2 (26 ml/min) at 100 °C for 30 min and exposed to reactant mixtures (point A), the conversion of crotonaldehyde was recovered to some extent (but less than the initial conversion). After that, the catalyst was in situ calcined in air at 400 °C for 1 h and subsequently reduced in H_2 (26 ml/min) at 500 °C for 30 min. (point B). When the treated sample was exposed to the reactant mixture, it was found that the initial conversion of crotonaldehyde could be fully recovered. The recovery of reactivity after N₂ purge (point A) could be attributed to the removal of chemisorbed CO on the catalyst surface, and the recovery of reactivity after calcination (point B) could be attributed to the combustion of surface organic compounds. Therefore, it could be validated that the deactivation of the catalyst is due to the CO chemisorption (mainly on Pt) and the deposition of organic compounds on the catalyst. It also could be concluded that the CO chemisorption on the surface Pt atoms is probably reversible as the CO molecules could be removed by N₂ purging.

It is interesting that the selectivities of crotyl alcohol on these two catalysts are different. In the case of the Pt/CeO₂, the selectivity decreases with reaction time, while it keeps stable in the case of Pt/ZrO₂. Chen [20] reported that carbon deposition formed on the catalyst surface during the hydrogenaton process may account for the decrease in selectivity for crotyl alcohol. In order to further verify this point, Raman spectroscopic measurements are carried out. Fig. 7 shows the Raman spectra of the used catalysts. For the used Pt/CeO₂ catalyst, two Raman bands at 1350 and 1600 cm⁻¹ are observed, which are assigned to the carbon deposit [21,22]. However, for the used Pt/ZrO₂ catalyst, no Raman peak associated to carbon deposit is observed. The deposition of carbon on the Pt/CeO₂ surface could result in the formation of Pt–C interface. It was reported that very low selectivity to crotyl alcohol (<10%) was obtained over Pt catalysts supported on activated carbon and carbon blacks, and it was concluded that Pt/C catalysts preferred the hydrogenation of C=C bond to C=O bond [23,24]. These findings indicate that the presence of carbon on the catalyst surface may suppress the selectivity. This point is also supported by the fact that the selectivity to butanal increases with reaction time. On the other hand, no peaks due to carbon deposit are observed on the surface of the Pt/ZrO₂ catalyst in the reaction, which could well explain the stable selectivity on this catalyst.



Fig. 7. Raman spectra of used Pt/CeO₂ and Pt/ZrO₂ catalysts.

In order to further explain the effects of the generation of carbon on the catalysts, in situ Raman spectroscopy of CO adsorption was performed on the reduced catalyst, as shown in Fig. 8. For the Pt/ZrO₂ catalyst, the Raman spectrum remains unchanged before and after CO adsorption. For the Pt/CeO₂ catalyst, the characteristic band at 460 cm^{-1} assigned to F_{2g} mode vibration of CeO₂ shifts to lower wave number at 445 cm^{-1} for the reduced catalyst compared to the as prepared catalyst. The shift is caused by lattice expansion of CeO₂ due to the presence of Ce³⁺ cations formed during the reduction treatment. Similar result has also been reported in a La³⁺doped CeO₂ material, in which replacement of Ce⁴⁺ by La³⁺ led to a lattice expansion and consequently a red shift of the 460 cm⁻¹ Raman band [25]. After the CO adsorption, the Raman band at 445 cm^{-1} returns to its initial position (460 cm^{-1}), indicating the oxidation of Ce³⁺ by reacting with CO. Meanwhile, two intensive bands at 1340 and 1600 cm^{-1} are observed on the Pt/CeO₂ catalyst, which could be assigned to the carbon deposit [21,22]. The results



Fig. 8. In situ Raman spectra of Pt/CeO2 and Pt/ZrO2 catalysts at 50°C (A) as prepared catalysts; (B) reduced catalysts; (C) after CO adsorption on catalysts.



Scheme 1. Proposed adsorption model of crotonaldehyde over Pt/CeO_2 and Pt/ZrO_2 catalysts.

suggest that the carbon deposits is formed by the reaction between CO and Ce³⁺ species on the catalyst surface (Ce₂O₃ + CO=2CeO₂ + C). It was reported that the reduced Ce³⁺ cations are beneficial to the selectivity of crotyl alcohol [26]. However, the reaction between CO and Ce³⁺ could results in carbon deposits and deactivate such Ce³⁺ sites, and consequently the Pt/CeO₂ catalyst turns unselective due to a poisoning of support sites, which could explain the loss of selectivity over the Pt/CeO₂ catalyst.

In summary, the comparison of these two catalysts suggests that the decline of crotyl alcohol selectivity on the Pt/CeO_2 catalyst may result from the formation of carbon species on the catalyst surface.

3.3. Adsorption model

Combined with the Raman and TPO results, adsorption models of crotonaldehyde over the Pt/CeO₂ and Pt/ZrO₂ catalysts are proposed in Scheme 1. $C_xH_yO_z$ stands for organic compounds such as C8 condensation product generated during the reaction on the catalysts surfaces. These organic compounds will cover the active sites of the catalyst, which consequently suppresses the reactivity. For the Pt/CeO₂ catalyst, the carbon deposits formed by CO reacting with Ce³⁺ cover the catalyst surface and produce Pt/C interfaces, which tends to C=C hydrogenation [19] and thus inhibits C=O hydrogenation. For the Pt/ZrO₂ catalyst, surface and the support is not reducible, the selectivity to crotyl alcohol remains unchanged during the reaction.

4. Conclusions

Catalytic behaviors of the Pt/CeO_2 and Pt/ZrO_2 catalysts are compared for selective hydrogenation of crotonaldehyde. It is found that both catalysts suffer deactivation due to the formation of organic compounds on the catalyst surface, and the poisoning effect of CO chemisorptions on Pt atoms. It is also found that the selectivity to crotyl alcohol decreases with reaction time for the Pt/CeO_2 catalyst, while it remains stable for the Pt/ZrO_2 catalyst. The decline of the selectivity on the Pt/CeO_2 catalyst could be attributed to the formation of carbon deposit on the catalyst surface. In contrast, no carbon deposits are formed on the surface of Pt/ZrO_2 catalyst in the reaction process, which could explain the stable selectivity.

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