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# **Graphical Abstract**



## Preparation and catalytic property of Pb-Zr mixed oxides for methyl

## phenyl carbonate disproportionation to synthesize diphenyl

## carbonate

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**Abstract:** Pb-Zr mixed oxides with 15.2 wt% PbO loading were prepared by four different preparation processes, and their catalytic performances for the disproportionation of methyl phenyl carbonate (MPC) to synthesize diphenyl carbonate (DPC) were evaluated. Physicochemical characterizations including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence spectroscopy (XRF), BET surface area measurement, H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR), ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) and infrared spectroscopy of pyridine adsorption (Py-IR), as well as catalytic tests of MPC disproportionation reaction showed that catalyst preparation process exerted significant influence on the composition, structural property, catalytic performance of obtained catalysts, and the catalyst prepared by co-precipitation method (PbZr-CP) demonstrated better dispersion of active phase, larger specific surface area and more Lewis acid sites on the surface due to the strong interaction of Pb and Zr, and thus exhibited higher catalytic activity than those prepared by other processes.

**Keywords:** diphenyl carbonate; methyl phenyl carbonate; disproportionaton; Pb-Zr catalyst

## 1. Introduction

Diphenyl carbonate (DPC), an important and eco-friendly chemical intermediate, was mainly used for the phosgene-free preparation of polycarbonates (PC) by a melt polymerization process, and also was often utilized in the synthesis of various organic compounds and polymer materials [1-4]. Nowadays, the transesterification of dimethyl carbonate (DMC) and phenol has attracted a great deal of attention as one of the most promising and suitable approach for DPC commercial production, due to no employment of the hazardous phosgene [5, 6]. Generally, this route has been recognized to be a two-step process. Firstly, methyl phenyl carbonate (MPC) was generated by the transesterification of phenol and DMC (Scheme 1, Eq. (1)). Secondly, DPC was produced by the disproportionation of MPC (Scheme 1, Eq. (2)) or the further transesterification of phenol and MPC (Scheme 1, Eq. (3)), but the equilibrium constants K<sub>2</sub> (0.19, 25 °C) and K<sub>3</sub> (1.2×10<sup>-5</sup>, 25 °C) showed that DPC was mainly generated through MPC disproportionation rather than the further transesterification [7-10]. For the two-step reaction, the first step was the rate-controlling step, owing to  $K_1$  (6.3×10<sup>-5</sup>, 25 °C) much smaller than  $K_2$ , even at elevated temperatures. Therefore, many efforts have especially been made on the first-step transesterification reaction [11-15], while few works have been paid to the second-step disproportionation yet [16-18]. In fact, MPC must undergo the disproportionation, and then can transfer into DPC. Moreover, it was found that the second-step disproportionation reaction could not process thoroughly for the most part, greatly restricting the generation of target product DPC. Thus, the second-step MPC disproportionation reaction was also regarded as the key step to synthesize DPC. To improve the yield of target product DPC, it would be of great significance to further study on the second-step MPC disproportionation.



Scheme 1. Transesterification reaction of DMC and phenol to produce DPC.

As a crucial part of our recent work, the development of attractive catalysts plays a vital role in the catalytic reaction. Previous research showed that the catalysts exhibited good catalytic performance in the first-step transesterification, whereas many of them suffered from low catalytic activities for MPC disproportionation [16, 17]. Hence, development of highly efficient catalysts for MPC disproportionation is quite desirable and useful. Mechanistic studies indicated that this process was Lewis acid catalysis because Brönsted acid often caused MPC decarboxylation into anisole [19, 20], and therefore some homogeneous or heterogeneous catalysts with Lewis acid properties had been preliminarily explored by our group. The results showed that homogeneous catalysts like organo-tin/titanium compounds displayed excellent catalytic performance [1, 21], while they were not easy to recover and recycle, as well as the product separation and/or purification was also very difficult. Subsequently, several heterogeneous catalysts have been developed including metal oxides, MoO<sub>3</sub>/SiO<sub>2</sub> and Pb-Zr mixed oxide catalyst [22-24]. Among them, Pb-Zr catalyst provided high conversion and yield, easy recovery, recyclability and long use lifetimes. However, for mixed metal oxide catalysts, it was well known that the preparation process had significant influences on the structural and textural properties of the catalysts, such as the dispersion of active species, specific surface area and the strength of interaction between active component and support, and these properties concomitantly determined the performance of the catalysts [25-32]. Therefore, as our continuous work for exploiting highly efficient reusable catalyst in practical

application, a systematic study of the influence on the preparation process of Pb-Zr mixed oxide catalyst would be very interesting to understand the relationship between the structure property of the catalyst and its catalytic performance.

Our group was always dedicated to the transesterification of DMC and phenol for the green synthesis of DPC and considering the fact that Pb-Zr mixed oxide appeared to be promising alternative catalyst for MPC disproportionation. The aim of the present work was to investigate the influence of preparation process on the structural properties and catalytic performances of Pb-Zr mixed oxide catalyst in detail, and it was conductive to screen a simple, facile and suitable method. Herein, Pb-Zr mixed oxide was prepared by four different methods and was employed to catalyze MPC disproportionation. Meanwhile, the obtained catalysts were evaluated by powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence spectroscopy (XRF), BET surface area measurement, H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR), ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) and infrared spectroscopy of pyridine adsorption (Py-IR).

## 2. Experimental

#### 2.1. Catalyst preparation

Zirconyl chloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O,  $\geq$ 99%), lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>,  $\geq$ 99%) and ammonia hydroxide (28-30%) were purchased from Sigma-Aldrich Chemical Reagent Company and used without further purification. Deionized water was used during the catalyst synthesis process.

The Pb-Zr mixed oxides were prepared with mechanical milling method, incipient wetness impregnation method, co-precipitation method and precipitation-impregnation method, respectively. The loading amount of PbO (wt%) in the mixed oxide was 15.2%, which was calculated by the stoichiometric molar ratio of Pb to Zr.

#### 2.1.1 Mechanical mill method

Firstly, pure ZrO<sub>2</sub> was prepared by precipitation method. Typically, a required amount of zirconyl chloride octahydrate were dissolved in distilled water and heated

to 90 °C. Thereafter, ammonium hydroxide aqueous was added drop-wise into the solution under magnetic stirring until the pH was controlled at 9-10. The resulting suspensions were aged for 24 h and then filtered, washed with distilled water. Finally, the sample was dried at 110 °C overnight and calcined at 600 °C for 5 h to obtain ZrO<sub>2</sub>. Subsequently, ZrO<sub>2</sub> and lead nitrate were mixed in a certain molar ratio and milled uniformly, and then calcinated at 600 °C for 5 h. The as-prepared catalyst was denoted as PbZr-MM.

#### 2.1.2 Incipient wetness impregnation method

Likewise, pure  $ZrO_2$  was also prepared using the same precipitation process. Thereafter,  $ZrO_2$  was impregnated with appropriate amount aqueous solution of lead nitrate, and then the mixture was kept at ambient temperature for 24 h. Afterwards, the mixture was dried at 110 °C overnight, followed by calcination in air at 600 °C for 5 h. The obtained catalyst was denoted as PbZr-WI.

#### 2.1.3 Co-precipitation method

A desirable amount of lead nitrate and zirconyl chloride octahydrate were added into deionized water, and then the aqueous mixture was heated to 90 °C completely dissolving the solids. Subsequently, an aqueous solution of ammonia was added drop-wise into the above solution until the solution pH was adjusted at 9-10. The resulting solution was aged at 60 °C with rigorous stirring for 24 h. The sediment was vacuum filtered, washed with distilled water until the absence of chlorides, and then dried at 110 °C overnight and calcinated at 600 °C in air for 5 h. The obtained catalyst was named as PbZr-CP.

#### 2.1.4 Precipitation-impregnation method

A certain amount of zirconyl chloride octahydrate was added into deionized water, and then heated to 90 °C to dissolve the solids under rigorous stirring. Afterwards, the aqueous solution of ammonia was added drop-wise into the solution until the pH constant was 9-10. The resulting white slurry was stirred at 60 °C for 24 h. The as-prepared solids were vacuum filtered, washed with distilled water, and then dried at

100 °C overnight to form the precipitate  $Zr(OH)_4$ . Thereafter, the sample was impregnated with appropriate amount aqueous solution of lead nitrate. The mixture was kept at ambient temperature for 24 h, and then dried and calcinated as described in the co-precipitation method. Finally, the obtained catalyst was referred to PbZr-PI.

In addition, pure PbO was also prepared by the similar precipitation process described above for comparison, and the sample would be used as reference when discussing some of the characterization results.

#### 2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were collected on a X'pert PRO MPD diffractometer (Philip) with Cu K $\alpha$  ( $\lambda$ =1.54056 Å) radiation in the 2 theta range from 5 to 90°. The operating voltage and current of X-ray tube were at 40 kV and 45 mA with a scanning rate of 1.2°/min. The crystalline phases were identified by comparison with the reference data from International Center for Diffraction Data (ICDD) files, and the crystallite sizes were calculated by Debye-Scherrer formula.

Temperature-programmed reduction (H<sub>2</sub>-TPR) experiments were conducted by using a chemisorption analyzer (Micro TP-5076, Xianquan Industry and Trade Development Co., Ltd., Tianjin, China). Before the reduction, about 50 mg catalyst was pretreated in N<sub>2</sub> flow (99.999%, 20 mL/min) at 400 °C for 1 h, and then cooled down to the ambient temperature. Thereafter, the baseline was stabilized at 30 °C in the flowing H<sub>2</sub>-N<sub>2</sub> mixture gas (10 vol.% H<sub>2</sub>/N<sub>2</sub>). After that, the reactor was carried out by heating the samples from 50 to 800 °C at a ramp rate of 10 °C/min. The H<sub>2</sub> consumption as a function of the reduction temperature was continuously detected with a thermal conductivity detector (TCD).

The ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) was carried out using the same chemical adsorption instrument (described above). Prior to the analysis, the catalyst (100 mg) was previously treated under flowing N<sub>2</sub> at 400 °C for 1 h and then cooled down to 50 °C, followed by saturating with flowing NH<sub>3</sub> (10

mL/min) for 30 min. The physically adsorbed  $NH_3$  was purged under a  $N_2$  flow for 1 h to remove physically bound ammonia until the TCD baseline was stabilized, and then the desorption experiment of  $NH_3$  was performed from 50 to 800 °C with a heating rate of 10 °C/min. All the profiles were simulated by Gaussian functions, and the quantification of the acid sites was calculated from the area of deconvolution peaks.

X-ray photoelectron spectroscopy (XPS) analyses were detected using a Kratos Model XSAM 800 apparatus with an Al K $\alpha$ =1486.6 eV exciting X-rays source (15 kV, 12 mA). The lines were recorded with a narrow sweep width in the range of 5-7 eV and an energy pass of 50 eV. The sample charge effect was compensated by calibrating the binding energy with adventitious C1s peak at 284.6 eV as internal standard.

The chemical element composition was determined by X-ray fluorescence spectroscopy equipped with Pd anode using an EDX1800B instrument (Jiangsu Skyray Instrument Co., Ltd., China).

Textural properties of the catalysts were evaluated by  $N_2$  adsorption/desorption at -196 °C using automatic JW-BK200C adsorption analyzer (Beijng JWGB Sci. & Tech. Co., Ltd, China). Prior to each measurement the samples were treated under high vacuum at 300 °C for 5 h. The total specific surface area was calculated by multi-point Brunauer-Emmett-Teller (BET) method, and the porous distribution was determined by Barrett-Joyner-Hallenda (BJH) method.

The numbers of Lewis and Brønsted acid sites on the catalysts were quantified by pyridine-adsorbed infrared spectroscopy (Py-IR). Generally, the samples were pressed into disks (30-40 mg, 2 cm<sup>2</sup> disk size). After the sample was pretreated at 200 °C for 2 h under vacuum and then cooled down to room temperature at which pyridine (99.5%) as probe molecule was adsorbed for 1 h. Subsequently, sample was vacuumed for 1 h and flushed with flowing He for 1 h at 50 °C to remove the physic-adsorbed pyridine before the analysis. Finally, Py-IR was tested on Thermo Nicolet 380 to measure the amount of acid sites.

#### 2.3. Catalyst tests

At present, there is no high purity MPC reagent on sale in the market. To our delight, MPC was synthesized and then purified in the laboratory, and its purity was 99.8% determined by high performance liquid chromatography. A detailed process was as follows: firstly, MPC was synthesized facilely by a reversible reaction of DMC and DPC, due to low equilibrium constant  $K_2$  (0.19, 25 °C) of MPC disproportionation. Subsequently, the separation and purity of MPC was conducted by reduced pressure distillation and rectification respectively, and then was identified by GC-MS, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectral techniques. Finally, the purity of MPC was analyzed quantitatively by high performance liquid chromatography.

The MPC disproportionation was carried out in a glass reactor. In a typical run, 150 mmol MPC and an appropriate amount of catalyst were added into a 100 mL three necked round bottom flask fitted with a fractionation column connected to a liquid dividing head under nitrogen atmosphere. The reaction mixture was gradually heated to desired temperature with a constant stirring rate in an oil bath and subsequently was kept at the desired temperature. During the reaction procedure, DMC distillate was slowly distilled out and collected continuously by the liquid dividing head attached to a receiver flask to break the equilibrium limit to promote the reaction towards the desired product formation of DPC.

After the reaction, the reactor was cooled to room temperature. All the reaction products were detected by GC-MS instrument with a HP-5 capillary chromatography packed column (30 m  $\times$  0.25 mm  $\times$  0.25 um) on a HP-6890/5973 system. The products were quantitatively analyzed with a gas chromatograph (Agilent Technologies 7820A) equipped with a flame ionization detector (FID) and a DB-35 capillary chromatography packed column (30 m  $\times$  0.32 mm  $\times$  0.25 µm).

## 3. Results and discussion

#### 3.1 Catalyst characterization

#### 3.1.1 XRD analysis

The composition of Pb-Zr mixed oxides prepared by different processes is determined by powder XRD, and the XRD patterns are shown in Fig. 1. As shown in Fig. 1,  $ZrO_2$  mainly existed the monoclinic crystalline phases (2 $\theta$ =24.8, 28.2, 31.5, 34.1 and 50.4°, JCPDS No. 37-1484), and only the few tetragonal crystalline phases appeared (20=30.2, 35.1, 50.2 and 60.2°, JCPDS No. 27-997) [33, 34]. The introduction of Pb by different preparation processes resulted in the great change of ZrO<sub>2</sub> crystalline structure. PbZr-MM and PbZr-WI mostly displayed the existence of monoclinic ZrO<sub>2</sub> crystalline phases, and there were also a few PbO crystalline phase appearances at ca. 31.9, 35.6, 45.7, 48.6, 54.7 and 59.9° [35, 36], probably related to the accumulation of partial PbO on the surface. However, for PbZr-CP and PbZr-PI samples, there was mostly the existence of tetragonal ZrO<sub>2</sub> crystalline phases, and no diffraction peak assigned to PbO crystalline phase was observed, which indicated that PbO was highly dispersed or amorphous type. The XRD results suggested that the dispersions of PbO in PbZr-CP and PbZr-PI were relatively higher than those in PbZr-MM and PbZr-WI. Besides, the average crystallite sizes of the samples were calculated by Scherrer equation, which were about 38, 45, 65 and 68 nm for PbZr-CP, PbZr-PI, PbZr-WI and PbZr-MM based on their maximum intensity diffraction peaks, respectively.



Fig. 1. XRD patterns of Pb-Zr catalysts prepared by different processes.

#### 3.1.2 H<sub>2</sub>-TPR analysis

The H<sub>2</sub>-TPR profiles of all the catalysts are shown in Fig. 2. As shown in Fig. 2, PbO showed a remarkable hydrogen reduction peak at 588 °C, which was attributed to the reduction of PbO species, and the reduction peak over ZrO<sub>2</sub> was very weak in the range of 450-600 °C and could hardly be observed. Compared with PbO, the reduction peaks of Pb-Zr catalysts were significantly shifted to lower temperatures, which indicated that there was strong or weak interaction of PbO with support [37, 38], but these peak shifts were clearly different. For PbZr-MM and PbZr-WI samples, PbZr-MM with a broad peak range exhibited two reduction peaks at around 375 and 425 °C, and a similar behavior was observed for PbZr-WI, which exhibited also two reduction peaks at around 355 and 382 °C in a broad peak range. The former shoulder peak was assigned to the reduction of highly dispersed lead species, and the latter reduction peak was presumably due to the reduction of bulk lead oxide. Such low reduction temperature range usually corresponded to a low dispersed metallic phase with a large crystallite size and low interaction with the support. However, for PbZr-CP and PbZr-PI samples, there was only a corresponding reduction peak appearance at 372 and 394 °C respectively, related to the reduction of highly dispersed lead species strongly interacting with the support, this was in accordance with the XRD results, whereas the comparison of reduction temperature implied that the interaction strength in PbZr-CP was greater than that in PbZr-PI. Thus, according to the reduction nature of PbO species, PbZr-PI exhibited the lowest reduction temperature and therefore possessed the strongest interaction between Pb and Zr, and the interaction strength among them was in the following order of PbZr-CP > PbZr-PI > PbZr-WI > PbZr-MM.



Fig. 2. H<sub>2</sub>-TPR profiles of all the catalysts.

#### 3.1.3 XPS analysis

XPS analysis was also performed, in order to elucidate the surface nature and composition of various elements over the catalyst surface. The XPS spectra of Zr  $3d_{5/2}$ , Pb  $4f_{7/2}$  and O 1s of the catalysts are shown in Fig. 3. The binding energy (BE) of Zr  $3d_{5/2}$  in ZrO<sub>2</sub> was 179 eV. As shown in Fig. 3(A), the BE of Zr  $3d_{5/2}$  increased, but the peak position shifts were different and PbZr-CP exhibited the biggest shift, and the order was PbZr-CP > PbZr-PI > PbZr-WI = PbZr-MM. The BE of Pb  $4f_{7/2}$  in PbO was 137 eV. As shown in Fig. 3(B), the BE of Pb  $4f_{7/2}$  also increased, and the variation trend was basically in accordance with that of Zr 3d<sub>5/2</sub>. The BEs of O 1s in ZrO<sub>2</sub> and PbO are 530.2 eV and 531.3 eV. As shown in Fig. 3(C), for a clear observation, O 1s band was resolved by two Gaussian component peaks, which were assigned to the surface absorbed oxygen (531.0–532.1 eV) and lattice oxygen (529.2–530.3 eV) [39], respectively. The BE for lattice oxygen at around 529.8 eV was shifted to lower value and PbZr-CP gave the largest shift, and the shift order was inconsistent with those of Zr 3d<sub>5/2</sub> and Pb 4f<sub>7/2</sub>. A shift towards lower BE in XPS was usually associated with an increased electron density or reduction to a lower oxidation state [40]. Thus, the above result indicated the flow of electron density from Zr and Pb to O by forming the Pb-O-Zr linkages due to higher electronegativity of O than those of Zr and Pb,

resulting in a rich electron state of O and a deficient electron state of Zr and Pb. However, these changes of BEs were remarkably different over the catalysts, suggesting that the interaction intensity between Zr and Pb through the Pb–O–Zr bonds was also different. Among them, PbZr-CP provided the maximum changes for the BEs of Zr  $3d_{5/2}$ , Pb  $4f_{7/2}$  and O 1s, illustrating the strongest interaction between Pb and Zr. Combined with the analysis of XRD and H<sub>2</sub>-TPR, it could be inferred that the strong interaction between Pb and Zr species was in favor of inhibiting the crystallization of PbO phase and promoting the dispersion of PbO, thus it was beneficial to improving the activity of the catalyst.



Fig. 3. Binding energies of Zr  $3d_{5/2}$  (A), Pb  $4f_{7/2}$  (B) and O 1s (C) of all the catalysts.

#### 3.1.4 BET analysis

The  $N_2$  adsorption-desorption isotherms and their corresponding pore size distribution of all the catalysts are shown in Fig. 4. Fig. 4(A) showed that all the catalytic samples presented typical IV isotherms with noticeable hysteresis loops at higher relative pressure, suggesting that mesoporous frameworks were formed for

them. Fig. 4(B) showed that the pore size distribution of pure  $ZrO_2$  mainly concentrated at 8.0 nm, and the pore sizes of PbZr-MM and PbZr-WI were similar to that of ZrO<sub>2</sub> support, retaining the average mesoporous size of the support, due to the weak interaction between PbO and ZrO<sub>2</sub> as described above. Evidently, for PbZr-CP and PbZr-PI, the strong interaction between Pb and Zr resulted in the appearance of new channels, and shifted the pores into the small distribution, exhibiting the narrow and smaller pore diameter ranges. Table 1 summarized the textural properties of all the samples. PbZr-CP displayed the largest BET specific surface area of  $62 \text{ m}^2 \cdot \text{g}^{-1}$  and pore volume of 0.110  $\text{cm}^3 \cdot \text{g}^{-1}$ , which was beneficial to the exposure of more active sites, resulting in improvement of the catalytic ability, and their surface areas were in the following sequence: PbZr-CP > PbZr-PI > PbZr-WI > PbZr-MM. Moreover, the surface composition of all the catalysts was determined by XRF technique, and the results were listed in Table 1. As shown in Table 1, the molar ratios of surface Pb to Zr over PbZr-CP and PbZr-PI were close to the bulk value estimated by theoretical calculation. Nevertheless, the molar ratios of surface Pb to Zr over PbZr-MM and PbZr-WI were far higher than the bulk value, suggesting the accumulation of PbO on the surface. The results further suggested that the dispersions of PbO over PbZr-CP and PbZr-WI were much better, and the crystalline PbO over PbZr-PI and PbZr-MM might be aggregated due to the low surface area, thus leading to poor dispersion. It was in accordance with the results of XRD measurement shown above, since high surface area was beneficial for the dispersion of PbO.



Fig. 4. N<sub>2</sub> adsorption-desorption isotherms (A) and pore diameter distributions (B) of all the

#### catalysts.

Catalyst	BET surface	Pore volume	Mean pore	Dh /7.ª	Pb/Zr <sup>b</sup>
	area $(m^2 \cdot g^{-1})$	$(\mathrm{cm}^3 \cdot \mathrm{g}^{-1})$	diameter (nm)	P0/Zľ	
PbZr-CP	62	0.110	5.0	0.099	0.111
PbZr-PI	58	0.067	3.8	0.099	0.115
PbZr-WI	35	0.088	8.3	0.099	0.122
PbZr-MM	28	0.083	7.9	0.099	0.131
ZrO <sub>2</sub>	53	0.123	8.0	-	_

Table 1 The textural properties of all the catalysts.

<sup>a</sup> Pb/Zr estimated by theoretical calculation.

<sup>b</sup> Pb/Zr determined by XRF.

#### 3.1.5 NH<sub>3</sub>-TPD and Py-IR analysis

The acid property of all the catalysts is carried out by NH<sub>3</sub>-TPD technique, and the amount of desorbed NH<sub>3</sub> which is reflected by the peak area, is proportional to the amounts of acidic sites. Fig. 5 showed the NH<sub>3</sub>-TPD profiles of all the catalysts. As shown in Fig. 5, all the profiles contained two NH<sub>3</sub> desorption peaks that the peak around 160 °C was assigned to weakly adsorbed NH<sub>3</sub>, and the peak above 400 °C was regarded as NH<sub>3</sub> coordinated to strong acid sites. Meanwhile, the acidity of all samples was summarized in Table 2. It could be seen that this preparation process apparently affected the acidic properties, and the adsorption amount of NH<sub>3</sub> was the most for PbZr-CP and the total number of acidic sites from large to small was as follows: PbZr-CP > PbZr-PI > PbZr-WI > PbZr-MM, indicating that PbZr-CP owned more acidic sites formed on the surface. Furthermore, above-mentioned discussion acknowledged that PbZr-CP had the highest specific surface area, and this was also beneficial for exposing more acidic sites, which would promote the adsorption and activation of MPC reactant molecules and enhance the catalytic performance.



Fig. 5. NH<sub>3</sub>-TPD profiles of all the catalysts.

Catalyst	Acid strength (°C)		Acid amount (mmol $\cdot$ g <sup>-1</sup> )		Total acid	I/D motio	
	Weak	Strong	Weak	Strong	$(\text{mmol} \cdot \text{g}^{-1})$	L/D Taulo	
PbZr- CP	290	702	0.094	0.018	0.112	0.466	
PbZr- PI	268	685	0.058	0.029	0.087	0.453	
PbZr-WI	303	703	0.055	0.015	0.070	0.286	
PbZr-MM	322	652	0.044	0.013	0.057	0.227	

Table 2 The surface acid properties of all the catalysts.

The amount of Lewis and Brønsted acid sites on the catalysts is quantified by FT-IR spectroscopy using pyridine as probe molecule. Fig. 5 showed FT-IR spectra of pyridine adsorbed on all the catalysts and the corresponding ratios of Lewis to Brønsted acid were presented in Table 2. All the samples displayed remarkable absorption peaks at 1436 and 1580 cm<sup>-1</sup>, which were assigned to Lewis acidity and Brønsted acidity, respectively [29, 33, 41]. Furthermore, PbZr-CP and PbZr-PI also exhibited weak absorption peak at 1480 cm<sup>-1</sup> and it was attributed to combination of both Brønsted (B) and Lewis (L) acid sites. As could be seen from the results in Table 2, the L/B ratio for PbZr-CP was obviously higher than others, and the sequence from high to low was as follows: PbZr-CP > PbZr-PI > PbZr-WI > PbZr-MM. Combined

with the results of NH<sub>3</sub>-TPD, it is obvious that PbZr-CP had more Lewis acidic sites, which was advantageous to catalyze MPC disproportionation.



Fig. 6. FT-IR spectra of pyridine adsorbed on all the catalysts.

## 3.2 Catalytic performance of all the catalysts for MPC disproportionation

The catalytic performances of all the catalysts for disproportionation of MPC to DPC were given in Fig. 7. The slight byproduct was mainly anisole. Noticeably, Pb-Zr mixed oxides prepared with different processes had remarkable catalytic activities, and the selectivities of DPC were more than 98.0%. Nevertheless, the catalytic activities were also evidently influenced by different preparation processes. It was clear that the best catalytic activity with MPC conversion of 74.7% and DPC selectivity of 99.3% was obtained over PbZr-CP, and the order of the activities was as follows: PbZr-CP > PbZr-PI > PbZr-WI > PbZr-MM. This trend was in agreement with the orders of the dispersion of PbO, specific surface area and Lewis acid sites. Based on the results of XRD, BET, NH<sub>3</sub>-TPD and Py-IR analysis, PbZr-CP exhibited better dispersion of PbO and a higher specific surface. Consequently, the superior catalytic activity of PbZr-CP should be ascribed to the presence of the higher specific surface area and the higher dispersion of PbO, which was as a result of the stronger interaction between Pb and Zr. PbZr-CP presented the strongest interaction between

Pb and Zr, resulting in the noticeable changes of  $ZrO_2$  pore structure, which was advantageous to highly disperse PbO and expose more active sites. Therefore, the strong interaction between Pb and Zr over PbZr-CP not only led to large surface area but also high dispersion of PbO, both of which accounted for the high catalytic activity in this system. The result suggested that Pb-Zr mixed oxide prepared by co-precipitation method was better than others, thus exhibiting higher catalytic activity.



Fig. 7. Catalytic performance of all the catalysts for MPC disproportionation. Reaction conditions: temperature 200 °C, reaction time 2.5 h, catalyst 1.2 g, MPC 150 mmol.

## 4. Conclusions

Pb-Zr mixed oxides prepared by different processes have been evaluated for MPC disproportionation. The synthesis process significantly affected the catalytic performance, and PbZr-CP catalyst prepared via co-precipitation method was more active than others, and the order of the conversion of MPC was PbZr-CP > PbZr-PI > PbZr-WI > PbZr-MM. XRD, XPS, H<sub>2</sub>-TPR, BET, NH<sub>3</sub>-TPD and Py-IR were employed to characterize the catalysts, and the results revealed that well-dispersed PbO, high specific surface area and more Lewis acid sites were responsible for the excellent catalytic performance of PbZr-CP, owing to the existence of strong interaction between Pb and Zr. In summary, this work provided a promising

technology for Pb-Zr catalyst preparation towards economic and efficient process to transform MPC disproportionation into DPC.

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## Highlights

► Preparation process exerts significant influence on structural property and catalytic performance of Pb-Zr mixed oxide.

▶ Pb-Zr mixed oxide prepared by co-precipitation is more active.

► Well-dispersed PbO and large specific surface area are formed on Pb-Zr catalyst prepared by co-precipitation.

► This work provides an effective technology for Pb-Zr catalyst preparation to transform MPC into DPC.