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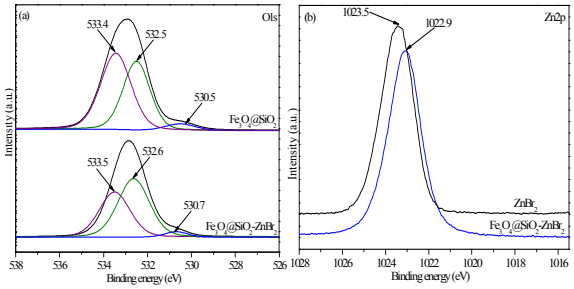

$ZnBr_2$ supported on SiO_2-coated Fe_3O_4 was developed as an effective and recyclable catalyst for diphenyl carbonate synthesis from CO_2.

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$ZnBr_2$ supported on silica-coated magnetic nanoparticles Fe_3O_4 for conversion of CO_2 to diphenyl carbonate

Guozhi Fan*, Shanshan Luo, Qiang Wu, Tao Fang, Jianfen Li and Guangsen Song

Magnetic Fe_3O_4@SiO_2-$ZnBr_2$ catalyst was prepared by supporting $ZnBr_2$ on silica-coated magnetic nanoparticles Fe_3O_4 and used as a recoverable catalyst for the direct synthesis of diphenyl carbonate (DPC) from CO_2 and phenol in the presence of carbon tetrachloride. The as-prepared catalyst was characterized by infrared spectroscopy (IR), powder X-ray diffraction (XRD), X-ray photoelectron spectrometer (XPS) and BET. Zn loading in supported catalyst and leaching during the reaction process were determined by atomic absorption spectroscopy (AAS). It was found that Fe_3O_4@SiO_2-$ZnBr_2$ showed higher catalytic activity than that of homogenous $ZnCl_2$ and ZnI_2 as well as homogenous $ZnBr_2$. With this new catalyst under optimized conditions, yield of DPC at 28.1% was obtained. The heterogeneous catalyst Fe_3O_4@SiO_2-$ZnBr_2$ can also be recovered by a permanent magnet after the reaction and reused for up to 4 times without noticeable deactivation.

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Introduction

Global warming is a concern due to the emission of greenhouse gases. It is known that CO_2 is the main cause of global warming because of overuse of petroleum, coal and natural gas. CO_2 is also regarded as a stable, safe and abundant C1 resource since it is nontoxic and available. The transformation of CO_2 to value-added chemicals is promising in organic synthesis from the chemical viewpoint.[1] In recent decades, much attention has been particularly paid to the chemical fixation of CO_2.[2–5] Direct synthesis of cyclic compounds, including cyclic carbonates, cyclic carbamates and cyclic ureas from CO_2 is an alternative way of using CO_2 as a resource. From the environmental and practical viewpoints, this alternative way can avoid using toxic and hazardous reagents such as phosgene. Many compounds including hydrogen, alkenes, acetals, epoxides, amines, phenol, etc. have been explored to react with CO_2 in the presence of metal catalysts.[6–14]

CO_2 is a highly oxidized and thermodynamically stable compound with low chemical reactivity which restricts the chemical conversion of CO_2, leading to significant challenges in using CO_2 as C1 feedstock. Therefore, the effort to convert CO_2 to useful chemicals is inevitably dependent on its activation via catalysts.[15] Although many homogenous catalysts such as salen-complex, metal oxide and Lewis acid have been employed in the reactions with CO_2 involved,[6-14] these catalysts often suffer from difficulty of separation. So far heterogeneous catalytic systems have been thought to be one of the most efficient ways to overcome these problems.[16,17] Heterogenization is generally achieved by grafting the active sites on solid materials such as inorganic particles, polymers and hybrid materials. Silica,[18] alumina,[19] active carbon,[20,21] ceria,[22] polystyrene[23] and polyvinylpyrrolidone[24] are typical examples. Recently magnetic nanoparticles Fe_3O_4 (MNPs-Fe_3O_4) has attracted much attention due to their convenient isolation and recovery.[16,17,25] It has been reported that the heterogeneous catalysts supported

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on MNPs-Fe_3O_4 reveal excellent performance in many reactions including hydrolysis, hydrogenation, oxidation, carbon-carbon coupling and reduction.[16,17] For example, ionic liquid-coated MNPs-Fe_3O_4 catalyst used in the reaction of CO_2 with epoxides could be reused up to 11 times without obvious activity loss.[26]

One of the most promising green reactions with CO_2 involved is to produce carbonates.[27] Many investigators have used CO_2 to couple with epoxide due to the atom economical process and nearly no by-product formation.[28,29] Diphenyl carbonate (DPC), an important carbonate and precursor of polycarbonate, is traditionally synthesized from phosgene (extremely toxic) and phenol. Since the process creates severe environmental pollution and equipment corrosion,[30] it is necessary to find an alternative process.[31] We previously reported the study on production of DPC from CO_2, phenol and tetrachloride carbon (CCl_4) catalyzed by $ZnCl_2$ alone and $ZnCl_2$/trifluoromethanesulfonic acid (CF_3SO_3H).[32–34] However, the process still showed the problems including requiring a large amount of catalyst and difficulty of recovering catalyst. Therefore, there is a need to explore an efficient and effective catalyst for direct synthesis of DPC from CO_2.

In this study, zinc halides including $ZnCl_2$, $ZnBr_2$ and ZnI_2 were supported on silica-coated MNPs-Fe_3O_4 (SiO_2@Fe_3O_4) and employed as catalysts for direct synthesis of valuable DPC from CO_2 and phenol in the presence of CCl_4. The catalytic performance of the magnetic supported catalysts was investigated, and the catalytic activity of heterogenized and homologous zinc halide was compared. The effects of active species, catalyst loading, amount of catalyst, reaction conditions including CO_2 pressure, reaction temperature and time were investigated as well. The reusability of Fe_3O_4@SiO_2-$ZnBr_2$ was also examined under the optimized reaction conditions.

Experimental

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Preparation of supported catalyst

In a typical experiment, 2.0 g MNPs-Fe_3O_4 (Supplied by Aladdin Co. Ltd., Shanghai, China) was added to a mixture solvent of ethanol and H_2O (70 mL/10 mL). After the mixture was dispersed by sonication for 20 min, 5 mL NH_3•H_2O and 5.0 mL tetraethoxysilane (TEOS) were slowly added. The mixture was vigorously stirred at 1200 rpm at room temperature for 24 h. The formed magnetic Fe_3O_4@SiO_2 was collected with a permanent magnet, rinsed repeatedly with deionized water until the filter became neutral, washed with ethanol and dried at 80 ^oC under vacuum for 12 h.[35]

Preparation of $ZnBr_2$ supported on Fe_3O_4@SiO_2

Typically, after 1.0 g Fe_3O_4@SiO_2 was added to a solution of 1.1 g $ZnBr_2$ (4.9 mmol) in 20 mL methanol, the mixture was heated under reflux for 3 h.[36] The formed Fe_3O_4@SiO_2-$ZnBr_2$ was collected with a permanent magnet and dried at 150 ^oC under vacuum for 10 h. The supported catalyst with particle size below 75 μm was collected by passing through a 200 mesh Tyler screen. The Zn loading was determined by atomic absorption spectroscopy (AAS).

Catalytic test

Typically, 12 mmol phenol, 40 mmol CCl_4 and as-prepared Fe_3O_4@SiO_2-$ZnBr_2$ (containing 1.2 mmol $ZnBr_2$) were charged into a 100 mL stainless steel autoclave. The autoclave was sealed and flushed with 2 MPa CO_2 three times to wash out the air in it. After the mixture was heated to the desired reaction temperature with stirring at 1200 rpm, CO_2 was then introduced into the autoclave to the desired pressure using a high-pressure pump. After a certain reaction time, the autoclave was cooled to room temperature and the pressure was gradually released. The mixture was centrifuged after the addition of 10 mL ethanol, followed by quantitatively analysis by gas chromatography (GC) using

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biphenyl as internal standard. The formation of DPC was also qualitatively identified by gas chromatography mass spectrometry (GC-MS).

Determination of conversion, yield and selectivity

All reactions were performed in triplicate. The conversion of phenol, the yield as well as the selectivity towards DPC were determined by averaging three reaction runs based on the charged phenol. The conversion, yield and selectivity were calculated according to the following equations, respectively:

$$\text{Conversion (\%)} = \frac{m_{\text{phenol}}}{m} \times 100\%$$

$$\text{Yield (\%)} = \frac{m_{\text{DPC}}}{\frac{m}{2 \times 94} \times 214} \times 100\%$$

$$\text{Selectivity (\%)} = \frac{\text{Yield}}{\text{Conversion}} \times 100\%$$

Where m is the mass of phenol taken for the reaction; m_{phenol} and m_{DPC} are the mass of phenol and DPC remained and detected in the reaction mixture; 94 and 214 are the molecular weights (in g mol^{-1}) of phenol and DPC, respectively.

Reuse of recovered catalyst

The residue containing Fe_3O_4@SiO_2-$ZnBr_2$ was collected by centrifugation after the reaction, followed by collecting with a permanent magnet after the addition of 10 mL dichloromethane (CH_2Cl_2), washing three times with CH_2Cl_2 (5 mL × 3) and drying at 150 ^oC under vacuum. After the Zn loading was detected by AAS, the recovered catalyst was reused in the next run without further pretreatment.

Measurements

Infrared spectroscopy (IR) was measured on an EQUINOX 55 spectrometer in the range from 4000 to

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500 cm^{-1} with resolution of 3.875 $cm^{-1}$and scan number of 32. The solid samples were ground with dried KBr powder, and compressed into a disc prior to analysis. Powder X-ray diffraction (XRD) measurements were performed on a D/MAX-RB RU–200BRU–200B diffractometer with Cu Kα radiation at 40 kV and 40 mA in the range of 2θ from 10 to 80° with scanning rate of 5° min^{-1}, respectively. The specific surface area of the sample was determined by nitrogen adsorption-desorption isotherm at 77 K using the one-point modified BET method on a Gemini 2360 analyzer. XPS were recorded on a Kratos XSAM800 spectrometer with Mg Kα radiation (1253.6 eV) operated at 12 kV and 10 mA. The energy scale was calibrated and corrected using the C1s (284.8 eV) line as the binding energy reference. The Zn loading of either fresh or leached catalyst from the reaction was determined by AAS with a Perkin-Elemer Analyst 300 using acetylene flame. The conversion of phenol, the yield and the selectivity towards DPC were analyzed using GC2020 gas chromatograph with HP-5 capillary column (30 m × 0.32 mm × 0.25 μm, 5% phenyl methyl-siloxane) and flame ionization detector (FID). GC-MS analysis was performed using Agilent 7890A/5975C GC equipped with HP-5 capillary column and EI source. The detection was performed in the scan mode from m/z 20 to 400. 1.0 mL min^{-1} helium was used as the carrier gas. The ionization voltage and source temperature were 70 eV and 230 ℃, respectively.

Results and discussion

Characterization of catalyst

Fig. 1 shows the IR spectra of SiO_2, Fe_3O_4, Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2-$ZnBr_2$ with 15.1 wt% Zn loading. The band at 3448 cm^{-1} is assigned to the symmetrical stretching vibration of hydroxyl groups (–OHs). The band at 1628 cm^{-1} is attributed to the bending vibration of adsorbed water.[35] The bands at

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1090 and 795 cm^{-1} in the IR spectra of SiO_2, Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2-$ZnBr_2$ are related to the asymmetric stretching vibration and symmetric stretching vibration of Si-O-Si, respectively.[37] The band at 960 cm^{-1} is assigned to symmetric stretching vibration of Si–OH.[35] In addition, the band at 565 cm^{-1} is attributed to the vibration of Fe-O bond.[38] It can be concluded from Fig. 1 that Fe_3O_4 is coated with silica because all the characteristic bands related to SiO_2 as well as Fe_3O_4 are shown in the spectrum of Fe_3O_4@SiO_2.

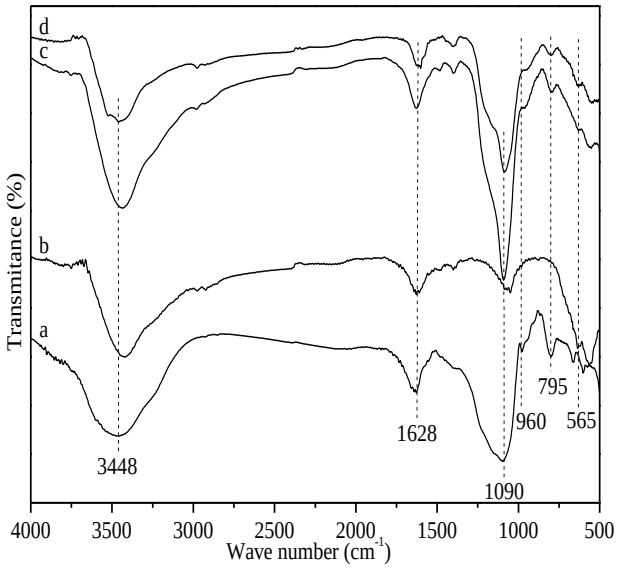

Fig. 1 IR spectra of (a) SiO_2 (b) Fe_3O_4, (c) Fe_3O_4@SiO_2 and (d) Fe_3O_4@SiO_2-$ZnBr_2$.

Fig. 2 shows the XRD patterns of SiO_2, $ZnBr_2$ (JCPDS: 75-1331), Fe_3O_4, Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2-$ZnBr_2$ with 15.1 wt% Zn loading. Only one wide and weak dispersion peak at 23.2° ascribed to the amorphous structure is observed in the pattern of pure SiO_2 (Fig. 2a). The peaks at 13.7°, 21.1°, 27.5°, 46.1° and 53.4° (Fig. 2b) are related to the characteristic diffraction of $ZnBr_2$. The peaks at 30.4°, 35.6°, 43.3°, 53.7°, 57.1° and 62.8° in the pattern of Fe_3O_4 (Fig. 2c) are associated with Miller indices values [hkl] of [220], [311], [400], [422], [511] and [440], respectively. These peaks are assigned to the inverse cubic spinel structure of Fe_3O_4.[39] All the characteristic diffraction peaks related

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to Fe_3O_4 also present in the pattern of Fe_3O_4@SiO_2 (Fig. 2d), indicating almost no change occurs in the structure of Fe_3O_4 after coating by SiO_2. Peaks assigned to the typical diffraction of $ZnBr_2$ are observed at 13.7°, 21.1°, 27.4°, 46.0° and 53.5° in the pattern of Fe_3O_4@SiO_2-$ZnBr_2$ (Fig. 2e). In addition, the characteristic diffraction peaks of Fe_3O_4 in the pattern of Fe_3O_4@SiO_2-$ZnBr_2$ become weaker than those observed in the patterns of Fe_3O_4 and Fe_3O_4@SiO_2, indicating that the cubic spinel structure of Fe_3O_4 could be slightly affected by introduction of $ZnBr_2$.

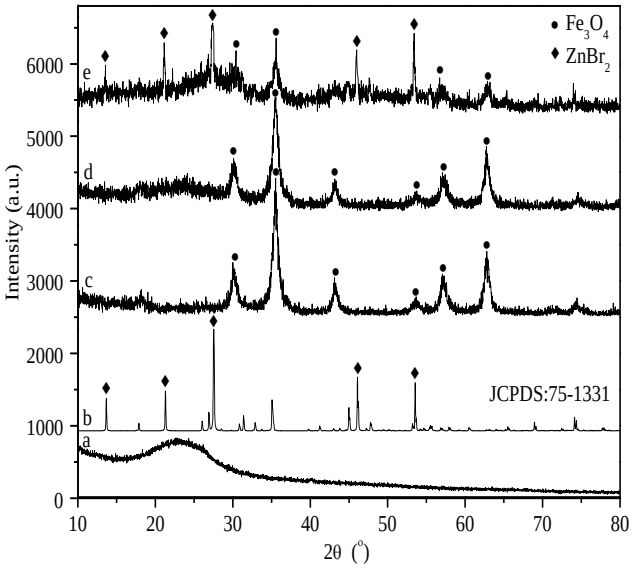

Fig. 2 XRD patterns of (a) SiO_2, (b)$ZnBr_2$, (c) Fe_3O_4, (d) Fe_3O_4@SiO_2 and (e) Fe_3O_4@SiO_2-$ZnBr_2$.

The XRD patterns of Fe_3O_4@SiO_2-$ZnBr_2$ with various Zn loadings are presented in Fig. 3. Fig. 3 reveals that the typical peaks ascribed to Fe_3O_4 become weaker while the intensity of the typical peaks assigned to $ZnBr_2$ is enhanced with increasing Zn loading. This can be ascribed to the decrease in the amount of Fe_3O_4 and increase in $ZnBr_2$. No typical peaks of $ZnBr_2$ are observed in the pattern of Fe_3O_4@SiO_2-$ZnBr_2$ with 4.5 wt% Zn loading while the intensity of such diffraction peaks become stronger in samples with higher $ZnBr_2$ content (curves b and c). It probably suggests that $ZnBr_2$ is uniformly distributed in the support of Fe_3O_4@SiO_2, and thus no characteristic peak could be observed with a lower Zn loading.

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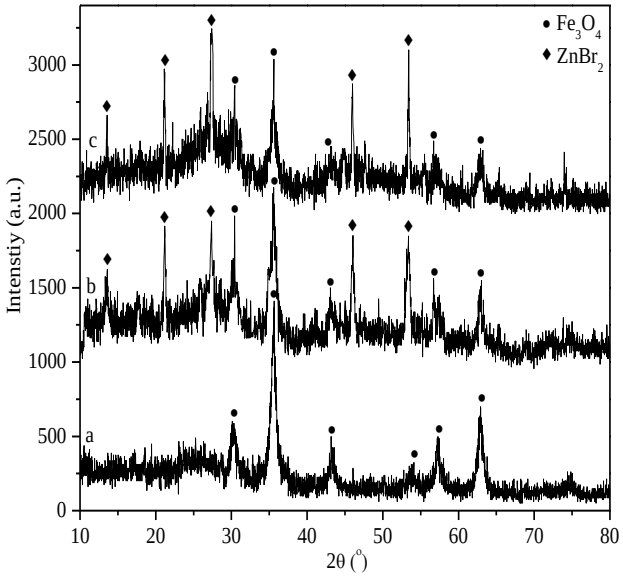

Fig. 3 XRD patterns of Fe_3O_4@SiO_2-$ZnBr_2$ with various Zn loadings (a) 4.5 wt% Zn loading, (b) 15.1 wt% Zn loading and (c) 17.5 wt% Zn loading.

Fig. 4 shows the XPS signals of Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2-$ZnBr_2$ with 15.1 wt% Zn loading. Three peaks at 530.5, 532.5 and 533.4 eV in the XPS spectrum of O1s (Fig. 4a) are assigned to lattice oxygen, adsorbed oxygen and oxygen species in –OHs on the surface, respectively.[40,41] It can be seen that these peaks shift to higher binding energies in the XPS resolution of Fe_3O_4@SiO_2-$ZnBr_2$ (Fig. 4a). In addition, the peak of Zn2p at 1022.9 eV is lower than that of $ZnBr_2$ at 1023.5 eV (Fig. 4b). The change in the binding energies of O1s and Zn2p reveals that there is a possible electronic interaction between Zn^{2+} and hydroxyl or surface oxide species, in which O atom donates electron to Zn^{2+}. As a result, the binding energy of Zn atom in $ZnBr_2$ shifts towards lower values while the O atom shifts to higher values.[42]

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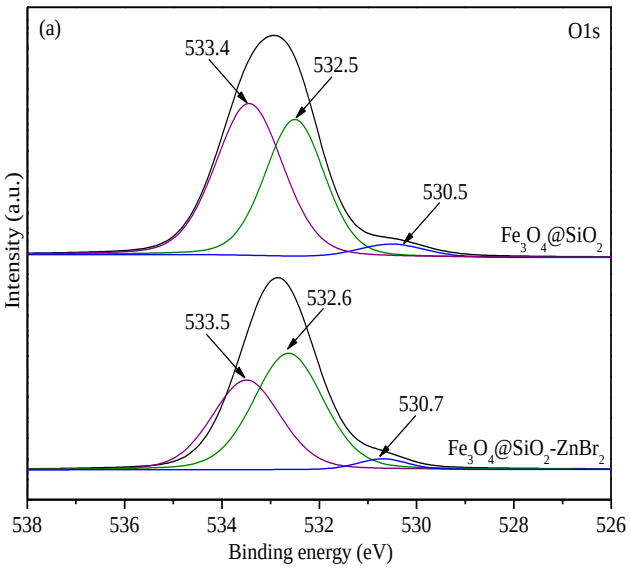

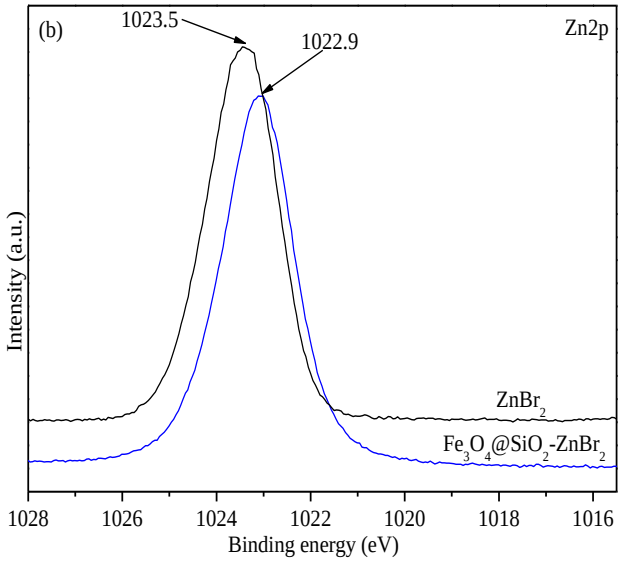

Fig. 4 XPS spectra of O1s and Zn2p.

Table 1 shows the values of the BET surface area for Fe_3O_4, $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$-$ZnBr_2$ with various Zn loading. It can be seen that the surface area of $Fe_3O_4@SiO_2$-$ZnBr_2$ is lower than that of $Fe_3O_4@SiO_2$, which can be ascribed to the dispersion and deposition of $ZnBr_2$ on the surface of $Fe_3O_4@SiO_2$. It is consistent with the observation of characteristic peaks of $ZnBr_2$ in the XRD patterns, as shown in Fig. 2 and Fig. 3. The results in Table 1 reveal that the heterogeneous catalyst still possesses acceptable surface area although it decreases after the introduction of $ZnBr_2$. The surface

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areas change from 75 to 86 m^2 g^{-1} indicates that Zn loading gives a negligible effect on the surface possibly due to its relatively low content.

Table 1 BET surface area for support and heterogeneous catalysts with various Zn loading

Sample	Fe_3O_4	$Fe_3O_4@SiO_2$	$Fe_3O_4@SiO_2$-$ZnBr_2$ (Zn wt%)					
			4.5	10.6	12.7	15.1	17.5	20.2
BET surface area (m^2 g^{-1})	63	158	86	79	80	77	79	75

Catalytic reaction

It has been reported that simple Lewis acids are effective catalysts for synthesis of DPC from CO_2, phenol and CCl_4.[15] The results in Table 2 showed that zinc halides displayed similar activity with respect to the total conversion of phenol, yield and selectivity towards DPC in the presence of zinc halides (entries 1–3), which is consistent with our previous work.[32] However, with 0.1 molar ratio of $ZnCl_2$ to phenol, the yield of DPC was only 5.8%. When a higher molar ratio ($ZnCl_2$/phenol = 0.5) or CF_3SO_3H was used, much higher yields of DPC at 22 and 25% were obtained.[32,34] Thus Lewis acids supported on $Fe_3O_4@SiO_2$ were further investigated based on the excellent performance of the magnetic catalyst in many reactions.[16] Although no activity was observed in the presence of $Fe_3O_4@SiO_2$ alone (entry 4), the catalytic performance of $Fe_3O_4@SiO_2$-$ZnBr_2$ was significantly enhanced as compared to that of $ZnBr_2$, giving 9.8% yield of DPC (entry 5). It has been known that the reactions with CO_2 involved can be activated by –OHs contained on the surface of support.[43] So it is

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logical to speculate that Fe_3O_4@SiO_2 may also play the role of a promoter besides support because the surface of Fe_3O_4 and SiO_2 contain a large number of accessible –OHs. The improvement in the catalytic performance of supported $ZnBr_2$ may also be ascribed to the possible interaction between Zn^{2+} and hydroxyl or surface oxide species, which was confirmed by XPS analysis (see Fig. 4). In addition, it can be seen from Table 2 that the catalytic performance of simple physical mixture of $ZnBr_2$ and Fe_3O_4@SiO_2 was far poorer than that of Fe_3O_4@SiO_2-$ZnBr_2$ obtained via impregnation (entries 5,6). The results further revealed that there is a possible interaction between Zn^{2+} and hydroxyl or surface oxide species, which may occur during the supported catalyst preparation.

The results in Table 2 also show that there is a difference in the yield of DPC with various zinc halides in heterogeneous system (entries 5,7,8). The yield of DPC with Fe_3O_4@SiO_2-$ZnCl_2$ or Fe_3O_4@SiO_2-ZnI_2 was lower than that with Fe_3O_4@SiO_2-$ZnBr_2$. It may be attributed to variation in the Lewis acidity as well as the steric hindrance of halide anions. It is generally accepted that increasing acidity gives a positive effect on the performance but the steric hindrance shows the opposite. The order of acidity is as following: $ZnCl_2$ < $ZnBr_2$ < ZnI_2 while the steric hindrance is on the contrary. These conflicting factors can compensate each other, thus generating better activity for Fe_3O_4@SiO_2-$ZnBr_2$. The tendency towards DPC yield in the supported catalytic systems (entries 5,7,8) is inconsistent with the results obtained in the presence of homogeneous zinc halides (entries 1–3), further indicating that the chemical environment in supported catalyst is different from that of simple zinc halide, which also support the possible interaction between Zn^{2+} and hydroxyl or surface oxide species.

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Table 2 Synthesis of DPC with various catalyst[a]

Entry	Catalyst	Conversion (%)	Selectivity (%)	Yield (%)
1	$ZnCl_2$	12.0	48.1	5.8
2	$ZnBr_2$	12.2	46.8	5.7
3	ZnI_2	11.7	48.5	5.7
4	$Fe_3O_4@SiO_2$	2.4	-	-
5[b]	$Fe_3O_4@SiO_2$-$ZnBr_2$	16.8	58.3	9.8
6[c]	$Fe_3O_4@SiO_2$/$ZnBr_2$	1.3	47.4	0.6
7[b]	$Fe_3O_4@SiO_2$-$ZnCl_2$	3.9	48.3	1.9
8[b]	$Fe_3O_4@SiO_2$-ZnI_2	9.4	43.6	4.1

[a] Reaction conditions: phenol=12 mmol, CCl_4=40 mmol, temperature=100 ℃, CO_2 pressure=8 MPa, reaction time=6 h, catalyst (containing zinc halide 1.2 mmol).

[b] Zn loading was 15.1 wt%.

[c] Simple physical mixture of $ZnBr_2$ and $Fe_3O_4@SiO_2$.

Table 3 shows the effects of heterogenized catalysts with different Zn loadings on the synthesis of DPC from CO_2. It can be seen that the yield and the selectivity towards DPC are significantly dependent on the Zn content. Both were enhanced by increasing Zn loading in the range from 4.5 to 15.1 wt% (entries 1–4) and a maximum yield of DPC at 9.8% was obtained in the presence of 15.1 wt% Zn loading. Then the conversion of phenol slightly dropped but the selectivity showed nearly no change when the Zn loading was increased to 20.2 wt%. It is possibly ascribed to the aggregation of the active sites with higher Zn content, thus leading to poor dispersion[37] and giving the negative effect on the reaction.

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Table 3 Synthesis of DPC with various Zn loading[a]

Entry	Zn loading (%)	Conversion (%)	Selectivity (%)	Yield (%)
1	4.5	11.1	9.8	1.1
2	10.6	15.6	33.5	5.2
3	12.7	16.3	41.1	6.7
4	15.1	16.8	58.3	9.8
5	17.5	15.5	54.8	8.5
6	20.2	13.1	55.1	7.2

[a] Reaction conditions: phenol=12 mmol, CCl_4=40 mmol, temperature=100 ℃, CO_2 pressure=8 MPa, reaction time=6 h, Fe_3O_4@SiO_2-$ZnBr_2$ (containing $ZnBr_2$ 1.2 mmol) was employed.

Table 4 shows the effects $ZnBr_2$ and CCl_4 on the reaction between CO_2 and phenol. Both the conversion of phenol and the yield of DPC were dependent on the molar ratio of $ZnBr_2$ to phenol in the range between 0.05 and 0.25 but the selectivity changed insignificantly. The maximum conversion and yield were observed at a molar ratio of 0.1 (entry 2) and then a decrease was observed. The yield of DPC was found to be 4.4% with a molar ratio of 0.25 (entry 5). The results are consistent with those previously obtained using CF_3SO_3H as co-catalyst[34] but not in accordance with those in the absence of co-catalyst. Both the conversion and the yield were enhanced with increasing the amount of zinc halide and no optimal ratio of catalyst to substrate was observed in the latter.[32] These results further indicate that Fe_3O_4@SiO_2 may not only play a role of support but also act a promoter in the present work. It has been reported that two phases including liquid and gas phase were present in the reaction mixture using pressured CO_2 as raw material as well as solvent for the synthesis of DPC, in which the reaction usually proceeds in the liquid phase mainly composed of CO_2.[32] As the molar ratio of $ZnBr_2$ to phenol

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increased, Fe_3O_4@SiO_2 increased more markedly due to relatively low content of $ZnBr_2$ in the heterogeneous catalyst. Thus catalyst and substrate may not be covered fully by liquid phase in the presence of excessive heterogeneous catalyst, leading to a decrease in the conversion of phenol and yield of DPC.

Table 4 Synthesis of DPC with various amounts of $ZnBr_2$ and CCl_4[a]

Entry	$ZnBr_2$/phenol (Molar ratio)	CCl_4 (mmol)	Conversion (%)	Selectivity (%)	Yield (%)
1	0.05	40	10.1	50.6	5.1
2	0.1	40	16.8	58.3	9.8
3	0.15	40	16.6	56.5	9.4
4	0.2	40	14.3	51.8	7.4
5	0.25	40	8.4	52.2	4.4
6	0.1	5	12.0	55.8	6.7
7	0.1	10	18.8	63.3	11.9
8	0.1	20	17.1	61.9	10.6
9	0.1	30	12.5	59.9	7.5
10	0.1	50	8.8	58.1	5.1

[a] Reaction conditions: phenol=12 mmol, temperature=100 ℃, CO_2 pressure=8 MPa, reaction time=6 h, Fe_3O_4@SiO_2-$ZnBr_2$ (15.1 wt% Zn loading) was employed.

The effect of CCl_4 was further investigated. Table 4 shows that increasing CCl_4 increased the conversion of phenol, yield and selectivity towards DPC. A lower yield of DPC with less CCl_4 (5 mmol, entry 6) can be related to the formation of smaller amount of CCl_3^+, which is believed to be an important intermediate for the synthesis of DPC from phenol and dense phase CO_2.[44] A maximum yield

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of DPC at 11.9% was obtained by the addition of 10 mmol CCl_4 (entry 7). Further increase in CCl_4 resulted in a drop in both the conversion and the yield but nearly no change in selectivity. Our previous investigation also indicated that two phases were always presented under the present reaction conditions and the reactions mainly occurred in the liquid phase.[32] Either concentration of phenol or $ZnBr_2$ in the liquid phase became smaller in the presence of a larger amount of CCl_4, and thus might reduce the conversion of phenol.[32] The results in Table 4 also show that a slightly excessive amount of CCl_4 is essential for the synthesis of DPC from CO_2, phenol and CCl_4. The optimal molar ratio of CCl_4 to phenol was 1:1.2 (entry 7), which is higher than the stoichiometric molar ratio of 1:4.[32]

Table 5 shows the effects of reaction variables including the CO_2 pressure, reaction temperature and time. Temperature was first tested over a range from 90 to 140 ^oC. It can be seen that the conversion of phenol was progressively improved with increasing temperature but the selectivity was low at lower and/or higher temperature. The selectivity of 21.1 and 38.1% were observed at 90 and 140 ^oC, respectively (entries 1, 6). The maximum yield of 27.2% was obtained at medium temperature of 130 ^oC. It has been reported that higher temperature favors the formation of phenoxide which would further transfer into DPC,[32] explaining why the selectivity to DPC increased with temperature as shown in Table 5 below 130 ^oC (entries 1–5). A further increase in temperature may be favorable to the formation of another intermediate *p*-hydroxybenzoic acid-like compound which would not change into the objective product. Thus temperatures above 130 ^oC led to the reduced yield and selectivity towards DPC.[45]

The CO_2 pressure has been considered one of the most crucial factors for the reactions using CO_2 as reactant as well as reaction medium. The conversion of phenol, yield and selectivity towards DPC were improved with an enhancement in the pressure of CO_2 below 8 MPa (entries 5,7,8). Although the conversion was slightly changed, a negative effect was observed in terms of selectivity with further increase in the pressure (entries 9,10). The unique properties appearing near the critical point are probably responsible for the positive effect observed around 8 MPa which is close to the critical

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pressure of pure CO_2. Due to phase change of CO_2 from gas to supercritical fluid, the variation of density around the critical point generally causes changes in chemical or physical equilibrium, possibly promoting the dissolution of phenol in liquid and the inter-solubility between supercritical CO_2 and CCl_4. Therefore, the rate and the selectivity were remarkably dependent on the pressure of CO_2 since it acts as both reactant and solvent in the present reaction. Similar results with a maximum selectivity at a pressure near the critical point of CO_2 were also reported elsewhere.[15,32,33]

Table 5 Optimization of reaction condition[a]

Entry	Temperature (^oC)	CO_2 pressure (MPa)	Time (h)	Conversion (%)	Selectivity (%)	Yield (%)
1	90	8	6	8.5	21.1	1.8
2	100	8	6	18.8	63.3	11.9
3	110	8	6	32.8	59.8	19.6
4	120	8	6	38.8	61.1	23.7
5	130	8	6	42.8	63.6	27.2
6	140	8	6	51.5	38.1	19.6
7	130	6	6	38.8	45.6	17.7
8	130	7	6	36.2	67.1	24.3
9	130	9	6	44.3	55.3	24.5
10	130	10	6	46.6	35.0	16.3
11	130	8	2	37.9	53.8	20.4
12	130	8	4	42.9	65.5	28.1
13	130	8	8	45.9	60.8	27.9
14	130	8	10	44.1	62.6	27.6

[a] Reaction conditions: phenol=12 mmol, CCl_4=10 mmol, Fe_3O_4@SiO_2-$ZnBr_2$ (Zn loading 15.1 wt%, containing $ZnBr_2$ 1.2 mmol) was employed.

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Table 5 also indicates that the synthesis of DPC was dependent on the reaction time. The conversion of phenol and the yield of DPC were increased from 2 to 4 h (entries 11,12) and then kept nearly constant (entries 5,13,14). This possibly suggests the reaction of CO_2 with phenol in the presence of CCl_4 reached equilibrium at 4 h.

Fe_3O_4@SiO_2-$ZnBr_2$ with 15.1 wt% Zn loading can be easily recovered with a permanent magnet after the reaction and reused in the next run without further treatment. The recyclable performance was shown in Fig. 5. It can be seen that Fe_3O_4@SiO_2-$ZnBr_2$ possessed excellent stability at the initial 4 runs, in which the yield of DPC changed in a small range from 27.6 to 28.1%, followed by a slight drop. The yield was decreased to 24.2% after the 5th runs. The amount of Zn in the recovered catalyst, which was determined after every recycle by AAS analysis, was 14.8%, 14.9%, 14.6%, 13.7% and 13.0%, respectively, after each cycle. These results revealed that the drop in the catalytic activity could be ascribed to $ZnBr_2$ leaching. The decrease in Zn content after the fourth run can be ascribed to the following reason: the active species $ZnBr_2$ supported on Fe_3O_4@SiO_2 by impregnation method may not be steadily adhere to the surface of the support under high pressure and temperature due to the weak interaction between them.

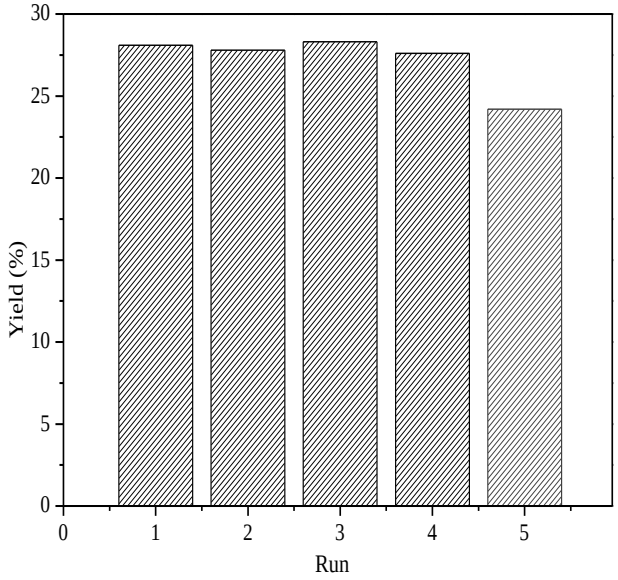

Fig. 5 Reusability of Fe_3O_4@SiO_2-$ZnBr_2$. Reaction conditions: phenol=12 mmol, CCl_4=10 mmol, temperature=130 ℃, CO_2 pressure 8=MPa, reaction time=4 h, Fe_3O_4@SiO_2-$ZnBr_2$ (Zn loading 15.1 wt%, containing $ZnBr_2$ 1.2 mmol for the first run) was employed.

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Conclusions

$ZnBr_2$ supported on MNPs-Fe_3O_4 coated by SiO_2 was developed as an effective and recoverable catalyst for the synthesis of DPC from CO_2 and phenol in the presence of CCl_4. It was found that the catalytic performance of Fe_3O_4@SiO_2-zinc halides was dependent on the kind of zinc halides. Fe_3O_4@SiO_2-$ZnBr_2$ showed better catalytic performance than that of the heteregenized $ZnCl_2$ and ZnI_2 as well as homologous $ZnBr_2$. Under the optimized conditions, 28.1% of DPC yield was obtained using Fe_3O_4@SiO_2-$ZnBr_2$ as the catalyst. The XPS result and the activity comparison between simple mixing $ZnBr_2$ with Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2-$ZnBr_2$ revealed that there is a possible interaction between Zn^{2+} and hydroxyl or surface oxide species in support Fe_3O_4@SiO_2. Fe_3O_4@SiO_2-$ZnBr_2$ can be easily recovered by using an external magnet and reused without significant loss in activity for 4 runs. The yield of DPC showed little change in the range 27.6 to 28.1%.

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