

# Pt Doped H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub> as a Heterogeneous and Recyclable Catalyst for the Synthesis of Carbonated Soybean Oil

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**ABSTRACT:** Carbonated soybean oil (CSBO) is a precursor of nonisocyanate polyurethanes (NIPUs). So far, the ruling catalysts for CSBO synthesis through the coupling of epoxidized soybean oil (ESBO) with CO<sub>2</sub> are homogeneous ones. In this work, a heterogeneous catalyst, 5 wt % H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (PW)/ZrO<sub>2</sub> was investigated for the coupling reaction and proved quite efficient. However, the catalyst showed poor reusability due to the difficult elimination of bulky by-products retained in the spent catalyst. To remedy this deficiency, the 5 wt % PW/ZrO<sub>2</sub> was modified with 0.3% Pt. It is found that Pt addition markedly

improved the reusability of the 5 wt % PW/ZrO<sub>2</sub> without loss in carbonation activity. An ESBO conversion of 78.3% was obtained at the end of third recycle, indicating that Pt species incorporated could promote the removal of the by-products and hence protect the active centres of 5 wt % PW/ZrO<sub>2</sub> catalyst. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4298–4306, 2012

**Key words:** carbonated soybean oil; coupling reaction; heterogeneous catalyst

## INTRODUCTION

Polyurethanes are a class of important polymers with broad spectrum of applications in nearly every aspect of modern life. Commercially, polyurethanes are produced via the polyaddition of polyisocyanate and polyol. The major drawbacks of the method include the use of noxious polyisocyanates and the excessive reliance on the petrochemicals. These are highly undesirable due to increasing threat of environmental deterioration and foreseeable depletion of the fossil resource.

As one of the promising alternatives to the traditional method, the coupling of epoxidized soybean oil (ESBO) with CO<sub>2</sub>, followed by reaction with amine allows nonisocyanate polyurethanes to be prepared (Scheme 1).<sup>1–3</sup> In this manner, polyisocyanate as indispensable building block for manufacturing conventional polyurethanes is rendered unnecessary. Furthermore, the novel route highlights the role of renewable resources like ESBO and CO<sub>2</sub> as starting

materials in the preparation. These are of great significance for the sustainable development of polyurethane industry.

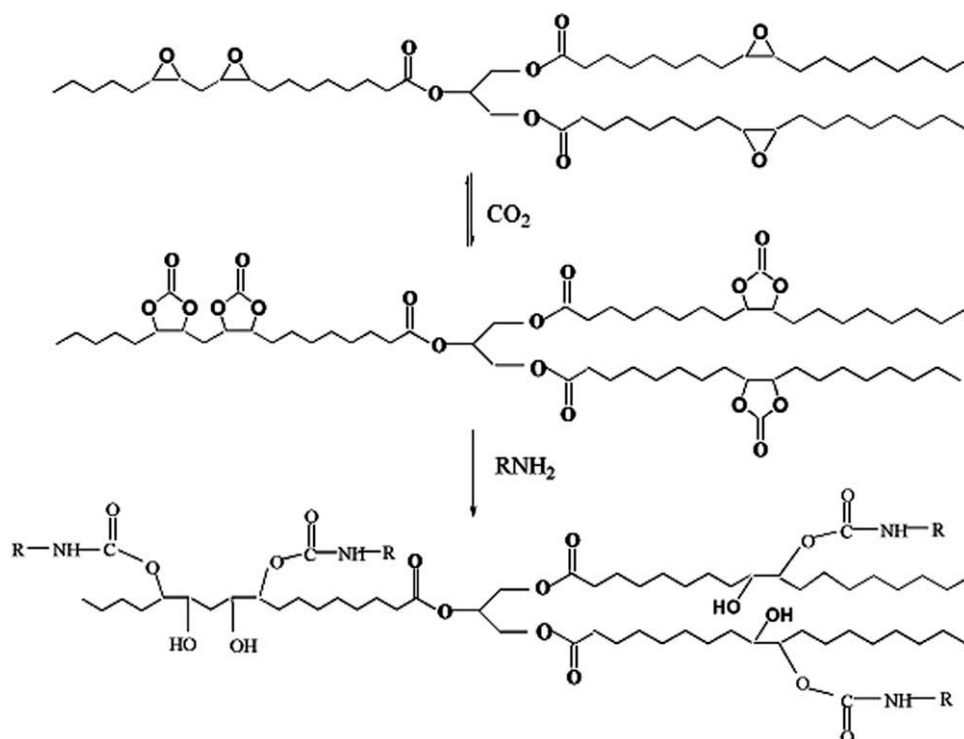
For the preparation of nonisocyanate polyurethane (NIPUs), coupling of ESBO and CO<sub>2</sub> is a crucial step because it furnishes the essential intermediate carbonated soybean oil (CSBO). Compared with cycloaddition of CO<sub>2</sub> to small epoxides such as ethylene oxide and propylene oxide yielding five-membered cyclic carbonates,<sup>4–7</sup> the transformation of ESBO into CSBO is not an easy task. The reason is that the limited oxirane groups in ESBO are located in interior of the molecular chain rather than in terminal position. Hence, the reactivity of these epoxy groups with CO<sub>2</sub> is lower than that of ethylene oxide or propylene oxide due to the steric hindrance.

Several research groups have investigated the carbonation reaction and proposed some catalysts. For example, Tamami et al. used homogeneous *n*-tetrabutyl ammonium bromide (TBABr) to implement the process. The reaction time as long as 70 hour was required to achieve an ESBO conversion of 94%.<sup>1</sup> Javni et al. employed the same catalyst in their work to prepare CSBO.<sup>8</sup> Doll and Erhan reported that the carbonation reaction rate could be markedly enhanced by using TBABr catalyst under supercritical condition.<sup>9</sup> Jalilian et al. found that a combination of TBABr with CaCl<sub>2</sub> could also considerably accelerate the reaction.<sup>10</sup> In our previous study, a composite catalyst comprising TBABr and SnCl<sub>4</sub> was applied to the

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**Scheme 1** Carbonation of ESBO and subsequent aminolysis of CSBO.

synthesis. It was discovered that very high purity of CSBO was unnecessary for the production of NIPU with good performance.<sup>3</sup> Moreover, Parzuchowski et al. described the synthesis of CSBO using KI activated with 18-crown-6 as catalyst under higher CO<sub>2</sub> pressure.<sup>11</sup> As far as we know, there is no report on the application of heterogeneous catalyst to the ESBO carbonation reaction till now. In comparison with heterogeneous catalyst, homogeneous one is less preferable in view of difficulty in separation of the spent catalyst from the reaction mixture and its poor reusability. To meet the requirement of future commercial production, development of efficient heterogeneous and recyclable catalyst is thus highly desirable.

In past decades, heteropoly acids (HPAs), in particular those of the Keggin structure have found a number of utilizations in catalysis. The HPAs can be used either directly as a bulk material or in a supported form. The supported one is preferable owing to its high specific surface area relative to the bulk one and better accessibility of reactants to the active sites.<sup>12</sup> Furthermore, they can be easily recovered from reaction mixtures and reused.<sup>13</sup> Of the solid catalysts, ZrO<sub>2</sub> supported H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (PW) is very useful for an array of reactions such as dehydration,<sup>14</sup> electrophilic substitution reaction,<sup>15</sup> alkylation,<sup>16</sup> oxidative bromination<sup>17</sup> and the like. Recently, bifunctional catalysts consisting of precious metals and HPA also attracted great attention due to their high catalytic performance for hydroisomerization of *n*-heptane, hydroxylation of benzene, one-pot conversion of citronellal to menthol.<sup>18–20</sup>

Musawir et al. found that CsPW doped with Pt made the catalyst regeneration easier.<sup>21</sup>

In this work, both unmodified and modified 5 wt % PW/ZrO<sub>2</sub> with Pt were investigated for the synthesis of CSBO from ESBO and CO<sub>2</sub>. Several operational parameters were examined. The effect of Pt addition on the reusability and carbonation activity of 5 wt %PW/ZrO<sub>2</sub> was explored.

## EXPERIMENTAL

### Materials

ESBO (EDENOL ® D81) with a molecular weight of ca. 935 g/mol and oxirane content of 6.3–7.0% provided by Cognis Company was used as received. CO<sub>2</sub> with a purity of 99.99% was purchased from Beijing Beiwen Gases Company, China. HPAs, zirconyl chloride hydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O), chloroplatinic acid hydrate (H<sub>2</sub>PtCl<sub>6</sub>·6 H<sub>2</sub>O), and other reagents of analytical grade were purchased from Sinopharm Chemical Reagent, China.

### Catalyst preparation

Zirconium hydroxide was synthesized by precipitation of ZrOCl<sub>2</sub> with ammonia at a pH value of 9.0. The precipitate gained was aged at room temperature for 2 h, followed by filtration, washing. The wet paste obtained was then dried at 100°C for 12 hour.

**TABLE I**  
**Synthesis of CSBO from ESBO and CO<sub>2</sub> Over Three HPAs**

Catalyst	Reaction temperature (°C)	CO <sub>2</sub> pressure (MPa)	ESBO conversion (%)
SiW	150	1.0	90.3
PW	150	1.0	94.5
PMo	150	1.0	91.6

Reaction time: 20 hour.

The PW/ZrO<sub>2</sub> catalysts having various PW contents were prepared by impregnating the as-synthesized zirconium hydroxide with aqueous solution of PW. While the Pt modified 5% PW/ZrO<sub>2</sub> catalyst was obtained by coimpregnating the hydrous zirconia with the aqueous solution containing required amount PW and H<sub>2</sub>PtCl<sub>6</sub>. After impregnation for 4 hour, the precursor was dried at 120°C for 12 hour and calcined at certain temperature under air for 4 hour. Other catalysts were also prepared by impregnating the commercial oxides with PW solution for comparison.

### Characterization

FT-IR spectra were collected on a Nicolet 380 spectrometer. <sup>1</sup>H-NMR spectra were recorded on a DRX 300 (300 MHz) spectrophotometer using tetramethylsilane as internal standard. Elemental analysis of products was performed on a Vario EL cube elemental analyzer. GPC measurements were conducted on a SHIMADZU RID-10A equipped with RI detector using DMF as the eluent. XRD measurement was performed on a Bruker AXS's D8 ADVANCE powder X-ray diffractometer using Cu K $\alpha$  radiation over

a 2 $\theta$  range of 5–80° with a step size of 0.017° at a scanning speed of 5°/min. Specific surface area and porosity of HPA catalysts were measured by nitrogen physisorption on a Micromeritics ASAP 2000 instrument. Elemental analysis of catalysts was done on an iCAP 6500 ICP Spectrometer quipped with an ASX-260 autosampler. Thermal gravimetric analysis (TGA) was carried out on a thermo gravimetric analyzer TGA-50 with a heating rate 10°C/min from ambient temperature to 600°C in air.

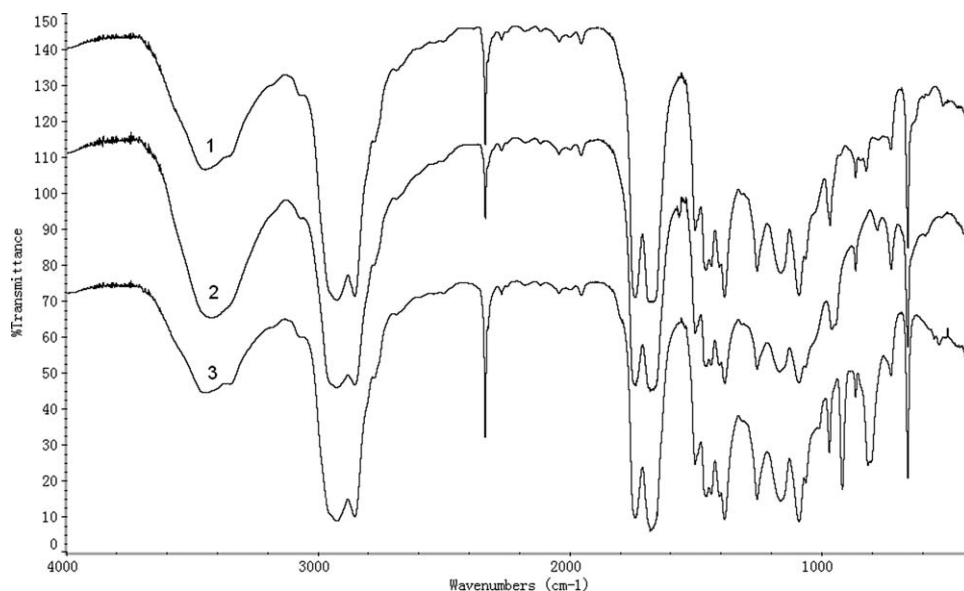
### CSBO synthesis

The synthesis of CSBO was carried out in a stainless steel autoclave with an inner volume of 500 cm<sup>3</sup>. ESBO (200g), solvent (DMF) (100g), and catalyst (10 g) were charged into the reactor. After purging the autoclave with N<sub>2</sub> for several times, the reaction mixture was heated to the desired temperature. At this temperature, the reactor was pressurized by CO<sub>2</sub> and kept for certain period when the reaction was taking place. After reaction the unreacted CO<sub>2</sub> was vented out. The catalyst was filtrated, washed with solvent, and dried at 100°C for 4 hour. The reaction progress was monitored via IR spectroscopy of small aliquots taken at certain intervals. In this way, the IR spectra were based on the samples containing solvent. The ESBO conversion was determined by a standard titration method described in reference.<sup>11</sup>

## RESULTS AND DISCUSSION

### Performance of 5 wt % PW/ZrO<sub>2</sub> catalyst

The catalytic performances of three Keggin type HPAs including H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> (SiW), H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>



**Figure 1** FTIR spectra of carbonated products acquired over bulk HPAs (1) SiW; (2) PW; (3) PMo.

**TABLE II**  
Effect of Carrier on Synthesis of CSBO

Catalyst	Reaction temperature (°C)	CO <sub>2</sub> pressure (MPa)	ESBO conversion (%)															
PW/In <sub>2</sub> O <sub>3</sub>	150	1.0	26.7															
PW/SiO <sub>2</sub>	150	1.0	81.3															
PW/V <sub>2</sub> O <sub>5</sub>	150	1.0 <td 64.3	PW/ZrO <sub>2</sub>	150	1.0	86.1	PW/MgO	150	1.0	40.7	PW/Nb <sub>2</sub> O <sub>5</sub>	150	1.0	41.6	PW/Al <sub>2</sub> O <sub>3</sub>	150	1.0	45.3
PW/ZrO <sub>2</sub>	150	1.0	86.1															
PW/MgO	150	1.0	40.7															
PW/Nb <sub>2</sub> O <sub>5</sub>	150	1.0	41.6															
PW/Al <sub>2</sub> O <sub>3</sub>	150	1.0	45.3															

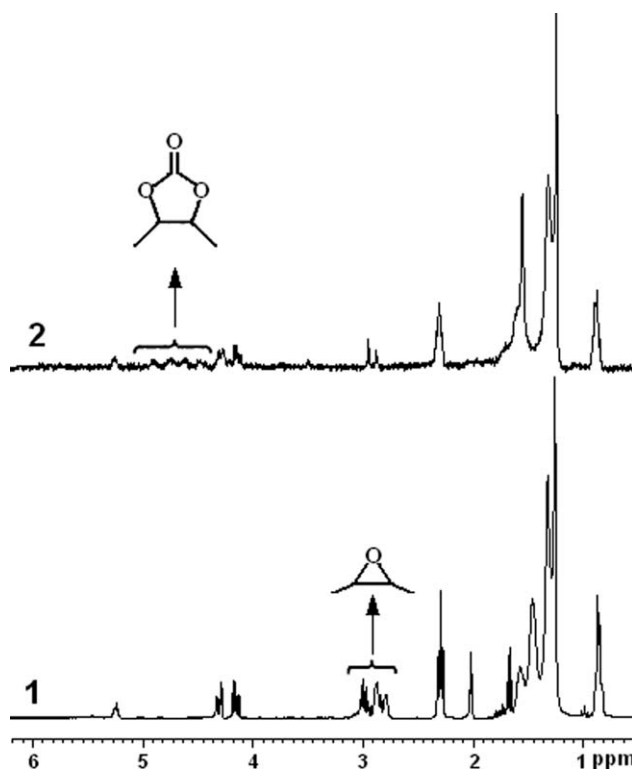
Active component loading of all catalysts was 5 wt %.

Reaction time was 20 hour.

Calcination of the catalysts was conducted at 300°C for 4 hours.

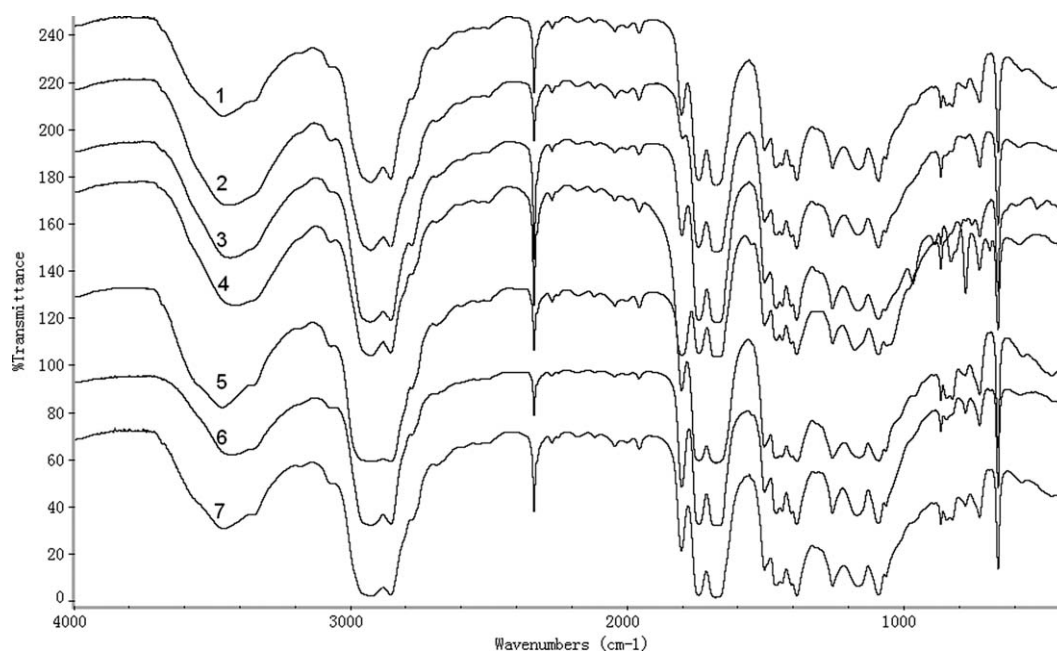
(PW), and H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (PMo) for CSBO synthesis by coupling of ESBO with CO<sub>2</sub> are listed in Table I. It is found that these bulk HPAs exhibited higher catalytic activity (>90% ESBO conversion in all instances). However, Figure 1 reveals that the intensity of characteristic absorption band of cyclic carbonyl group at 1805 cm<sup>-1</sup> was too weak to be observed, suggesting that these bulk HPAs did not promote the formation of CSBO.

To cope with the problem, the oxide supported PW was investigated as shown in Table II. It is clear that the type of support influenced the ESBO conversion significantly. The catalytic activity determined by chemical titration was in the sequence of PW/ZrO<sub>2</sub> > PW/SiO<sub>2</sub> > PW/V<sub>2</sub>O<sub>5</sub> > PW/Al<sub>2</sub>O<sub>3</sub> > PW/Nb<sub>2</sub>O<sub>5</sub> > PW/MgO > PW/In<sub>2</sub>O<sub>3</sub>.



**Figure 3** <sup>1</sup>H-NMR spectra of (1) ESBO and (2) CSBO.

Figure 2 shows that the effective transformation of ESBO into CSBO occurred over these catalysts, witnessed by the diminishing epoxy absorption at 845, 823 cm<sup>-1</sup>, and reinforcing carbonyl band at 1805 cm<sup>-1</sup>. It appears that the marriage of PW and the oxide better impel the reaction. The CSBO formation



**Figure 2** FTIR spectra of products acquired over various catalysts 1–5 wt % PW/In<sub>2</sub>O<sub>3</sub>; 2–5 wt % PW/SiO<sub>2</sub>; 3–5 wt % PW/V<sub>2</sub>O<sub>5</sub>; 4–5 wt % PW/ZrO<sub>2</sub>; 5–5 wt % PW/MgO; 6–5 wt % PW/Nb<sub>2</sub>O<sub>5</sub>; 7–5 wt % PW/Al<sub>2</sub>O<sub>3</sub>.

**TABLE III**  
Elemental Analysis of Isolated CSBO

Sample	Composition (wt %)			Formula
	C	H	O	
ESBO	71.5	11.2	17.2	C <sub>56.4</sub> H <sub>106</sub> O <sub>10.2</sub>
CSBO	65.9	9.8	24.2	C <sub>59.5</sub> H <sub>106</sub> O <sub>16.4</sub>

The calculation was based on ESBO having 3.8 epoxy groups per triglyceride molecule. ESBO conversion was 86.1%.

was also strongly dependent on the support used and was not exactly the same with the ESBO conversion. For example, 5% PW/SiO<sub>2</sub> having quite high ESBO conversion only exhibited low CSBO formation. Presumably, this catalyst may only facilitate the ring-opening of epoxy groups of ESBO. Among the catalysts tested, ZrO<sub>2</sub> bearing 5 wt % PW was the most active and selective to CSBO preparation. Therefore, it was chosen as a base for further study.

Distinct catalytic behavior of ZrO<sub>2</sub> supported PW from bulk PW could be related to their acid-base properties. A possible reaction mechanism is suggested as follows: for PW/ZrO<sub>2</sub>, strong acidic center originating from PW could promote its combination with oxygen of epoxy group in ESBO, yielding carbonium ion. On the other hand, quite a large number of strong basic sites created on the surface of ZrO<sub>2</sub> during calcinating PW/ZrO<sub>2</sub> at 300°C could benefit the adsorption and activation of CO<sub>2</sub>.<sup>22</sup> As a result, five-membered cyclic carbonate is easily produced through the interaction between activated CO<sub>2</sub> and neighbouring carbonium ion. The recombination of proton dissociated from hydroxyl group with (H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>)<sup>-</sup> gets the catalyst recovered. It appears that the synergic effect between acidic and basic site is prerequisite for successful synthesis of CSBO. As for the bulk PW, it only provides acidic centers and has no basic site for CO<sub>2</sub> activation. Therefore, poor CSBO formation is not surprising.

The transformation of ESBO to CSBO was also traced by <sup>1</sup>H-NMR spectroscopy. Figure 3 shows

**TABLE IV**  
Effect of PW Content on CSBO Preparation

PW content (wt %)	Reaction temperature (°C)	CO <sub>2</sub> pressure (MPa)	ESBO conversion (%)
0	150	1.0	21.4
3	150	1.0	82.7
5	150	1.0	86.1
7	150	1.0	84.3
10	150	1.0	73.6
15	150	1.0	61.1

Calcination treatment of catalyst and reaction time were identical with of Table I.

**TABLE V**  
Effect of Calcination Temperature of 5 wt % PW/ZrO<sub>2</sub> on CSBO Synthesis

Calcination temperature (°C)	Reaction temperature (°C)	CO <sub>2</sub> pressure (MPa)	ESBO conversion (%)
200	150	1.0	83.5
300	150	1.0	86.1
400	150	1.0	70.6
500	150	1.0	51.4

Reaction time: 20 hour.

that the original epoxy groups reduced after the reaction of ESBO with CO<sub>2</sub> over 5 wt % PW/ZrO<sub>2</sub> (ESBO conversion = 86.1%), while new cyclic carbonate groups emerged.

It was observed during the synthesis that the viscosity of CSBO product was acutely augmented to 15,400 cp/25°C from 418 cp/25°C of pristine ESBO. GPC analysis showed that the discrepancy in molecular weight (*M<sub>w</sub>*) of these two samples was unobvious (1282 vs. 935). Therefore, the increase of viscosity should mainly be ascribed to the enhanced intermolecular interaction caused by the formation of highly polar cyclic carbonate groups instead of the polymerization of ESBO.<sup>3,9</sup>

CSBO is composed of carbon, hydrogen, and oxygen. Analyzing the elemental content in isolated CSBO could provide useful information about the CO<sub>2</sub> combination with ESBO. Table III indicates that about 3.1 CO<sub>2</sub> molecules, on average, were incorporated into end product.

Previously, reaction temperature and CO<sub>2</sub> pressure for the synthesis have been optimized.<sup>3</sup> In this work, the other parameters with respect to PW/ZrO<sub>2</sub> catalyst were further examined. Table IV shows the effect of PW content on the synthesis of CSBO. As the PW content ascended from 3 to 5 wt %, ESBO conversion slightly increased from 82.7 to 86.1%. Further increasing PW content, ESBO conversion decreased drastically. Exorbitant PW may block the pores of ZrO<sub>2</sub>, thus reducing the catalyst activity.

Table V shows the effect of calcination temperature of 5 wt % PW/ZrO<sub>2</sub> on the synthesis. It is observed that ESBO conversion increased with

**TABLE VI**  
Effect of Reaction Time 5 wt % PW/ZrO<sub>2</sub> on CSBO Synthesis

Entry	Reaction time (hour)	Reaction temperature (°C)	CO <sub>2</sub> pressure (MPa)	ESBO conversion (%)
1	10	150	1.0	67.8
3	20	150	1.0	86.1
4	30	150	1.0	91.6
5	40	150	1.0	94.3

**TABLE VII**  
Reuse of 5 wt % PW/ZrO<sub>2</sub>

Regeneration method	Reaction temperature (°C)	CO <sub>2</sub> pressure (MPa)	ESBO conversion (%)
Fresh catalyst	150	1.0	91.6
Washed, spent catalyst <sup>a</sup>	150	1.0	35.5
Calcined, spent catalyst-300 <sup>b</sup>	150	1.0	45.7
Calcined, spent catalyst- 400 <sup>c</sup>	150	1.0	48.6

Reaction time: 30 hour.

<sup>a</sup> After first run, catalyst was washed by DMF.

<sup>b</sup> After first run, catalyst was washed by DMF and calcined at 300°C for 4 hour.

<sup>c</sup> After first run, catalyst was washed by DMF and calcined at 400°C for 4 hour.

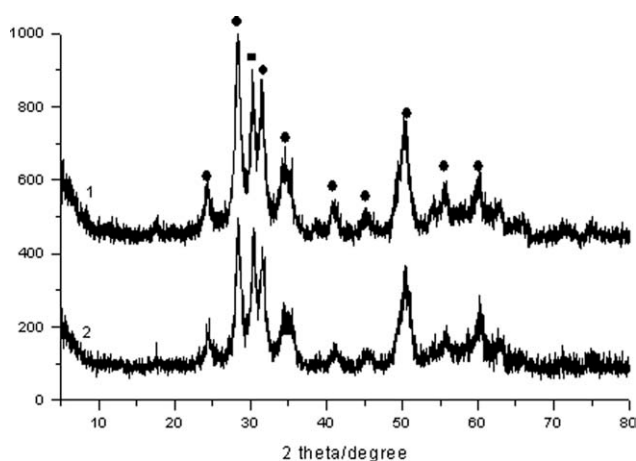
increasing calcination temperature up to 300°C and decreased thereafter.

Table VI shows the effect of reaction time on the formation of CSBO. On the whole, longer reaction time benefited the ESBO conversion. However, the conversion only increased slightly with the reaction time when it exceeded 30 hour. In view of practical application, reaction time of 30 hour is optimal.

In summary, reaction of ESBO and CO<sub>2</sub> over 5 wt % PW/ZrO<sub>2</sub> calcined at 300°C with reaction time of 30 hour are considered to be optimal conditions in terms of CSBO formation.

To check the stability and reusability of 5 wt % PW/ZrO<sub>2</sub>, regeneration tests using different methods were carried out as shown in Table VII. It is clear that simple washing or combination of washing and calcination treatment at different temperatures did not get the spent 5 wt % PW/ZrO<sub>2</sub> rejuvenated available.

The XRD patterns of the fresh and used 5 wt % PW/ZrO<sub>2</sub> are shown in Figure 4. The diffraction



**Figure 4** XRD patterns of the catalysts 1–5 wt % PW/ZrO<sub>2</sub> (fresh); 2–5 wt % PW/ZrO<sub>2</sub> (used) (●-tetragonal ZrO<sub>2</sub>; ■-monoclinic ZrO<sub>2</sub>).

**TABLE VIII**  
N<sub>2</sub> Adsorption and ICP-AES Results of the Catalysts

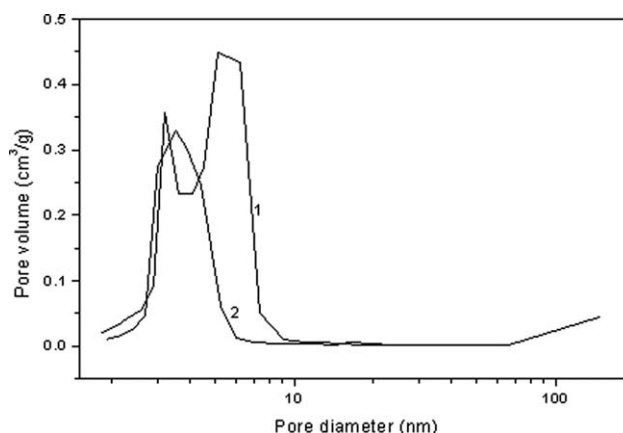
Catalyst	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	W/Zr ratio <sup>a</sup>
5 wt % PW/ZrO <sub>2</sub> (fresh)	100.28	0.143	5.25
5 wt % PW/ZrO <sub>2</sub> (used)	53.32	0.076	5.21

<sup>a</sup> The data were calculated based on ICP-AES measurement.

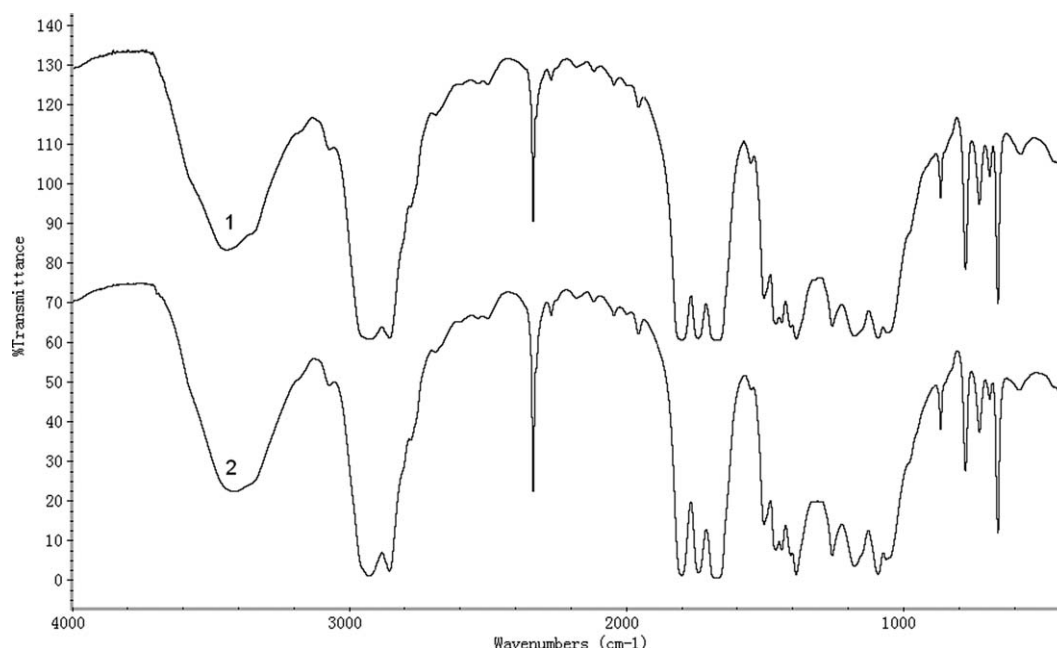
peaks at  $2\theta = 24.5, 28.3, 31.6, 34.2, 35.3, 40.7, 49.4, 50.1, 55.4,$  and  $60.2^\circ$  are due to the monoclinic form of ZrO<sub>2</sub>, while peak at  $30.8^\circ$  is assigned to the tetragonal phase of ZrO<sub>2</sub>.<sup>23,24</sup> The absence of PW diffraction peaks suggests that the active ingredient is highly dispersed on the ZrO<sub>2</sub>. There is no obvious difference between these two spectra, showing that the activity loss of the used catalyst should not be imputed to the structure alternation of the catalysts.

Elemental analysis of the catalysts by ICP-AES is listed in the fourth column of Table VIII. It is found that W/Zr ratio of the used 5 wt % PW/ZrO<sub>2</sub> is very close to that of the fresh one. This implies that the catalyst deactivation was not due to the leaching of PW during the reaction process. BET specific surface area and pore volume of the used catalyst were reduced by about 50%, compared with the fresh one. These might be attributed to the plugging of pores. It is also found from Figure 5 that smaller pores unfavorable for conversion of ESBO were predominated in the used catalyst.

It is deduced from above results that that the bulky by-products retained in the used catalyst may account for the performance degradation. A comprehensive analysis of the by-products and a study on their formation mechanism are underway. The catalyst deactivation caused by the surface coverage and the pore blockage with bulky molecular species has been reported in literatures.<sup>25–27</sup> For example, Wang



**Figure 5** Pore volume-pore diameter curves of catalysts 1–5 wt % PW/ZrO<sub>2</sub> (fresh); 2–5 wt % PW/ZrO<sub>2</sub> (used).



**Figure 6** IR spectra of products acquired over different catalysts 1–5 wt % PW/ZrO<sub>2</sub>; 2–0.3 wt % Pt–5 wt % PW/ZrO<sub>2</sub>.

et al. proposed that the deactivation of TS-1 catalyst for epoxidation of propylene was caused by such reasons. Unlike present work, the catalytic activity of the used catalyst could be mostly recovered by calcination and washing with dilute peroxide in their study.<sup>25</sup> This means that different catalyst systems may need dissimilar regeneration methods.

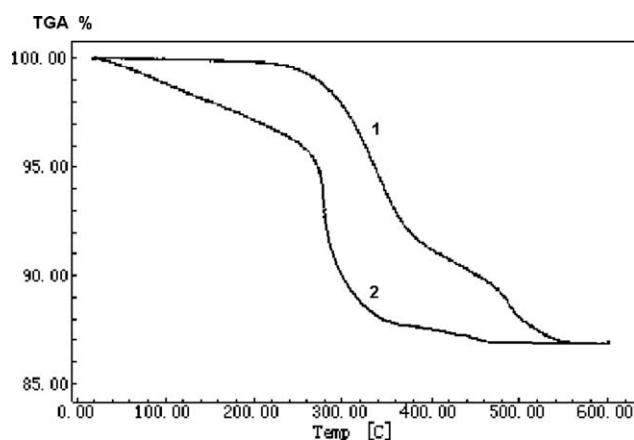
#### Performance of Pt modified 5 wt % PW/ZrO<sub>2</sub> catalyst

Because some by-products in the spent catalyst could hardly be removed by the existing methods, it is obligatory to search for a novel way to tackle the problem. It is reported that supported Pt catalysts could promote low temperature oxidation reactions.<sup>28,29</sup> The elimination of the bulky by-products

through Pt catalyzed oxidation may be viable and deserves investigation.

The incorporation of Pt component had no notable influence on the performance of 5 wt % H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. Under the same reaction conditions, ESBO conversion over 0.3 wt % Pt–5 wt % PW/ZrO<sub>2</sub> and Pt free, 5 wt % PW/ZrO<sub>2</sub> is almost identical (93.0% vs. 91.6%). Moreover, the results in Figure 6 reveal that the inherent function of 5 wt % PW/ZrO<sub>2</sub> to form CSBO did not change either.

The oxidation behaviors of Pt modified 5 wt % PW/ZrO<sub>2</sub> and unmodified one are shown in Figure 7. After first run, washing, and drying, the total weight loss of 5 wt % PW/ZrO<sub>2</sub> up to 530°C was 13.3% (curve 1). The whole oxidation was a staged process: the first stage corresponding to temperature ranging from 250 to 360°C was a fast weight drop process (about 8%). This may be ascribed to the oxidation of the residue on exterior surface of the catalyst. Second stage occurring at temperatures between 360 and 530°C could be attributed to the oxidation of residues penetrated into the inner

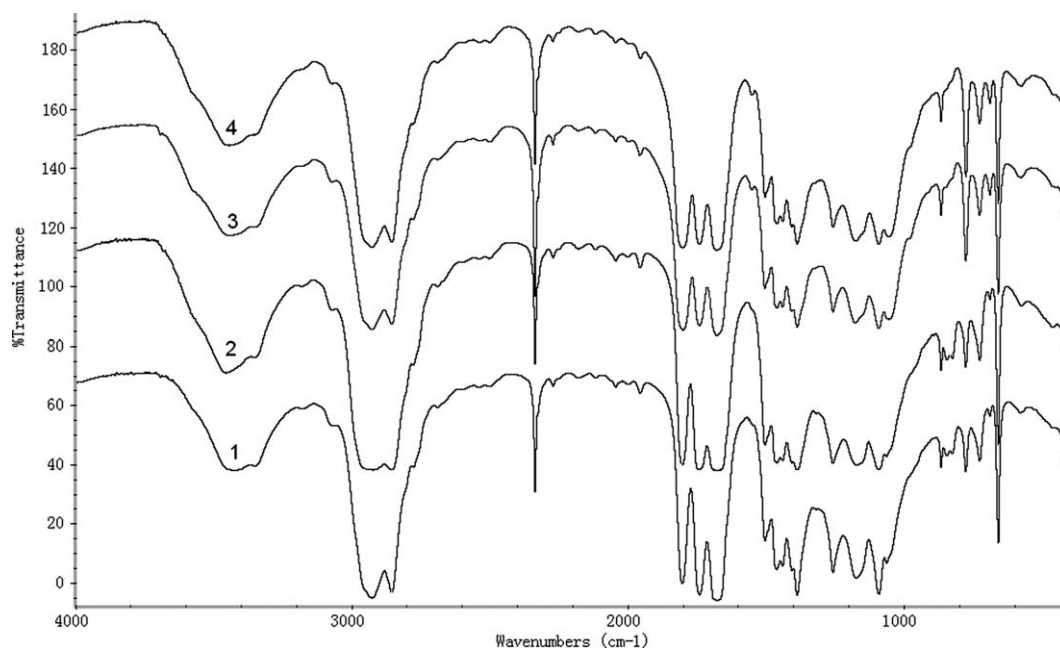


**Figure 7** TG curves of catalysts after first run (1) Used 5 wt % PW/ZrO<sub>2</sub>; (2) Used 0.3 wt % Pt–5 wt % PW/ZrO<sub>2</sub>.

**TABLE IX**  
Effect of Recycle Times on CSBO Synthesis

Entry	Recycle run	Reaction temperature (°C)	CO <sub>2</sub> pressure (MPa)	ESBO conversion (%)
1	Fresh catalyst	150	1.0	93.0
2	First recycle	150	1.0	83.2
3	Second recycle	150	1.0	80.4
4	Third recycle	150	1.0	78.3

Reaction time: 30 hour.



**Figure 8** IR spectra of products acquired over recycled 0.3 wt % Pt-5 wt % PW/ZrO<sub>2</sub> (1) Fresh catalyst; (2) First recycle run; (3) Second recycle run; (4) Third recycle run.

pore of catalyst (5% of weight loss). Since the Pt free 5 wt % PW/ZrO<sub>2</sub> has no ability to catalyze oxidation reaction, the combustion processes are noncatalytic ones and thus the complete oxidation requires higher temperature, which may result in the serious damage of catalyst performance. Compared with the pristine 5 wt % PW/ZrO<sub>2</sub>, the Pt-modified one exhibited quite strong oxidation ability. The oxidation began from ca. 50°C and the majority of residue was removed from the catalyst below 300°C (curve 2). The marked difference in these two cases should be related to the Pt participation. Such mild operation also held extra advantage, being nondestructive for the catalyst. It is reasonably to infer that isothermal treatment of used, Pt modified catalyst at 300°C for 4 hour could eliminate the residual by-products from catalyst basically. Therefore, the procedure was applied for reusability examination of 0.3 wt % Pt-5 wt % PW/ZrO<sub>2</sub>.

As shown in Table IX, after three runs, the modified catalyst still maintained a reasonable activity. ESBO conversion in the three runs was 83.2%, 80.4%, and 78.3%, respectively, showing pretty good reusability. Figure 8 backs the results above. According to our previous study, all these CSBO products could meet the requirement for producing NIPUs with high performance.<sup>3</sup>

## CONCLUSIONS

Although 5 wt % PW/ZrO<sub>2</sub> could well catalyze the CSBO synthesis by the reaction of ESBO with CO<sub>2</sub>,

the catalyst was incapable of being reused due to the difficulty in removing bulky by-products residue in the spent catalyst. A novel way to resolve the problem was proposed. Experimental results demonstrated that the incorporated Pt in 5 wt % PW/ZrO<sub>2</sub> could promote the removal of the by-products and protect the active centres of 5 wt % PW/ZrO<sub>2</sub>, which are essential for the consecutive carbonation of ESBO. Present work provides valuable information on preparation of heterogeneous, recyclable catalyst for the practical production of CSBO.

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