Direct Synthesis of Diethyl Carbonate from CO\textsubscript{2} over ZnO@Na\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} Heterogeneous Material

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To cite this article:
Meng Zhang. Direct Synthesis of Diethyl Carbonate from CO\textsubscript{2} over ZnO@Na\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} Heterogeneous Material. Science Journal of Chemistry. Special Issue: The Application of Catalytic Materials, Polymers and Li Batteries in New Energy and Environmental Protection. Vol. 7, No. 6, 2019, pp. 105-109. doi: 10.11648/j.sjc.2019070611

Received: November 4, 2019; Accepted: November 26, 2019; Published: December 4, 2019

Abstract: At present, the world is facing two major problems: energy crisis and CO\textsubscript{2} emission. Diethyl carbonate is an effective gasoline additive which can greatly improve octane number. The route of diethyl carbonate synthesis from CO\textsubscript{2} is green and economical technique, which can effectively solve both energy crisis and CO\textsubscript{2} emission problems together. However, the design and preparation of catalysts is the core and key to realize the conversion from CO\textsubscript{2} to diethyl carbonate. This paper mainly described a novel synthesis of ZnO@Na\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} heterogeneous material that applied in the direct synthesis of diethyl carbonate from CO\textsubscript{2} and ethanol. The special pore and channel structure of Na\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} was used to maximize the catalytic capacity of ZnO material. The prepared catalysts were fully characterized by means of temperature-programmed desorption (TPD) and X-ray powder diffraction (XRD). The properties of acid-base sites on the surface of ZnO@Na\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} were measured by temperature-programmed desorption technique. The catalytic performance over ZnO@Na\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} heterogeneous material was examined on micro-reactor. The experiment results indicated that synthesized novel ZnO@Na\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} heterogeneous material had large number of acid-base sites and high catalytic activity. This novel ZnO@Na\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} catalyst had great ability to realize the effective conversion from CO\textsubscript{2} to diethyl carbonate. This technology not only improved the utilization rate of energy materials, but also reduced CO\textsubscript{2} emissions.

Keywords: Carbon Dioxide, Diethyl Carbonate, Material, Ethanol, Heterogeneous

1. Introduction

Diethyl carbonate (DEC) have attracted widespread attention during the last ten years due to its extensive industrial applications [1-3]. DEC is a type of good green solvent [4, 5] instead of phosgene, dimethyl sulphate and alkyl halide. And DEC is a kind of good electrolyte in lithium ion batteries [6-9]. More importantly, DEC can be used as an ideal additive for gasoline in order to increase octane number of gasoline [10-12]. Recently, DEC can be synthetized by several routes: phosgenation of ethanol [13, 14], oxidative carbonylation of ethanol [15-17], transesterification of organic carbonates [18-20], direct synthesis from CO\textsubscript{2} and ethanol, among which the last route is particularly promising due to cost effectiveness, mild reaction conditions and safe operations. Furthermore, this process involves the activation of CO\textsubscript{2} resulting in very low conversion yield. Therefore, the exploration of highly efficient, stable catalysts is desirable. Many literatures [21-26] have shown that both acid sites and base sites are crucial to determine the catalytic activity. Yet, the cooperation of acid–base sites as well as their respective contribution to catalytic activity is not confirmed. Therefore, how to adjust the acid–base sites of catalysts in order to obtain high stable and efficient catalysts is still a challenge.

In this work, a novel heterogeneous material of ZnO@Na\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} catalyst was synthesized. After temperature-programmed desorption (TPD) measurement, on the surface of ZnO@Na\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} catalyst there were many acid and base sites that were enough to make CO\textsubscript{2} and ethanol activated. According to catalytic performance results, this heterogeneous material had high activity for CO\textsubscript{2} conversion to DEC.
2. Experimental

2.1. Catalysts Preparation

Prepare the ammonia solution of octyl nitrate, in which Zn is 0.4mol/L. The ammonia complex solution of zinc nitrate is placed in the spray bottle of 75mL. Take a glass plate and lay aluminum foil on the glass plate. Evenly sprinkle Na₃PW₁₂O₄₀ powder on the aluminum foil, and place an infrared lamp beside it. Intermittently spray of powdered samples on aluminum foil with spray bottle. Put in the oven and dry at 100°C. The precursor of the catalyst is obtained by grinding in an agate mortar and sieving through a 200 mesh sieve. Put it into muffle furnace and calcine it at 500°C for 6 hours under air atmosphere. The final ZnO@Na₃PW₁₂O₄₀ heterogeneous material is obtained.

2.2. Catalytic Characterization

2.2.1. Powder X-ray Diffraction (XRD)

The X-ray diffraction was obtained on Rigaku Dmax 2200 diffractometer with graphite monochromatized Cu Kα radiation (λ=0.154178nm) at 40kV and 20mA. The sample was scanned from 5° to 80° at a rate of 3°/min. The crystallite sizes of the particles were calculated from the XRD peaks using the Scherrer equation.

2.2.2. Temperature Programmed Desorption (TPD)

Temperature programmed desorption (TPD) was obtained on Quanta ChromChem 3000 to determine the surface acid-base properties of catalysts. Before adsorption experiments, 0.1g of the samples were pretreated at 120°C in a quartz U-tube in an nitrogen flow with a flow rate of 50 mL per minute for 2h to remove absorbed water. Upon cooling to room temperature, the samples were saturated with 10%CO₂/90%N₂, 10%NH₃/90%N₂ for 1 h. Then the physical adsorbed CO₂, NH₃ were removed by streaming with 30%N₂/70% He for 3h under a flow rate of 50mL/min. The samples were then heated up to 500°C at a heating rate of 4°C/min in N₂/He under a flow rate of 80mL/min.

2.3. Catalytic Evaluations

Synthesis of DEC from ethanol and CO₂ was carried out in a continuous fixed-bed reactor. N₂ was purged into reactor to replace the air inside before the reaction temperature was heated up to a set temperature. CO₂ was purged into ethanol container to get CO₂/ethanol mixed gas. The mixed gas was then charged into the reactor. The results of the reaction were measured by GC-112N equipped with a flame ionization detector (FID) through a six-way valve to connect with the reactor.

3. Results and Discussion

3.1. Structure Characterization

XRD patterns of synthesized ZnO@Na₃PW₁₂O₄₀ heterogeneous material was shown in Figure 1. The main peak was around 8.0 degree and all the peaks belonged to the characteristic peaks of Na₃PW₁₂O₄₀. There were no peaks of ZnO in the XRD pattern, which was due to excellent dispersion of ZnO particles.

![Figure 1. XRD pattern of ZnO@Na₃PW₁₂O₄₀ Heterogeneous Material.](image1)

3.2. Lewis Acid-base Characterization

To investigate the base sites characteristics of ZnO@Na₃PW₁₂O₄₀ material, CO₂-TPD was measured as shown in Figure 2. The amount of peaks stands for types of base sites on the surface of ZnO@Na₃PW₁₂O₄₀ material. Peaks from 100°C to 300°C, it is weak base site. Peaks from 300°C to 500°C, it is moderate base site. Peaks from 500°C to 700°C, it is strong base site. The area of peaks stands for numbers of a certain type of base site. According to measured CO₂-TPD pattern, there was only one big peak around 240°C, which indicates that only one type of weak base site exists on the surface of synthesized ZnO@Na₃PW₁₂O₄₀ material. The area of peak was large, which indicates that there are a large number of weak base sites. The CO₂-TPD pattern implied that synthesized ZnO@Na₃PW₁₂O₄₀ material had the ability to make CO₂ activated.

![Figure 2. CO₂-TPD pattern of ZnO@Na₃PW₁₂O₄₀ Heterogeneous Material.](image2)
To investigate the acid sites characteristics of ZnO@Na₃PW₁₂O₄₀ material, NH₃-TPD was measured as shown in Figure 3. The amount of peaks stands for types of acid sites on the surface of ZnO@Na₃PW₁₂O₄₀ material. Peaks from 100°C to 300°C, it is weak acid site. Peaks from 300°C to 500°C, it is moderate acid site. Peaks from 500°C to 700°C, it is strong acid site. The area of peaks stands for numbers of a certain type of acid site. According to measured NH₃-TPD pattern, there was only one big peak around 170°C, which indicates that only one type of weak acid site exists on the surface of synthesized ZnO@Na₃PW₁₂O₄₀ material. The area of peak was large, which indicates that there are a large number of weak acid sites. Different from CO₂-TPD, NH₃ was used instead of base reactants to measure the acid sites of catalysts. The NH₃-TPD pattern implied that synthesized ZnO@Na₃PW₁₂O₄₀ material had the ability to make ethanol activated.

### 3.3. Performance of Catalyst

Different reaction temperature was measured for direct synthesis of diethyl carbonate from CO₂ over synthesized ZnO@Na₃PW₁₂O₄₀ material. According to experimental results as shown in Table 1, the best ethanol conversion was 0.89% and the best DEC selectivity was 94.2% when reaction temperature was 140°C. Totally, ethanol conversion was less than 1% and DEC selectivity was more than 90%.

| Temperature/°C | Ethanol Conversion/% | DEC Selectivity/% | DEC Yield/% |
|----------------|----------------------|-------------------|-------------|
| 80             | 0.13                 | 90.1              | 0.12        |
| 100            | 0.44                 | 90.9              | 0.40        |
| 120            | 0.51                 | 92.3              | 0.47        |
| 140            | 0.89                 | 94.2              | 0.84        |
| 160            | 0.62                 | 91.6              | 0.57        |

In order to study the rule of catalytic activity with reaction temperature more clearly, Figure 4 was drawn based on experimental results. Clearly, ethanol conversion was increased with the increasing reaction temperature. Beyond 140°C, ethanol conversion started to decline. DEC selectivity was improved with the increasing reaction temperature.

Different reaction pressure was measured for direct synthesis of diethyl carbonate from CO₂ over synthesized ZnO@Na₃PW₁₂O₄₀ material. According to experiment results as shown in Table 2, the best ethanol conversion was 0.89% and the best DEC selectivity was 94.2% when reaction pressure was 2.0 MPa. Totally, ethanol conversion was less than 0.9% and DEC selectivity was more than 90%.

| Pressure/MPa | Ethanol Conversion/% | DEC Selectivity/% | DEC Yield/% |
|--------------|----------------------|-------------------|-------------|
| 0.8          | 0.11                 | 90.8              | 0.10        |
| 1.2          | 0.43                 | 93.2              | 0.40        |
| 1.6          | 0.66                 | 94.1              | 0.62        |
| 2.0          | 0.89                 | 94.2              | 0.84        |
| 2.4          | 0.59                 | 95.4              | 0.56        |
| 2.8          | 0.32                 | 93.7              | 0.30        |
In order to study the rule of catalytic activity with reaction pressure more clearly, Figure 5 was drawn based on experimental results. Clearly, ethanol conversion was increased with the increasing reaction pressure. Beyond 2.0 MPa, ethanol conversion started to decline. DEC selectivity was improved slightly with the increasing reaction pressure.

4. Conclusions

Heterogeneous material of ZnO@Na\(\text{PW}_{12}\text{O}_{40}\) catalyst was successfully synthesized by a novel method. According to temperature-programmed desorption (TPD) measurement, there was only one type of weak acid site and a type of weak base site on the surface of ZnO@Na\(\text{PW}_{12}\text{O}_{40}\) catalyst. And the amount of weak acid sites and weak base sites was much large, which indicated that synthesized ZnO@Na\(\text{PW}_{12}\text{O}_{40}\) material had the ability to make both CO\(_2\) and ethanol activated. The catalytic performance of ZnO@Na\(\text{PW}_{12}\text{O}_{40}\) heterogeneous material was measured on micro-reactor. The best ethanol conversion was 0.89\% and DEC selectivity was 94.2\% on conditions of reaction temperature 140°C and pressure 2.0 MPa. In order to study the rule of catalytic activity with reaction pressure more clearly, Figure 5 was drawn based on experimental results. Clearly, ethanol conversion was increased with the increasing reaction pressure. Beyond 2.0 MPa, ethanol conversion started to decline. DEC selectivity was improved slightly with the increasing reaction pressure.

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Conflicts of Interest

There are no conflicts of interest to declare.

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