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# Effects of NaCl on Pt/ZrO<sub>2</sub> catalysts for selective hydrogenation of crotonaldehyde

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## ABSTRACT

A series of NaCl-modified Pt/ZrO<sub>2</sub> catalysts were prepared and tested for vapor phase selective hydrogenation of crotonaldehyde. It was found that the reactivities of the catalysts increased with NaCl contents, with the highest selectivity to crotyl alcohol (60%) at a NaCl content of 1%. Ammonia temperature programmed desorption and Fourier transmission infrared spectra of pyridine adsorption results indicated that the strengths of surface Lewis acids of the catalysts were weakened with increasing NaCl contents, such weakening was responsible for the enhancement of the reactivity. Diffuse reflectance infrared transform spectra of CO adsorption and X-ray photoelectron spectrometer results suggested that increased electron density on Pt species with the NaCl modification was responsible for the enhanced selectivity. However, high NaCl content (>3%) in the catalyst resulted in the growth of Pt particles and fewer interfacial Pt sites contacting with the surface Lewis acid sites, such changes were unfavorable for the selectivity.

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## 1. Introduction

Unsaturated alcohols are very important intermediates for pharmaceutical, agrochemical, and fragrance productions [1–3]. Selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes using heterogeneous catalysts is of great interest because it can facilitate the reaction process and lower the cost. More importantly, the heterogeneous method can avoid the waste that is produced in the present process using NaBH<sub>4</sub> or AlLiH<sub>4</sub> [4]. However, the challenge for heterogeneous processes lies in the fact that the reduction of the C=C bond is usually preferred over the reduction of the C=O bond on monometallic catalysts due to both thermodynamic and kinetic factors [5,6].

Intensive studies have been performed on the Pt based catalysts, the most commonly used catalysts for selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes. Usually, the selectivity to the desired unsaturated alcohol is low on the monometallic Pt catalysts supported on non-reducible support, due to the preferential reduction of C=C bond. In order to obtain high selectivity, people have tried to modify the Pt catalysts. For example, it was reported that the addition of electropositive metals such as Fe, Sn and Ni could enhance the selectivity [7–9]. Also, Cl species in the catalysts, which originated from the H<sub>2</sub>PtCl<sub>6</sub> were considered important for the reaction [10]. These findings indicated that such electronic mod-

ification could enhance the catalytic performance, probably by changing the electronic structure of the active Pt metal. Riguetto et al. [11] demonstrated that the electronic properties of the active metal exerted important impacts on the selectivity and concluded that the surface electron density of the active metal particles was crucial to improving the adsorption and reactivity of the C=O bond. On the other hand, the structure of the Pt metal is also essential to the reaction, especially the selectivity. Abid et al. [12] reported high selectivity to unsaturated alcohol on Pt/CeO<sub>2</sub> catalysts. They concluded that the selectivity of Pt/CeO<sub>2</sub> catalyst is mainly determined by the metal particle size. The large particles of Pt containing high fractions of Pt(111) surfaces favored the adsorption of crotonaldehyde via the C=O bond, leading to a higher selectivity of unsaturated alcohol. Similar conclusions were also drawn by Plomp et al. for the selective hydrogenation of cinnamaldehyde [13].

Surface properties of the support are also reported to be crucial to the reactivities of the Pt catalysts. Englisch et al. [14] found that Lewis acid sites enhanced the adsorption strength of the C=O bond, thus resulting in the enhanced selectivity to crotyl alcohol. So the appropriate strength of Lewis acid sites is critical for the reaction.

In this work, the role of NaCl as a promoter for the  $Pt/ZrO_2$  catalysts for gas phase hydrogenation of crotonaldehyde is investigated and reported. The addition of NaCl in the catalysts not only affects the electronegativity and particle size of Pt metal, but also the surface acidity of the support, which greatly influences the catalytic behavior of the catalysts for selective hydrogenation of crotonaldehyde.

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Table 1	
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Contents of Pt, Cl and Na in Pt/NaCl/ZrO2 catalysts.

Catalyst	Content (wt	Content (wt.%)				
	Pt <sup>a</sup>	Cl <sup>a</sup>	Na <sup>b</sup>			
Pt/ZrO <sub>2</sub>	2.99	2.49	_			
Pt/NaCl(0.5)/ZrO <sub>2</sub>	2.92	2.53	0.12			
Pt/NaCl(1)/ZrO <sub>2</sub>	2.83	2.69	0.23			
Pt/NaCl(3)/ZrO <sub>2</sub>	2.79	3.07	0.66			
Pt/NaCl(6)/ZrO <sub>2</sub>	2.81	3.84	1.20			

<sup>a</sup> Detected by XRF.

<sup>b</sup> Detected by ICP-AES.

## 2. Experimental

#### 2.1. Catalyst preparation

All reagents were analytically pure and were purchased from Sinopharm Chemical Reagent Co.  $ZrO_2$  was prepared from hydrochloride precursors by a precipitation method. An NH<sub>3</sub> aqueous solution was added to a  $ZrOCl_2$  solution under constant stirring. The pH of the resulting mixture was controlled at  $10 \pm 0.5$ . The mixture was stirred at room temperature for 24 h, and the precipitate was then filtered after aging at 90 °C for 5 days and washed with distilled water several times. The achieved white powder was dried at 70 °C for 4 h under vacuum, followed by calcination at 400 °C for 4 h, leading to the final support with a specific surface area of  $263 \text{ m}^2/\text{g}$ .

The NaCl/ZrO<sub>2</sub> supports were prepared by impregnating  $ZrO_2$  with a NaCl aqueous solution (0.1 mol/L). The NaCl-modified support was dried at 120 °C overnight and calcined at 400 °C for 4 h. The modified supports were denoted as NaCl(x)/ZrO<sub>2</sub>, where x (0, 0.5, 1, 3 and 6) refers to the molar ratio of NaCl/ZrO<sub>2</sub> (%).

The supported Pt catalysts were prepared by impregnating the supports with aqueous solution of  $H_2PtCl_6$ , with a nominal Pt content of 3 wt.%. Excess solution was removed by mild evaporation. Finally, the catalysts were dried overnight at 120 °C. The catalysts were denoted as Pt/NaCl(x)/ZrO<sub>2</sub>.

For comparison, a chlorine free catalyst (denoted as  $Pt(N)/ZrO_2$ ) was also prepared. The  $ZrO_2$  was prepared using  $ZrO(NO_3)_2$  as the precursor, and the synthesis process was the same as that for the chlorine-containing  $ZrO_2$ . Then an aqueous solution of  $Pt(NO_3)_2$  was impregnated to the support. The nominal Pt content was 3 wt.%.

#### 2.2. Catalyst characterizations

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

X-ray diffraction (XRD) patterns were recorded with a PANalytic X'Pert PW3040 diffractiometer using Cu K $\alpha$  radiation. The working voltage was 40 kV and the working current was 40 mA. The patterns were collected in a  $2\theta$  range from  $20^{\circ}$  to  $110^{\circ}$ , with scanning steps of  $0.15^{\circ}$  s<sup>-1</sup>.

Elemental compositions of the reduced catalysts were determined by X-ray fluorescence (XRF) analysis, with an ARL ADVANT'X Intelli Power 4200 scanning X-ray fluorescence spectrometer. The results were analyzed using UniQuant non-standard sample quantitative analysis software. The sodium content was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) technique. The results are listed in Table 1.

CO-chemisorption experiments were carried out on a Quantachrame CHEMBET-3000 instrument. The sample was placed in a quartz U-tube, and purified He was used as the carrier gas. The sample was reduced in a  $H_2-N_2$  mixture (5 vol%  $H_2$ ) stream at 500 °C for 1 h and cooled down to 30 °C in a pure He flow. Then pulses of CO were fed into the stream of carrier gas with a precision analytical syringe. Pt dispersion was evaluated from the consumption of CO, assuming that CO:Pt = 1:1.

The acidic properties of the catalysts were studied by ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) and Fourier transmission infrared spectra (FTIR) analysis of pyridine adsorption. For the NH<sub>3</sub>-TPD experiment, the catalyst was pretreated in a flow of  $N_2$  (30 ml/min) at 500 °C for 1 h, and then cooled to room temperature. Afterwards, a flow of NH<sub>3</sub> (30 ml/min) was introduced into the reactor for 15 min, followed by purging with a N<sub>2</sub> flow (30 ml/min at  $100 \circ \text{C}$ ) to remove the physisorbed NH<sub>3</sub>. The NH<sub>3</sub>-TPD profile was measured using a TECHTEMP GC 7890 II with a thermal conductivity detector (TCD) when the sample was heated at a rate of 10°C/min from 200 to 560°C. Meanwhile, the above process at the same conditions was repeated 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. 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. For the FTIR experiment, the spectra were recorded at room temperature on a NEXUS 670 Fourier transform infrared spectroscope equipped with a diffuse reflectance accessory. The self-supported sample wafer was dried in an oven for 1 h at 100 °C prior to pyridine treatment for IR measurements. The catalyst was exposed first to pyridine directly, and then kept in a vacuum oven at 120 °C for 1 h to remove physisorbed pyridine. After the sample was cooled down to room temperature, each IR spectrum was recorded in a spectral range of 1200-2250 cm<sup>-1</sup> with 64 scans and at a resolution of  $4 \, \text{cm}^{-1}$ .

In order to study the oxidation state of Pt, we performed in situ diffuse reflectance infrared transform spectra (DRIFTS) measurement of CO-chemisorption. Prior to the measurement, the sample was in situ reduced in a  $H_2-N_2$  mixture (30 ml/min, 5 vol%  $H_2$ ) at 500 °C for 1 h. After the pretreatment, the sample was cooled down to 25 °C and a flow of He (30 ml/min) was fed to remove the residual  $H_2$ . Then the sample was exposed to CO for 30 min. Finally, the sample was purged by He for another 30 min and the spectra were recorded. In all cases the spectra were taken at 25 °C, with a resolution of  $4 \text{ cm}^{-1}$  and a cumulative averaging of 64 scans.

The crotonaldehyde chemisorption on catalyst surface was performed by DRIFTS measurement. The pretreatment condition was the same as that in the in situ DRIFTS of CO adsorption. When the sample had cooled down to  $50 \,^{\circ}$ C, a flow of crotonaldehyde was introduced by pure He for 15 min. The crotonaldehyde was introduced in a trap set maintained at  $0 \,^{\circ}$ C to achieve a constant crotonaldehyde partial pressure (1062 Pa). Finally, the sample was purged by He for 120 min and a spectrum was recorded. In all cases, the spectra were taken at  $50 \,^{\circ}$ C with a resolution of 4 cm<sup>-1</sup> and with a cumulative averaging of 64 scans.

For the Pt/ZrO<sub>2</sub> and Pt/NaCl(3)/ZrO<sub>2</sub> catalysts, after the ultrapure H<sub>2</sub> reduction at 500 °C treatment, the oxidation states of Pt were measured on a VG ESCALAB MK-2 X-ray photoelectron spectrometer (XPS) with Al K $\alpha$  monochromatic X-rays. 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 maintained at 2 × 10<sup>-10</sup> mbar. The binding energies were calibrated for the surface charge by referencing to the C<sub>1S</sub> peak of the contaminant carbon at 284.6 eV.

#### 2.3. Catalytic test

The gas phase crotonaldehyde hydrogenation was carried out in a fixed bed reaction system at atmospheric pressure, using a quartz tube (10 mm i.d.) reactor. One hundred mg of catalyst was loaded in the reactor with a thermocouple placed in the middle of



Fig. 1. XRD pattern of Pt/NaCl/ZrO<sub>2</sub> catalysts.

the catalyst bed to monitor the reaction temperature. Before the catalytic test was run, the catalyst was reduced at 500 °C for 1 h in ultra-pure H<sub>2</sub> (26 ml/min) and then it was cooled down to 50 °C. The crotonaldehyde was introduced in a trap set before the reactor tube and was maintained at 0 °C to achieve a constant crotonaldehyde partial pressure (1062 Pa). The gas line was kept at about 60 °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 column ( $0.32 \text{ mm} \times 30 \text{ m}$ ) capillary column.

## 3. Results and discussion

#### 3.1. Phase and composition of Pt/NaCl/ZrO<sub>2</sub> catalysts

Table 1 lists the contents of Pt, Cl and Na elements analyzed by XRF and ICP-AES in the reduced catalysts. Note that the Na content was measured by ICP-AES in order to avoid any disturbance of  $ZrO_2$  due to using the XRF technique. It is found that the Pt content in all catalysts is about 2.8%, which is close to the nominal Pt loading (3%). Also, Cl is present in the catalysts even after H<sub>2</sub> reduction, which is due to the fact that  $ZrO_2$  support was prepared from  $ZrOCl_2$  and H<sub>2</sub>PtCl<sub>6</sub> precursors. It is also found that the contents of Na and Cl increase with the increasing of NaCl contents.

Fig. 1 shows the XRD patterns of the Pt/NaCl/ZrO<sub>2</sub> catalysts. It can be seen that the diffraction peaks of the ZrO<sub>2</sub> support are very weak, indicating that the support is amorphous. No diffraction peaks due to Pt or PtO<sub>x</sub> are observed when the NaCl content is lower than 3%, indicating the presence of very small Pt particles in the catalysts. However, for the Pt/NaCl(6)/ZrO<sub>2</sub> catalyst, weak diffraction peaks assigned to metal Pt are observed at  $2\theta = 39.9^{\circ}$  (1 1 1), 46.7° (2 0 0), 68.1° (2 2 0) and 81.8° (3 1 1). This suggests that the Pt particles grow larger with the increasing of NaCl contents.

Table 2 lists the Pt dispersion and particle size in  $Pt/NaCl/ZrO_2$  catalysts, based on the CO-chemisorption analysis. The dispersion of Pt particles decreases with increasing NaCl content, and therefore the average particle size of Pt grows from 2.3 to 6.0 nm. This is in agreement with the XRD results, further suggesting the growth of Pt particles with the addition of NaCl.

Table 2	
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Dispersion and particle size of Pt in Pt/NaCl/ZrO<sub>2</sub> catalysts.

Catalyst	Dispersion (%)	Particle size (nm)
Pt/ZrO <sub>2</sub>	50	2.3
Pt/NaCl(0.5)/ZrO <sub>2</sub>	43	2.8
Pt/NaCl(1)/ZrO <sub>2</sub>	37	3.1
Pt/NaCl(3)/ZrO <sub>2</sub>	31	3.7
Pt/NaCl(6)/ZrO <sub>2</sub>	19	6.0

## 3.2. Surface acidity of the Pt/NaCl/ZrO<sub>2</sub> catalysts

Fig. 2 shows the NH<sub>3</sub>-TPD profiles and the amount of acid of the Pt/NaCl/ZrO<sub>2</sub> catalysts. The NH<sub>3</sub>-TPD results (Fig. 2) indicate that the amount of acid sites decreased with NaCl content, which suggests that the acidic sites decrease with NaCl content. Considering that NaCl is not a basic compound, it is more likely that NaCl blocked the acidic sites of the ZrO<sub>2</sub>, instead of neutralizing the acidic sites. Meanwhile, we found that the initial temperature of NH<sub>3</sub> desorption decreases, from 196 °C for the Pt/ZrO<sub>2</sub> catalyst down to 179 °C for the Pt/NaCl(6)/ZrO<sub>2</sub>. At the same time, the NH<sub>3</sub> desorption peak temperatures shift from 304 and 337 °C for the Pt/ZrO<sub>2</sub> catalyst to 292 and 322 °C for the Pt/NaCl(6)/ZrO<sub>2</sub>, respectively. The results here indicate that the addition of NaCl has weakened the acid strength of the catalysts.

In order to determine the nature of acidic sites, we conducted pyridine adsorption experiments. Fig. 3 shows the FTIR spectra of pyridine adsorption of the Pt/NaCl/ZrO<sub>2</sub> catalysts. The band at 1445 cm<sup>-1</sup> is characteristic of Lewis acid sites, and the broad band near  $1629 \, {\rm cm^{-1}}$  is assigned either to Lewis acid centers or to the vibrations of some remaining water molecules [15]. The band at  $1542 \, {\rm cm^{-1}}$  attributed to Brønsted acid sites (L/B) can be calculated by comparing the peak area of the band at  $1445 \, {\rm cm^{-1}}$  and that of the band at  $1542 \, {\rm cm^{-1}}$ . The ratio is about 5/1, indicating that the surfaces of the catalyst are mainly occupied by Lewis acid sites.

## 3.3. In situ DRIFTS of CO adsorption on Pt/NaCl/ZrO<sub>2</sub> catalysts

Fig. 4 shows the in situ DRIFTS spectra of CO adsorption on  $Pt/NaCl/ZrO_2$  catalysts. It can be seen that the areas of IR peaks decrease with increasing of NaCl content, that is because the parti-



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



Fig. 3. FTIR spectra of pyridine adsorbed on Pt/NaCl/ZrO<sub>2</sub> catalysts.

cle size of Pt increases, which leads to the reduction of the number of Pt particles [17]. For the Pt/ZrO<sub>2</sub> catalyst without NaCl, the spectrum showed a band centered at 2065 cm<sup>-1</sup>, which is assigned to CO linearly adsorbed on Pt particles [18]. However, no bridge CO species ( $\sim$ 1855 cm<sup>-1</sup>)[19] are observed for any of the catalysts, suggesting that the CO adsorption on the catalysts is in linear mode. The adsorptions of linear CO bands shift to lower wavenumbers with the increasing of NaCl contents. The variation of wavenumbers for CO adsorption band has been extensively studied [19,20]. For instance, Rades et al. [19] concluded that the reason for the shift to a lower frequency in Pt/NaY catalysts was due to negative charging of supported metal particles, which resulted from the transfer of electrons from the basic oxygen anions of the carrier to the metal. Panagiotopoulou and Kondarides [20] studied Pt/TiO<sub>2</sub> catalysts modified with Na and Cs; they found that Pt particles on Pt/TiO2 modified with alkali metals had higher electron density values than these on Pt/TiO2. From the above-mentioned findings, it can be concluded that the addition of NaCl in the Pt/ZrO<sub>2</sub> catalysts leads to an electronic modification of the metal phase. The addi-



Fig. 4. In situ DRIFTS spectra of CO adsorbed on Pt/NaCl/ZrO<sub>2</sub> catalysts.



Fig. 5. XPS Pt 4f spectra of reduced Pt catalysts.

tion of NaCl brings an increase in the electron density of Pt and is considered to be the reason for the shift [20].

#### 3.4. XPS analysis of Pt/NaCl(x)/ZrO<sub>2</sub> catalysts

Fig. 5 shows the XPS spectra of Pt 4f for the Pt/ZrO<sub>2</sub> and Pt/NaCl(3)/ZrO<sub>2</sub> catalysts after in situ reduction treatment. For all the catalysts, the spectra show two broad bands, corresponding to the Pt  $4f_{7/2}$  (at low binding energies) and Pt  $4f_{5/2}$  levels (at high binding energies). For the Pt/ZrO<sub>2</sub> catalyst, the binding energies of Pt  $4f_{5/2}$  and Pt  $4f_{7/2}$  are 74.7 and 71.4 eV, respectively; while for the Pt/NaCl(3)/ZrO<sub>2</sub> catalyst, these values are 74.4 and 71.1 eV. These results clearly show that the Pt species in the reduced catalysts are metallic Pt [21]. However, compared with the Pt/ZrO<sub>2</sub> catalyst, a shift of about 0.3 eV toward lower binding energies for the Pt/NaCl(3)/ZrO<sub>2</sub> catalyst is observed, which can be attributed to an increase in the electron density of Pt due to the addition of NaCl [22]. This is in agreement with the in situ DRIFTS spectra of CO adsorption (Fig. 4), further demonstrating that the addition of NaCl enhances the electronegativity of Pt.

## 3.5. Reactivities of Pt/NaCl/ZrO<sub>2</sub> catalysts

Fig. 6 shows crotonaldehyde conversion and selectivities to hydrogenation products as a function of reaction time on the Pt/NaCl(1)/ZrO<sub>2</sub> catalyst for selective hydrogenation of crotonaldehyde. The products are crotyl alcohol (formed by hydrogenation of the carbonyl C=O bond), butanal (formed by hydrogenation of the C=C bond), butanol (formed by hydrogenation of the C=O and C=C bands) and hydrocarbons (formed by polymerization).

Fig. 6 clearly shows that the catalyst gives a conversion of 20% during the first 30 min of reaction, but it is deactivated and reaches a quasi-steady state after 1.5 h. Such deactivation is commonly observed for this reaction, and it has been explained as due to polymerization and decarbonylation reactions that lead to a loss of active sites [23]. In the quasi-steady state regime of the catalyst, a conversion of 7% is obtained after 5 h of reaction. The selectivity to crotyl alcohol increases quickly during the first 30 min and reaches a stable level (about 60%) afterwards.

In order to explain the loss of the activity of the catalyst with the reaction time, we performed an FTIR examination of used catalyst. Fig. 7 shows the FTIR spectra of the  $Pt/NaCl(1)/ZrO_2$  catalyst. Com-



**Fig. 6.** Crotonaldehyde conversion and selectivities to hydrogenation products as functions of time on stream for Pt/NaCl(1)/ZrO<sub>2</sub> catalyst.

pared with the fresh catalyst, it is found that the adsorption bands are very different for the used one. Used catalyst exhibits bands at 1171, 1082, 799, 788, 674 cm<sup>-1</sup>. The adsorption bands at 1171 and 1082 cm<sup>-1</sup> are assigned to  $\nu_{C-O}$  [24,25], while the bands at 799, 788, 674 cm<sup>-1</sup> are assigned to  $\delta_{C-H}$ . This result suggests that during the reaction, organic compounds are formed on the catalyst surface by polymerization of reaction products; such formation may lead to a partial loss of active sites and thus suppress the reactivity.

Table 3 shows the reactivities of the Pt/NaCl/ZrO<sub>2</sub> catalysts for selective hydrogenation of crotonaldehyde. For comparison, we give the reactivities of the catalysts to which other additives such as KOH, KCl, NaOH and Na<sub>2</sub>CO<sub>3</sub> are added. It can be seen that the catalytic activities of Pt/NaOH(3)/ZrO<sub>2</sub> and Pt/Na<sub>2</sub>CO<sub>3</sub>(3)/ZrO<sub>2</sub> are similar to that of Pt/NaCl(3)/ZrO<sub>2</sub> catalyst. Considering that many works pointed out that the presence of Cl has great influence on the reaction [10], NaCl was selected as an additive to be investigated in detail. From Table 3, one can see that the conversion of the catalyst increases with increasing NaCl content, from 6% to 14%. However, the selectivity to crotyl alcohol reaches a maximum



Fig. 7. FTIR spectra of Pt/NaCl(1)/ZrO<sub>2</sub> (A: fresh, B: reacted).



 $\label{eq:scheme1} Scheme1. \ Proposed adsorption model of crotonal dehyde on Pt/NaCl/ZrO_2 catalysts.$ 

at the NaCl content of 1% (60%) and decreases with the further increasing of NaCl contents. In contrast, the selectivity to butanal first decreases but then increases when the NaCl content is higher than 1%. In addition, the TOFs of the catalysts based on particle size of Pt show a more pronounced enhancement with the increasing of NaCl contents, from 1.6 to  $11.1 \times 10^{-3} \, \text{s}^{-1}$ . Adding excess NaCl is disadvantageous to C=O hydrogenation. The reason is that the reaction rate of C=O hydrogenation continued to increase with NaCl content; however, the C=C hydrogenation rate increased more intensively, so the selectivity to crotyl alcohol decreased.

#### 3.6. Active sites of Pt/NaCl(1)/ZrO<sub>2</sub> catalysts

The activity of the supported Pt catalysts for selective hydrogenation of crotonaldehyde is affected by various factors, such as the surface acidity and electronic property of the Pt metal, as described in Section 1. In this work, the NH<sub>3</sub>-TPD (Fig. 2) and the pyridine adsorption (Fig. 3) results indicate that the support surface contains mainly Lewis acid sites, and that the strength of the Lewis acid sites weakens with the increasing of NaCl contents. The CO-chemisorption (Fig. 4) and XPS (Fig. 5) results suggest that the electron density of Pt increases with the increasing of NaCl contents. According to the adsorption model proposed by Englisch et al. [14] and based on the co-existence of the surface Lewis acid sites and the Pt active sites in this system, a proposed model for crotonaldehyde adsorption on Pt/NaCl/ZrO<sub>2</sub> catalyst is shown in Scheme 1. The carbonyl oxygen is suggested to strongly interact with Lewis acid sites (electron pair donor sites) and the Pt particle is the adsorption center of C=C band and carbonyl carbon.

In order to further explain the influence of Pt active sites and the Lewis acid sites on selective hydrogenation of crotonaldehyde, we studied in situ DRIFTS of crotonaldehyde adsorption, as shown in Fig. 8. The bands due to free crotonaldehyde molecules  $(\nu_{C=0} \text{ at } 1694 \text{ cm}^{-1}, \nu_{C=C} \text{ at } 1639 \text{ cm}^{-1}, \delta_{asCH3} \text{ at } 1445 \text{ cm}^{-1}, \delta_{CH3})$ at 1395 cm<sup>-1</sup>,  $\delta_{CH}$  at 1376 cm<sup>-1</sup>) can be clearly identified [26,27]. However, when the crotonaldehyde molecules adsorb on the NaCl(1)/ZrO<sub>2</sub> support and on the Pt/NaCl(1)/ZrO<sub>2</sub> catalyst, the bands undergo remarkable shifts. The band at 1677 cm<sup>-1</sup> is close to the main band of crotonaldehyde molecules, and its intensity becomes weaker with purging He. Therefore, the band at 1677 cm<sup>-1</sup> is attributed to  $v_{C=0}$  of physisorbed crotonaldehyde. The band at  $1586 \text{ cm}^{-1}$  for the support and the band at  $1576 \text{ cm}^{-1}$  for the catalyst are attributed to  $\nu_{C=0}$  of chemisorbed of crotonaldehyde. The relevant down shift of the crotonaldehyde  $v_{C=0}$  (from 1694 to 1586 cm<sup>-1</sup>) indicates that crotonaldehyde molecules partially adsorb on Lewis acid sites through carbonyl oxygen, which is consistent with the previous study [27]. Moreover, due to the stronger surface acidity of the NaCl(1)/ZrO<sub>2</sub> support compared to that of the TiO<sub>2</sub> in Ref. [27], the shift is more pronounced. For the Pt/NaCl(1)/ZrO<sub>2</sub> catalyst, the band of  $\nu_{C=0}$  is observed at 1576 cm<sup>-1</sup>, which is 10 cm<sup>-1</sup> lower than that on the support. This indicates that the interaction of carbonyl group with the catalyst is even stronger than that with the support. Moreover, this result further validates

Tab	le	3			
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Effect of NaCl content on reactivities of  $Pt/NaCl/ZrO_2$  catalysts.

Catalyst <sup>a</sup>	Conversion (%)	$TOF^{b} (10^{-3} s^{-1})$	Selectivity (%)	
			Crotyl alcohol	Butanal
Pt/ZrO <sub>2</sub>	5.9	1.6	31	35
Pt/NaCl(0.5)/ZrO <sub>2</sub>	4.8	1.6	41	28
Pt/NaCl(1)/ZrO <sub>2</sub>	7.2	2.6	60	21
Pt/NaCl(3)/ZrO <sub>2</sub>	9.1	4.1	50	24
Pt/NaCl(6)/ZrO <sub>2</sub>	14.6	11.1	46	35
Pt/NaOH(3)/ZrO <sub>2</sub>	13.5	-	53	27
Pt/KOH(3)/ZrO <sub>2</sub>	6.4	-	43	28
Pt/Na <sub>2</sub> CO <sub>3</sub> (3)/ZrO <sub>2</sub>	10.2	-	52	25
Pt/KCl(3)/ZrO <sub>2</sub>	6.2	-	47	30

<sup>a</sup> Data obtained at 5 h of time on stream.

<sup>b</sup> Turnover frequency (TOF) in hydrogenation is calculated on the basis of conversion and the amount of CO adsorption at room temperature.

the proposed adsorption model, that is, carbonyl carbon adsorbs on the Pt sites and carbonyl oxygen adsorbs on the Lewis acid sites.

According to the adsorption model of Scheme 1, it can be seen that the catalytic activity is mainly affected by both the Pt active sites and the Lewis acid sites. The increase of the electron density on Pt is beneficial to the adsorption of carbonyl carbon, which leads to the hydrogenation of C=O bond. Furthermore, it was reported that high acidity can result in high catalytic activity at the initial stage of reaction, but it also can lead to high coking and easy deactivation for the reaction [28]. In this work, the strength of Lewis acidity weakens with the increasing of NaCl in the catalyst, which could well explain the enhanced reactivity on the NaCl-modified Pt/ZrO<sub>2</sub> catalysts in the quasi-steady state.

In order to further explain the influence of the Lewis acidity on the reactivity, we prepared the chlorine free  $Pt(N)/ZrO_2$  catalyst. The particle size of Pt in the  $Pt(N)/ZrO_2$  catalyst measured by CO-chemisorption is 2.0 nm, which is very close to that of the chlorine-containing  $Pt/ZrO_2$  catalyst (Table 2). The NH<sub>3</sub>-TPD profiles of the  $Pt/ZrO_2$  and  $Pt(N)/ZrO_2$  catalysts are shown in Fig. 9. It is obvious that the amount of NH<sub>3</sub> desorbed on the  $Pt/ZrO_2$  catalyst is much larger than that on the  $Pt(N)ZrO_2$ , with a relative peak area ratio of 5. This indicates that the Lewis acidity of the  $ZrO_2$  support prepared by  $ZrOCl_2$  precursor can be reinforced by chlorine [29]. The desorption temperature of NH<sub>3</sub> for the  $Pt/ZrO_2$  catalyst also is higher than that for the  $Pt(N)/ZrO_2$ , indicating that the acid strength of  $Pt/ZrO_2$  is stronger than that of the  $Pt(N)/ZrO_2$ . This result tells us that the Lewis acid sites are mainly generated by chlorine species in the catalyst. Fig. 9 also presents the conversion of crotonaldehyde on the two catalysts (obtained at 5 h reaction). We found that the conversion of crotonaldehyde on the  $Pt/ZrO_2$  (6%) is lower than that on the  $Pt(N)/ZrO_2$  (11%). This result is consistent with the hypothesis mentioned above, that is, a Lewis acid with too great strength is disadvantageous to the catalytic activity [28]. Therefore, for the  $Pt/NaCl/ZrO_2$  catalysts, the addition of NaCl leads to the weakened strength of Lewis acid (Fig. 2), which could be one reason of the improvement of the reactivity.

Considering the selectivity to the desired product crotyl alcohol, we found that when NaCl content is 1%, the selectivity to crotyl alcohol is the highest, while that for butanal is the lowest. The factors that influence the selectivity have been extensively discussed in the literature. Ammari et al. [10] concluded that the Pt catalysts prepared from platinum chloride precursor with strong Lewis acidity have high selectivities toward  $\alpha$ , $\beta$ -unsaturated alcohol. Englisch et al. [14] reported that the terminal oxygen of crotonaldehyde strongly interacted with the Lewis acid sites and this interaction led to high selectivity to crotyl alcohol. Therefore, Lewis acid sites are considered to be one of the key factors leading to high crotyl alcohol selectivity. In this study, the strength of Lewis acid becomes weaker with the increasing of NaCl contents (Fig. 2), which could have led to a decrease for the selectivity to crotyl alcohol. But in fact,



Fig. 8. DRIFTS analysis of crotonal dehyde adsorption over  $NaCl(1)/ZrO_2$  support and  $Pt/NaCl(1)/ZrO_2$  catalyst.



Fig. 9.  $\rm NH_3-TPD$  profiles of  $\rm Pt(N)/ZrO_2$  and  $\rm Pt/ZrO_2$  catalysts, the inserted profile is the conversion of crotonaldehyde on these catalysts.

the selectivity to crotyl alcohol increases and reaches the maximum when the NaCl content is 1% in the catalyst (Table 3).

In order to explain the enhancement of selectivity on the NaClmodified catalysts, the electronic state of Pt must be taken into account [30]. When the NaCl content is below 1%, the Pt particle size does not change much (about 3 nm, Table 1), so the Pt particle size is not considered to be the major factor that affects the selectivity to crotyl alcohol. The DRIFTS results of CO adsorption (Fig. 4) and XPS results (Fig. 5) clearly show that with the increasing of NaCl contents, the electron density of Pt increases; such higher density can easily attract the electron positive carbonyl carbon. The strong interaction of the electronegative Pt particles with electropositive carbonyl carbon could certainly improve the selectivity to the crotyl alcohol; such improvement probably plays a key role as it compensates the opposite effect of the weak acidic strength of the NaCl-containing catalysts on the decline of selectivity.

When the NaCl content is higher than 1% in the catalyst, the particle size of Pt changes significantly and grows from 3.7 to 6.0 nm. Thus, the influence of Pt particle size on the selectivity must be taken into account. Previous studies pointed out that large Pt particles are favorable for the formation of crotyl alcohol [31], however, the selectivity declines with the increase of Pt particles (Table 3) in the present work. According to the crotonaldehyde adsorption model (Scheme 1), the formation of crotyl alcohol takes place on the interface region, which involves both Pt and Lewis acid sites. The growth of Pt particle results in a decline in the amount of interfacial sites of Pt contacting with Lewis acid sites, while the sites for the C=C bond adsorption increase. Therefore, the competing adsorption of C=C bond on large Pt particles suppresses the selectivity to crotyl alcohol. Moreover, the weakened Lewis acidity on the high NaCl content catalyst may suppress the adsorption of C=O bond, which would result in the lowered selectivity to crotyl alcohol. This is consistent with the reaction results (Table 3), as the selectivity to butanal increases when the NaCl content is higher than 1%, accompanied by the loss of selectivity to crotyl alcohol.

In summary, the selectivity to the desired product crotyl alcohol is influenced by several factors: the strength of Lewis acid sites, the electronegativity of Pt species and the Pt particle size. The weak strength of Lewis acid sites will suppress the selectivity, while highly electronegative Pt species are beneficial to the enhancement of the selectivity. Moreover, when the Pt particles grow larger, the interfacial sites for C=O adsorption decline while the adsorption of C=C bond becomes more pronounced, thus suppressing the selectivity to crotyl alcohol.

#### 4. Conclusions

In this work, we demonstrated that the selective hydrogenation of crotonaldehyde can be enhanced by the modification of the Pt/ZrO<sub>2</sub> catalyst. By adding NaCl to Pt/ZrO<sub>2</sub> catalysts, one can remarkably enhance the reactivity of the catalyst and the selectivity to crotyl alcohol. The characterization results show that the addition of NaCl decreases the strength of the Lewis acid sites; such lower strength is believed to be the main factor for the enhanced activity. With a low NaCl content ( $\leq$ 1%), the increase in the electron density on Pt leads to the increase of the selectivity to crotyl alcohol; however with a high NaCl content (>1%), the growth of Pt particle size and the weakened strength of Lewis acid lead to the decrease of the selectivity.

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