The direct reaction between CO_2 and phenol catalyzed by bifunctional catalyst ZrO_2

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Abstract

The systematic investigation was carried out to elucidate the direct reaction between CO_2 and phenol over multiphase catalyst. Reactions carried out over ZrO_2, TiO_2, and KF/NaY + Mn^{2+} gave the high selectivity to 4-[4-hydroxybenzyl]phenol and 2-[2-hydroxybenzyl]phenol (HBP), and the maximum HBP selectivity of 68% was obtained with ZrO_2 as catalyst. XRD patterns showed that metastable tetragonal ZrO_2 was the active phase for HBP synthesis, and the bidentate carbonate on ZrO_2 surface was responsible for high HBP selectivity. If Hbeta, HZSM-5, and Al_2O_3 were used as catalyst, the main product was diphenyl ether (DPE). But when reactions were catalyzed by KY and KF/NaY, xanthone became the main product; however, xanthone disappeared when KF/NaY coexisted with $Mn(OCOCH_3)_2$ as catalyst. The optimized reaction conditions for HBP synthesis over tetragonal ZrO_2 are 350 °C, 12 h, and 4.0 MPa CO_2 pressure.
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1. Introduction

Carbon dioxide is an attractive C_1 building block in organic synthesis as it is highly functional, abundant, inexpensive, non-toxic, and nonflammable. As petroleum reserves are depleted, the development of efficient catalytic processes employing CO_2 as a feedstock has become increasingly important as evidenced by the intense research in this area in recent years [1]. For example, it has been shown that using CO_2 as reactant one can generate formic acid [2], dimethyl formamide [3], formic acid [4,5], methanol [6], dialkyl carbonate [7], urea, carbamate [8,9], copolymer, cyclic carbonate [10], and salicylic acid [11]. Among the above mentioned researches, the synthesis of salicylic acid from phenoxide (Na or K) and carbon dioxide through Kolbe–Schmitt method has been practiced commercially for more than one century [12]; however, no studies on the direct reaction between phenol and CO_2 under supercritical conditions were carried out until now. The reaction between phenol and CO_2 might provide a new application of phenol and CO_2 in organic synthesis just like the synthesis of dimethyl carbon-

ate from methanol and CO_2 [13,14]. Furthermore, the reaction between phenol and CO_2 might also provide a new method for the treatment of organic pollutant phenol [15].

In the catalytic reactions of carbon dioxide, ZrO_2 is widely used as active catalyst for hydrogenation of carbon dioxide and carbon oxide. Previous studies [16–18] indicated that CO_2 reacted with amorphous ZrO_2 to give HCO_3^- which largely disappeared as temperature increased to 400 °C. When tetragonal ZrO_2 reacted with CO_2 at 25 °C, CO_3^{2-} and HCO_3^- ions were formed, and bidentate carbonate became the main species after reaction temperature increased to 400 °C. If monoclinic ZrO_2 reacted with CO_2 at 400 °C, a large amount of unidentate carbonate existed on the zirconia surface in addition to bidentate carbonate. The formation of bidentate and unidentate carbonate was due to coordinative unsaturated Zr^{4+}–O^{2-} pairs which was detected by the temperature-programmed desorption (TPD) experiment [18,19]. Modes of the phenol adsorption on ZrO_2 surface are non-planar and co-planar to the surface [20] and are governed by acid–base properties of ZrO_2 [21,22].

Phenol and CO_2 could compete for adsorption on the ZrO_2 surface or reaction with ZrO_2, since both phenol and CO_2 are acids. If phenol adsorbs onto ZrO_2, non-planar or co-planar phenoxide will be formed which might further react with CO_2 to give salicylate, phenyl salicylate, or other derivatives

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through the Kolbe–Schmitt reaction. If CO_2 adsorbs onto ZrO_2, bidentate carbonate and unidentate carbonate will be formed at higher temperature, which might stop the Kolbe–Schmitt reaction and result in new products.

Here, studies were carried out on the reaction between CO_2 and phenol under supercritical conditions. Among the catalyst screened, ZrO_2 is the best catalyst for this reaction. At the same time, effects of ZrO_2 phase, reaction temperature, reaction duration, and CO_2 pressure were investigated.

2. Experimental

2.1. Catalyst preparation

The preparation of zirconia by the hydrolysis of zirconium chloride with excess of NH_4OH has been described previously [23]. A 10% solution of zirconium chloride was slowly added to a well-stirred precipitating solution of NH_4OH (5 M, *ca.* 50% excess base) at room temperature. After the addition of all the zirconium chloride, the base concentration was 0.55 M. The precipitate was placed in a round-bottomed pyrex flask and refluxed at 100 °C in the supernatant liquid for 48 h. The precipitate was filtered and dried at 80 °C for 6 h. Pure ZrO_2 was obtained and activated at certain temperature (400 °C) for 3 h before use.

TiO_2 was synthesized according to an earlier paper [24]. Titanium chloride ($TiCl_4$) was dissolved in deionized water. Then, titanium hydroxide was precipitated from $TiCl_4$ solution by adding ammonium hydroxide until pH 8.0. The precipitate was filtered and washed with distilled water until complete elimination of chlorine ions in the liquid phase. The precipitate was filtered and dried at 80 °C for 6 h. Pure TiO_2 was obtained and activated at 550 °C for 3 h before use.

Commercial Hbeta (Si/Al = 30) and HZSM-5 (Si/Al = 50) were purchased from Nankai University. $γ$-Al_2O_3 was obtained from Shan Xi Commodity Chemistry Institute and NaY was purchased from QiLu Corporation. KY was obtained by exchange of NaY with a KCl solution (1 mol L^{-1}) for three times. KF/NaY (10 wt.%) was prepared by impregnation. Hbeta, HZSM-5, $γ$-Al_2O_3, KY, and KF/NaY were activated at 550 °C in air for 3 h before use.

2.2. Synthesis procedure

A definite quantity of catalyst and phenol were placed in an autoclave of 250 ml (inner volume). The autoclave was then sealed and flushed with CO_2 to remove the air. After that, the CO_2 was pressurized in the autoclave to a given pressure and the autoclave was heated to a given temperature. After reaction, the autoclave was cooled down to room temperature. The contents was diluted with THF and discharged to separate the catalyst by the simple filtration.

2.3. Analysis

The structure of the products was confirmed by GC–MS (HP5972) (capillary column: 30 m SE-30, 0.25 mm i.d., and 0.25 μm film thickness) and compared with authentical samples.

Quantitative analysis was carried out on a gas chromatograph (Shimadzu GC-14B with a FID detector, DB-1 capillary column) with cetane as interior standard.

Powder X-ray diffraction (XRD) pattern characterization of the catalyst samples was measured on a Bruker AXS (Germany) diffractometer using Cu K$α$ radiation. The data were recorded from 20° to 70° (2$θ$).

N_2 adsorption–desorption isotherms of the mesoporous ZrO_2 samples were measured at 77 K on a micromeritics Tristar 3000 sorptometer (Micromeritics Instrument Corporation, USA). Prior to the measurement, all samples were outgassed at 473 K and 1.33×10^{-4} Pa over night. The specific surface areas of the mesoporous samples were calculated by the BET method. The pore size distribution of the samples was determined from the adsorption branch of the isotherms using the BJH method, and the pore size was obtained from the peak position of the distribution curves.

3. Results and discussion

3.1. Effect of catalyst on the product distribution

The reaction results are listed in Table 1. The product distribution was greatly affected by the use of the catalyst (see Scheme 1).

When Hbeta, HZSM-5, and $γ$-Al_2O_3 were used as catalyst, the main products were DPE and HBP. In addition, a trace of *ortho*- or *para*-phenyl phenol, bis(4-hydroxyphenyl)methanone, bis(2-hydroxyphenyl)methanone, salicylic acid, *para*-hydroxyl benzoic acid, phenyl salicylate, and phenyl 4-hydroxy benzoate were detected. If KY and KF/NaY were used as catalyst, xanthone was found as the main product. For example, xanthone selectivity was 64 and 46% with KY and KF/NaY as catalyst, respectively. However, xanthone disappeared and HBP became the main product when KF/NaY coexisted with Mn $(OOCCH_3)_2$ as catalyst. When ZrO_2, TiO_2, and KF/NaY + Mn^{2+} were used as catalyst, the high selectivity to HBP was obtained, and ZrO_2 was the best catalysts for HBP formation of 67%.

Table 1
The activity of various catalysts for the reaction between carbon dioxide and phenol

Catalysts	Product distribution (mol%)				Yield (%) (HBP)
	DPE	HBP	Xanthone	Others	
Hβ	69	16	–	15	5.2
HZSM-5	65	28	–	8	5.9
$γ$-Al_2O_3	40	23	–	37	3.9
ZrO_2	11	68	10	12	4.7
TiO_2	9	36	15	41	2.9
KY	14	9	64	12	0.8
KF/NaY	19	29	37	15	2.4
KF/NaY + Mn^{2+}	8	60	–	25	6.3

Reaction condition: phenol, 0.2 mol; catalyst, 3 g (activated at 550 °C for 3 h); P_{CO_2}, 5.0 MPa; temperature, 400 °C; time, 6 h. DPE: diphenyl ether; HBP: 2-(2-hydroxybenzyl)phenol and 4-(4-hydroxybenzyl)phenol. Others include little of *ortho*- or *para*-phenyl phenol (PPH), bis(4-hydroxyphenyl)methanone, bis(2-hydroxyphenyl)methanone, salicylic acid, *para*-hydroxyl benzoic acid (PHBA), phenyl salicylate (PS), phenyl 4-hydroxy benzoate (PHB), and xanthene.

Scheme 1. The reaction between CO_2 and phenol.
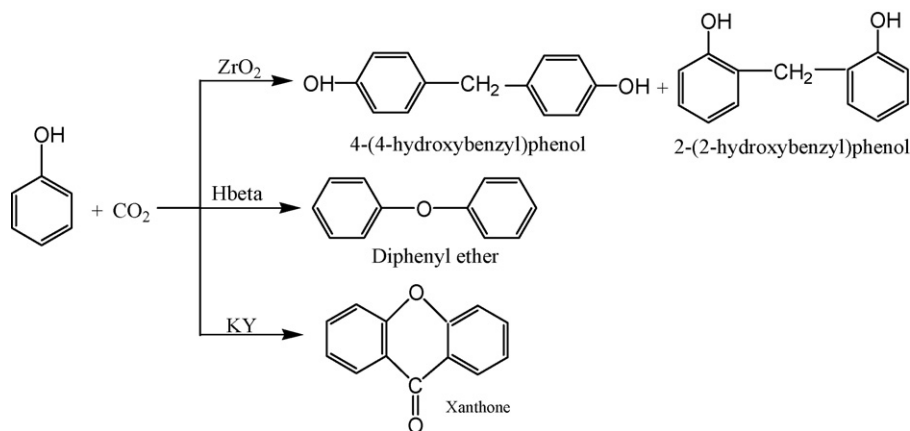
3.2. Effect of ZrO_2 morphology

ZrO_2 was activated at 200, 300, 400, 500, and 600 °C for 3 h. XRD patterns of ZrO_2 are shown in Fig. 1. When ZrO_2 was calcined at 200 and 300 °C, the morphology of ZrO_2 was amorphous. Both monoclinic and tetragonal phases were observed in the ZrO_2 calcined at 500 and 600 °C, and monoclinic phase became the main component. But only tetragonal phase was found in the ZrO_2 calcined at 400 °C.

The textural and physical properties of the samples are summarized in Table 2. The elevating of calcination temperature led to a continuous decrease of the specific surface area and the cumulative pore volume, while pore diameter increased from 6.3 to 12.2 nm.

Reactions catalyzed by ZrO_2 were carried out, and results are listed in Fig. 2. When amorphous ZrO_2 calcined at 200 and 300 °C was used as catalyst, HBP selectivity was 29 and 31%. The by-products including DPE, phenyl phenol, phenyl salicylate, xanthone, and xanthene were found. When tetragonal ZrO_2 calcined at 400 °C was used as catalyst, HBP selectivity

Table 2
The texture properties of ZrO_2

ZrO_2	BET surface $(m^2 g^{-1})$	Total pore volume $(cm^3 g^{-1})$	Pore diameter (nm)
200	368	0.47	6.3
300	284	0.42	6.4
400	173	0.36	7.5
500	99	0.33	8.9
600	73	0.33	12.2

was 45%. While ZrO_2 calcined at 500 and 600 °C were used as catalyst, HBP selectivity declined to 24 and 20%, but DPE selectivity increased to 5 and 19%. In addition, the others including xanthone and phenyl salicylate increased to 58 and 35%. Those results indicated that the most active phase for HBP formation was metastable tetragonal, while the BET surface and pore diameter were not the determined factor in HBP formation.

Previous study [15] indicated that CO_2 reacted with amorphous ZrO_2 at 25 °C to give HCO_3^- which largely disappeared
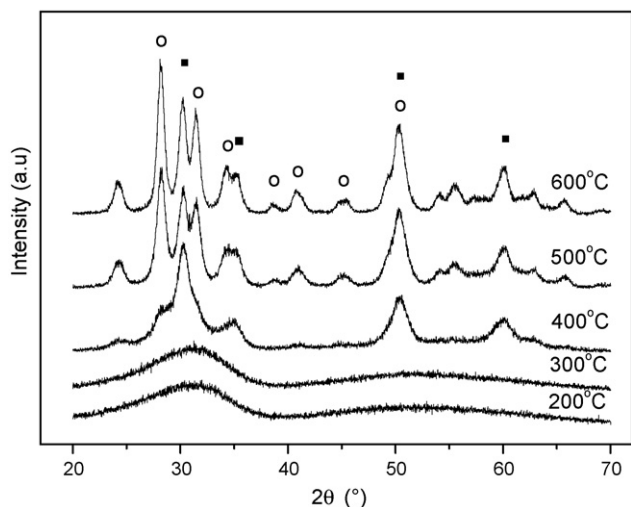

Fig. 1. XRD patterns of ZrO_2 calcined at different temperature. Crystal structure: metastable tetragonal (■); monoclinic (○).
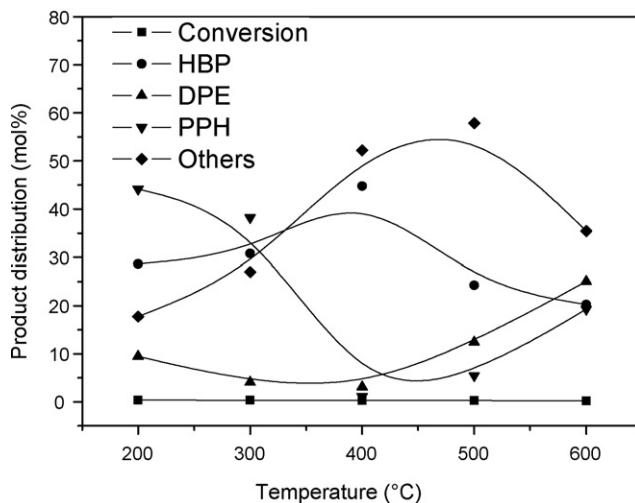

Fig. 2. Effect of ZrO_2 phase on the reaction between phenol and CO_2 (reaction condition: ZrO_2, 2 g; phenol, 0.1 mol; P_{CO_2}, 4.0 MPa; reaction temperature, 350 °C; reaction time, 3 h).

as temperature increased to 400 °C. The tetragonal ZrO_2 reacted with CO_2 at 25 °C to produce two principal CO_3^{2-} and HCO_3^- ions. After temperature increased to 400 °C, bidentate carbonate became the main species. When monoclinic ZrO_2 reacted with CO_2 at 400 °C, a large amount of unidentate carbonate existed on the zirconia surface in addition to bidentate carbonate. According to above described results, the conclusion could be drawn that the formation of HBP might be relevant with bidentate carbonate.

$Zr^{4+}O^{2-}$ Lewis acid/base pairs [25,26] might serve as active centers for the synthesis of HPB from phenol and carbon dioxide over zirconia. The formation of bidentate carbonate required an acid–base pair center associated with an anionic vacancy which would generate electron-rich zirconium cations [17]. As for amorphous ZrO_2, there were less anionic vacancy and acid–base pair centers on the surface of ZrO_2. The scarcity of bidentate carbonate on surface of amorphous zirconia might result in less HBP formation. Monoclinic ZrO_2 had the strong Lewis acidity and Lewis basicity, which were investigated by the temperature-programmed desorption (TPD) experiment [18,19]. Lewis acid site Zr^{4+} is responsible for DPE formation from phenol, while O^{2-} promotes the Kolbe–Schmitt reaction between phenol and CO_2 into phenyl salicylate and xanthone.

3.3. Effect of temperature

Reactions were carried out at different temperature and results are shown in Fig. 3. The reaction was hardly observed at 300 °C because of the inert property of CO_2. When reaction was carried out at 350 °C, the highest HBP selectivity of 90% was achieved and the conversion of phenol amounted to 1.4%. After the reaction temperature increased to 400 °C, much more coke, xanthene, xanthone, bis(2-hydroxyphenyl)methanone, and bis(4-hydroxyphenyl)methanone produced. In addition, the methylation of phenol detected at 400 °C was due to the reaction among CO_2, phenol and hydrogen. The hydrogen came from the thermolysis of phenol [27].

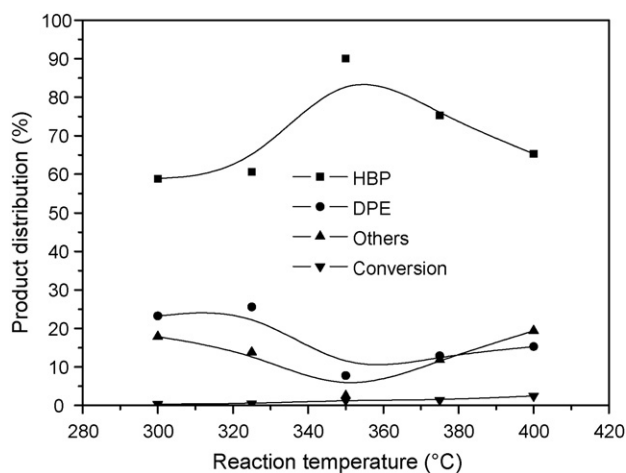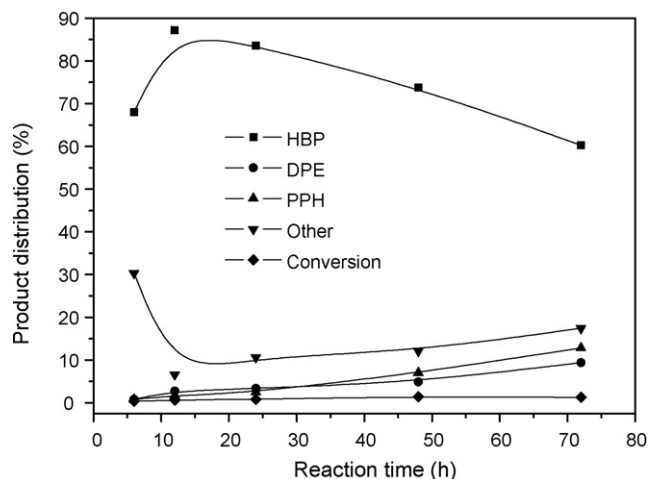Fig. 4. Effect of time on the reaction between phenol and CO_2 under supercritical condition (reaction condition: phenol, 4.7 g; metastable tetragonal ZrO_2, 0.5 g; temperature, 350 °C; P_{CO_2}, 5.0 MPa).

3.4. Effect of duration

Effect of reaction duration on the reaction between CO_2 and phenol at 350 °C was investigated and the results are listed in Fig. 4. As the reaction time extended, both the selectivity to HBP and the conversion of phenol increased. The optimized reaction time for HBP synthesis was 12 h, and HBP selectivity amounted to 87%. When reaction time exceeded to 12 h, the selectivity to HBP declined due to ZrO_2 lost activity from coke.

3.5. Effect of CO_2 pressure

The effects of CO_2 pressure on reaction are listed in Fig. 5. When reactions were carried out at low CO_2 pressure, HBP was difficult to be synthesized while DPE was the main production. In addition, by-products including *ortho-*, *para*-phenyl phenol and benzofuranl were detected. After CO_2 pressure increased
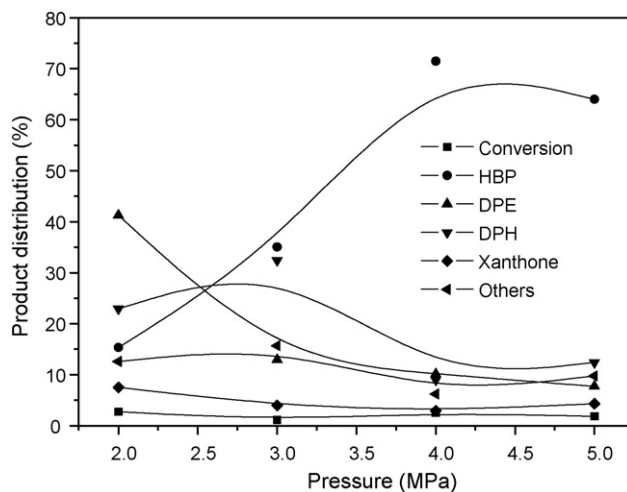
Fig. 3. Effect of temperature on the reaction between phenol and CO_2 over ZrO_2 (reaction condition: phenol, 4.7 g; metastable tetragonal ZrO_2, 0.5 g; P_{CO_2}, 5.0 MPa; reaction time, 4 h).

Fig. 5. Effect of CO_2 pressure on the reaction between phenol and CO_2 (reaction condition: phenol, 4.7 g; metastable tetragonal ZrO_2, 0.5 g; reaction temperature, 350 °C; reaction time, 4 h).

to 4.0 MPa, HBP selectivity achieved maximum of 72%. But when CO_2 amounted to 5.0 MPa, the selectivity to HBP declined, which was contrary to our primary expectation. High HBP selectivity was obtained at 4 MPa due to the following reasons: first, high CO_2 pressure was in favor of the formation of bidentate carbonate species; secondly, high density of CO_2 facilitated the removal of compounds from the catalyst surface to keep catalyst from being deactivated. The reason for the decline of HBP selectivity at 5 MPa might be that ZrO_2 surface was occupied by CO_2 molecule which kept phenol from reaction.

4. Conclusion

In the reaction between phenol and CO_2 under supercritical conditions, high HBP selectivity was achieved with ZrO_2, TiO_2 and KF/Ac + Mn^{2+} as catalysts, which might be ascribed to their bifunctional sites. If Hbeta, HZSM-5, and Al_2O_3 were used as catalyst, reactions gave a large amount of DPE. But when alkali KY and KF/NaY were used as catalyst, xanthone becomes the major compound because alkali site promotes reaction to adopt the Kolbe–Schmitt reaction.

The high HBP selectivity was achieved over ZrO_2, and metastable tetragonal ZrO_2 was suggested to be active. The high HBP selectivity achieved over tetragonal ZrO_2 may be relevant with bidentate carbonate on the surface of ZrO_2. The optimized reaction conditions for HBP synthesis over tetragonal ZrO_2 are 350 °C, 12 h, and 4.0 MPa for reaction temperature, duration, and CO_2 pressure, respectively.

Acknowledgment

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