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RESEARCH ARTICLE

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# Ce cooperated layered double oxide with enhanced base sites activity for the synthesis of polycarbonate diols

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**Abstract**

The development of highly efficient alkaline catalysts with abundant base sites is of paramount importance for the synthesis of polycarbonate diols (PCDLs). And the application of heterogeneous catalysts is an effective strategy to address the effect of residual catalysts on the quality of PCDLs. Here, Ce cooperated layered double oxide (LDO-Ce) was used as a catalyst for the preparation of PCDLs via transesterification between dimethyl carbonate (DMC) and 1,4-butanediol (BDO). $CO_2$ temperature-programmed desorption ($CO_2$-TPD) profiles demonstrated that the introduction of Ce led to an increase in strong base sites of LDO-Ce, thus endowing LDO-Ce with excellent catalytic performance. Besides, LDO-Ce possessed satisfactory specific surface area and pore size. A possible catalytic mechanism was proposed to illustrate the transesterification process. The effects of the reaction conditions on the hydroxyl value, yield, and BDO conversion were further investigated in detail. The yield of PCDLs with a hydroxyl value of 112.2 mg KOH/g (corresponding to a number average molecular weight [$M_n$] of 1000 g/mol) was 92.44% under its optimum reaction conditions (w (catalyst) = 0.5%, $n(\text{DMC})/n(\text{BDO}) = 1.25$, $T\text{-}_{\text{transesterification}} = 130°\text{C}$, $t\text{-}_{\text{transesterification}} = 5$ h, $T\text{-}_{\text{polycondensation}} = 170°\text{C}$, $t\text{-}_{\text{polycondensation}} = 4$ h, $P\text{-}_{\text{polycondensation}} = 10$ kPa). Moreover, LDO-Ce was easily removed after the transesterification process (Step 1), ensuring the quality of PCDLs, and it was recycled three times without significant loss of catalytic activity.

KEYWORDS
basic sites, Ce cooperated, layered double oxide, polycarbonate diols

## 1 | INTRODUCTION

Polyurethane (PU), a kind of versatile polymer material, has been widely used in medical science, automobiles, textile, and construction fields.[1] The main chain of PU consists of soft segments (composed of polyols) and rigid segments (composed of isocyanate). The properties of PU are closely related to the composition of raw materials. Compared with traditional PU produced from polyether diols or polyester diols, the PU generated by polycarbonate diols (PCDLs) shows better mechanical performance, hydrolysis resistance, heat resistance, etc.[2] Therefore, PCDLs are the important intermediates to synthesize PU elastomers with high performance.

PCDLs can be synthesized via various methods, for instance, the conventional phosgene route,[3] copolymerizations

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Kaiyan Zhao and Xiaowei Tantai contributed equally to this work.

of $CO_2$ with oxiranes,[4] regulated polymerizations of cyclic carbonates,[5] and transesterification.[6] The phosgene route has been considered behind the times because of the generation of hydrogen chloride phosgene, which is harmful to the environment and human health,[7] and the polymerization is also eliminated due to the usage of phosgene. Although $CO_2$ is easy to produce or separate from the air, only PCDLs with finite chemical structures can be obtained.[8] Transesterification between dimethyl (diethyl) carbonate and diols for the synthesis of PCDLs with multiple structures has the advantages of environmental friendliness and mild reaction conditions.[9] Furthermore, the maturity of dimethyl carbonate (DMC) industrial production technology renders this route better prospect.[10]

The application of Lewis or Brønsted base catalysts in the transesterification process has been studied for decades. Researchers have verified that the activity of alkaline catalysts is positively correlated with their basic sites,[11,12] that is to say, the more strong the basic sites, the higher the reaction activity. Generally, these catalysts can be divided into two categories: homogeneous catalysts and heterogeneous catalysts. Homogeneous catalysts possess high catalytic activity, but they are difficult to remove from the products, which not only affects the quality of products but also causes a potential hazard to the environment because of the as-produced wastewater. Heterogeneous catalysts have enjoyed growing attention due to the reusable nature and easy separation from the reaction mixtures. For instance, Feng et al.[13] employed alumina-supported potassium fluoride as the solid base catalyst for the synthesis of PCDLs, which demonstrated that its active basic sites depended on the interaction between KF and $Al_2O_3$. Song et al.[11] reported a solid base catalyst via loading $KNO_3$ on the alumina for the preparation of PCDLs, revealing that the performance of $KNO_3/\gamma Al_2O_3$ catalyst was highly influenced by the amount and strength of basic sites.

Layered double hydroxides (LDHs) have been widely used as heterogeneous solid base catalysts due to the tunable structure, favourable thermal stability, high specific surface area (SSA), and abundant base sites. However, the catalytic activity of traditional binary LDHs was lower than alkali metals in the transesterification process,[14] which inspired the development of ternary LDHs. Wang et al.[15] utilized Mg-Fe/Ti LDHs as an acid–base bifunctional catalyst for the transesterification between dimethyl carbonate and aliphatic diols, and the strength matching of the acidic and basic active sites was regulated by the introduction of $Ti^{4+}$. Noticeably, after being calcined at 450–600°C, LDHs can be converted into highly dispersed mixed metal oxides (LDO) with a higher SSA and multiple Lewis basic sites.[16] Zhu et al.[12] considered the calcined Mg-Al hydrotalcite doped with $Ni^{2+}$ (HTC-Ni-T) as the catalyst in the synthesis of PCDLs, which indicated that the Mg-O and Ni-O pairs contributed the most to the increase in the base strength, thus endowing HTC-Ni-T with excellent catalytic performance. Apparently, the introduction of a third metal into the LDHs or LDO can significantly improve the basicity of catalysts and further enhance the catalytic activity in the preparation of PCDLs.

In this paper, the third metal cooperated LDHs (LDH-M, M = Ce, Ni, Zn, Fe, Co, and Cu) were prepared with the method of double-drop co-precipitation, and the LDH-M was calcined at 500°C to obtain metal oxide LDO-M. LDO-M was used as the catalyst for the synthesis of PCDLs via transesterification between 1,4-butanediol (BDO) and DMC. The studied catalysts were characterized by X-ray diffraction (XRD), Brunauer, Emmett, and Teller (BET), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and $CO_2$-TPD to explore the relationship between the properties of catalysts (structure properties and basicity) and the catalytic performance in the synthesis of PCDLs. Furthermore, the effects of the reaction conditions on the synthesis of PCDLs were systematically investigated.

## 2 | EXPERIMENTAL

### 2.1 | Materials

Gamma-aluminium oxide ($\gamma$-$Al_2O_3$) (size distribution of 20~40 nm, 99%), dimethyl carbonate (DMC, 99%), 1,4-butanediol (BDO), $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and ethanol (99.5%) were purchased from Tianjin Yuanli Chemical Co., Ltd. (China). Sodium hydroxide (98.0%), anhydrous $Na_2CO_3$, $Ce(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 9H_2O$, and *N,N*-dimethylformamide (DMF) were obtained from Tianjin Kermel Co., Ltd. (China). And, 1-methylimidazole was provided by Tianjin Heowns Biochemical Technology Co., Ltd. (China). Acetic anhydride was bought from Tianjin Jiangtian Chemical Co., Ltd. (China). Deionized water was used in all experiments. All chemicals were used as received, without further purification.

### 2.2 | Catalyst preparation

Tri-metal hydrotalcite LDH-M (M = Ce, Ni, Zn, Fe, Co, and Cu) catalysts were prepared based on the double-drop coprecipitation method.[17] In a typical process, a certain amount of metallic nitrates ([Mg + M]/Al molar ratio of 4; Mg/M molar ratio of 5) were dissolved in 50 ml deionized water to obtain solution A. The compositions of solution B were $\gamma$-$Al_2O_3$ and anhydrous $Na_2CO_3$.

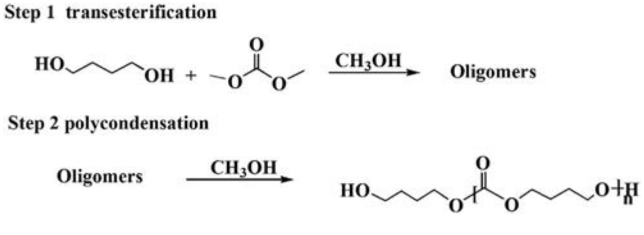
Briefly, 0.1 g γ-$Al_2O_3$ was uniformly dispersed in 50 ml deionized water by ultrasound for 30 min, and 0.636 g anhydrous $Na_2CO_3$ was added as precipitating agent. Then solution B was transferred into a three-necked flask, and solution A was added dropwise into the flask at room temperature with vigorous stirring for 1 h. Meanwhile, the pH was controlled at 9.2 ± 0.2 by adding 1 M NaOH solution. After that, the slurry was aged overnight at 65°C. Then, the sample was filtered and washed with deionized water, Finally, the solid product was dried at 80°C for 6 h. LDO-M samples were obtained by calcination of LDH-M at 500°C for 4 h. The preparation route of Mg/Al hydrotalcite (LDH) and corresponding metal oxide LDO was completely consistent with the above process.

## 2.3 | Catalyst characterization

The X-ray diffraction (XRD) measurements were conducted on a D8-Focus powder diffractometer (AXS, Germany) with Cu Kα ($\lambda = 1.54$ Å) radiation in a $2\theta$ range of 10–80° at a speed of 8°/min. The SSA of the samples was measured on a Micromeritics ASAP 2020 Sorptometer apparatus by $N_2$ adsorption–desorption. The morphologies of the samples were observed by field-emission scanning electron microscopy (SEM, Hitachi S-4800, Japan). X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi, USA) was used to investigate the composition of the elements. $CO_2$ temperature-programmed desorption ($CO_2$-TPD, AutoChem II 2920, USA) experiments were carried out for the measurement of the basicity of the catalysts. Fourier-transform infrared spectroscopy (FTIR, Bruker TENSOR 27, Germany) spectra were recorded in the range of 4000–500 $cm^{-1}$ using the KBr pellet technique.

## 2.4 | Synthesis of PCDLs

The synthesis of PCDLs from DMC and BDO was briefly divided into two steps: transesterification and polycondensation (Scheme 1).



SCHEME 1 The synthesis process of polycarbonate diols (PCDLs)

The typical procedure is explained as follows.

In the first step: the transesterification process was proceeded first by adding the appropriate amount of BDO, DMC, and the obtained catalyst into a four-necked flask (250 ml), equipped with a magneton stirrer, a thermometer, a Vigreux column, and a nitrogen inlet, which avoided the dropwise addition of DMC. Initially, the mixture was heated to 100°C and kept for 1 h, which prevented the excess loss of DMC (b.p. = 90°C) caused by high temperature. Then the temperature was gradually raised to 130°C and stirred continually for 4 h under a nitrogen atmosphere. The distillate was collected with the temperature of the distillation head lower than 65°C. According to the reversibility of the transesterification process, the by-product methanol must be removed in time to promote the formation of oligomers. However, part of the methanol might be encased in the oligomers, making it hard to be completely removed from the system. As a result, the polycondensation could not be accomplished under atmospheric pressure, and only oligomers could be obtained in Step 1. In the second step: the catalyst was removed through centrifugation at 8000 rpm for 10 min at room temperature, and the supernatant was transferred into the flask. The temperature and pressure of the reaction were changed from 130 to 170°C and 70 to 10 kPa, respectively. Finally, the white, waxy, solid PCDLs were obtained when the temperature cooled down to 25°C. In conclusion, the transesterification process (Step 1) can ensure the formation of sufficient oligomers, which are crucial to the production of PCDLs, and the yield and a hydroxyl value of the PCDLs are mainly determined by the polycondensation step.

The analysis of distillate was performed by a gas chromatograph (GC, 7820, HP-5, China) equipped with an FID detector. The BDO conversion and the yield of PCDLs were calculated based on the following equations:

$$\text{BDOconversion}\,(\%) = \frac{n(\text{methanol distilled in the first step})}{2n(\text{Diols})} \times 100\% \tag{1}$$

$$\text{Yield}\,(\%) = \frac{\dfrac{m(\text{PCDLs})}{\text{molecular weight of repeating units}}}{n(\text{Diols})} \times 100\% \tag{2}$$

The hydroxyl value ($V_{OH}$) of PCDLs was measured with an acid-imidazole method, and the number average

TABLE 1 Comparative relationship between $V_{OH}$ and $M_n$

| $V_{OH}$ (mg KOH/g) | $M_n$ (g/mol) |
|---|---|
| 112.2 | 1000 |
| 56.1 | 2000 |
| 37.4 | 3000 |

molecular weight ($M_n$) of the PCDLs was calculated using Equation (3). Additionally, the comparative relationship between $V_{OH}$ and $M_n$ was listed in Table 1. In industry, PCDLs with $M_n$ between 500 g/mol and 3000 g/mol are widely used. Hence, the synthesis of PCDLs with $M_n$ of 1000 g/mol, corresponding to $V_{OH}$ of 110 ± 10 mg KOH/g was explored in detail.

$$M_n = (1000 \times 2 \times 56.1)/V_{OH} \tag{3}$$

# 3 | RESULTS AND DISCUSSION

## 3.1 | Screening of the catalysts

The catalyst evaluation of LDO-M based on different nitrates for the transesterification between BDO and DMC was performed. As shown in Figure 1, all the samples exhibited catalytic activity in the transesterification reaction, and the LDO-Ce achieved the highest BDO conversion. Besides, the yield calculated by Equation (2) using different catalysts featured the same trend with BDO conversion. Importantly, the target PCDLs with a $V_{OH}$ of 112.2 (mg KOH/g) could only be obtained by using LDO-Ce as a catalyst, which turned into the white waxy solid at room temperature (Figure 1C). Among the catalysts examined, the $V_{OH}$ followed the order of LDO-Ce < LDO-Ni < LDO-Zn ≈ LDO-Fe ≈ LDO-Co ≈ LDO-Cu, which was contrary to the viscosity variation of the resultant products. Based on the above discussion, LDO-Ce can be listed as a candidate catalyst for transesterification process between BDO and DMC.

## 3.2 | Catalyst characterization

The XRD patterns of the LDO and LDO-Ce samples were presented in Figure 2. Both of the LDO and LDO-Ce showed characteristic peaks at $2\theta = 29.32°$, $42.91°$, and $62.30°$, corresponding to the reflections from the ($\bar{3}$02), (123) and (404) crystal faces, respectively, which were well consistent with the poorly crystallized layered hydrotalcite-type phase (JCPDS:10-0238). Moreover, the characteristic peaks at 42.91° and 62.30° highly correlated with the structure of MgO (periclase), revealing the formation of mixed oxides.[12] Compared with LDO, the

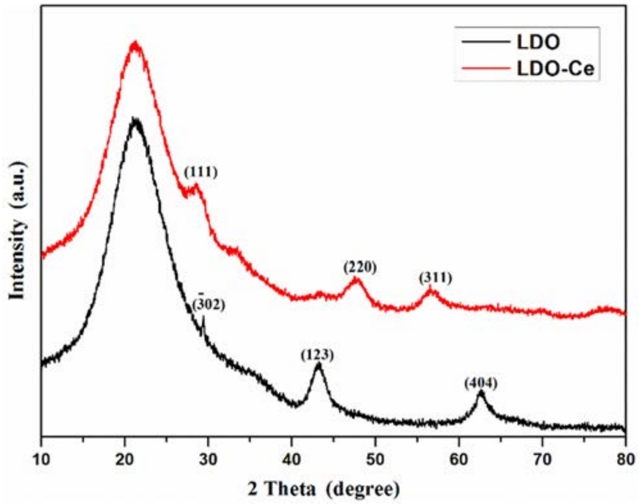


FIGURE 2 X-ray diffraction (XRD) patterns for the layered double oxide (LDO) and Ce cooperated layered double oxide (LDO-Ce)

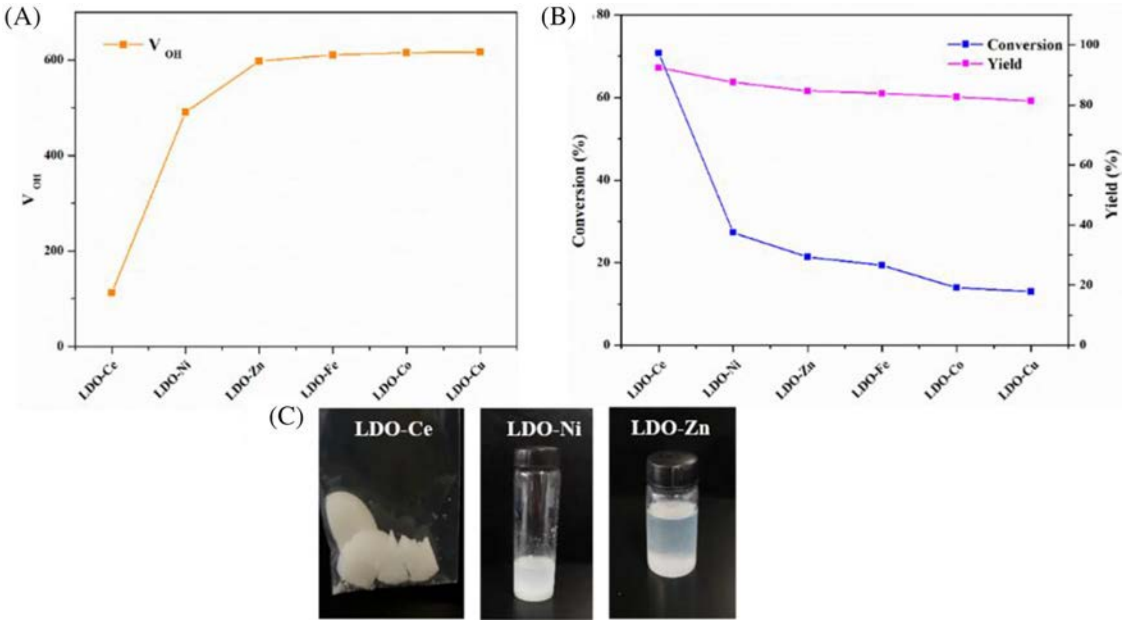


FIGURE 1 Catalytic activities of different catalysts (A) hydroxyl value of PCDLs, (B) yield and BDO conversion, and (C) product appearance

characteristic peak intensity of LDO-Ce at the same location significantly diminished, which probably was attributed to the introduction of Ce (1.02 Å) with larger ionic radius and the highly dispersed amorphous of Al and Mg in oxidic form.[18,19] For LDO-Ce, the characteristic peaks related to the $CeO_2$ phase appeared at $2\theta = 28.55°$, 47.47°, and 56.33°, corresponding to the reflections from the (111), (220), and (311) crystal faces, respectively, which were consistent with previous studies.[20,21]

The morphology of LDO and LDO-Ce was observed by SEM analysis (Figure 3). Compared with the flower-like structure of LDO, the hierarchical structure of LDO-Ce exhibited slight collapse but still possessed nanosheet morphology. This phenomenon was probably due to the larger cationic size of $Ce^{4+}$ compared with the LDO brucite layers,[18] affecting the growth process of hydrotalcite lamella.

The composition of LDO and LDO-Ce was studied by XPS. Figure 4B depicts the full XPS spectrum of LDO-Ce, which revealed the presence of Mg 1s, Al 2p, and Ce 3d signals. The oxidation states of Ce and O elements in the catalyst samples were also investigated. Figure 4C presents the O 1s XPS spectra of LDO and LDO-Ce samples. The peaks at 529.7–531.3 and 531.3–532.8 eV were corresponding to the lattice oxygen ($O_\alpha$) and the surface adsorbed oxygen ($O_\beta$), respectively.[22] The results implied that with the introduction of Ce, the intensity of $O_\beta$ increased, which might be conducive to improving the catalytic activity of LDO-Ce.

The XPS spectra of Ce $3d_{3/2}$ and Ce $3d_{5/2}$ core levels of the LDO-Ce catalyst were presented in Figure 4D. The XPS spectrum of pure Ce(IV) oxide presented six peaks (three pairs of spin-orbit doublets), named in order of decreasing energy as U‴, U″, U (related to the Ce $3d_{3/2}$ level) and V‴, V″, V (related to the Ce $3d_{5/2}$ level). The remaining four peaks, named as U′, $U^0$, and V′, $V^0$, were related to the $3d_{3/2}$ and $3d_{5/2}$ levels of Ce(III), which were consistent with the previous research.[23]

The results of $N_2$ adsorption–desorption isotherms of LDO and LDO-M are shown in Table 2. The SSA, pore volume ($V_t$), and average pore size of LDO were $260.21\ m^2 \cdot g^{-1}$, $0.93\ cm^3 \cdot g^{-1}$, and 9.70 nm, respectively. Compared with those of LDO, the SSA and $V_t$ of LDO-Ce decreased, but the average pore size increased, implying the the presence of Ce possibly destroyed pore structure and enlarged the pores of LDO.[24] Meanwhile, the introduction of Ce oxide-side phase with high crystallinity also resulted in a reduction to the SSA of catalyst.[20] Furthermore, the SSA of LDO-M was in the order of LDO-Ni > LDO-Fe > LDO-Ce > LDO-Zn > LDO-Co > LDO-Cu, which was not consistent with their catalytic activities, indicating that the activity of LDO-M was not completely related to SSA.

As shown in Figure 5, the desorption peaks with maxima at about 120, 370, and 500°C indicated the presence of three types of basic centres. The peak at 120°C related with the weak basic strength was mainly due to the adsorption at the $OH^-$ groups.[16] The peak at 370°C was corresponding with the Mg—O of LDO and LDO-M,[25] and M—O of LDO-M (M = Ce, Ni, Zn, Fe, Co, and Cu),[26] indicating the medium base strength. The peak at 500°C could be ascribed to the adsorption of the $O^{2-}$ sites, which implied the strong base strength.[27] Among the LDO-M, the strong base sites only appeared when the LDO was cooperated with Ce, which demonstrated that the introduction of low electronegativity of the Ce induced a general enhancement of the negative charge of oxygen ions,[28] resulting in the increase of strong base sites.

## 3.3 | Reaction mechanism

According to the results of $CO_2$-TPD, the addition of Ce with low electronegativity reinforced the negative charge of oxygen ions and generated strong base sites, which were critical to the catalytic activity of LDO-Ce. Based on the above analysis in this work and previous studies, the oxygen ions of LDO-Ce were considered the major active centres, and a reaction mechanism was speculated as presented in Figure 6.[29,30] The hydroxyl of BDO was polarized and broken by the oxygen ions, which possessed

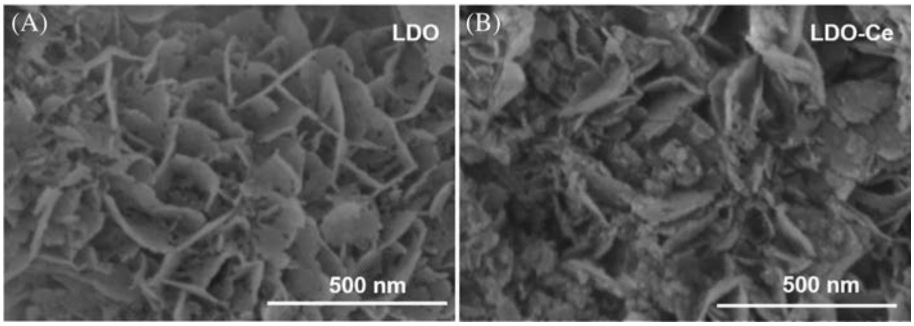


**FIGURE 3** Scanning electron microscopy (SEM) images of (A) layered double oxide (LDO) and (B) Ce cooperated layered double oxide (LDO-Ce) catalysts

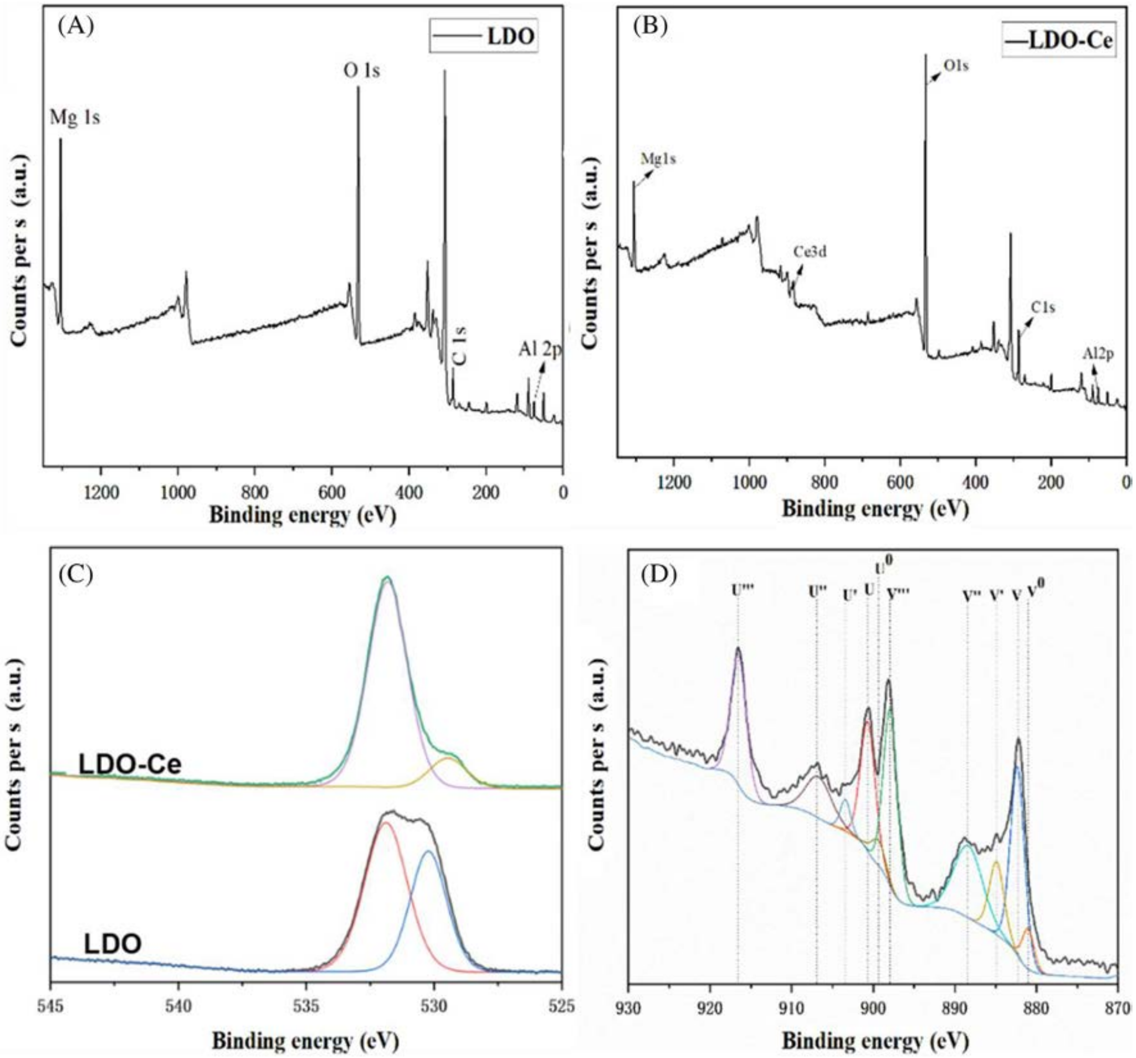


**FIGURE 4** X-ray photoelectron spectroscopy (XPS) spectra of (A) layered double oxide (LDO), (B) Ce cooperated layered double oxide (LDO-Ce), (C) O1s of LDO and LDO-Ce, and (D) Ce 3d of LDO-Ce

**TABLE 2** Structural properties of different samples

| Sample | SSA ($m^2\ g^{-1}$) | $V_t$ ($cm^3\ g^{-1}$) | Pore size (nm) |
|---|---|---|---|
| LDO | 260.21 | 0.93 | 9.70 |
| LDO-Ce | 116.72 | 0.43 | 17.88 |
| LDO-Ni | 186.14 | 0.49 | 7.89 |
| LDO-Zn | 84.52 | 0.33 | 12.56 |
| LDO-Fe | 179.86 | 0.47 | 8.21 |
| LDO-Co | 82.12 | 0.32 | 12.02 |
| LDO-Cu | 69.77 | 0.27 | 12.43 |

Abbreviations: LDO, layered double oxide; LDO-Ce, Ce cooperated layered double oxide; LDO-Co, Co cooperated layered double oxide; LDO-Cu, Cu cooperated layered double oxide; LDO-Fe, Fe cooperated layered double oxide; LDO-Ni, Ni cooperated layered double oxide; LDO-Zn, Zn cooperated layered double oxide; SSA, specific surface area.

favourable negative charge, and were the Lewis base sites of LDO-Ce, generating the nucleophilic species HO-R-O$^-$. And the hydrogen atom of BDO transferred to the catalyst. Then, HO-R-O$^-$ attacked the carbonyl carbon of DMC, and an intermediate compound (a) was obtained. Subsequently, the H$^+$ on the surface of the catalyst was captured by (a), while the chain of (a) was broken and the methoxy group dropped to form methanol. In this way, the transesterification process continuously proceeded depending on the catalyst.

## 3.4 | Effect of reaction conditions

To further optimize the synthesis conditions of the target PCDLs ($M_n = 1000$ g/mol, $V_{OH} = 110 \pm 10$ mg KOH/g), the influences of catalyst amount, molar ratio of DMC to BDO, temperature, and reaction time on the synthesis of PCDLs by using LDO-Ce as the catalyst were systematically investigated.

### 3.4.1 | Effect of catalyst amount

According to the above procedure, the transesterification reaction was performed with the catalyst amount ranging from 0.05 to 1 wt.% (with respect to the mass of raw materials). As shown in Figure 7, the hydroxyl value of the PCDLs decreased from 167.8 to 94.7 mg KOH/g with the increase of the amount of catalyst. PCDLs with an appropriate hydroxyl value could be obtained when the amount of catalyst was 0.5 wt.%. And the yield apparently decreased when the amount was higher than 0.5 wt.%. Therefore, 0.5 wt.% was determined as a suitable amount of catalyst for the following study.

### 3.4.2 | Effect of monomer feed ratio

The molar ratio of DMC to BDO played an important role in the synthesis of PCDLs. As shown in Figure 8, the hydroxyl value of PCDLs dropped sharply when the molar ratio increased from 1.10 to 1.20 and reduced gradually above 1.25. The BDO conversion and yield increased continuously with the improved molar ratio and changed gently between 1.25 and 1.30. However, the purity of PCDLs declined when the molar ratio was beyond 1.25, which was confirmed by the appearance of absorption peak of —$CH_3$ at 1380 $cm^{-1}$ in the FTIR spectrum when the molar ratio was 1.3 (Figure 9).[24] Besides, the intensity of peak of —C—H at 2970 $cm^{-1}$ increased when the molar ratio was up to 1.3, which was also attributed to the augment of —$CH_3$. Thus, 1.25 was chosen as a suitable molar ratio of DMC to BDO.

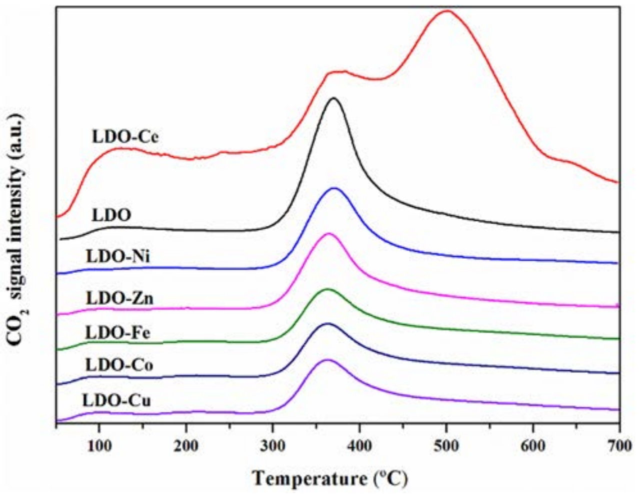


**FIGURE 5** $CO_2$ temperature-programmed desorption ($CO_2$-TPD) profiles of layered double oxide (LDO) and LDO-M

### 3.4.3 | Effect of temperature and time of the transesterification section

Temperature was important for the transesterification process. High temperature was beneficial to the activation of the catalyst and the improvement of reaction efficiency. However, if the temperature was increased continuously, the side reaction might occur and affect the formation of oligomers. Thus, the influence of temperature on the transesterification between DMC and BDO was studied, ranging from 120 to 170°C. As shown in Figure 10A, the hydroxyl value of PCDLs decreased from 139.6 to 104.7 mg KOH/g when the temperature elevated from 120 to 130°C, and then increased rapidly when the temperature was above 150°C. This may be ascribed to the generation of side-product tetrahydrofunan[12] and the side reaction of the obtained oligomers at high temperature, affecting the content of oligomers in the system, so that the second step of polycondensation was hard to be carried out. Hence, desired PCDLs can be prepared when the temperature of the transesterification process was 130°C, which was lower than the160°C reported in some literature,[12,13] reducing the energy consumption

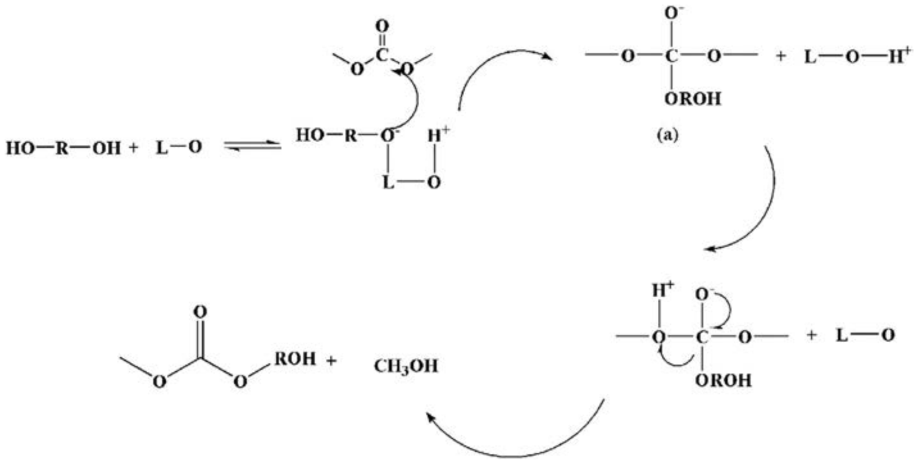


**FIGURE 6** Speculated mechanism for the transesterification between 1,4-butanediol (BDO) and dimethyl carbonate (DMC)

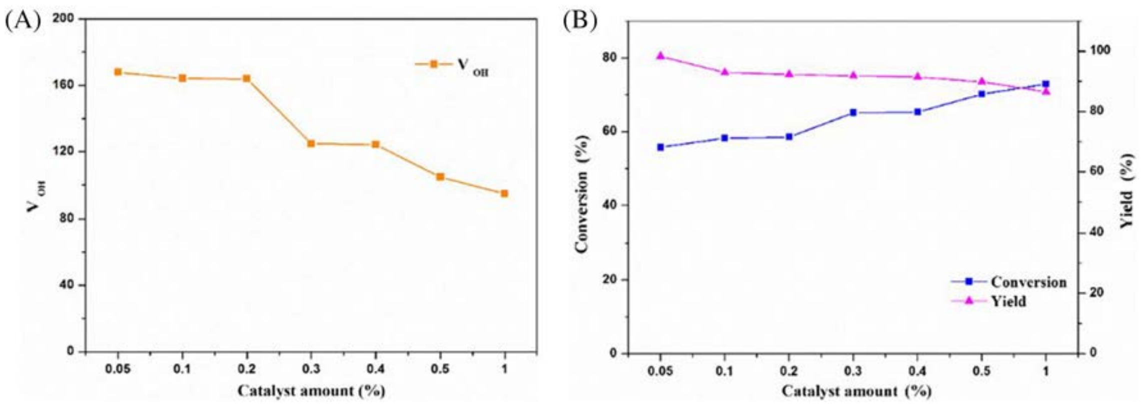


**FIGURE 7** Effect of catalyst amount on the (A) hydroxyl value of polycarbonate diols (PCDLs) and (B) yield and 1,4-butanediol (BDO) conversion

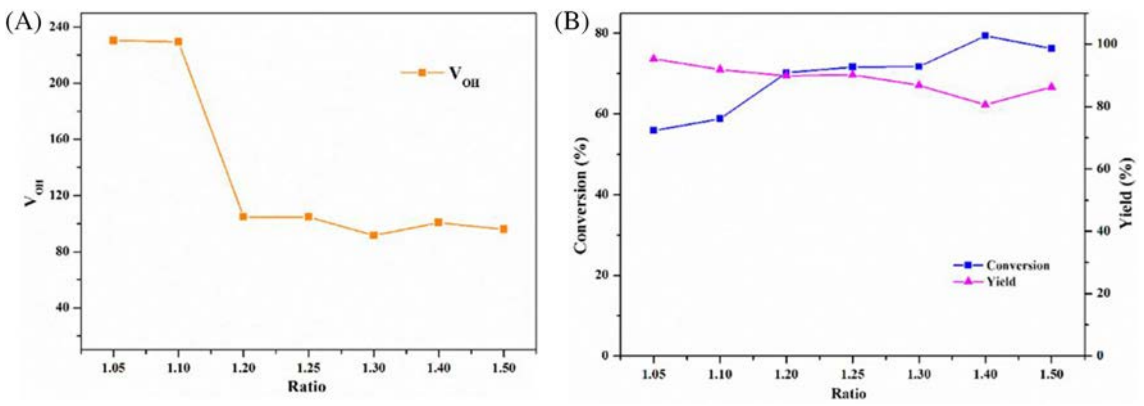


**FIGURE 8** Effect of molar ratio on the (A) hydroxyl value of polycarbonate diols (PCDLs) and (B) yield and 1,4-butanediol (BDO) conversion

required for the reaction. And 130°C of transesterification process was confirmed to accomplish the following study.

Figure 10C,D presents the effect of $t_{\text{transesterification}}$ on the hydroxyl value of PCDLs, yield, and BDO conversion. As the time prolonged, the hydroxyl value decreased slightly and the target PCDLs could be obtained at 5 h. The yield increased initially and then decreased as reaction time prolonged, and reached the maximum at 5 h, owing to the deficiency of transesterification reaction with a short time and the generation of by-products with a longer time. It appeared that 5 h was an acceptable choice for the ideal product.

### 3.4.4 | Effect of temperature, pressure, and duration time of the polycondensation section

The vacuum condition is necessary for the polycondensation process, which can not only remove the residual methanol but also boost the polymerization of oligomers. At the same time, to overcome the adverse effect of the increased system viscosity on the progress of the polycondensation stage, a high temperature was also essential. But the temperature could not exceed 200°C, at which PCDLs would be decomposed.[31] Therefore, the temperature, pressure, and reaction time of the polycondensation stage directly impacted the $V_{OH}$ and the yield of PCDLs. In this step, the investigation of temperature was finished in the range of 160 to 190°C. As shown in Figure 11A, the hydroxyl value of PCDLs decreased rapidly when the temperature went up from 160 to 170°C and kept constant with further increase in the temperature. The BDO conversion showed an opposite trend to the hydroxyl value, but both reached suitable degrees at 170°C. The yield dropped when the temperature was above 170°C, on account of the decomposition of the products at high temperature (Figure 11B). Thus, the temperature of the polycondensation process was determined as 170°C.

It is well known that a vacuum operation was necessary to gain the desired PCDLs. Figure 11C,D shows the effect of vacuum pressure on the reaction. When the pressure was reduced from 12 to 4 kPa, both BDO conversion and yield were stable at around 70% and 90%, respectively. However, the hydroxyl value presented a downward trend with the decrease in pressure, and the desired PCDLs could be obtained at 10 kPa.

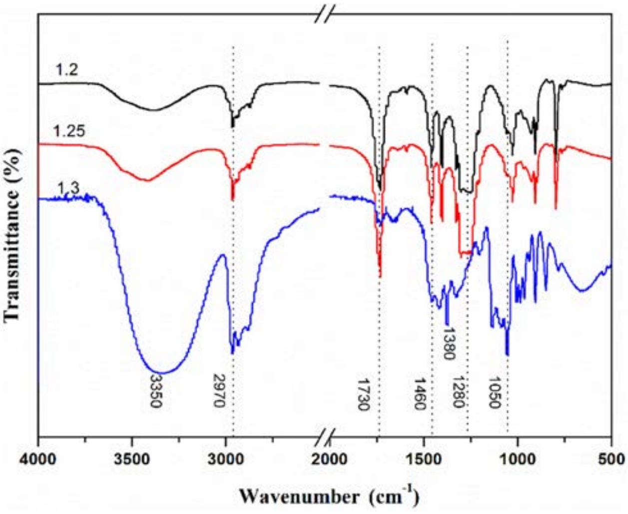


**FIGURE 9** Fourier-transform infrared spectroscopy (FTIR) spectra of polycarbonate diols (PCDLs) with different molar ratio of dimethyl carbonate (DMC) to 1,4-butanediol (BDO)

The $t$-$_{\text{polycondensation}}$ was theoretically more than 2 h,[31] which was beneficial to the removal of methanol. Figure 11E indicated that the hydroxyl value declined with the going up of $t$-$_{\text{polycondensation}}$ from 2 to 4 h and no longer showed a further decrease. BDO conversion and yield did not change apparently within the change in time (Figure 11F). Thus, 4 h was confirmed as the duration time of polycondensation process.

Consequently, the target PCDLs ($M_n$ = 1000 g/mol, $V_{OH}$ = 112.2 mg KOH/g) can be acquired at 170°C and 10 kPa for 4 h.

### 3.4.5 | Reuse of catalyst

In order to study the stability and cycle durability of the catalyst, the LDO-Ce after reaction was recovered by centrifugation, followed by washing with ethanol three times and drying at 80°C for 6 h, and then used in the next cycle. As shown in Figure 12, the hydroxyl value remained constant after three successive cycles, and then went up from 115.2 to 220.7 mg KOH/g when the catalyst was recycled for more than three times. Interestingly,

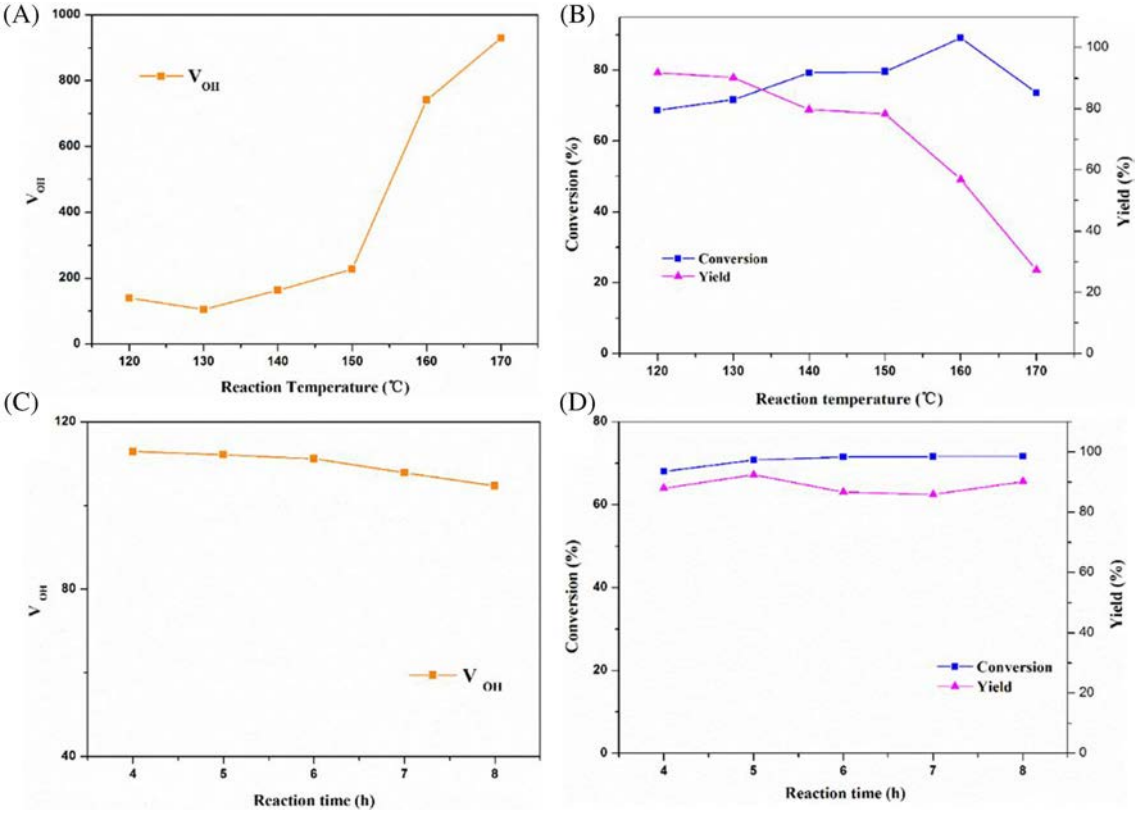


**FIGURE 10** Effect of transesterification temperature on the (A) hydroxyl value of polycarbonate diols (PCDLs), (B) yield and 1,4-butanediol (BDO) conversion; and effect of transesterification time on the (C) hydroxyl value of PCDLs and (D) yield and BDO conversion (reaction conditions: $w$ (catalyst) = 0.5%, $n$(DMC)/$n$(BDO) = 1.25, $T$-$_{\text{polycondensation}}$ = 170°C, $t$-$_{\text{polycondensation}}$ = 4 h, $P$-$_{\text{polycondensation}}$ = 10 kPa).

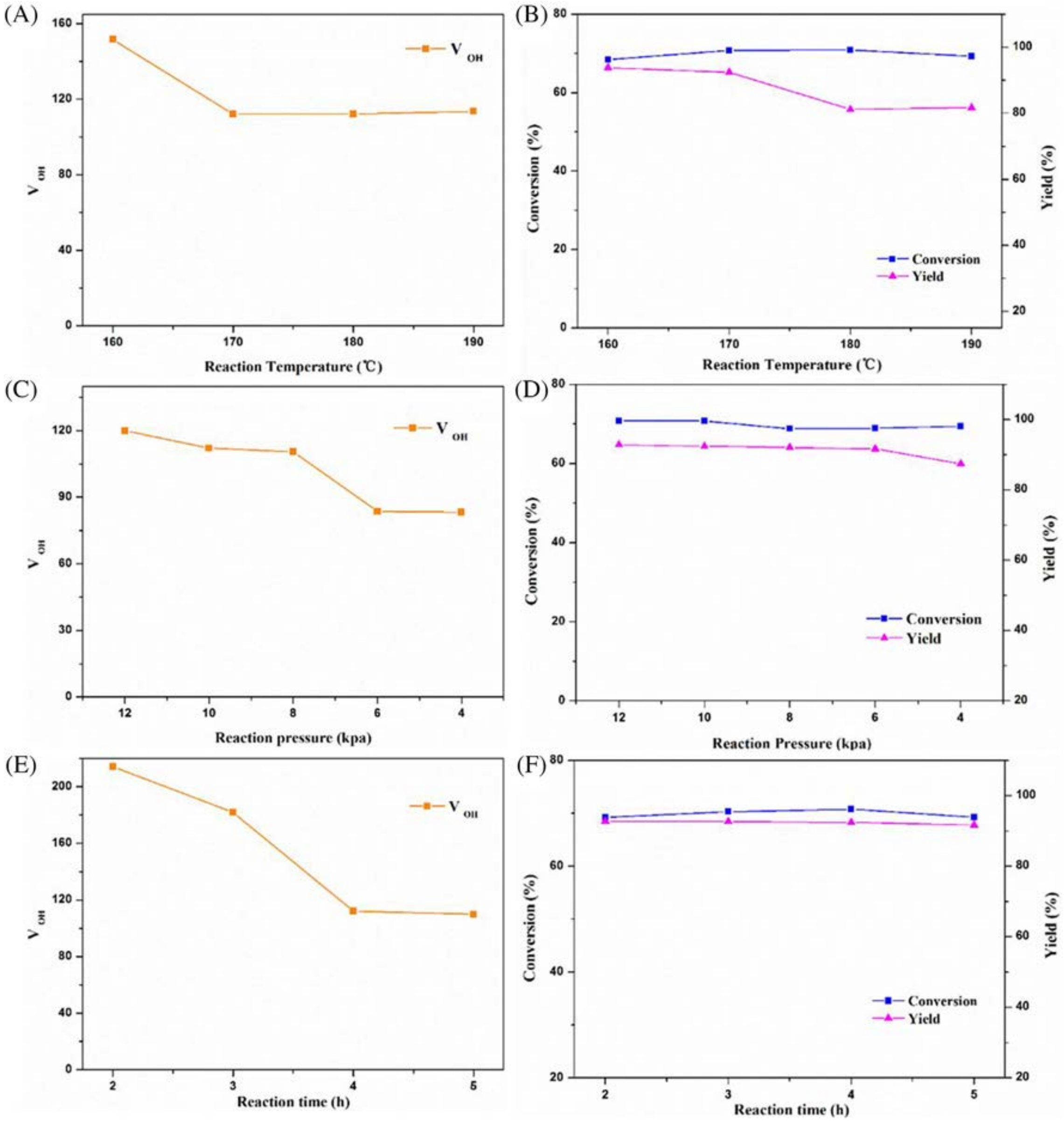


**FIGURE 11** Effect of various reaction conditions on the hydroxyl value of PCDLs. (A) Polycondensation temperature, (C) pressure and (E) duration time. Effect of various reaction conditions on the yield and 1,4-butanediol (BDO) conversion. (B) Polycondensation temperature, (D) pressure, and (F) duration time (reaction conditions: $w$ (catalyst) = 0.5%, $n$(DMC)/$n$(BDO) = 1.25, $T$-$_{\text{transesterification}}$ = 130°C, $t$-$_{\text{transesterification}}$ = 5 h)

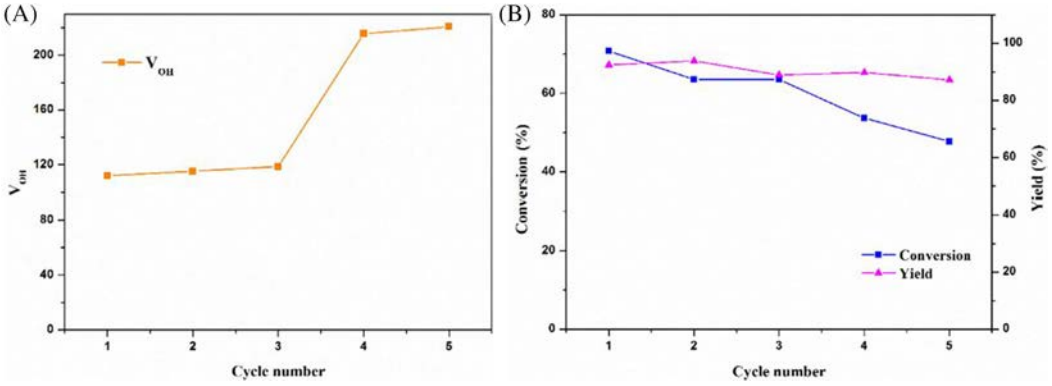


**FIGURE 12** Cycle durability of the Ce cooperated layered double oxide (LDO-Ce) catalyst: (A) hydroxyl value of PCDLs and (B) yield and BDO conversion

**TABLE 3** Effect of different catalysts on the synthesis of polycarbonate diols

| Entry | Catalyst | Catalyst amount (%) | Types of catalysts | $V_{OH}$ (mg KOH/g) | Yield (%) | References |
|---|---|---|---|---|---|---|
| 1 | $CH_3COONa$ | 0.3 | Homogeneous | 56.1 | 64.7 | Song et al.[31] |
| 2 | $Zn(CH_3COO)_2$ | 1.0 | Homogeneous | 46.8 | 78.1 | Wang et al.[32] |
| 3 | $KNO_3/\gamma\text{-}Al_2O_3$ | 0.7 | Heterogeneous | 70.1 | 68.4 | Song et al.[11] |
| 4 | Zn-Al LDHs | 0.2 | Heterogeneous | 69.7 | 76.8 | Wang et al.[33] |
| 5 | Mg-Fe/Ti LDHs | 1.0 | Heterogeneous | 43.5 | 89.1 | Wang et al.[15] |
| 6 | HTC-Ni-T | 0.1 | Heterogeneous | 59.7 | 95.0 | Zhu et al.[12] |
| 7 | $KF/Al_2O_3$ | 0.3 | Heterogeneous | 112.2 | 96 | Feng et al.[13] |
| 8 | LDO-Ce | 0.5 | Heterogeneous | 112.2 | 92.4 | This work |

after five cycles, PCDLs with a hydroxyl value of 220 mg KOH/g ($M_n$ was around 500 g/mol) were still obtained. The results indicated that LDO-Ce catalyst showed favourable recyclability in the synthesis of PCDLs.

## 3.5 | Comparison of catalytic activity

A summary of the activity of the representative catalysts for the synthesis of PCDLs is listed in Table 3, allowing a comparison between LDO-Ce and reported catalysts. The results showed that the prepared LDO-Ce exhibited excellent performance for synthesizing PCDLs. Specifically, LDO-Ce could be separated from the product compared with homogeneous catalysts, ensuring the quality of PCDLs. Moreover, abundant strong base sites endowed LDO-Ce with the desired catalytic activity. In addition, compared with the supported catalyst, utilization of LDO-Ce in the transesterification process avoided the loss of an active component, which might affect the quality of product and the activity of the catalyst.[34] Therefore, LDO-Ce can be regarded as a potential solid base catalyst for the synthesis of PCDLs.

## 4 | CONCLUSIONS

The Ce-containing layered double oxide was prepared and used as a heterogeneous solid base catalyst for the transesterification process between DMC and BDO. The results showed that the strong base sites of LDO were enhanced with the addition of Ce, which contributed to improving the catalytic activity of LDO-Ce. And the benign BET surface area of LDO-Ce was also beneficial to its catalytic activity. The effects of the reaction conditions were investigated. Under the optimal reaction conditions, the yield of PCDLs with the hydroxyl value of 112.2 (mg KOH/g) was up to 92.44%. In addition, a LDO-Ce catalyst could be easily recovered and reused. Consequently, LDO-Ce is a promising heterogeneous solid base catalyst for the industrial production of PCDLs.

## AUTHOR CONTRIBUTIONS

**Kaiyan Zhao:** Data curation; formal analysis; investigation; methodology; supervision; validation; writing – original draft; writing – review and editing. **Xiaowei Tantai:** Conceptualization; investigation; methodology; resources; supervision; validation; writing – review and editing. **Yongli Sun:** Funding acquisition; project administration; writing – review and editing. **Luhong Zhang:** Funding acquisition; project administration; writing – review and editing. **Bin Jiang:** Funding acquisition; project administration; writing – review and editing. **Na Yang:** Project administration; resources.

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## CONFLICT OF INTEREST

There are no conflicts of interest to declare.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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