

# Synthesis of styrene carbonate from styrene oxide and CO<sub>2</sub> over ZnBr<sub>2</sub> supported on MCM-41—Coated magnetic Fe<sub>3</sub>O<sub>4</sub>



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## ABSTRACT

ZnBr<sub>2</sub> supported on magnetic nanoparticles Fe<sub>3</sub>O<sub>4</sub> coated by MCM-41 (Fe<sub>3</sub>O<sub>4</sub>@MCM-41/ZnBr<sub>2</sub>) was prepared and characterized by infrared spectroscopy (IR), powder X-ray diffraction (XRD) and nitrogen adsorption–desorption isotherms. The as-prepared samples were used as a recyclable catalyst for solvent-free synthesis of styrene carbonate (SC) from styrene oxide (SO) and carbonate dioxide (CO<sub>2</sub>). The results showed that Fe<sub>3</sub>O<sub>4</sub>@MCM-41/ZnBr<sub>2</sub> exhibited similar catalytic activity to homologous ZnBr<sub>2</sub>. It was found that the reaction depended on the reaction conditions in terms of the yield of SC. The yield of SC at 81.5% was obtained with 8 MPa CO<sub>2</sub> pressure at 90 °C for 3 h. The supported catalyst Fe<sub>3</sub>O<sub>4</sub>@MCM-41/ZnBr<sub>2</sub> can be easily recovered by a permanent magnet after the reaction and reused without further treatment. No significant change in the structure and loss in activity were observed. The yield of SC changed in a small range from 79.2 to 82.6% during 5 cycles.

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## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is one of the main greenhouse gases resulted from human activities. It causes global warming and climate change as the concentration in the atmosphere increases at an accelerating rate. Factually, CO<sub>2</sub> is not only a sort of greenhouse gas but also the most abundant carbon resource on earth. The conversion of CO<sub>2</sub> into useful chemicals is one of the most important and fascinating fields in organic chemistry from the chemical science perspective. In recent decades, it has attracted extensive interest with the increase in the emission of CO<sub>2</sub>.

Cyclic compounds, including cyclic carbonates, cyclic carbamates and cyclic ureas are conventionally synthesized by using toxic and hazardous phosgene as raw reagent. CO<sub>2</sub> is a promising alternative to conventional toxic chemicals such as phosgene, isocyanate or carbon monoxide due to its non-toxic, non-flammable, inexpensive and available in large quantities. Greener processes could be expected by using CO<sub>2</sub> as carbon resource [1]. Many compounds including hydrogen, alkenes, acetals, epoxides, amines, phenol and carbon–carbon unsaturated compounds etc. have been explored to react with CO<sub>2</sub> [2–4], in which carbonates, urea derivatives as well as formates and so on have been efficiently obtained [5–7]. Unfortunately, CO<sub>2</sub> is a highly oxidized and thermodynamically stable compound with low chemical reactivity

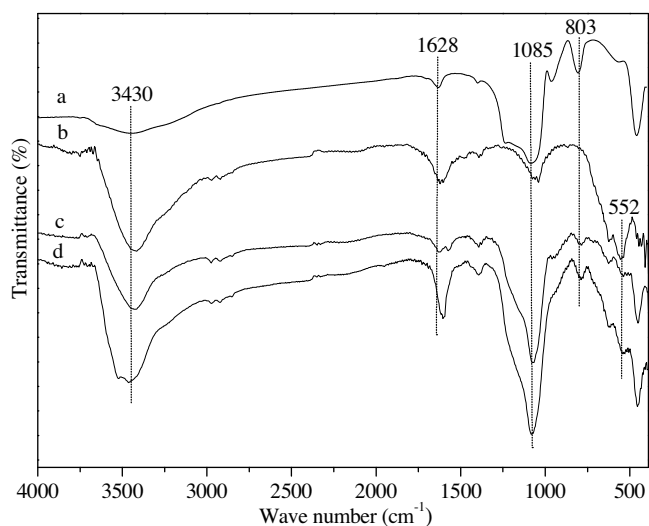
[8]. As a result, the kinetic and thermodynamic stability of CO<sub>2</sub> molecule presents significant challenges in designing efficient chemical transformations. The conversion of CO<sub>2</sub> into chemicals is generally focused on developing catalysts to activate CO<sub>2</sub> [6]. A variety of homogenous catalysts such as salen-complexes, metal oxides and Lewis acids have been employed in the reactions with the conversion of CO<sub>2</sub> involved [5,6,9]. However, few works focused on the heterogeneous catalytic system so far.

Homogeneous catalysts have been widely employed because of its excellent catalytic activity and selectivity, mild reaction conditions and more understandable mechanism. However, these catalysts often suffer the difficulty of isolation and separation. Heterogeneous catalytic systems have thought to be one of the most to overcome these problems since they can be effectively recovered from a reaction mixture in a straightforward manner [10]. Generally, heterogenization is achieved by grafting the active sites on solid materials including inorganic supports, polymers and hybrid materials. Silica, alumina, active carbon, ceria, polystyrene, polyvinylpyrrolidone are typical examples [11–13]. Recently, heterogeneous catalysts possess excellent activity and selectivity as well as the ease of separation and recovery have been developed by using magnetic nanoparticle Fe<sub>3</sub>O<sub>4</sub> (MNPs-Fe<sub>3</sub>O<sub>4</sub>) as the support. Heterogenized magnetic catalysts such as noble metal Pd, Ru, Pt, and Au supported on Fe<sub>3</sub>O<sub>4</sub> reveal excellent activity in a variety of reactions such as hydrolysis, hydrogenation, oxidation, carbon–carbon coupling and reduction [1,14–16].

A number of investigations have been focused on the synthesis of carbonates via the coupling of CO<sub>2</sub> with epoxide due to its atom

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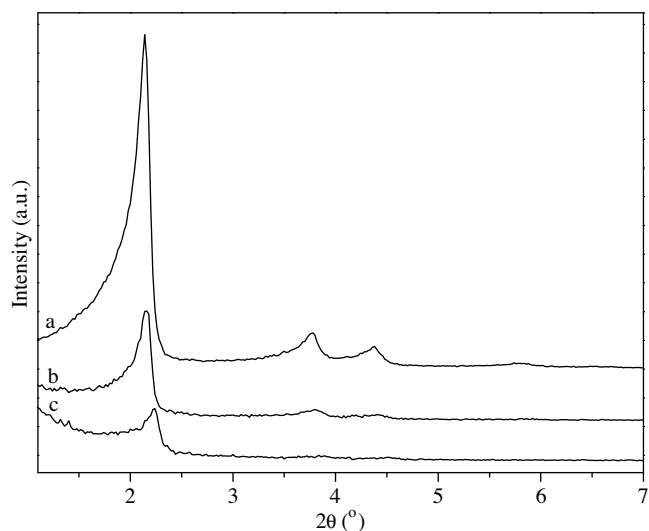
**Fig. 1.** IR spectra of (a) MCM-41, (b) Fe<sub>3</sub>O<sub>4</sub>, (c) Fe<sub>3</sub>O<sub>4</sub>@MCM-41 and (d) Fe<sub>3</sub>O<sub>4</sub>@MCM-41/ZnBr<sub>2</sub>.

economy process and nearly no formation of by-product [17,18]. The synthesis of styrene carbonate (SC) via CO<sub>2</sub> and styrene oxide (SO) catalyzed by salen complexes is one of them [19,20]. The aim of this work is to develop an effective and recyclable catalyst for the direct synthesis of valuable SC from CO<sub>2</sub> and SO. Zinc halides supported on MNPs-Fe<sub>3</sub>O<sub>4</sub> coated by MCM-41 were employed as the catalyst and the catalytic performance of the supported zinc halides was investigated by varying the loading and amount of ZnBr<sub>2</sub>, material ratio, CO<sub>2</sub> pressure, reaction temperature and time. Moreover, Fe<sub>3</sub>O<sub>4</sub>@MCM-41/ZnBr<sub>2</sub> was recovered and reused without further treatment to evaluate its recyclable performance.

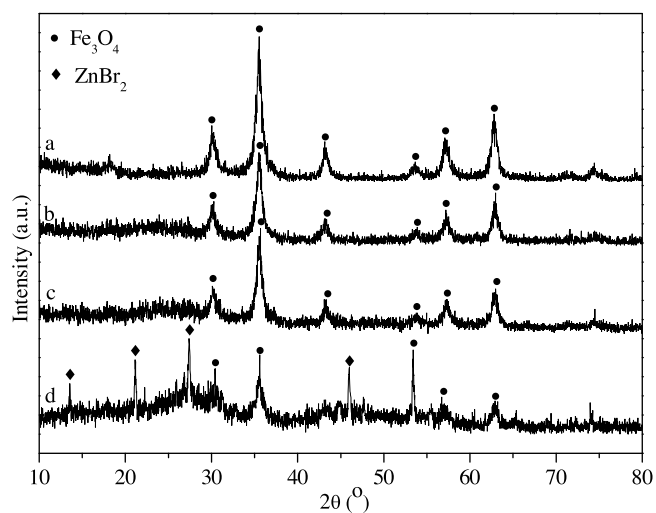
## 2. Experimental

### 2.1. Materials

All reagents were of analytical grade, purchasing commercially and used without further purification. The purity of CO<sub>2</sub> was 99.99%.



**Fig. 2.** XRD patterns of (a) MCM-41, (b) Fe<sub>3</sub>O<sub>4</sub>@MCM-41 and (c) Fe<sub>3</sub>O<sub>4</sub>@MCM-41/ZnBr<sub>2</sub>.



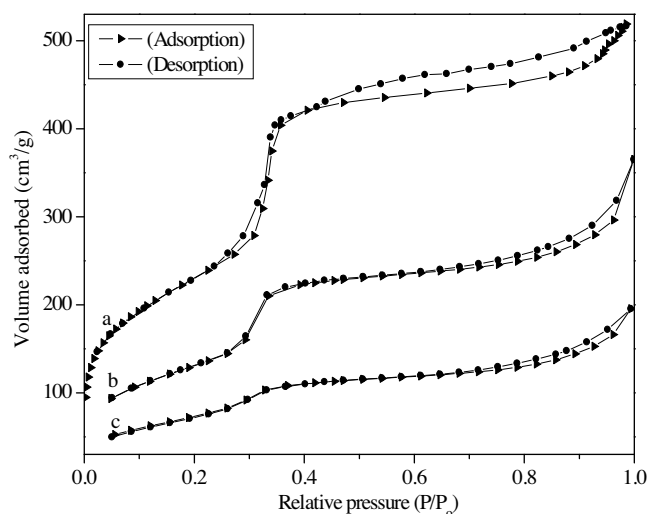
**Fig. 3.** XRD patterns of (a) Fe<sub>3</sub>O<sub>4</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>@MCM-41, (c) Fe<sub>3</sub>O<sub>4</sub>@MCM-41/ZnBr<sub>2</sub> and (d) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnBr<sub>2</sub>.

### 2.2. Preparation of catalyst

#### 2.2.1. Preparation of Fe<sub>3</sub>O<sub>4</sub>@MCM-41/ZnBr<sub>2</sub>

Mesoporous MCM-41 was prepared as the methods reported previously [21,22]. A typical procedure is as follows: 2.2 g (0.6 mmol) cetyltrimethylammonium bromide was added to a solution of 53.4 g aqueous ammonia (26 wt%, 40 mmol NH<sub>3</sub>·H<sub>2</sub>O) before stirring for 30 min in a closed polyethylene bottle. Then 10.4 g (10 mmol) tetraethoxysilane (TEOS) was slowly added to the base/surfactant solution under stirring. The resulting solution was stirred for further 2 h at room temperature followed by aging at 80 °C for 96 h. White powder was then recovered by filtration and washed with distilled water thoroughly, dried at ambient temperature and calcined at 560 °C in air for 8 h.

In a typical experiment, 2.0 g MNPs-Fe<sub>3</sub>O<sub>4</sub> was added to a mixture of ethanol and deionized water (70 mL ethanol/10 mL deionized water). After the mixture was dispersed by sonication for 20 min, 5 mL aqueous ammonia (26 wt%) and 1.72 g MCM-



**Fig. 4.** Nitrogen adsorption–desorption isotherms of (a) MCM-41, (b) Fe<sub>3</sub>O<sub>4</sub>@MCM-41 and (c) Fe<sub>3</sub>O<sub>4</sub>@MCM-41/ZnBr<sub>2</sub>.

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