



# Influence of ZrO<sub>2</sub> properties on catalytic hydrodechlorination of chlorobenzene over Pd/ZrO<sub>2</sub> catalysts

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## ABSTRACT

Pd/ZrO<sub>2</sub> catalysts using different ZrO<sub>2</sub> as supports were prepared using the deposition–precipitation method and were characterized by X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, N<sub>2</sub> adsorption, temperature programmed reduction, H<sub>2</sub> chemisorption and measurement of surface hydroxyl group. Catalytic hydrodechlorination (HDC) of chlorobenzene was used to evaluate the activity and stability of the catalyst. The results showed that ZrO<sub>2</sub> support calcined at 300 °C was amorphous in nature, whereas ZrO<sub>2</sub> supports calcined at 500 and 600 °C consisted of both monoclinic and tetragonal phases. In addition, increasing calcination temperature led to the decrease of specific surface area and surface hydroxyl group content of the ZrO<sub>2</sub> support. For temperature programmed reduction of PdO/ZrO<sub>2</sub> samples, two H<sub>2</sub> consumption peaks with varied reduction temperature were distinctly observed, implying the existence of different Pd species in Pd/ZrO<sub>2</sub> catalysts. In addition, Pd/ZrO<sub>2</sub> catalyst with ZrO<sub>2</sub> calcined at 500 °C had a relatively higher content of Pd species with strong metal–support interaction than other catalysts. For catalytic HDC of chlorobenzene, Pd/ZrO<sub>2</sub> catalyst with ZrO<sub>2</sub> support calcined at 500 °C exhibited a higher initial activity and stability as compared to other catalysts, indicative of a strong dependence of the catalytic behavior of the Pd/ZrO<sub>2</sub> catalyst on the support properties for catalytic HDC of chlorobenzene.

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## 1. Introduction

Chlorinated organic compounds which have been intensively used in and produced by the chemical industry are unambiguously recognized as highly toxic contaminants due to their strong mutagenic and carcinogenic activities [1,2]. In addition, the release of chlorinated organic compounds into the atmospheric environment is strongly linked to negative environmental effects such as ozone depletion and global warming [3,4]. It is, therefore, highly desirable to develop effective methods for the abatement of chlorinated organic compounds prior to their release into the environment.

Catalytic combustion provides an effective method to decompose chlorinated organic compounds at relatively low reaction temperature [5,6]. Alternatively, catalytic hydrodechlorination (HDC) to convert chlorinated organic compounds to corresponding hydrocarbons is generally considered as one of the most prominent approaches to eliminate the negative environmental risks from chlorinated organic compounds, concomitantly offering additional advantages in the recovery of valuable chemicals. In principle, the catalytic HDC of chlorinated organic compounds over supported

noble metal catalyst proceeds by the cleavage of carbon–chlorine bond via a reaction between chlorinated organic compounds and dissociated hydrogen on the metal surface [7,8]. For catalytic HDC, supported Pt, Pd and Ru catalysts have been intensively investigated and supported Pd catalysts are believed to be especially active [9,10]. However, severe catalyst deactivation can be usually observed in catalytic HDC over supported Pd catalysts, generally attributed to the strong adsorption of chlorine on Pd surface [8,11], aggregation of active Pd particles [12–14] and/or carbonaceous deposits on Pd surface [15–17].

The activity and stability of supported Pd catalyst can be feasibly tuned using different preparation methods. For example, Seshu Babu et al. [18] studied the catalytic reduction of chlorobenzene over Pd/TiO<sub>2</sub> catalysts and observed substantially higher catalytic activity and stability of Pd/TiO<sub>2</sub> obtained using the deposition–precipitation method due to the higher Pd dispersion as compared to that using the impregnation method. In parallel, Gopinath et al. [19] reported the high stability of Pd/CeO<sub>2</sub> catalysts prepared using the deposition–precipitation method for catalytic HDC of chlorobenzene resulting from the strong interaction between metal and support. Similar results were also observed for catalytic HDC of chlorobenzene over Pd/ZrO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts [20,21]. Recently, Vinod Kumar et al. [22] prepared Pd/Al<sub>2</sub>O<sub>3</sub> catalyst with high Pd dispersion using a novel radiolysis method

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and observed superior catalytic behavior for chlorobenzene HDC in terms of catalytic activity and stability.

The catalytic behavior of supported Pd catalysts are found to be dependent on the support properties. For Pd/C catalysts, for example, Amorim et al. [23] studied catalytic HDC of chlorobenzene over Pd/C catalysts with activated carbon, graphite and carbon nanofiber as the supports and observed a higher activity and stability of carbon nanofiber supported Pd catalyst as compared to other catalysts. Liu et al. [24] used ammonia-treated carbon nanofiber as the support and obtained enhanced catalytic activity and stability due to the presence of pyridine-type species on the surface of carbon nanofiber acting as effective chlorine trap. Aramendia et al. [25] compared the catalytic behavior of Pd/ZrO<sub>2</sub> with those of Pd/SiO<sub>2</sub>-AlPO<sub>4</sub> and Pd/MgO for liquid-phase HDC of chlorobenzene and found that Pd/ZrO<sub>2</sub> was more stable due to the effective adsorption of chlorine on ZrO<sub>2</sub> surface although its initial activity was relatively lower. It should be pointed out that for a particular support the catalytic behavior of supported metallic catalysts were found to be closely linked to the properties of the support [26,27]. However, the impact of the support properties on the catalytic behavior of supported Pd catalyst for catalytic HDC has been seldom addressed.

In this study, Pd/ZrO<sub>2</sub> catalysts using different ZrO<sub>2</sub> as the supports were prepared using the deposition-precipitation method and catalytic HDC of chlorobenzene over these catalysts was investigated. The results showed that the catalytic activity and stability of Pd/ZrO<sub>2</sub> catalyst varied with ZrO<sub>2</sub> properties, highlighting the strong impact of support properties on the catalytic behavior.

## 2. Experimental

### 2.1. Catalyst preparation

ZrO<sub>2</sub> precursor was prepared by the precipitation method. Under vigorous stirring 2 M ammonia solution was added dropwise to 400 ml of 0.5 M ZrOCl<sub>2</sub>·8H<sub>2</sub>O till aqueous solution pH reached 10. After ageing at room temperature for 2 h, the ZrO<sub>2</sub> precursor was recovered by filtration, washing with distilled water and drying at 105 °C for 6 h. ZrO<sub>2</sub> supports with different properties were obtained by calcining the ZrO<sub>2</sub> precursor at 300, 500 or 600 °C for 4 h. ZrO<sub>2</sub> supports calcined at 300, 500 and 600 °C are referred to as ZrO<sub>2</sub>-300, ZrO<sub>2</sub>-500 and ZrO<sub>2</sub>-600, respectively.

ZrO<sub>2</sub> supported Pd catalyst was prepared using the deposition-precipitation method. Due to the high HDC activity of supported Pd catalyst [7,10,20,21], a Pd loading amount around 1 wt.% was used for ZrO<sub>2</sub> supported Pd catalyst. Briefly, 3 g of ZrO<sub>2</sub> was suspended in 30 ml distilled water, to which PdCl<sub>2</sub> solution was added. The solution pH was slowly adjusted to 10.5 using 1.0 M Na<sub>2</sub>CO<sub>3</sub> solution under vigorous stirring, followed by filtration and repeated washing with distilled water. The resultant solid was dried at 105 °C for 6 h, calcined at 300 °C in air for 4 h and eventually reduced at 300 °C in a H<sub>2</sub> flow (40 ml/min) for 4 h.

**Table 1**  
Properties of ZrO<sub>2</sub> supports and Pd/ZrO<sub>2</sub> catalysts.

Sample	Pd content (%)	BET surface area (m <sup>2</sup> /g)	Crystalline phase composition	ZrO <sub>2</sub> particle size (nm)	Pd dispersion <sup>a</sup> (%)	Pd particle size <sup>b</sup> (nm)	Surface hydroxyl content (mmol/g)
Zr-300	–	236	Amorphous	–	–	–	–
Zr-500	–	68	T+M <sup>c</sup>	11.9	–	–	–
Zr-600	–	38	T+M <sup>c</sup>	18.0	–	–	–
Pd/ZrO <sub>2</sub> -300	1.02	212	Amorphous	–	25	4.4	0.352
Pd/ZrO <sub>2</sub> -500	1.01	67	T+M <sup>c</sup>	12.0	34	3.3	0.094
Pd/ZrO <sub>2</sub> -600	1.03	32	T+M <sup>c</sup>	18.0	29	3.9	0.050

<sup>a</sup> Obtained from H<sub>2</sub> chemisorption.

<sup>b</sup> Calculated from H<sub>2</sub> chemisorption.

<sup>c</sup> T: tetragonal; M: monoclinic.

### 2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku D/max-RA powder diffraction-meter. Pd contents in the catalysts were determined using X-ray fluorescence (ARL-9800). Transmission electron microscopy (TEM) images of the samples were obtained on a JEM-2100 transmission electron microscope. BET specific surface areas of ZrO<sub>2</sub> and Pd/ZrO<sub>2</sub> samples were measured using the nitrogen adsorption method on a Micromeritics ASAP 2200 instrument. Prior to the measurement the samples were pre-treated at 300 °C under vacuum (1.33 Pa) for 1 h. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250 instrument equipped with a monochromatized Al K $\alpha$  excitation source ( $h\nu = 1486.6$  eV). The C 1s peak (284.6 eV) was used for the calibration of binding energy values.

Pd dispersion in the catalyst was measured using the H<sub>2</sub> chemisorption method. Typically, 100 mg of the reduced catalyst was loaded in a U-shaped quartz tube, in which the catalyst was activated in a H<sub>2</sub> flow (20 ml/min) at 300 °C for 1 h. After purging in an Ar flow (40 ml/min) for 1 h, the catalyst was cooled to room temperature. The H<sub>2</sub> chemisorption was performed using the pulse titration model and H<sub>2</sub> contents in the pulses were monitored by a thermal conductivity detector (TCD). Preliminary experiment showed that H<sub>2</sub> adsorption on ZrO<sub>2</sub> was negligible and the experimental error of H<sub>2</sub> adsorption measurement was below 5% under our experimental conditions.

Prior to H<sub>2</sub> reduction, the calcined samples were characterized using temperature programmed reduction (TPR), which was performed on a home made apparatus consisting of a gas chromatograph equipped with a TCD detector. Briefly, 100 mg of the sample was pressed into wafers, broken into small platelets and charged into a U-shaped quartz tube. The sample was preheated at 300 °C in a He flow (30 ml/min) for 2 h. After cooling to room temperature, the sample was heated from room temperature to 500 °C under a flow gas consisting of 10% H<sub>2</sub> in Ar (30 ml/min) at a ramping rate of 10 °C/min. The H<sub>2</sub> consumption amount of the sample was monitored by an on-line GC and the H<sub>2</sub> consumption peaks were normalized based on sample mass.

The content of surface hydroxyl group of the sample was measured using the conventional acid-base titration method. Briefly, 0.5 g of the sample was shaken with 20 ml of 0.05 M NaOH solution at 298 K for 24 h. After filtration, 5.0 ml of filtrate was titrated with 0.01 M HCl solution.

### 2.3. Catalytic hydrodechlorination of chlorobenzene

The gas phase HDC of chlorobenzene was carried out in a down-flow glass reactor at 100 °C under atmospheric pressure. Typically, 100 mg of sample was pressed into wafers, sieved to 20–40 mesh, and loaded between two layers of quartz wool. The upper portion of the reactor was filled with quartz sand to preheat the reactant before contacting the catalyst bed. Prior to cat-

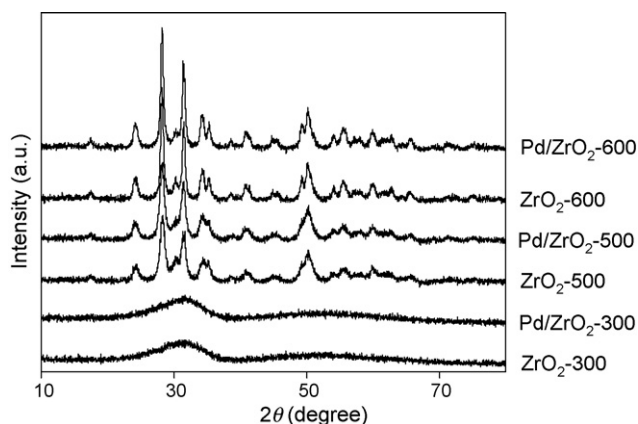


Fig. 1. XRD patterns of ZrO<sub>2</sub> supports and Pd/ZrO<sub>2</sub> catalysts.

alytic chlorobenzene HDC, the catalyst was activated in a H<sub>2</sub> flow (60 ml/min) at 300 °C for 2 h. After cooling to 100 °C, chlorobenzene was injected at 1.5 ml/h into a H<sub>2</sub> flow (60 ml/min) using a microprocessor-controlled infusion pump. The products were analyzed using an on-line gas chromatograph equipped with a flame-ionization detector (FID).

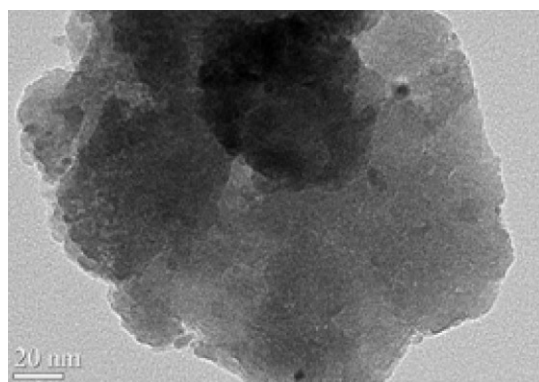
### 3. Results and discussion

#### 3.1. Catalyst characterization

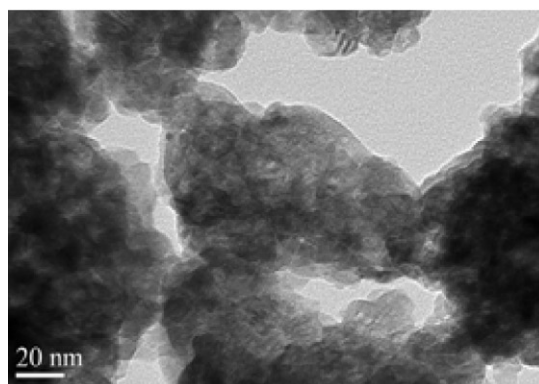
XRD patterns of ZrO<sub>2</sub> supports and Pd/ZrO<sub>2</sub> catalysts are shown in Fig. 1. For ZrO<sub>2</sub>-300, only a broad XRD peak was observed, suggesting that ZrO<sub>2</sub> support calcined at 300 °C is amorphous in nature. Increasing support calcination temperature to 500 and 600 °C led to the presence of both tetragonal and monoclinic phases. For ZrO<sub>2</sub>-500 and ZrO<sub>2</sub>-600, the particle sizes were estimated using the Scherrer equation [28] and the results are listed in Table 1. As shown in Table 1, increasing the calcination temperature from 500 to 600 °C led to a slightly increased particle size. After Pd supporting and H<sub>2</sub> reduction, no marked changes in the crystalline phases and particle sizes of ZrO<sub>2</sub> support in Pd/ZrO<sub>2</sub> catalysts were observed. In addition, the diffraction peaks characteristic of metallic Pd were not observed, probably due to the low Pd loading amounts of the catalysts.

N<sub>2</sub> adsorption results are listed in Table 1. The specific surface areas of ZrO<sub>2</sub>-300, ZrO<sub>2</sub>-500 and ZrO<sub>2</sub>-600 were 236, 68 and 38 m<sup>2</sup>/g respectively, reflecting that increasing calcination temperature results in decreased BET surface area of the ZrO<sub>2</sub> support. In principle, the thermal treatment process leads to the dehydroxylation of ZrO<sub>2</sub> precursor in concomitance with the growth of particle size, decrease of specific surface area and crystalline phase transformation [29]. Therefore, the contents of the surface hydroxyl group of the catalysts were determined using the acid–base titration method and the results are compared in Table 1. The surface hydroxyl group contents of Pd/ZrO<sub>2</sub>-300, Pd/ZrO<sub>2</sub>-500 and Pd/ZrO<sub>2</sub>-600 were found to be 0.352, 0.094 and 0.050 mmol/g respectively, also indicating the gradual dehydroxylation of ZrO<sub>2</sub> support during the thermal treatment process.

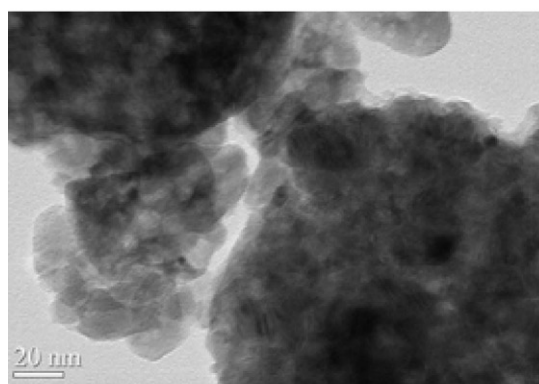
TEM images of the supported catalysts are compared in Fig. 2. For Pd/ZrO<sub>2</sub> catalysts, Pd particles with size around 3–4 nm were observed and no marked difference in Pd particle sizes could be differentiated among these catalysts, suggesting that the Pd particle sizes in Pd/ZrO<sub>2</sub> catalyst are not strongly associated with the properties of ZrO<sub>2</sub> support under our experimental conditions. This observation was also supported by the Pd dispersion measurements using H<sub>2</sub> chemisorption adsorption. As shown in Table 1, Pd



Pd/ZrO<sub>2</sub>-300



Pd/ZrO<sub>2</sub>-500



Pd/ZrO<sub>2</sub>-600

Fig. 2. TEM images of Pd/ZrO<sub>2</sub> catalysts.

dispersions were found to be 25%, 34% and 29%, corresponding to Pd particle sizes of 4.4, 3.3 and 3.9 nm respectively in Pd/ZrO<sub>2</sub>-300, Pd/ZrO<sub>2</sub>-500 and Pd/ZrO<sub>2</sub>-600, which indicates a slightly higher Pd dispersion in Pd/ZrO<sub>2</sub>-500 as compared to other catalysts.

XPS analysis can provide valuable information about the oxidation states and compositions of superficial metals, and the XPS profiles of the fresh and used catalysts are compared in Fig. 3. As Pd 3d<sub>5/2</sub> was partially overlapped with Zr 3p<sub>3/2</sub> in the XPS spectra of Pd/ZrO<sub>2</sub>, the XPS profiles of the samples were deconvoluted and the results are listed in Table 2. For the fresh catalysts (see Fig. 3a), the binding energies of Pd 3d<sub>5/2</sub> were found to be 335.6, 335.5 and 335.5 eV for Pd/ZrO<sub>2</sub>-300, Pd/ZrO<sub>2</sub>-500 and Pd/ZrO<sub>2</sub>-600, respectively. The binding energies of Pd 3d<sub>5/2</sub> for metallic Pd and PdO were reported to be around 335.0 and 336.7 eV [30], respectively. The slightly higher binding energies of Pd 3d<sub>5/2</sub> for metallic Pd in the XPS profiles of the catalysts are indicative of the presence of



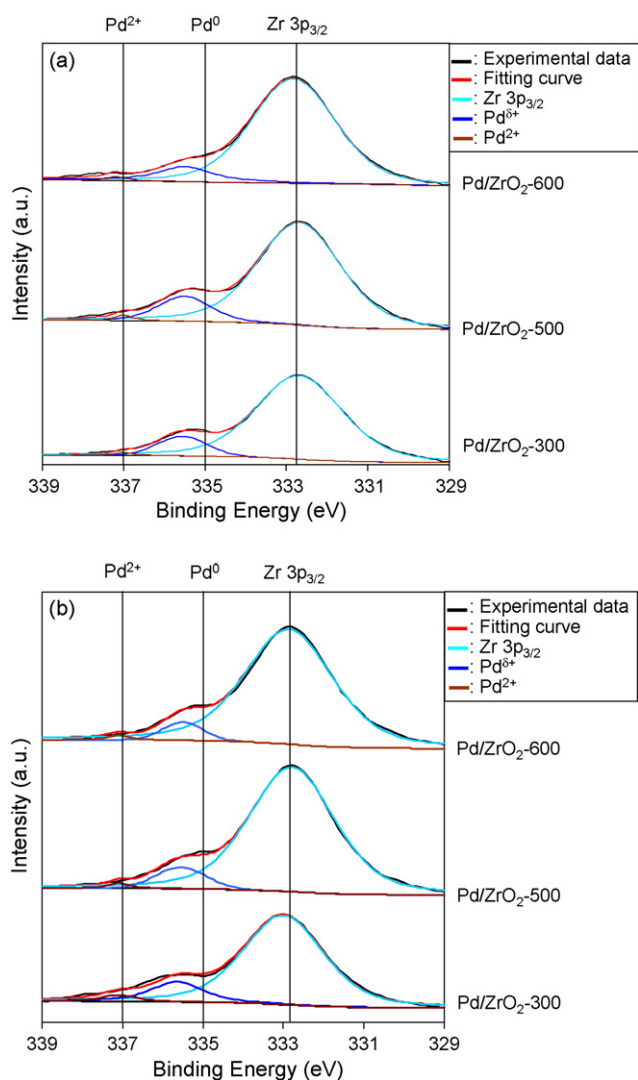


Fig. 3. XPS profiles of (a) reduced Pd/ZrO<sub>2</sub> catalysts and (b) used Pd/ZrO<sub>2</sub> catalysts.

cationic palladium species, attributed to the electron transfer from palladium to zirconia due to the strong interaction between metallic Pd and ZrO<sub>2</sub> [31]. In addition, minor peaks at around 337.0 eV were also observed, reflecting the existence of Pd<sup>2+</sup> species in the fresh catalysts [32,33].

As for the used catalysts, the atomic ratios of chlorine to Zr were found to be 0.29, 0.22 and 0.20 respectively for Pd/ZrO<sub>2</sub>-300, Pd/ZrO<sub>2</sub>-500 and Pd/ZrO<sub>2</sub>-600, which is substantially higher as compared to the fresh catalysts (see Table 2). In addition, catalytic HDC of chlorobenzene led to the increase of Pd<sup>2+</sup> contents in the catalysts. It should be pointed out that the Pd<sup>2+</sup> content in Pd/ZrO<sub>2</sub>-300 increased from 7.5% to 18.0% after catalytic HDC for 10 h, which is most prominent among the tested catalysts.

Table 2  
XPS analysis of Pd/ZrO<sub>2</sub> catalysts.

Sample	Binding energy (eV)		Pd <sup>2+</sup> /(Pd + Pd <sup>2+</sup> ) (%)	Cl/Zr
	Pd	Pd <sup>2+</sup>		
Pd/ZrO <sub>2</sub> -300 (reduced)	335.6	337.0	7.5	0.09
Pd/ZrO <sub>2</sub> -300 (used)	335.7	337.2	18.0	0.29
Pd/ZrO <sub>2</sub> -500 (reduced)	335.5	337.0	8.3	0.13
Pd/ZrO <sub>2</sub> -500 (used)	335.6	337.1	12.5	0.22
Pd/ZrO <sub>2</sub> -600 (reduced)	335.5	337.2	9.1	0.09
Pd/ZrO <sub>2</sub> -600 (used)	335.5	337.2	16.0	0.20

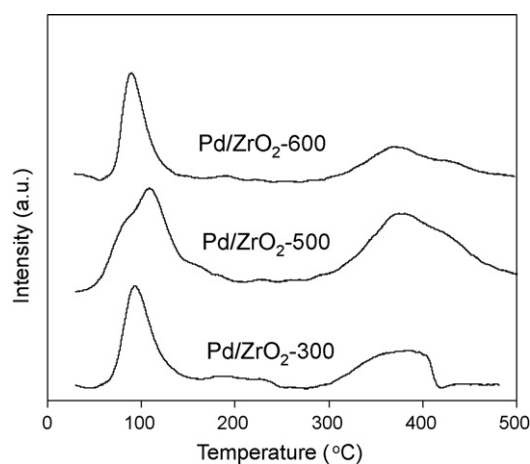


Fig. 4. TPR profiles of PdO/ZrO<sub>2</sub> samples.

Prior to H<sub>2</sub> reduction of ZrO<sub>2</sub> supported Pd catalysts, TPR measurements of the calcined samples were performed and the TPR profiles are compiled in Fig. 4. For all samples, two positive H<sub>2</sub> consumption peaks were distinctly observed at around 100 °C and 300–500 °C, suggesting the existence of different Pd species in Pd/ZrO<sub>2</sub> catalysts. Gopinath et al. [33] studied H<sub>2</sub>-TPR of PdO/ZrO<sub>2</sub> obtained by the deposition–precipitation method and observed different surface Pd species over ZrO<sub>2</sub> support. The H<sub>2</sub> consumption peaks at low and high reduction temperatures were assigned to the reduction of PdO having weak and strong interaction with ZrO<sub>2</sub> support [33]. For PdO/ZrO<sub>2</sub>-500, the presence of shoulder peak is due to the non-uniform distribution of Pd particle sizes [33]. It is general consensus that the deposition–precipitation method for the preparation of Pd/ZrO<sub>2</sub> is susceptible to invoking the strong interaction between Pd and ZrO<sub>2</sub> support. For the interaction mechanism, Narui et al. [34] proposed that the strong interaction between PdO and ZrO<sub>2</sub> is similar to a solid solution. Matsumura et al. [32] suggested that Pd–O–Zr could be formed in the sample prepared by the deposition–precipitation method. It is interesting to note that the ratios of the H<sub>2</sub> consumption peak area at high reduction temperature to that at low reduction temperature were estimated to be 0.83, 1.11 and 0.97 for Pd/ZrO<sub>2</sub>-300, Pd/ZrO<sub>2</sub>-500 and Pd/ZrO<sub>2</sub>-600 respectively, implying that the content of Pd with strong metal–interaction is closely linked with the properties of ZrO<sub>2</sub> support. For supported Pd catalysts, Chary et al. [27] concluded that the presence of surface hydroxyl groups is essential for the metal–support interaction. Furthermore, PdO is believed to be susceptible to having strong interaction with surface acid sites of the support via formation of Pd–O–Zr species [35,36]. It is noteworthy that ZrO<sub>2</sub> possesses both acid and basic sites [25]. Rhodes and Bell [37] further concluded that the presence of crystalline phase in ZrO<sub>2</sub> support resulted in surface anionic defects, which enhanced the acidity of adjacent hydroxyl groups [38]. Characterization results showed that increasing ZrO<sub>2</sub> calcination temperature led to the increase in the contents of both monoclinic and tetragonal phases at the expense of surface hydroxyl group content. As for Pd/ZrO<sub>2</sub>-300, the content of Pd with strong metal–support interaction is relatively lower, reflected by the fact that the intensity of H<sub>2</sub> consumption peak at high reduction temperature is lower as compared to Pd/ZrO<sub>2</sub>-500 and Pd/ZrO<sub>2</sub>-600. This could be attributed to the low content of surface defects due to the amorphous nature of ZrO<sub>2</sub>-300. For Pd/ZrO<sub>2</sub>-600, however, the intensity of H<sub>2</sub> consumption peak at high reduction temperature is higher than Pd/ZrO<sub>2</sub>-300 but lower than Pd/ZrO<sub>2</sub>-500, which is probably ascribed to its lower hydroxyl group content as compared to Pd/ZrO<sub>2</sub>-500 although the content of crystalline phases of ZrO<sub>2</sub>-600 is higher than that of ZrO<sub>2</sub>-500.

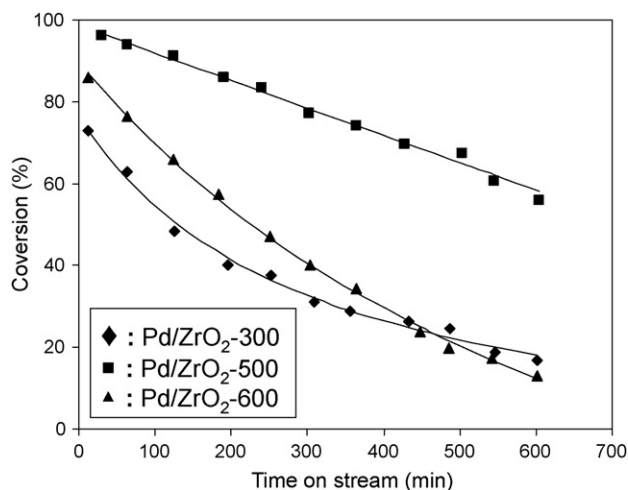


Fig. 5. Catalytic chlorobenzene HDC over Pd/ZrO<sub>2</sub> catalysts. Solid lines represent the fitting curves using Eq. (1).

### 3.2. Catalytic hydrodechlorination of chlorobenzene

For catalytic HDC of chlorobenzene over Pd/ZrO<sub>2</sub> catalysts, benzene was found to be the main product and only a minor amount of cyclohexane was detected in the initial reaction stage. The activity of the supported catalysts for catalytic HDC of chlorobenzene as a function of time on stream is compiled in Fig. 5. The supported catalysts exhibited varied catalytic activities for chlorobenzene HDC. In addition, HDC activities of the catalysts declined with time on stream, indicative of gradual deactivation of the catalysts during HDC process. For catalytic HDC, the behavior of catalyst deactivation could be well described by following equation [39]:

$$\frac{a_t - a_0}{a_{ss} - a_0} = \frac{\Delta t}{\beta + \Delta t} \quad (1)$$

where  $a_t$  is chlorobenzene conversion at time  $t$ ,  $a_0$  is the initial conversion,  $a_{ss}$  is conversion after reaction for 10 h,  $\beta$  is time fitting parameter and  $\Delta t$  is the reaction time, respectively.

The fitting results showed that the initial chlorobenzene conversions were 76.5%, 99.0% and 89.7% respectively for Pd/ZrO<sub>2</sub>-300, Pd/ZrO<sub>2</sub>-500 and Pd/ZrO<sub>2</sub>-600, indicative of a higher catalytic activity of Pd/ZrO<sub>2</sub>-500 as compared to other catalysts. Moreover, the ratios of chlorobenzene conversion at 10 h to the initial conversion were calculated to be 0.24, 0.59 and 0.13 for Pd/ZrO<sub>2</sub>-300, Pd/ZrO<sub>2</sub>-500 and Pd/ZrO<sub>2</sub>-600 respectively, reflecting a deactivation order of Pd/ZrO<sub>2</sub>-500 < Pd/ZrO<sub>2</sub>-300 < Pd/ZrO<sub>2</sub>-600.

For catalytic HDC, the initial activity is related to the properties of surface Pd particles. Jujjuri et al. [40] studied catalytic HDC of chlorobenzene, 1,2-dichlorobenzene and 1,3-dichlorobenzene over Ln-Pd/SiO<sub>2</sub> catalysts and observed a positive correlation between initial HDC activity and the H<sub>2</sub> chemisorption amount of the catalyst. Similarly, Seshu Babu et al. [18] compared Pd/TiO<sub>2</sub> catalysts prepared using different preparation methods and concluded that Pd/TiO<sub>2</sub> catalyst prepared using the deposition-precipitation method had a higher Pd dispersion, concurrently exhibiting a higher activity for catalytic HDC of chlorobenzene. For Pd/ZrO<sub>2</sub>-500, Pd dispersion (34%) is slightly higher than other catalysts, accounting for its higher activity for chlorobenzene HDC. Furthermore, the catalytic activity for chlorobenzene HDC may be also associated with the metal-support interaction. For catalytic HDC of chlorobenzene over Pd/Al<sub>2</sub>O<sub>3</sub>, Seshu Babu et al. [21] concluded that the strong interaction between Pd and Al<sub>2</sub>O<sub>3</sub> resulted in the formation of cationic Pd species, consequently offering higher catalytic

activity than that of surface metallic Pd. As for Pd/ZrO<sub>2</sub> catalysts, a higher content of Pd with strong metal-support interaction was observed in Pd/ZrO<sub>2</sub>-500, which may also contribute to its higher initial activity than other catalysts for catalytic HDC of chlorobenzene.

As shown in Fig. 5, the gradually declined chlorobenzene conversion with time on stream is indicative of the catalyst deactivation during HDC process. In principle, catalyst deactivation generally results from strong HCl adsorption, coke deposition on the Pd surface and Pd particle aggregation during the HDC process. For the supported Pd catalyst prepared using the deposition-precipitation method, Pd particles are believed to be highly stable against aggregation and catalyst deactivation is generally attributed to the detrimental effects resulting from strong HCl adsorption on Pd surface. XPS analysis of the used catalysts revealed that the atomic ratios of chlorine to Zr in Pd/ZrO<sub>2</sub>-300, Pd/ZrO<sub>2</sub>-500 and Pd/ZrO<sub>2</sub>-600 were 0.29, 0.22 and 0.20 respectively, demonstrating the marked chlorine accumulation on catalyst surface. It is noteworthy that the increased Cl/Zr ratio in the used catalyst results from the chlorine accumulation on both ZrO<sub>2</sub> support and Pd surface, which cannot be differentiated using the XPS analysis method. Therefore, the structural information about the chlorine accumulation on Pd surface of the used catalyst is not available. For Pd/ZrO<sub>2</sub> deactivation, however, Gopinath et al. [20] concluded that Pd with strong metal-support interaction was relatively stable against deactivation. This is also supported by XPS analysis of Pd species in used Pd/ZrO<sub>2</sub> catalysts. The contents of Pd<sup>2+</sup> in the used catalysts were found to be 18.0%, 12.5% and 16.0% for Pd/ZrO<sub>2</sub>-300, Pd/ZrO<sub>2</sub>-500 and Pd/ZrO<sub>2</sub>-600 respectively (see Table 2), reflecting the increased Pd<sup>2+</sup> contents in the used catalysts as compared with the fresh catalysts due to the strong binding of chlorine with Pd or the generation of palladium chloride in the catalytic HDC process [41]. Moreover, catalytic HDC led to a more prominent increase of Pd<sup>2+</sup> content in Pd/ZrO<sub>2</sub>-300, suggesting that Pd sites in Pd/ZrO<sub>2</sub>-300 are more susceptible to deactivation during HDC process probably due to its low content of Pd with strong metal-support interaction as compared with Pd/ZrO<sub>2</sub>-500 and Pd/ZrO<sub>2</sub>-600. It should be further pointed out that the ratios of the conversion at 10 h to the initial conversion are 0.13 and 0.24 respectively for Pd/ZrO<sub>2</sub>-600 and Pd/ZrO<sub>2</sub>-300, reflecting the higher catalytic stability of Pd/ZrO<sub>2</sub>-300 although the content of Pd with strong metal-support interaction in Pd/ZrO<sub>2</sub>-300 is lower than that of Pd/ZrO<sub>2</sub>-600. The results also suggest that the stability of Pd/ZrO<sub>2</sub> catalyst for chlorobenzene HDC is not solely dependent on the content of Pd with strong metal-support interaction. Benites and Angel [42] studied the catalytic HDC of chlorobenzene over Pd/SiO<sub>2</sub>, Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub> and attributed the higher catalytic stability of Pd/SiO<sub>2</sub> to the higher capability of SiO<sub>2</sub> to act as chlorine trap, which consequently suppressed the detrimental effect resulting from chlorine adsorption on the Pd surface. Liu et al. [24] studied chlorobenzene HDC over supported Pd catalyst with ammonia-treated carbon nanofiber as the support and concluded that ammonia treatment of carbon nanofiber led to the formation of pyridinic-type basic species on the carbon nanofiber surface, facilitating the transport of resultant HCl from Pd to support surface and eventually inhibiting catalyst deactivation. Similarly, Aramendia et al. [25] compared the catalytic behavior of supported Pd catalysts with different supports, e.g. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>, for chlorobenzene HDC and attributed the high stability of Pd/ZrO<sub>2</sub> to the strong adsorption of chlorine on ZrO<sub>2</sub>, inhibiting the passivation of Pd during reaction. It is noteworthy that for Pd/ZrO<sub>2</sub>-300 the abundant surface hydroxyl groups of ZrO<sub>2</sub> support may act as the adsorption sites to transfer chlorine from the Pd surface, which alleviates the detrimental effects from chlorine adsorption on the Pd surface and eventually leads to a higher catalytic stability of Pd/ZrO<sub>2</sub>-300 than that of Pd/ZrO<sub>2</sub>-600.

#### 4. Conclusions

In this study, Pd/ZrO<sub>2</sub> catalysts with varied support properties were prepared using the deposition–precipitation method and the catalytic HDC of chlorobenzene over the catalysts was investigated. Increasing calcination temperature of ZrO<sub>2</sub> support leads to the decreased content of the surface hydroxyl groups and to the formation of crystalline ZrO<sub>2</sub> consisting of monoclinic and tetragonal phases. For the catalytic HDC of chlorobenzene, a higher initial activity is observed for Pd/ZrO<sub>2</sub>-500 due to its higher Pd dispersion and higher content of Pd species with strong metal–support interaction. In addition, Pd/ZrO<sub>2</sub>-500 exhibits higher stability against catalyst deactivation as compared to other catalysts, attributed to its high content of Pd with strong metal–support interaction. Moreover, the abundant surface hydroxyl groups in ZrO<sub>2</sub> support are beneficial for the alleviation of the deactivation of Pd/ZrO<sub>2</sub>-300 via ZrO<sub>2</sub> acting as the surface chlorine trap.

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