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Application of Modified Organic-Inorganic Hybrid Zirconium Phosphate Material ZAMPS-PVPA-Salen-Mn(III) in Chemical Fixation of CO₂

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Abstract. The modified organic-inorganic hybrid zirconium phosphate materials were used to catalyze the addition reaction of propylene epoxide with carbon dioxide. The catalytic materials of different carbon chains were investigated. The optimal catalytic materials were screened out. At the same time, the reaction time, pressure, temperature and the optimum amount of catalytic materials were also studied. The results show that the catalytic material 1c modified by Salen Mn(III) has good catalytic performance for the carbon dioxide addition reaction, the yield of propylene carbonate are over 90%. In addition, the modified catalytic material 1c is easily separated from the reaction system, and can be recycled at least 5 times, and the catalytic activity is not significantly reduced.

1. Introduction
Carbon dioxide, which exists in the three states of gas, liquid and solid, is widely used as a product in various sectors of industry and the national economy. According to statistics, the amount of carbon dioxide emitted by various fossil fuels (such as coal, oil, natural gas) in the world is rapid increased [1]. The waste of carbon dioxide resources has intensified the global warming tendency [2]. The average temperature of the earth is increased by 1.5 to 4.5°C annually [3]. Therefore, the control of carbon dioxide emissions, the recovery, fixation, utilization and recycling of carbon dioxide have become a matter of great concern to all countries in the world [4].

The high and new technology of using CO₂ as carbon resource for chemical utilization has become the research focus of the scientific community [5]. The chemical utilization of CO₂ is to convert CO₂ into bulk basic chemicals, organic fuels or to fix it directly into macromolecule materials. At present, industrialized projects on chemical utilization of carbon dioxide include synthesis of urea, salicylic acid, organic carbonate, inorganic carbonate and so on. The synthesis of cyclic carbonates from CO₂ and epoxy compounds is one of the most typical success stories of CO₂ resource utilization. During the reaction, without the use of organic solvents, the process is an atomic economic response, conforming to the standards of green chemistry. The product cyclic carbonates are widely used in textiles, printing and dyeing, polymer synthesis and electrochemistry, as well as in pharmaceutical and fine chemical intermediates [6].

A large number of catalysts have been developed to catalyze the coupling of CO₂ with epoxy compounds to form cyclic carbonates, such as alkali metal salts [7], metal oxides [8], transition metal
compounds [9], Schiff base [10], ion exchange resin [11], functional polymer material [12], quaternary ammonium salt and quaternary phosphonium salt [13-15], gold nanoparticle support resin [16-18] and so on. However, many catalytic systems have disadvantages such as low catalytic stability and low catalytic activity, or requiring harsh conditions such as organic solvents. Both homogeneous [19] and heterogeneous systems have their own advantages and disadvantages. Usually the homogeneous catalytic system has higher catalytic activity than the heterogeneous catalytic system, but the latter is favored because of its simple preparation, easy separation, easy operation, good stability and recyclability.

The organic-inorganic hybrid zirconium phosphate is an excellent carrier material for the heterogeneous catalytic system [20]. One of its outstanding features is the designability of organic group. The organic-inorganic hybrid zirconium phosphate with different organic group can meet a variety of purposes [21]. Meanwhile the organic-inorganic hybrid zirconium phosphate is a kind of multifunctional material with a layered structure, and has high thermal stability, good resistance to acid and alkali [22]. As a peculiar material, it can be modified by various catalytic groups. It has become a new research hotspot in recent years [23]. In this paper, we have extended the research of application of modified organic-inorganic hybrid zirconium phosphate material to the field of activated carbon dioxide reaction, and found that it has a good effect on the catalytic carbon dioxide and propylene oxide to form cyclic carbonate [24-26].

2. Materials and Methods

2.1. Chemicals and Instruments

Propylene epoxide (PO) was supplied by Alfa Aesar, CO2 was technical grade and was received from Guiyang shenjian Air Company. Other commercially available chemicals were laboratory grade reagents from local suppliers. Both the salen ligand and the salen Mn(III) homogeneous catalyst were prepared according to the reference [26]. The yield of propylene carbonate (PC) was determined by gas chromatography (Shimadzu GC-14C).

2.2. Preparation of Organic-Inorganic Hybrid Zirconium Phosphate Materials (Scheme 1)

According to the reference [26], organic-inorganic hybrid zirconium phosphate materials (ZAMPS-PVPA) a-c was successfully prepared. And their compositions and structures have been proved by 1H NMR, 31P NMR and FT-IR.
2.3. Materials Modified with Salen-Mn(III) as Catalytic Materials 1a-1c (Scheme 2)
ZAMPS-PVPA a-c (0.5 g) separately, salen Mn(III) (2.5 g), NaOH (0.35 g) and 60 mL of tetrahydrofuran as solvent was added to a 150 mL three-necked flask. The mixture was stirred and heated to reflux for 24 hours. The mixture was filtered and washed with CH$_2$Cl$_2$ until no Mn ions were detected in the filtrates. The filter cake is dried under vacuum to obtain tan powdery solids catalytic materials as 1a, 1b, 1c.

2.4. The Addition Reaction of Propylene Oxide with Carbon Dioxide
20.0 mL of propylene oxide, catalytic material and co-catalyst ZnBr$_2$ were mixed in a 50 mL autoclave. After sealing the autoclave, a certain pressure of CO$_2$ was introduced to remove the air in the reaction vessel to prevent oxidation of the reactants by O$_2$ during the reaction. This reaction was carried out at a certain pressure, time and temperature. After completion of the reaction, the autoclave was cooled to remove residual gas. 10.0 mL of ethyl acetate was poured into the reaction vessel. The reaction product was taken out and washed twice with ethyl acetate to remove the catalyst. Finally the solvent in the product was removed by a rotary evaporator to give a colorless liquid.

3. Results and Discussion
3.1. Catalytic Properties of the Different Catalytic Materials 1a-1c
This study investigated the catalytic properties of the different modified materials 1a-1c. The results are shown in figure 1. At 130 °C, with ZnBr$_2$ (0.2mmol) as co-catalyst, along with the growth of the carbon chain of catalytic materials from 1a to 1c (0.5 mmol based on Mn in it), after a catalytic reaction for 6h, the yields of PC was increased from 80.3% to 90.2%. It can be seen that as the length of the arm increases, the catalytic effect of the modified materials is significantly improved. Mainly because in the catalytic process, the longer "molecular arm" makes the complex molecules away from the skeleton structure of the organic-inorganic hybrid zirconium phosphate material, and has more
spatial freedom, which is beneficial to the deformation of the molecule and the participation of the promoter molecules, and at the same time the activity of the reaction. In general, catalytic material 1c has the best catalytic effect.

![Figure 1. Catalytic properties of the different catalytic materials 1a-1c](image)

3.2. Effect of various factors on catalytic performance of catalytic material 1c

The optimum conditions for the cycloaddition reaction are: ZnBr₂ (0.2mmol) as co-catalyst, reaction temperature 130 °C, reaction time 6h, filling with CO₂ 5MPa, catalytic material 1c dosage 0.5 mmol based on Mn in it. Under the above conditions the yield of PC is the highest 90.2%.

![Figure 2. Effect of the amount of catalytic material 1c (mmol)](image)
Figure 2. (a) Effect of the dosage of catalytic material 1c on the reaction; (b) Effect of reaction temperature on catalytic performance of 1c; (c) Effect of CO$_2$ pressure on catalytic performance of 1c; (d) Effect of reaction time on catalytic performance of 1c
3.3. **The Recycling of the catalytic material 1c**

In order to detect the stability and recyclability of the catalytic material, we investigated the 1c under the optimal conditions. The catalytic performance of 1c for the catalytic cycloaddition of PO and CO₂. It can be seen from figure 3 that the catalytic results of the catalysts 1c was repeated 5 times. It is obvious that after 5 times of use, the catalyst 1c has a decrease in catalytic performance slightly.

![The yields of PC % vs Recycling Time of 1c graph](image.png)

*a* Reaction conditions: catalytic material 1c (0.5 mmol based on Mn in it), co-catalyst ZnBr₂ (0.2 mmol), PO (20 mmol), temperature 130°C, CO₂ pressure 5.0 MPa, reaction time 6h

**Figure 3. Recycling of 1c in the cycloaddition of PO and CO₂**

3.4. **Proposed Mechanism of the Cycloaddition Reaction**

We believe that the quaternary phosphonium salt and the salen Mn (III) groups on the modified organic-inorganic hybrid zirconium phosphate material can activate propylene oxide in the course of the reaction. So we proposed the acceleration mechanism of the catalytic material and zinc bromide, as shown in the scheme 3.

![Scheme 3. Possible acceleration mechanism on the catalytic material and ZnBr₂](image.png)

**Scheme 3. Possible acceleration mechanism on the catalytic material and ZnBr₂**

4. **Conclusions**

In this study, propylene oxide was used as substrates to carry out the cycloaddition reaction, and the catalytic performances of the catalytic materials were evaluated. The effects of the different modified materials 1a-1c, reaction temperatures, the dosage of catalytic material, CO₂ pressure and reaction time were investigated. The results indicate that the cyclic carbonate reaction can be activated by the catalytic material 1c. The yield of propylene carbonate can reach up to 90.2%. Furthermore, the
reusability of the catalytic material 1c was investigated in the PO catalytic system. The results showed that the catalytic activity of 1c was not significantly decreased after 5 cycles, and the yield was still higher than 70%. The research in this article is of great significance for the stable catalytic performance of the catalytic material 1c. At the same time, it also opens up a new field for the application of organic phosphonic acid zirconium materials.

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