Efficient and recyclable performance of organic-inorganic zirconium phosphonates supported salen-Mn(III) as catalysts for CO₂ cycloaddition

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Abstract. In this research, organic-inorganic zirconium phosphonates were modified by salen-Mn(III) and formed novel heterogeneous catalysts using to CO₂ cycloaddition for the first time. Specially, the supported catalyst 1c indicate excellent catalytic activities (conv%, up to 95.8; sele%, up to 94.8) in the absence of solvent. Moreover, this heterogeneous catalyst could still show good catalytic ability after recycling seven times.

1. Introduction

Even though carbon dioxide is a stable and kinetically inert molecule, but it is also abundant, renewable, nontoxic and inexpensive C1-feedstock [1-3]. So the effective utilization of CO₂ has been one of the major challenges in the world [4]. In particular, the synthesis of CO₂ to renewable resources will be especially desirable [5]. Cyclic carbonate is considered to be one of the best products for this purpose, as it can be used as excellent aprotic polar solvents, precursors for producing polycarbonates, fine chemicals, etc [6].

The search for green catalytic processes to the synthesis of cyclic carbonates in highly-selective pathways becomes extremely important in this years. There are a number of catalytic systems used for producing cyclic carbonates, including simple alkali metal salts [7], ionic liquids [8-11], phosphines [12], main group metal complexes [13], transition metal complexes [14] and porous metal oxides [15-18].

Among those systems, metal-salen complexes have attracted significant attention to promote the activity and selectivity of the cycloaddition reaction from carbon dioxide and epoxides. High conversion rate has been achieved with homogeneous metal-salen catalysts [19]. The main disadvantages of them are separation, recovery, and reuse which limited their practical applications.

In order to overcome these disadvantages, the present method is immobilizing salen Mn(III) complexes onto solid supports. It is desired to develop solid catalysts with high activity for the cycloaddition reaction. Organic-inorganic zirconium phosphates have been extensively researched in the decades [20-22]. They are easily obtained as low dimensional layered solids having different structures, which correspond to different chemical features [23]. They are also used as catalyst
supports, owing to their controlled layers and concentration of surface which can increase the activity of the catalysts [24-26].

Very recently, our research group successfully immobilized salen-Mn(III) into organic-inorganic zirconium phosphates framework by direct synthesis method. The supported catalyst 1c exhibited great activity and selectivity in the cycloaddition reaction. It can produce cyclic carbonates from epoxides and carbon dioxide at 120 °C under 3MPa in a short reaction time of 4 h without solvent. Especially, the supported catalyst 1c was easily recovered by simple filtration and could be reused at least seven times with little loss of activity.

2. Materials and methods

2.1. Chemicals and Instruments

1,2-Diaminocyclohexane, Styrene, Ethyl acetate, Mn(OAc)2•4H2O, 3,5-Di-tert-butylsalicylaldehyde, Benzoyl peroxide (BPO), Ethyl acetate (EtOAc), Sodium formaldehyde bisulfite, Sodium hydroxyethyl sulfonate, ZrOCl2 • 8H2O and Potassium iodide (KI) were 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. All solvents used were previously dried and distilled according to the usual methods. Salen ligand and homogeneous catalyst Salen Mn(III) were synthesized according to the standard reference procedures [26] and further identified by analysis and comparison of IR spectra with the reference [26].

GC was performed on a gas chromatograph (Shimadzu GC-14C) equipped with an FID detector and N2 was the carrier gas. The supported Mn contents of catalysts were determined by a TAS-986G (Pgeneral, China) atomic absorption spectroscopy (AAS). Proton and carbon magnetic resonance spectra were recorded on a Varian 400 MHz spectrometer with the solvent resonance as the internal standard.

2.2. Preparation of the supports a-c (Scheme 1)

The supports organic-inorganic zirconium phosphates (ZSPS-PVPA) a-c were synthesized according to the reference [26] and their structures were confirmed by 1H NMR, 31P NMR and FT-IR.

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\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \xrightarrow{\text{THF}} \text{Zr(HPO}_4)_2 \cdot 3\text{H}_2\text{O} \xrightarrow{\text{BPO, EtOAc}} \text{Zr(HPO}_4)_2 \cdot 3\text{H}_2\text{O} \xrightarrow{\text{CH}_3\text{OCH}_2\text{Cl, ZnCl}_2, 38^\circ\text{C, 20h}} \text{ZSPS-PVPA (a-c)}
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Scheme 1. Preparation of the supports ZSPS-PVPA (a-c).
2.3. Salen-Mn(III) immobilized on organic-inorganic zirconium phosphonates as efficient catalysts 1a-1c (Scheme 2)

Referring to references [26], the supports a-c (0.5 g, separately) and 50 ml tetrahydrofuran were put into 100 ml single-port flask, keeping 40 °C and stirring 1 h. Then 2.5 g Salen Mn ((III) and 0.35 g NaOH were added into the single bottle, with the temperature increasing to 80 °C for 12 h. Stopping the reaction until the temperature coming to room temperature, the solvent was removed by filtration. The filter cakes were washed with dichloromethane and water separately until pH = 7. By drying filter cake, the brown powder solid were obtained which recorded as 1a, 1b, 1c. The supported Mn contents of catalysts were determined by AAS, which show Salen Mn ((III) complexes are grafted onto ZPS-PVPA successfully.

![Scheme 2: The synthetic route to catalysts 1a-1c.](image)

2.4. General procedure for synthesis of cyclic carbonates

All coupling reactions were carried out in a 50 ml stainless steel autoclave which was equipped with a magnetic stirrer, charged with epoxide (20 mmol) and the desired amount of catalysts 1a-1c and co-catalyst KI respectively. The autoclave was pressurized with CO₂ to the desired pressure and then heated to the desired temperature. After the reaction, the autoclave was cooled in ice-water and extra CO₂ was vented slowly. An aliquot of sample was taken from the resultant mixture and dissolved in EtOAc for GC analysis. The crude product was purified by distillation and cyclic carbonates were obtained and identified by IR, ^1^H NMR and ^13^C NMR.

3. Results and discussion

3.1. Catalytic properties of the different catalysts 1a-1c

According to other literatures [7-18], we choose cheap and easy-to-get propylene oxide (PO) as the representative substrate. The substrate dosage is 20 mmol, and the reaction temperature is set at 120°C. The reaction was carried out for 4 hours at a carbon dioxide pressure of 3MPa. The catalysts 1a-1c (2.5 mol%) in reaction are determined by the Mn content in them, and the co-catalyst KI is 0.3 mmol. The effects of different catalysts 1a-1c on the reaction were investigated. As can be seen from Figure 1, the conversions of propylene oxide changed from 88.1 to 95.8% with the catalysts from 1a to 1c, and the selectivities of propylene carbonate are similar. Considering the catalytic properties, the catalyst 1c has the highest efficiency.
3.2. Effect of various factors on catalytic performance of 1c

![Bar charts showing the effect of various factors on catalytic performance of 1c: amount of catalyst, reaction temperature, CO$_2$ pressure, reaction time.]

Figure 2. (a) Effect of the amount of catalyst 1c on catalytic performance; (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
Organic-inorganic zirconium phosphonate supported salen-Mn(III) catalyst 1c was designed to effectively realize the cycloaddition from carbon dioxide to cyclocarbonates. In the reaction process, propylene oxide was used as the representative compound, and the effects of the amount of catalyst 1c, temperature, time, and the pressure of carbon dioxide on the reaction were investigated. As shown in Figure 2, the optimal condition is catalyst 1c (2.5mol% based on Mn in it), co-catalyst KI (0.3mmol), epoxides (20 mmol), temperature 120°C, CO₂ pressure 3.0 MPa, reaction time 4h.

3.3. Catalytic Behavior for the Synthesis of Other Carbonates
The cycloaddition of CO₂ with other epoxides was also studied at 120 °C and 3.0 MPa. Clearly, the catalyst 1c system was also very efficient for other epoxides, producing the corresponding cyclic carbonates with epoxides conversions of 90.9-94.2% and cyclic carbonates selectivities of 90.7-96.1% as in Table 1. Moreover, the catalyst 1c of this work is very cheap, simple, and is easily obtained in large quantity, which has industrial application value in future.

| Entry | R’          | Time (h) | Epoxides Conv.% | Cyclic carbonates Selec.% |
|-------|-------------|----------|-----------------|---------------------------|
| 1     | Ph          | 6        | 93.7            | 96.1                      |
| 2     | CH₃(CH₂)₂OCH₂ | 6        | 94.2            | 92.7                      |
| 3     | CH₂=CH-CH₂OCH₂ | 6        | 92.5            | 93.8                      |
| 4     | CH₃(CH₂)₅ | 10       | 90.9            | 90.7                      |

* Reaction conditions: catalyst 1c (2.5 mol% based on Mn in it), co-catalyst KI (0.3mmol), epoxides (20 mmol), temperature 120°C, CO₂ pressure 3.0 MPa.

3.4. The Recycling of the Catalyst 1c
To assess the long-term stability and reusability of the supported catalysts, PO was also used as a mode substrate with CO₂ system, and recycling experiments were carried out with the catalyst 1c. After each experiment, the catalyst 1c was filtrated from the reaction system by adding ethyl acetate and subsequently used without further purification. The results of the recovered catalyst 1c after seven recycling are listed in Figure 3. Obviously, the reuse of the catalyst 1c in seven times decreased slightly both in the conversion and the selectivity. The Mn content of the heterogeneous catalyst 1c is 0.38 mmol/g after recycling for 7 times, compared with the total amount (around 0.52 mmol/g) in fresh catalyst 1c. On account of this, it could be deduced that the decrease of the activity may also be attributed to the decomposition of the manganese complex under cycloaddition conditions.

3.5. Proposed Mechanism of the Cycloaddition Reaction
The exact mechanism of this reaction is not very clear. However, based on the experimental results and previous reports, we proposed that the cycloaddition of carbon dioxide with epoxides to generate cyclic carbonates. It probably requires activation through both the salen Mn(III) groups and the iodides. The former activates the epoxide, while the latter acts as a nucleophile to open the epoxide ring. The catalytic cycle is depicted in Figure 4.
Figure 3. Recycling of 1c in the cycloaddition of PO and CO$_2$.$^a$

$^a$ Reaction conditions: catalyst 1c (2.5 mol% based on Mn in it), co-catalyst KI (0.3mmol), PO (20 mmol), temperature 120°C, CO$_2$ pressure 3.0 MPa, reaction time 4h.

Figure 4. A proposed mechanism for the formation of cyclic carbonate.

4. Conclusions

In this work, a series of heterogeneous catalysts 1a-1c have been successfully synthesized by immobilization of Salen Mn(III) onto organic-inorganic zirconium phosphonate supports a-c. The resultant catalysts 1a-1c exhibited significantly enhanced activity towards the production of cyclic carbonates. Particularly catalyst 1c is a versatile, recyclable, and reusable solid catalyst for the cycloaddition reaction of CO$_2$ and epoxides up to 90.9-94.2% conversion levels with 90.7-96.1% selectivities of products under mild reaction conditions. In the consideration of reaction activity and selectivity due to addition of the heterogeneous catalysts in the reaction, the proposed mechanism of cycloaddition from CO$_2$ and epoxides to cyclic carbonate catalyzed by the catalysts was proposed.
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