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# Oxidative lactonization of diethylene glycol to high-value-added product 1, 4-dioxan-2-one promoted by a highly efficacious and selective catalyst ZnO- $ZnCr_2O_4$

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after 10 consecutive cycles.

# A R T I C L E I N F O A B S T R A C T *Keywords:*Oxidative lactonization I,4-dioxan-2-one Tono-ZnCr<sub>2</sub>O<sub>4</sub> catalyst Heterogeneous catalysis *Keywords:*Discrete the desired product 1,4-dioxan-2-one (PDO) was successfully synthesized via the oxidative lactonization of diethylene glycol (DEG) under mild conditions. After screening several catalysts (M-Cr-O), we found ZnO-ZnCr<sub>2</sub>O<sub>4</sub> (Zn-Cr-O) catalyst exhibited excellent catalytic performance and this chemical transformation obtained moderate to excellent selectivity (96.22%) and conversion (81.95%) within a 4 h reaction time. Subsequently, the morphology of calcined M-Cr-O was investigated by FT-IR, XRD, FESEM, TEM, and N<sub>2</sub> adsorption-desorption tests for further study on catalytic performances. The strength and quantity of acid and base sites over Zn-Cr-O were also detected by NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD, and it was worth noting that the acid/base sites over ZnO-ZnCr<sub>2</sub>O<sub>4</sub> (Zn-Cr-O) catalyst could promote this catalytic process well. Recycle studies demonstrated

#### 1. Introduction

Lactones and their derivatives have attracted extensive attention to both academic and industrial chemists. Due to the promising and interesting biological activities, their applications are in a wide range of yields, including polymer production, drug discovery, as building blocks for synthesis *etc* [1–8]. In general, oxidative lactonization of diols is considered as one of the most advanced methodologies for industrial process with enormous economic efficiency. However, practical applications are notoriously facing the limitations of requiring fierce reaction conditions as well as employing costly and toxic oxidants. These shortcomings currently have been proved to be the biggest obstacles in industrial manufacture [9]. With an environmental view to the oxidative lactonization, proposing a mild catalytic protocol incorporative uses "soft" oxidants (*e.g.*  $O_2$ ,  $H_2O_2$ ) to tackle the above mentioned problems is of great importance in chemical industry [10,11].

Among the lactones, 1,4-dioxan-2-one (PDO), an industrially valuable precursor to Poly (1,4-dioxan-2-one) (PPDO), is a fundamental building block for ranges of well-known derivative materials such as degradable surgical sutures, osteosynthesis products, and drug-delivery supporters [12–16]. Considering the degradation of ether bond, the scientific community pays more attention to a robust and flexible catalytic system capable of manufacturing high-quality lactones. Recently, researchers have studied the synthesis of lactones under bifunctional PCP pincer catalyst system [17] and other M/TEMPO system [18] with O<sub>2</sub> as oxidants. Many noble metals, such as gold [19-21], palladium [22,23], ruthenium [24,25] and iridium [26] have been also reported, exhibiting excellent catalytic performances in the process of aerobic oxidative lactonization of diols. Compared with noble metals, nonnoble transitional metals performed less active in this chemical transformation. But employing cheap and effective economic transition metals like Cu [27], Co [28,29], are an urgent matter due to the scarcity and price of noble metals in chemical industry. Zhu Q et al. synthesized WO3/ZrO2 catalyst and applied it in the oxidative lactonization of 1,2benzenedimenthanol with H<sub>2</sub>O<sub>2</sub>. This catalyst exhibited high activities in the first run. With the leaching of WO<sub>6</sub> units and the appearance of WO<sub>x</sub>-O-Zr bonds, however, the catalytic selectivity decreased when the recovered catalyst participated in the reaction [30]. Indeed, an efficient oxidative lactonization that uses  $H_2O_2$  as an oxidant in combination with economical, reusable, and more efficacious catalysts under mild conditions is still an unmet challenge in catalytic transformation.

exceptional stability and recyclability of the prepared catalyst without significant efficiency and selectivity loss

Recently, a mixed metal oxide, prepared by LDH precursor, has attracted significant attention. It displays broad application prospects in

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the field of catalyst and exhibits potential abilities on the dehydrocyclization reactions [31-35]. In addition, acid sites accelerate the dehydration reactions and basic sites promote the dehydrogenation reactions. These properties make them competitive in catalysis field compared to other catalysts [36-38]. For example, Venugopal A et al. successfully produced 2-methylpyrazine using prepared ZnO-ZnCr<sub>2</sub>O<sub>4</sub> (Zn-Cr-O) catalyst obtained by Zn-Cr-HT precursor. Meanwhile, extensive and comprehensive studies toward the influences of acid-base sites on that catalyst were also included [39]. Min Wei et al. obtained an acid-base-promoted Ni nanocatalyst on the basis of NiAl-layered double hydroxide precursor, and successfully applied it in the dehydrogenation reaction of 2-octanol to obtain 2-octanone. Both excellent catalytic performances (the yield of the target product was nearly 100%, 3.9 times larger than typical catalysts) and characterization results revealed a vital role of the acid-base sites [40]. As mentioned in the literature, acid-base bifunctional catalysts can facilitate the formation of C-C bond in order to obtain a complex and stable molecule [41-44]. Ramesh C. Deka et al. synthesized several mixed metal oxides calcined from their precursors and found NiMgAl was the best catalyst for nitro-aldol condensation in comparison to other prepared catalysts. The condensation reaction catalyzed by NiMgAl was completed in two hours at room temperature with excellent conversion (99%). Meanwhile, the catalyst had good activities in the reaction of nitromethane with other different aldehydes as well [45]. These remarkable performances make mixed oxides catalyst a better choice to conduct a highly efficient catalytic process.

Here, we successfully tailored mixed metal oxides (M-Cr-O) and firstly applied them in the oxidative latonization of DEG to obtain PDO under mild conditions. With diligent investigations of the reaction parameters, we found that ZnO-ZnCr<sub>2</sub>O<sub>4</sub>(Zn-Cr-O) obtained by Zn-Cr-HT exhibited highly catalytic activity and excellent reusability. Especially, accompanied with the acid and base sites, diethyl glycol (DEG) can undergo either dehydration or dehydrogenation reactions to produce PDO, and the highest conversion of DEG could reach 81.95% and the selectivity of PDO was 96.22% within a 4 -h reaction time. Accordingly, different characterization methods were employed to reveal the correlations between the catalyst properties and the catalytic activities toward oxidative lactonization of DEG.

#### 2. Experimental section

#### 2.1. General

Transmission electron microscopy (TEM) and high-resolution TEM were performed on a FEI Tecnai G<sup>2</sup> F20 operated at 200 kV. Field emission scanning microscopy (FESEM) imagines were collected on a Hitachi SU-70 microscope and energy dispersive X-ray spectrometer (EDS) connected with FESEM was employed for elemental distribution. The amount of Zn and Cr species in catalysts was measured by ICP method (Varian-730ES). XRD was carried out on PANalytical X' Pert diffractometer with Cu Ka radiation. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific Escalab 250Xi spectrometer using Al Ka radiation at 1486.6 eV, and the binding energies were calibrated at 284.8 eV from C 1s peak. FT-IR spectra were tested in an IRAffinity-1S (Shimadzu, Japan) spectrometer using KBr pellets in a scope of 400–4000 cm<sup>-1</sup>. UV–vis spectra of the samples were recorded on a UV/ vis UNICO UV-3820 spectrophotometer. N2 adsorption-desorption test was performed on a Micromeritics ASAP 2020 analyzer at -196 °C to determine the surface areas, pore size and volume of the catalysts using the Brunauer-Emmett-Teller (BET) method and BJH method.

#### 2.2. Catalyst preparation

A series of Zn-Cr-O catalysts were synthesized via a facile co-precipitation method. Typically, dissolving  $Zn(CH_3COO)_2$ :2H<sub>2</sub>O and Cr (NO<sub>3</sub>)<sub>3</sub>:9H<sub>2</sub>O in deionized water with a constant Zn/Cr ratio of 2 to produce hydrotalcite structure. Subsequently, an alkaline mixture of NaOH and Na<sub>2</sub>CO<sub>3</sub> was slowly added to the metallic solution until the pH = 9 under vigorous stirring. The resulting gel was then washed to neutral with deionized water, and filtered followed by drying at 120 °C in an oven for 12 h. After that, the samples were collected and calcined at specific temperature (350, 450, 550 and 650 °C) for 5 h. For convenience, the Zn-Cr-O samples calcined at different temperatures were nominated as ZC350, ZC450, ZC550, and ZC650, respectively. Under the same condition, Mn-Cr-O, Fe-Cr-O and Cu-Cr-O samples were also prepared to compare the catalytic performances.

#### 2.3. Activity tests

All catalysts were evaluated for the oxidative lactonization of diethylene glycol (DEG) to obtain 1,4-dioxan-2-one (PDO). The reaction was carried out in a three-neck flask (25 ml) equipped with a reflux condenser at 80 °C under magnetic stirring. First of all, 0.5 mmol of DEG, 1.2 ml of CH<sub>3</sub>CN and 0.2 mmol of NaOH (0.2 M) were added into a three-neck flask with vigorous stirring at room temperature. 15 min later, the catalyst (5 mol%) was added. After stirring for 30 min, 30 wt. % aqueous H<sub>2</sub>O<sub>2</sub> (1.5 mmol) was dropwise added into the above mixture and maintained the temperature at 80 °C for 4 h. In addition, a series of experiments have been conducted to optimize the reaction conditions such as hydrogen peroxide dosage, catalyst amounts, and solvent nature. The solid catalyst was separated by filtration when the reaction was completed, then washed with deionized water and ethanol thoroughly, followed by drying in an oven at 120 °C overnight for reuse. With external standard method, the filtrate was analyzed by GC (FULI 9790II, FID detector, 30 m AT-FFAP capillary column).

#### 3. Results and discussion

#### 3.1. Catalyst characterization

The crystalline phase and the structure of the Zn-Cr-O samples calcined at different temperatures ranged from 350 to 650 °C were characterized by XRD (Fig. 1). Better crystallinity was obtained when the samples were calcined at higher temperature. The peaks appeared at  $31.78^{\circ}$ ,  $34.42^{\circ}$ ,  $36.35^{\circ}$ ,  $47.54^{\circ}$ ,  $56.60^{\circ}$ ,  $62.86^{\circ}$ , and  $66.38^{\circ}$  might reveal the (100), (002), (101), (102), (110), (103), and (200) planes of ZnO phase [JCPDS NO. 36-1451] and the resulting 'd' values of 0.28 nm, 0.26 nm, 0.25 nm, 0.19 nm, 0.16 nm, 0.15 nm and 0.14 nm, respectively. The peak appeared at  $30.30^{\circ}$ ,  $35.73^{\circ}$ ,  $37.36^{\circ}$ ,  $43.41^{\circ}$ ,  $53.90^{\circ}$ ,  $57.46^{\circ}$ ,  $63.11^{\circ}$ ,  $66.31^{\circ}$ , and  $71.60^{\circ}$  were attributed to the (220), (311), (222), (400), (422), (511), (440), (531), and (620) facets of ZnCr<sub>2</sub>O<sub>4</sub> [JCPDS NO. 22-1107] phase, and the 'd' values were



Fig. 1. XRD patterns of the Zn-Cr-O catalysts calcined at various temperatures: (a) ZC350, (b) used ZC450, (c) ZC450, (d) ZC550 and (e) ZC650.

#### Table 1

The textural parameters of catalysts.

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Catalysts	$S_{BET}(m^2g^{-1})^{[a]}$	$V_p(cm^3 g^{-1})^{[a]}$	r <sub>p</sub> (nm) <sup>[a]</sup>	Crystallite size, nm <sup>[b]</sup>	
				ZnO(100)	ZnCr <sub>2</sub> O <sub>4</sub> (311)
ZC350	118.03	0.2863	9.702	nd	nd
ZC450	53.29	0.2428	18.23	26.69	16.94
ZC550	30.81	0.1467	19.05	38.95	19.13
ZC650	21.47	0.0619	11.53	44.97	23.27

[a] Determined from  $N_2$  adsorption-desorption at -195.96 °C and calculated using the BET and BJH methods ( $S_{BET}$  and  $r_p$ ), t-polt method ( $V_p$ ), respectively. [b] Crystallite size calculated from XRD patterns by Scherrer's equation.

calculated of 0.30 nm, 0.25 nm, 0.24 nm, 0.21 nm, 0.17 nm, 0.16 nm, 0.15 nm, 0.14 nm, and 0.13 nm, respectively. These findings were also consistent with the results of other authors [46–48]. However, there were no detection of ZnO and ZnCr<sub>2</sub>O<sub>4</sub> peaks in ZC350, probably caused by the pre-existence of amorphous phase [49]. Table 1 illustrated the average crystallite sizes of ZnO (100) phase and ZnCr<sub>2</sub>O<sub>4</sub> (311) phase of the calcined catalysts and the XRD patterns of the M-Cr-O catalysts were shown in Fig. S1. Compared to the Zn-Cr-O, there was no diffraction peaks for MCr<sub>2</sub>O<sub>4</sub> phase in M-Cr-O, indicating that the spinel phase of them might be too small to be detected by XRD. Meanwhile,  $Cr_2O_3$  phase unexpectedly occurred in Mn-Cr-O and Fe-Cr-O catalysts.

Fig. 2 depicts the  $N_2$  adsorption-desorption isotherms and the pore distributions of Zn-Cr-O samples. A type of IV isotherm with the occurrence of an evident H3 hysteresis loop in each sample, inferring that the structure was mesoporous, and slit-shaped pore channels were existed in our catalysts [50]. At low relative pressure, the adsorption amount gradually decreased along with increasing calcination temperature. All the detailed textural parameters of calcined catalysts were listed in Table 1. It could be seen that only mesopores exhibited in our samples and the specific surface area and the pore volumes ( $V_p$ ) of Zn-Cr-O catalysts obviously decreased with increasing calcination temperature.

FI-IR spectra of ZnO-ZnCr<sub>2</sub>O<sub>4</sub> (Zn-Cr-O) samples calcined at different temperatures were shown in Fig. 3. The vibration of tetrahedral M–O and the octahedral M–O bond was presented at the bands v1 and v2 at 627 and 502 cm<sup>-1</sup> [51], which are in good correlation with XRD results for the formation of a spinel phase. With increasing calcination temperature, the absorption bands of Zn-Cr-O apparently enhanced and became sharped, but the broad absorption bands in the range of 3500–3400 cm<sup>-1</sup> were weakened. Meanwhile, a small absorption band at 1636 cm<sup>-1</sup> was related to the hydroxyl deformation mode of water [52] and the band at around 928 cm<sup>-1</sup> was an evidence of Cr<sup>6+</sup> species,



Fig. 2. (a)  $N_2$  adsorption-desorption isotherms and (b) Pore size distributions of the calcined catalysts.



Fig. 3. FT-IR spectra of the Zn-Cr-O catalysts calcined at various temperatures: (a) ZC350, (b) used ZC450, (c) ZC450, (d) ZC550 and (e) ZC650.



Fig. 4. UV-vis spectra of Zn-Cr-O samples calcined at different temperatures: (a) ZC350, (B) used ZC450, (C) ZC450, (d) ZC550, and (e) ZC650.

which were partly decreased with increasing calcination temperature [53,54].

UV-visible spectroscopy can identify the  $Cr^{3+}$  and  $Cr^{6+}$  species in the calcined Zn-Cr-O samples, as presented in Fig. 4, the charge transferred from O  $2p \rightarrow Cr^{6+}$  of the samples leading two characteristic bands located at about 280 and 360 nm [55]. With increasing calcination temperature, there was a blue-shift of the band around 360 nm, suggesting a decreasing concentration of the surface chromate species [56]. This result was consistent with the phenomenon in FT-IR analysis. Same tendency was also found in the spectra of recovered Z450, and this



**Fig. 5.** TEM and FESEM images (a, b) of ZC450, HRTEM imagines (c) of ZC450 sample, selected area diffraction (SAED) pattern (e) recorded at the marked area of (d), and the corresponding elemental distribution mapping(g–i) of (f), Zn(orange), Cr(green), O(red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

might be the reason why the XRD result of used ZC450 was similar to the high-temperature calcined one (Fig. 1b). An absorption band at around 220 nm was attributed to the ZnO phase, presenting in all samples [57]. Importantly, there are no bands located at around 440 nm, implying no occurrence of  $Cr_2O_3$  phase in our samples, and XRD results did not observe  $Cr_2O_3$  phases in all the catalysts as well.

The microstructure of the ZC450 was tested by TEM and FESEM measurements (Fig. 5), the FESEM image of ZC450 in Fig. 5b shown that there was clearly existing the ZnO entity and ZnCr<sub>2</sub>O<sub>4</sub> particles on ZC450 surface. The lattice fringes are periodical, meaning a good single crystal in prepared catalyst. And the measured inter-planar spacing of 0.251 nm was identical with the dominant exposed plane (311) of ZnCr<sub>2</sub>O<sub>4</sub>, and the inter-planar spacing of 0.244 nm, 0.275 nm and 0.293 nm matched well with the (101), (100), and (220) facets of ZnO, respectively (Fig. 5c). These results were consistent fitly with the peaks shown in XRD spectra. Additionally, the corresponding SADE pattern (Fig. 5e) was indicating a polycrystalline structure of ZC450. Meanwhile, we collected the corresponding energy dispersive spectroscopy (EDS) spectra (Fig. S2) and further analyzed the component elements. As presented in Fig. 5g-i, only three elements of Zn, Cr and O were identified in the spectrum. In addition, the amount of metal species was characterized by ICP-OES, giving a percentage of Zn and Cr of 0.56.

The X-ray photoelectron spectra of Zn-Cr-O samples are presented in Fig. 6, and the existence of Zn, Cr and O elements are distinctly identified by the wide-range XPS spectrum of ZC450 in Fig. S3. The Zn 2p spectra of Zn-Cr-O calcined at various temperatures are shown in Fig. 6a. The BE values of Zn in these samples ranging from 1021.5 to 1021.7 eV along with 1044.9 eV are characteristic to ZnO and ZnCr<sub>2</sub>O<sub>4</sub>, respectively. Meanwhile, a shift in BE towards the low energy region with increasing calcination temperature is evident for the formation of ZnO-ZnCr<sub>2</sub>O<sub>4</sub>. Chromium shows a binding energy at 575.9 eV along with 585.4 eV (Fig. 6b) attributed to Cr<sup>3+</sup> species for all catalysts, and

this phenomenon means the formation of  $ZnCr_2O_4$  as well.  $Cr^{6+}$  species was responded to 578.9–579.6 eV [58–60], and the shift in Cr 2p peak towards low BE with increasing calcination temperature means the transition of  $Cr^{6+}$  to  $Cr^{3+}$ . These observations are also found in the FT-IR spectra (Fig. 3) of high temperature treated samples.

To gain a better understanding of our calcined catalysts, the temperature-programed desorption (TPD) of NH<sub>3</sub> and CO<sub>2</sub> were used to evaluate the correlations between the quantity of acid/base sites and their chemical performances. According to the desorption temperature, these profiles were deconvoluted to several peaks. As shown in Fig. 7a. Zn-Cr-O samples displayed a broad CO<sub>2</sub> desorption peak in the temperature region of 100-300 °C with a shoulder at 250-270 °C. Three desorption peaks were clearly noticed in ZC450 and ZC550, those were weak base site (150-160 °C), moderate base sites (250-270 °C) and strong base sites (350-370 °C). In addition, the peak appearing at and above 250 °C corresponded to moderate base sites were slightly greater for ZC450 when compared to ZC550. The low temperature peak (weak base sites) might cause by the occurrence of OH<sup>-</sup> groups, because ZC350 with the pre-existence of amorphous hydroxyl zinc chromate phase showed the highest intensity [53,54]. Similarly, the NH<sub>3</sub>-TPD profiles of all samples were shown the peaks with maximal temperatures in the regions of 100-105 °C (weak acid sites), 245-255 °C (moderate acid sites), and 395-405 °C (strong acid sites).

TPD studies demonstrated that all catalysts possessed both acid and base sites in different calcination temperatures, and total number of weak and moderate acid/base sites decreased while strong acid/base sites formed at higher calcination temperature (Table 2). We thought the increasing crystallite size in ZnO and ZnCr<sub>2</sub>O<sub>4</sub> species of high-temperature-treated catalyst may cause the decrease of acid-base strength. In addition,  $T_{max}$  of CO<sub>2</sub> desorption curves (Fig. 7a) in high-temperature-treated samples were slightly shifted to low temperatures and  $T_{max}$  of NH<sub>3</sub> desorption curves were moved toward high



Fig. 6. XPS analysis (a) Zn2p, (b) Cr2p spectra of calcined Zn-Cr-O.

temperature in contrary (Fig. 7b). It was worth noting that the moderate acid site in ZC550 disappeared and strong acid site occurred. We also calculated the ratio of acid to base sites, as listed in Table 2, the ratio value of ZC350 was inferior to others. ZC450 and ZC550 had similar ratio values, which were approximately 4 times higher than their basicity. Reportedly the surface acid (base) sites were conductive to either dehydration or dehydrogenation reactions [36–38]. These findings could help us make a deliberation that DEG was first oxidized to the monoaldehyde, then the carbonyl group might be activated by the acid sites of ZC450. After receiving a nucleophilic attack on the carbocation, the intermolecular cyclization occurred to form the intermediate product 1,4-dioxan-2-ol (Fig. S4). The cooperativity between the basicity and acidity might be an important factor for the formation of PDO in Zn-Cr-O catalysts.

#### 3.2. Catalytic oxidative lactonization of diethyl glycol (DEG)

The main product 1,4-dioxan-2-one (PDO) is successfully prepared via the catalytic oxidation of DEG according to the GC analysis after compared to a standard sample. And the occurrence of main by-product glycol may due to the R-O-R chain scission. The catalytic performances we concerned about are based on the yield of PDO.

The catalytic performances of the oxidation reaction over various molar ratios of  $H_2O_2$  to DEG were verified and the results were shown in Fig. 8. With increasing amount of  $H_2O_2$  to DEG molar ratio, *i.e.*, 1.0 to 2.0, the conversion of DEG kept steady (65%) might on account of the theoretically needs 2 mol  $H_2O_2$  for lactonization of 1 mol DEG. Then the conversion ascended continuously from 65% to 95% with

increasing oxidant dosage. However, the selectivity observed above 6.0: 1 oxidant: substrate ratio was no appreciable increased. It was speculated that a competitive reaction of the chain degradation might occur to hamper the formation of PDO at high ratio of oxidant to substrate. This phenomenon might be explained by the acidity of Zn-Cr-O and the generation of OH radicals from the excess amounts of  $H_2O_2$  [61].

Also, we have attempt the oxidative lactonization of DEG over ZC450 with the bubble of  $O_2$ , but the reaction failed to give the desired product. Considering both catalytic performance and  $H_2O_2$  utility, the best dosage of  $H_2O_2$  was chosen to be 3.0 equivalents in the following investigations.

For comparison, a series of four M-Cr-O catalysts were prepared by a simple co-precipitation method, and the samples were collected and calcined in static air at 450 °C for 5 h. The DEG conversion and PDO selectivity were depicted in Fig. 9, indicating ZC450 became the best choice as the yield of PDO was superior to other catalysts. The FI-IR spectra of M-Cr-O samples calcined at different temperatures were also shown in Fig. S5. The brand at  $501 \text{ cm}^{-1}$  can be assigned to the vibration of the octahedral M-O bond [51]. When we used XRD to characterize the crystalline phase and the structure of the M-Cr-O samples (Fig. S1), only Cu-Cr-O have formed a combination of M<sub>x</sub>O<sub>v</sub>-MCr<sub>2</sub>O<sub>4</sub> species, and M<sub>x</sub>O<sub>v</sub> and Cr<sub>2</sub>O<sub>3</sub> phases formed rather than M<sub>x</sub>O<sub>v</sub>-MCr<sub>2</sub>O<sub>4</sub> species in Fe-Cr-O and Mn-Cr-O. Also, the FESEM image of M-Cr-O catalysts in Fig. S6 told us that the morphology of M-Cr-O (M = Cu, Fe, Mn) were different from Zn-Cr-O. There was no composite structure of MCr<sub>2</sub>O<sub>4</sub> particles existed and agglomerate spherical particles could be seen clearly in prepared M-Cr-O catalysts. The ZnO particles were well embedded into the pores of ZnCr<sub>2</sub>O<sub>4</sub> particles in ZC450,



Fig. 7. TPD patterns of calcined samples. (a) CO<sub>2</sub>-TPD and (b) NH<sub>3</sub>-TPD of calcined samples.

#### Table 2 Amounts of acid and base sites according to NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD patterns.

Catalysts	The amounts of Base/Acid sites (mmol/g)							Ratio of acid to base site	
	B <sub>CO2</sub> <sup>[c]</sup>	Bw	B <sub>M</sub>	B <sub>S</sub>	A <sub>NH3</sub> <sup>[d]</sup>	A <sub>W</sub>	A <sub>M</sub>	As	
ZC350 ZC450 ZC550	0.2031 0.1428 0.1162	0.1613 0.0801 0.0612	0.0418 0.0442 0.0237	/ 0.0185 0.0313	0.6464 0.5508 0.4553	0.2778 0.1970 0.2227	0.3686 0.3334 /	/ 0.0204 0.2326	3.18 3.86 3.92

[c]  $CO_2$  uptakes measured by TPD of  $CO_2$ ,  $B_W$ ,  $B_M$ , and  $B_S$  are the amounts of weak, moderate, and strong base site, respectively. [d]  $NH_3$  uptake calculated by TPD of  $NH_3$ ,  $A_W$ ,  $A_M$ , and  $A_S$  are the amounts of weak, moderate, and strong acid site, respectively.



Fig. 8. Effect of  $\rm H_2O_2$  dosage on catalytic performances of oxidation of DEG over ZC450.



Fig. 9. Catalytic performances of oxidation of DEG over various catalysts.

but it couldn't be found in other catalysts.

The performance of catalysts exposed to various calcination temperatures was examined, suggesting 450 °C was the optimum calcined temperature of the catalyst. The yield of PDO increased firstly and then decreased steadily over prepared catalysts as the calcination temperature increased (Fig. S7). As Jiangping Xiao et al. reported the long-term stability of the ZnCr<sub>2</sub>O<sub>4</sub> species in the catalytic oxidation of HCl to produce Cl<sub>2</sub> [62]. The prepared catalyst calcined at 350 °C do shows comparable results with the rest of the samples but the absence of the ZnO and ZnCr<sub>2</sub>O<sub>4</sub> peaks make it less stable after the reaction. Meanwhile, the pores or channels of prepared catalysts were in favor of the absorption of active components, but they collapsed as calcination temperature increased (Fig. S6). That mean the decrease of the PDO yield might be explained by the changing density of acid/base sites and the increasing crystallite size in both ZnO and ZnCr<sub>2</sub>O<sub>4</sub> species in high



Fig. 10. The effect of amounts of base on the reaction. Reaction condition: DEG (0.5 mmol),  $H_2O_2$ /DEG molar ratio (6.0), 8 mg of ZC450 (5 mol %), reaction temperature (80 °C), reaction time (4 h).

calcination temperature. For the basicity of the reaction played a very assignable role both in PDO selectivity and catalyst efficiency.

As shown in Fig. 10, the reaction didn't go well without base additive, maybe basicity environment had a positive impact upon the acid sites in prepared catalyst and promoted the catalytic function of the acid and base sites. Meanwhile, the influence of the base type of oxidative lactonization reaction was also studied (Fig. S8). It can be found that both DEG conversion and PDO selectivity were very poor when Et<sub>3</sub>N or pyridine as an additive. When inorganic bases participated in the reaction, the target product was obtained with a satisfactory yield. Considering all the information, we have a hypothesis that prepared catalysts which have detected the ZnO and ZnCr<sub>2</sub>O<sub>4</sub> peaks could provide more active sites when they have larger specific surface areas and are more stable than non-calcined precursor. ZC450 possessed moderate basic sites and slightly lower acidity, but ZC550 had the position of strong acid sites. The inferences are that an appropriate amounts of acid/base sites and a larger surface area of effective catalytic components which can adsorb more reactant molecules can exhibited higher catalytic oxidation performance, and the ZnO and ZnCr<sub>2</sub>O<sub>4</sub> phases make prepared catalysts more stable in the cycling reaction [62].

Some studies were investigated to attest to that the oxidative lactonization of DEG was a catalytic process (Fig. 11). The experiment in the absence of Zn-Cr-O catalyst was first carried out with a poor conversion and selectivity, proving that the particular oxidation process was catalytic. Better performance was observed in the case of the catalyst. With a high dosage of ZC450, the DEG conversion rose apparently whereas the PDO selectivity decreased from 95.36% to 80.29% by the decomposition of DEG. It could be concluded that the optimal dosage of ZC450 was 5 mol% under the typically identical conditions. It was also pleasure to find that ZC450 exhibited the highest selectivity of 95.36% with a conversion of 74.82% when used the optimized dosage we have found.

Hot filtration tests are carried out in order to verify that our catalyst is indeed heterogeneous, and to ensure that there is no existence of homogeneous catalysis owning to the leaching of Cr into the solution.



Fig. 11. The effect of catalyst dosage on catalytic performance of ZC450.

Table 3 The results of hot filtration tests<sup>[e]</sup>.

Entry	Reaction time (h)	Cat. dosage	Conv. (%)	Sel. (%)
А	1 h	8 mg	69.63%	95.80%
	1 h + 1 h	0 mg	69.41%	95.46%
	1 h + 3 h	0 mg	69.17%	95.45%
В	2 h	8 mg	72.33%	95.53%
	2h + 2h	0 mg	71.53%	95.31%

[e] Reaction conditions: DEG (0.5 mmol), H<sub>2</sub>O<sub>2</sub>/DEG molar ratio (3.0), CH<sub>3</sub>CN (1.2 ml), 0.2 M NaOH/DEG molar ratio (0.4), 8 mg of ZC450 (5 mol %), reaction temperature (80 °C).

Considering that the reaction is completed in four hours (Fig. S9), we performed the tests in one (Table 3, Entry A) and two hours (Table 3, Entry B), respectively. Firstly, 0.5 mmol of DEG, 1.2 ml of CH<sub>3</sub>CN and 0.2 mmol of NaOH (0.2M) were added into a three-neck flask with vigorous stirring at room temperature. 15 min later, ZC450 (5 mol%) was added, after stirring for 30 min, 30 wt. % aqueous  $H_2O_2$  (1.5 mmol) was dropwise added into the above mixture. The catalyst was separated from the hot reaction mixture after maintaining the temperature at 80 °C for 1 h (2 h). Then filtrate continued to be heated at 80 °C. After the completion of 4 h, the filtrate was analyzed by GC and no increase in the conversion of DEG was achieved. These results clarified that the reaction heterogeneous in nature.

It was vital to investigate the solvent effect due to its significant role in reaction. As listed in Table 4, the highest conversion and selectivity were achieved when using CH<sub>3</sub>CN as a solvent. Unfortunately, other water-soluble solvents such as tetrahydrofuran and methanol (Table 4, Entry 4, 7) obtained chaotic systems and had no tendency to give the

Table 4						
The effect	of the	different	solvents	over	the	rea

Entry	Solvents	T. °C	Conv. (%)	Sel. (%)
1	Acetonitrile	80	81.95	96.22
2	Cyclohexane	80	51.83	10.74
3	Toluene	80	46.74	12.56
4	Water	80	18.95	29.77
5	Tetrahydrofuran	60	/	/
6	Ethyl acetate	60	48.82	17.25
7	Methanol	60	/	/

[f] Reaction conditions: DEG (0.5 mmol), H<sub>2</sub>O<sub>2</sub>/DEG molar ratio (3.0), Solvent (1.2 ml), 0.2 M NaOH/DEG molar ratio (0.4), 8 mg of ZC450 (5 mol %), reaction time (4 h).



Fig. 12. Recycling experiments of ZC450 catalyst.

desired product PDO. Fat-soluble solvents (Table 4, Entry 2, 3, 6) were also tested in the same reaction conditions but the results were disastrous. All the results revealed a strong dependence on the nature of used solvent and the presence of acetonitrile was essential to this reaction.

#### 3.2.1. Catalyst reusability

The life cycle and stability of the heterogeneous catalysts are crucial in practical applications. Hence, recycle studies were carried out to assess the stability of ZC450 catalyst for the oxidative lactonization of diethylene glycol (DEG) (Fig. 12). After the completion of reaction, ZC450 was separated from the reaction mixture by simple filtration, then washed thoroughly with ethanol and dried at 120 °C in an oven for next use. It was worth mentioning that ZC450 had a robust reusability for it could be reused more than ten runs without significant loss in catalytic activity. XRD analysis confirmed that ZC450 maintains its stability after the reaction and even more stable than prepared. FI-IR, UV-vis, and SEM spectra of used ZC450 were in good agreement with that of freshly prepared sample (Figs. 1, 3 and S6). All the results indicated a better recyclability of present catalyst system, and verified its application potential in chemical transformation.

#### 4. Conclusion

A facile, recyclable and effective method for the oxidative lactonization of diethylene glycol (DEG) has been proposed for the first time in order to prepare the high-valued product 1,4-dioxan-2-one (PDO). With H<sub>2</sub>O<sub>2</sub> as an oxidant, the Zn-Cr-O oxide catalyst exhibited good performances on the target reaction and well received the product PDO in a satisfactory yield. We also used NH3-TPD and CO2-TPD to discover the properties of acid/base sites over ZnO-ZnCr<sub>2</sub>O<sub>4</sub> (Zn-Cr-O) catalyst and found the cooperativity between the basicity and acidity might be an important factor for the formation of PDO in Zn-Cr-O catalysts. Although, the ZC350, which does not have the ZnO and ZnCr<sub>2</sub>O<sub>4</sub> XRD reflections, shows comparable results with the rest of the samples, those have the ZnO and ZnCr<sub>2</sub>O<sub>4</sub> peaks are more stable after the reaction. As far as we knew, this was the first report of oxidative lactonization of DEG with such an economical and efficacious catalyst under mild conditions with H<sub>2</sub>O<sub>2</sub> as oxidant. Furthermore, existing catalytic reaction system had provided a safe, sustainable and low-cost process for this chemical transformation and the prepared catalyst can be easily reused more than ten runs without significant deactivation. Accompanied with long term economic viability, this catalytic protocol is a promising approach and may herald a new era for low-cost lactones construction.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110643.

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