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Unexpected malformations in  
*Xenopus tropicalis*



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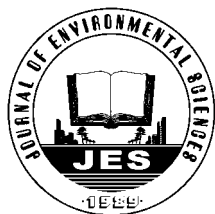
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## Effects of metal and acidic sites on the reaction by-products of butyl acetate oxidation over palladium-based catalysts

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### ABSTRACT

Catalytic oxidation is widely used in pollution control technology to remove volatile organic compounds. In this study, Pd/ZSM-5 catalysts with different Pd contents and acidic sites were prepared via the impregnation method. All the catalysts were characterized by means of N<sub>2</sub> adsorption-desorption, X-ray fluorescence (XRF), H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR), and NH<sub>3</sub> temperature programmed desorption (NH<sub>3</sub>-TPD). Their catalytic performance was investigated in the oxidation of butyl acetate experiments. The by-products of the reaction were collected in thermal desorption tubes and identified by gas chromatography/mass spectrometry. It was found that the increase of Pd content slightly changed the catalytic activity of butyl acetate oxidation according to the yield of CO<sub>2</sub> achieved at 90%, but decreased the cracking by-products, whereas the enhancement of strong acidity over Pd-based catalysts enriched the by-product species. The butyl acetate oxidation process involves a series of reaction steps including protolysis, dehydrogenation, dehydration, cracking, and isomerization. Generally, butyl acetate was cracked to acetic acid and 2-methylpropene and the latter was an intermediate of the other by-products, and the oxidation routes of typical by-products were proposed. Trace amounts of 3-methylpentane, hexane, 2-methylpentane, pentane, and 2-methylbutane originated from isomerization and protolysis reactions.

## Introduction

Volatile organic compounds (VOCs), which are widely emitted from industrial processes, are hazardous to the environment and public health. They are organic compounds that can participate in photochemical reactions with nitrogen oxides in the presence of sunlight, thereby producing more toxic compounds (Diaz et al., 2005). Among various kinds of VOCs abatement treatments, catalytic oxidation is considered to be one of the most effective and energy-saving techniques because it can convert VOCs into carbon

dioxide (CO<sub>2</sub>) and water at low reaction temperatures. Catalysts for the treatment of VOCs are supported noble metals (Bendahou et al., 2008) and transition metal oxides (Saqr et al., 2011; Choudhary and Deshmukh, 2005). The catalytic activity of noble metal-based catalysts is generally higher than that of metal oxides. Palladium (Pd) nanoparticles are especially active for a wide range of VOCs oxidation states (Giraudon et al., 2008). In recent years, studies on catalysts have not only focused on catalysts with superior performance for catalytic oxidation, but also on the reaction processes and mechanisms of VOCs oxidation. Researchers tend to understand the reaction mechanism of catalytic oxidation over Pd-supported catalysts via kinetic models, which include the power-

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rate law model, the Mars-van Krevelen (MvK) model, and the Langmuir-Hinshelwood (L-H) model. Among these models, the MvK model has been widely accepted for VOCs oxidation over Pd-supported catalysts. During the active phase of VOCs oxidation over a Pd-supported catalyst, Pd<sup>2+</sup> has been proposed to catalyze hydrocarbon oxidation, and Pd<sup>0</sup> can promote the catalytic activity by maintaining a Pd<sup>2+</sup>-Pd<sup>0</sup> cycle during the dissociation of VOCs. Thus, the reaction rate is accelerated (Nag, 2001). However, the validity of each mechanism strongly depends on the properties of the catalyst (noble metal and nature of the support) as well as the features of the VOCs; thus, the validity is difficult to generalize. A certain amount of incompletely combusted product that is formed during catalytic oxidation is inevitable. Thus, the reaction by-products and processes need to be addressed.

In our previous work, the relation between reaction by-products and the acidity of the catalyst was investigated (Yue et al., 2013). In this article, we selected butyl acetate oxidation, a subject that has not been studied in-depth, to obtain more information about the influence of metal and acidic sites on by-product distribution. Furthermore, we explored the oxidation process by using the thermal desorption/gas chromatography-mass spectrometry GC-MS technique over Pd-supported catalysts.

## 1 Experimental

### 1.1 Catalyst preparation

ZSM-5 zeolite (Si/Al = 25, Tianjin Chemical Plant, China) was impregnated in aqueous solutions of Pd(NO<sub>3</sub>)<sub>2</sub> (0.3 wt%, 0.5 wt% and 1 wt%) to obtain 0.3PdZ, 0.5PdZ, and 1PdZ catalysts, respectively. Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (99.9%, Alfa Aesar, USA) was prepared using the same impregnation process. Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was then mixed with pure ZSM-5 to obtain a mixture named MIX (Pd: 0.5 wt%). All samples were dried at 80°C for 24 hr, and calcined at 500°C for 4 hr.

### 1.2 Catalyst characterization

The N<sub>2</sub> adsorption/desorption isotherms of the catalysts were collected at 77 K using a gas sorption analyzer (NOVA 1200, Quantachrome Corp., USA). All samples were degassed in vacuum at 300°C for 3 hr before measurement. The total pore volume was estimated from the amount of adsorbed nitrogen at a relative pressure ( $P/P_0$ ) of about 0.99. The specific surface area ( $S_{\text{BET}}$ ) was calculated using the Brunauer-Emmett-Teller (BET) method. The elemental composition of each sample was analyzed via X-ray fluorescence (XRF) (XRF-1800 spectrometer, Shimadzu, Japan) using a Rh tube as the excitation source.

The H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) was performed using a Chemisorb analyzer (ChemiSorb

2720, Micrometrics, USA). The TPR profiles were obtained by passing a 5% H<sub>2</sub>/He flow (50 mL/min) through the catalysts (approximately 100 mg), which were previously dried in helium (50 mL/min) at 300°C for 1 hr.

The NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD) was also performed using a Chemisorb 2720 analyzer. Prior to each TPD test, the sample (100 mg) was pretreated in helium (50 mL/min) at 300°C for 1 hr. The samples were then adsorbed with NH<sub>3</sub>/He (2%/98%, V/V) to saturate them with NH<sub>3</sub>. The catalyst was flushed with He (50 mL/min) at room temperature to remove the physisorbed NH<sub>3</sub>. The desorption profile of NH<sub>3</sub>-TPD was then recorded from 25°C to 800°C at a heating rate of 10°C/min.

### 1.3 Activity measurements

The experiments were conducted in a continuous-flow fixed-bed reactor, which consists of a steel tube (6 mm, i.d.) at atmospheric pressure. In each test, 0.3 g of the catalyst (40–60 mesh) was placed into the tube reactor. A gas that contains VOCs was generated by bubbling air through the VOCs saturator, which was further diluted with another airstream before reaching the reaction bed. The total flow rate was kept at 300 mL/min, i.e., a gas hourly space velocity (GHSV) of 30,000 hr<sup>-1</sup>, with a butyl acetate concentration of 1500 ppm. The reaction temperature was first increased to 100°C as the feed stream passed over the reactor bed and was then stabilized for 30 min. The reaction bed temperature was increased to the following setting and was maintained for 20 min for online detection before performing the next procedure.

Online analysis was performed via simultaneous gas chromatography (GC; model 6820, Agilent, USA) and GC-mass chromatography (MS; Agilent 6890, Agilent, USA). A gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) was employed for quantitative analysis, and GC-MS was used for qualitative analysis. The by-products were collected on a mixed Tenax/carbon tube for several min at each temperature point and then desorbed by a thermal desorber (Unity 2 series, Markes International Ltd., UK) before passing into the GC-MS device.

## 2 Results and discussion

### 2.1 Catalyst characterization

The Pd loading, surface area, and total pore volume of the catalysts are listed in **Table 1**. For the Pd-supported catalysts, the percentage of Pd loading increased from 0.09 wt% to 0.40 wt%. The value for 0.5PDZ was similar to that of MIX, which indicates that the Pd contents in these two catalysts were similar. Meanwhile, pure ZSM-5 had a relatively high  $S_{\text{BET}}$  (346.0 m<sup>2</sup>/g), which was larger than

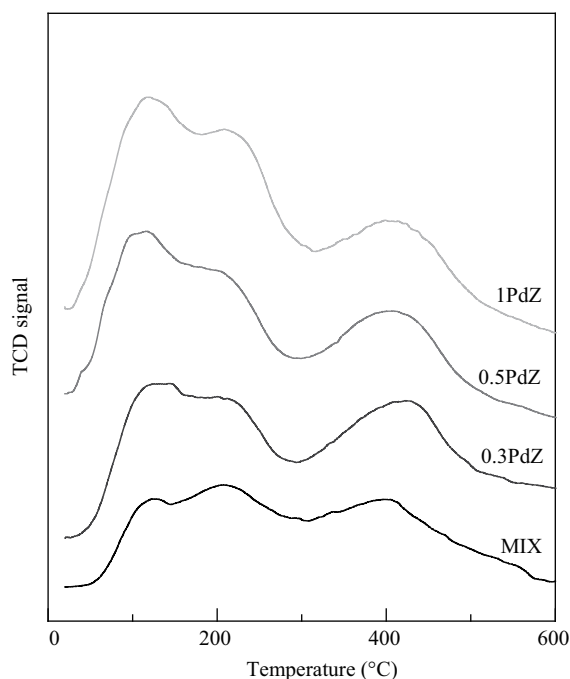
**Table 1** Physicochemical properties of the synthesized catalysts

Catalyst	Pd content <sup>a</sup> (wt.%)	$S_{\text{BET}}^{\text{b}}$ ( $\text{m}^2/\text{g}$ )	$D_v^{\text{c}}$ ( $\text{cm}^3/\text{g}$ )
MIX	0.15	186.6	0.21
ZSM-5	–	346.0	0.17
0.3PdZ	0.09	306.3	0.14
0.5PdZ	0.16	290.4	0.15
1PdZ	0.40	234.4	0.14

<sup>a</sup>Pd content by XRF analysis; <sup>b</sup>BET specific surface area; <sup>c</sup>total pore volume estimated at  $P/P_0 = 0.99$ .

the other Pd-supported catalysts. The MIX catalyst had the smallest value ( $186.6 \text{ m}^2/\text{g}$ ). For the PdZ series, the value of  $S_{\text{BET}}$  decreased with the increase of Pd content as follows:  $0.3\text{PdZ}$  ( $306.3 \text{ m}^2/\text{g}$ ) >  $0.5\text{PdZ}$  ( $290.4 \text{ m}^2/\text{g}$ ) >  $1\text{PdZ}$  ( $234.4 \text{ m}^2/\text{g}$ ). The total pore volume ( $D_v$ ) of the prepared samples was  $0.21 \text{ cm}^3/\text{g}$  for MIX,  $0.17 \text{ cm}^3/\text{g}$  for ZSM-5,  $0.14 \text{ cm}^3/\text{g}$  for  $0.3\text{PdZ}$ ,  $0.15 \text{ cm}^3/\text{g}$  for  $0.5\text{PdZ}$ , and  $0.14 \text{ cm}^3/\text{g}$  for  $1\text{PdZ}$ .

$\text{NH}_3$ -TPD was performed to evaluate the acid strength and the acid site numbers. The results are shown in **Fig. 1**. The temperature was kept above  $100^\circ\text{C}$  to eliminate the physisorption of  $\text{NH}_3$  (Zhou et al., 2009). Three types of  $\text{NH}_3$  desorption peaks were observed for all catalysts investigated, corresponding to three types of acid sites. The desorption temperature and quantitative molar number of the acid sites are listed in **Table 2**. The peaks in the range of  $100^\circ\text{C}$  to  $200^\circ\text{C}$  correspond to the weak acid sites (He et al., 2010). The high desorption temperature peak (HT peak) in the range of  $300^\circ\text{C}$  to  $500^\circ\text{C}$  was caused by the desorption of ammonia from the strong acid sites, and this

**Fig. 1**  $\text{NH}_3$ -TPD profiles of MIX,  $0.3\text{PdZ}$ ,  $0.5\text{PdZ}$  and  $1\text{PdZ}$  catalysts.

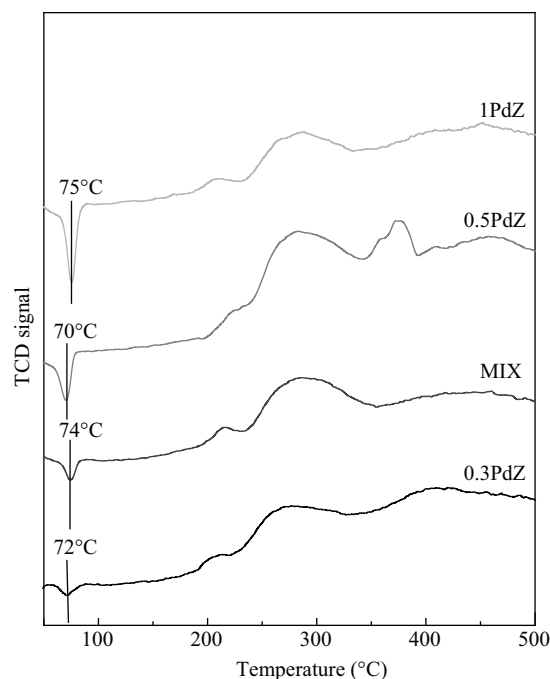
process has an important function in the catalytic reaction. The MIX catalyst ( $0.47 \text{ mmol NH}_3/\text{g-cat}$ ) had fewer strong acid sites than the other catalysts ( $0.3\text{PdZ}$ ,  $0.5\text{PdZ}$  and  $1\text{PdZ}$ ), and the quantities of strong acid sites over  $0.3\text{PdZ}$ ,  $0.5\text{PdZ}$  and  $1\text{PdZ}$  were about  $0.8 \text{ mmol NH}_3/\text{g-cat}$ . The strong acidity was not changed when the Pd content was increased.

The  $\text{H}_2$ -TPR profiles for the MIX,  $0.3\text{PdZ}$ ,  $0.5\text{PdZ}$ , and  $1\text{PdZ}$  catalysts are displayed in **Fig. 2**. A negative peak ( $70^\circ\text{C}$  to  $75^\circ\text{C}$ ) can be observed for all samples because of the desorption of weakly adsorbed hydrogen and the decomposition of  $\text{PdH}_x$  (Bonarowska et al., 2002). This result indicated that  $\text{PdCl}_2$  or  $\text{PdO}$  was easily reduced to Pd metal in an  $\text{H}_2$  atmosphere at ambient temperature (Sangeetha et al., 2009), as expected in a hydrocarbon atmosphere. The temperatures of the desorption peaks over these catalysts were quite the same, while the intensity of desorption peaks increased with increasing Pd contents. The intensity of the desorption peak is associated with the metal sites and the structure of the support (Sangeetha et al., 2009). Thus the different amounts of metal sites caused the discrepancies in the intensity of desorption peaks.

## 2.2 Butyl acetate oxidation

### 2.2.1 Catalytic behavior

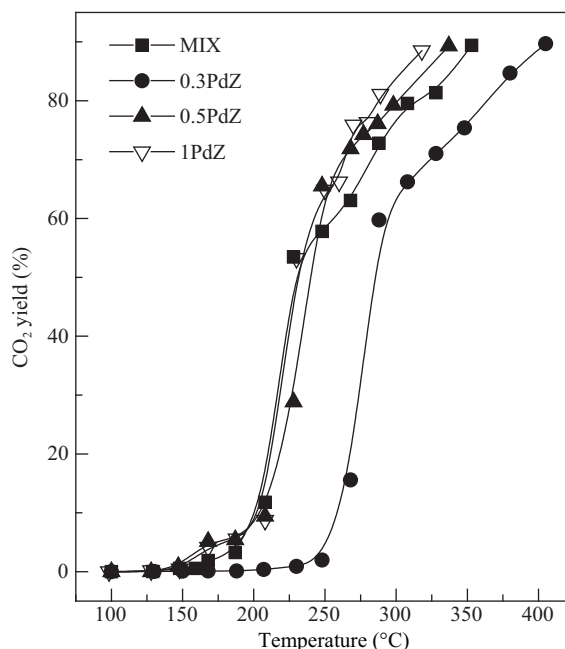
The  $\text{CO}_2$  yields of the MIX,  $0.3\text{PdZ}$ ,  $0.5\text{PdZ}$ , and  $1\text{PdZ}$  catalysts during butyl acetate oxidation are presented in **Fig. 3**. The catalytic activity over Pd-based catalysts had slight differences, and the activity order decreased as follows:  $1\text{PdZ}$  ( $310^\circ\text{C}$ ) >  $0.5\text{PdZ}$  ( $337^\circ\text{C}$ ) > MIX ( $351^\circ\text{C}$ ) >  $0.3\text{PdZ}$  ( $406^\circ\text{C}$ ), based on the  $T_{90}$  values (the temperature

**Fig. 2**  $\text{H}_2$ -TPR profiles of MIX,  $0.3\text{PdZ}$ ,  $0.5\text{PdZ}$  and  $1\text{PdZ}$  catalysts.

**Table 2** Acidity of MIX, 0.3PdZ, 0.5PdZ and 1PdZ catalysts

Catalyst	Desorption temperature (°C)			Acidity <sup>a</sup> (mmol NH <sub>3</sub> /g-cat)			ΣAcidity (mmol NH <sub>3</sub> /g-cat)
	123	209	401	0.23	0.51	0.47	
MIX	123	209	401	0.23	0.51	0.47	1.21
0.3PdZ	118	211	425	0.39	0.46	0.77	1.62
0.5PdZ	108	208	396	0.78	0.46	0.89	2.13
1PdZ	117	223	395	1.05	0.31	0.89	2.25

<sup>a</sup>Amounts of NH<sub>3</sub> desorbed at different temperatures.



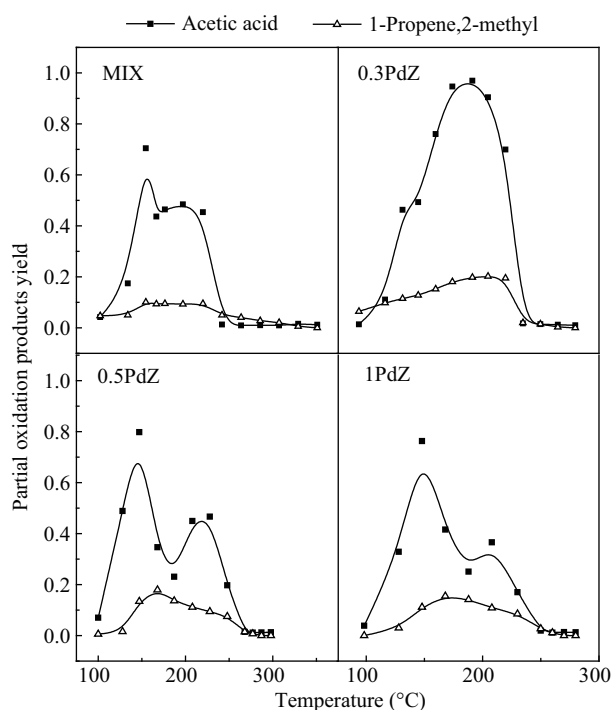
**Fig. 3** CO<sub>2</sub> yield of butyl acetate oxidation over MIX, 0.3PdZ, 0.5PdZ and 1PdZ catalysts.

required to achieve 90% CO<sub>2</sub> yield). Compared with the acidity of the catalysts, the quantities of the strong acid sites were almost the same for the PdZ catalysts. This result implied that the acidities of PdZ catalysts were not proportional to the catalytic performance in butyl acetate oxidation. However, the catalytic activities of PdZ series catalysts were related to the results of H<sub>2</sub>-TPR. The catalytic activity was enhanced over the 1PdZ catalyst because the amounts of metal sites of the catalyst were greater. The MvK kinetic model is usually preferred for VOCs catalytic oxidation over supported noble metals (such as Pd catalysts) to describe an alternative redox cycle of the metal catalyst by oxygen and hydrocarbons (Aranzabal et al., 2006). During the active phase of VOCs oxidation over a Pd-supported catalyst, Pd<sup>2+</sup> has been proposed to catalyze the hydrocarbon oxidation, and Pd<sup>0</sup> has been proposed to promote the catalytic activity by maintaining a Pd<sup>2+</sup>-Pd<sup>0</sup> cycle during the dissociation of VOCs. Thus, the reaction rate is accelerated. Therefore, larger amounts of metal sites brought about higher reducibility, which resulted in an enhancement of catalytic activity. In addition, 0.5PdZ and MIX showed differences

in strong acidity even though they had similar Pd content. Generally, only the tetrahedral Al species contribute to the strong acidity of materials (Wu et al., 2004). He et al. (2012) proposed that the acidity of the catalysts was in good accordance with the Pd dispersion order, which proved that the support acidity had positive influence on Pd particle dispersion and catalytic activity. Clearly, the catalytic activity of butyl acetate oxidation over 0.5PdZ was better than that over MIX due to its larger quantities of strong acid sites (presented in Table 2).

### 2.2.2 Distribution of butyl acetate oxidation by-products

For efficient VOCs catalytic oxidation, understanding the catalytic activity is essential, and the reaction process must also be investigated (Arzamendi et al., 2009; Ai, 1984). **Figure 4** displays the yield (moles of butyl acetate converted into a given product/moles of butyl acetate into the reactor) of the main products from the partial oxidation of butyl acetate over MIX, 0.3PdZ, 0.5PdZ, and 1PdZ



**Fig. 4** Yields of butyl acetate oxidation products as a function of reaction temperature over MIX, 0.3PdZ, 0.5PdZ and 1PdZ catalysts.

catalysts. The yield of acetic acid increased when the reaction temperature was increased from 100°C to 150°C, and then decreased when the reaction temperature was further increased. For PdZ catalysts, the maximum yields of acetic acid decreased with increasing Pd content, and the maximum values were 0.70 for MIX, 0.97 for 0.3PdZ, 0.80 for 0.5PdZ, and 0.76 for 1PdZ. 2-Methylpropene was also observed during butyl acetate oxidation, and the maximum values were 0.09 for MIX, 0.21 for 0.3PdZ, 0.18 for 0.5PdZ, and 0.16 for 1PdZ. This result indicates that 2-methylpropene had the same tendency with acetic acid with increasing Pd content. This phenomenon can be elucidated by the redox process of metallic sites. Based on the results of H<sub>2</sub>-TPR, the maximum amounts of the by-products were reduced with increasing reducibility. A fast conversion over 1PdZ can transform these by-products to CO<sub>2</sub> and H<sub>2</sub>O in a short reaction time. This result was in agreement with the superior catalytic performance of the 1PdZ catalyst. Compared with MIX, 0.5PdZ had a similar Pd content but had larger quantities of strong acid sites. Therefore, a stronger acidity is related to more by-products. In addition, by-products (acetic acid and 2-methylpropene) were formed before the formation of CO<sub>2</sub> over Pd-based catalysts. A cracking reaction of butyl acetate occurred on the strong acid and metallic sites, thereby resulting in the formation of acetic acid and 2-methylpropene over the Pd-based catalyst at lower temperatures.

Acetic acid and 2-methylpropene should be equivalent. Indeed, the yields of acetic acid were larger than that of 2-methylpropene. Thus, 2-methylpropene could be an intermediate by-product that could be transformed to other products. The molar ratio of 2-methylpropene to acetic acid presented in Fig. 5 clarified the conversion extent of 2-methylpropene over the 0.5PdZ and MIX catalysts. Compared with the MIX catalyst, the molar ratio over the 0.5PdZ catalyst was low because the transformation of 2-methylpropene to other by-products was fast, whereas the strong acidity of 0.5PdZ was higher than that of MIX. The results indicate that more side reactions occurred when the acidity was further increased. Some trace amounts of by-products were detected via the thermal desorption/GC-MS method, which included 2-butanone, 1-butene, 3-methylpentane, hexane, 2-methylpentane, pentane, and 2-methylbutane. Based on the by-product distribution, the catalytic oxidation processes of butyl acetate was proposed as shown in Fig. 6. 2-Methylpropene underwent a rearrangement of cations and oxidation in air to form 2-butanone. 1-Butene was derived from the isomerization process of 2-methylpropene. As shown in Fig. 6, more high-energy intermediates (carbenium ions) were formed through isomerization and  $\beta$ -cracking reactions. This result coincides well with the fact that  $\sigma_{C-H}$  and  $\sigma_{C-C}$  bonds are directly protonated by strong acid sites (Louis et al., 2010). Therefore, the formation of more by-products should be

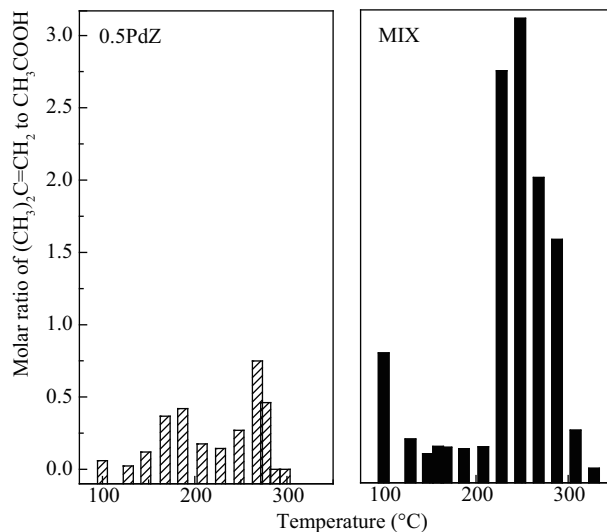


Fig. 5 Molar ratio of 1-propene, 2-methyl to acetic acid during butyl acetate oxidation as a function of reaction temperature over MIX, and 0.5PdZ catalysts.

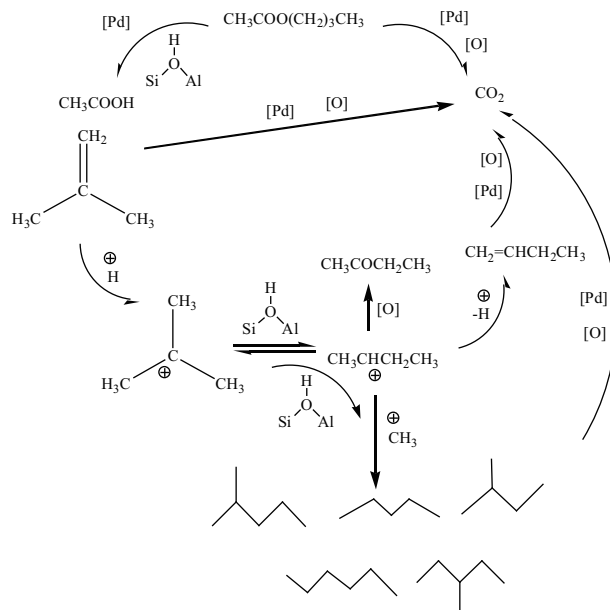


Fig. 6 Main frame for butyl acetate oxidation process over MIX, 0.3PdZ, 0.5PdZ and 1PdZ catalysts.

attributed to the strong acidity of the catalysts.

### 3 Conclusions

In summary, a series of ZSM-5-based Pd catalysts with different amounts of metal content and acidic sites was prepared via an impregnation method. The catalytic processes of butyl acetate oxidation over the MIX, 0.3PdZ, 0.5PdZ, and 1PdZ catalysts were studied by GC and thermal desorption/GC-MS techniques. The by-products



of butyl acetate oxidation include 2-methylpropene, acetic acid, 1-butene, 2-butanone, 3-methylpentane, hexane, 2-methylpentane, pentane, 2-methylbutane, and CO<sub>2</sub> through a series of reactions such as dehydrogenation, dehydration, cracking, and isomerization. The strong acidity of the support favored the formation of carbenium ions for PdZ catalysts, and secondary or tertiary reactions occurred. A larger quantity of strong acid sites led to the formation of more types of by-products. In addition, more amounts of metal sites accelerated the reaction to complete oxidation, which was thought to benefit the reduction of by-products. Thus, a catalyst with a lower quantity of strong acid sites and higher redox ability should be suitable for butyl acetate oxidation.

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