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Synthesis of ethyl methyl carbonate via transesterification over molecular sieves and ZIF-8

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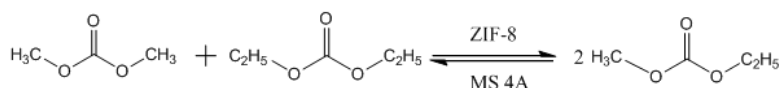[1]School of Materials and Environment, Beijing Institute of Technology, Zhuhai, China.
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Abstract. An efficient catalyst system of molecular sieves and ZIF-8 was developed for preparing ethyl methyl carbonate from dimethyl carbonate and diethyl carbonate under mild conditions. We used a number of tools to characterize ZIF-8, including X-ray diffraction instrument and physical adsorption instrument and thermogravimetric analyzer. Chemisorption instrument was used to characterize its acid-base properties. We studied different factors associated with the yield. The catalyst leaching test showed that the reaction took place heterogeneously.The results indicated that the catalyst system of molecular sieves and ZIF-8 displayed excellent activity, selectivity and reusability. Furthermore, the addition of molecular sieves to ZIF-8 resulted in dramatic increases from 50.3% to 84.7% in the yield.

1. Introduction

Ethyl methyl carbonate (EMC) is attracting great interests in recent decades because EMC can be used as a kind of co-solvent for commercial lithium ion batteries[1-3]. Generally, we can use esterification or transesterification to synthetize ethyl methyl carbonate[4-5]. But the above route is either not environmentally benign or difficult to separate from other impurities. We can also synthetize ethyl methyl carbonate using dimethyl carbonate (DMC) and diethyl carbonate (DEC)[6], the products can avoid separating. Yet, the homogeneous catalysts is difficult for separation and recovery, which limits their application. Therefore, many people have investigated heterogeneous catalysts, including the acids[7], the bases[8] and acid-base bifunctional materials[9] for transesterification of DEC and DMC. When using Al-Zn-MCM-41 catalyst in 180 °C, the EMC yield was 85%[9]. In this paper, we develop a new kind of heterogeneous catalyst with highly activity under mild conditions.

Scheme 1. Transesterification of DMC with DEC to produce EMC.

Recently, the yield of transesterification from DMC and DEC was about 50% using MOF as catalyst[10]. Unfortunately, MOF-5 is unstable and can easily deteriorate in the presence of water or air. ZIF, which is a subclass of MOF, has many excellent properties[11-19]. Previously, Shen et al[8] revealed that the moderately basic sites on MgO play a crucial role in the transesterification for synthesis of EMC, while La_2O_3 with strong basic sites and CeO_2 with weak basic sites both performed relatively poorly. Inspired by this, we hypothesis the strength of acid and base of catalyst system affect on the

yield of EMC. Therefore, we chose low-priced and easy accessible molecular sieves as co-catalyst to improve the acid strength of catalyst system and further promote the yield of EMC. Interestingly, the addition of molecular sieves to ZIF-8 led to a boost in the activity, and a high yield of 84.72% was obtained under mild conditions. Besides, the catalytic system of molecular sieves and ZIF-8 could be easily recycled without any special treatment. To the best of our knowledge, this is the first report to use the catalyst system of molecular sieves and ZIF-8 for the transesterification reaction of DMC and DEC.

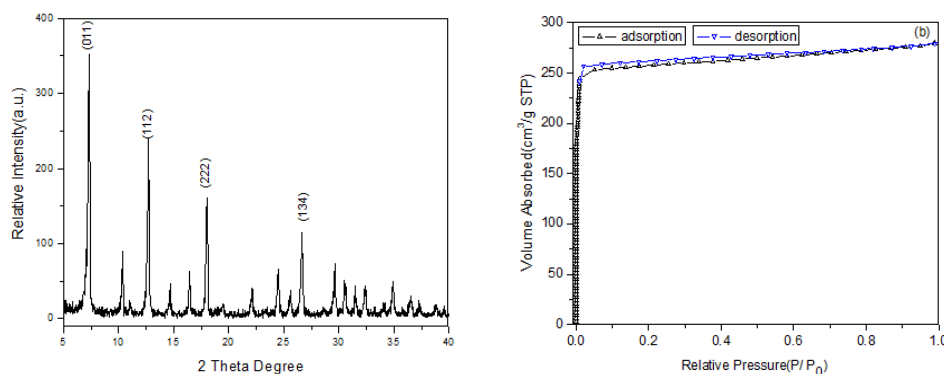## 2. Experimental Section
2.1. Preparation of catalyst
We prepared the ZIF-8 catalyst according to the procedure as followed[20]: 2-methylimidazole ($C_4H_6N_2$) and zinc nitrate hexahydrate ($[Zn(NO_3)_2] \cdot 6H_2O$) were dissolved in methanol respectively, then stirred for quite a time vigorously. Subsequently, we obtained the white polyhedral crystals. Finally, we collected white polyhedral crystals from the solution through filtration, washing and drying. We used a number of tools to characterize ZIF-8, including X-ray diffraction instrument and physical adsorption instrument and thermogravimetric analyzer. Chemisorption instrument was used to characterize its acid-base properties.
2.2. Evaluation of Catalytic Activity
All the chemicals were of analytical grade. DMC, DEC, ZIF-8 and molecular sieves were put in a flask, then heated and continuous stirring. After reaction, the product was collected and analyzed by a GC instrument with FID detector. ZIF-8 was separated by filtration, washing and drying for the reusability experiment. Molecular sieves was washed using water and dried at 350 °C for the next reaction.

3. Results and Discussions
3.1. Characterization

Figure 1. Characterization of ZIF-8 catalyst: (left) powder X-ray diffraction pattern, (right). N_2 adsorption-desorption isotherm at 77K

We used a number of tools to characterize ZIF-8, including X-ray diffraction instrument and physical adsorption instrument and thermogravimetric analyzer. Fig.1(left) is the XRD pattern of ZIF-8[21], while ZIF-8 exhibits N_2 adsorption and desorption isotherms in Fig.1(right). Generally, relatively narrow the pore size was narrower, the diffusion of reactants was worse, then the reaction rate was smaller. However, Jia etal[7] demonstrated the pore diffusion limitation was unimportant for this reaction. The surface area of ZIF-8 was as high as 750 m^2/g with the presence of micro-pores [21]. The Thermal stability test of ZIF-8 shows only approximately 6% weight loss in 500 °C [11]. Chemosorption results demonstrate ZIF-8 is both acidic and alkaline[22].

3.2. The synthesis of ethyl methyl carbonate with different catalysts

Table 1. The synthesis of ethyl methyl carbonate with different catalysts .[a]

Entry	Catalyst	catalyst amount [b](g)	Yield[c](%)	Selectivity[c](%)	TOF[d](mmolg^{-1}h^{-1})
1	None	-	-	-	-
2	ZIF-8	0.20	50.32	97.26	41.93
3	MS 4A [e]	10.00	34.89	94.14	29.08
4	ZIF-8+MS 4A [e]	0.30	67.94	96.44	56.62
5	ZIF-8+MS 4A [e]	0.20	84.72	98.39	70.60
6	ZIF-8+MS 4A [e]	0.10	62.70	93.41	52.25
7	ZIF-8+MS 4A [e]	0.05	58.68	97.25	48.90
8	ZIF-8+MS 4A [e,f]	0.20	47.15	99.22	39.29
9	ZIF-8+MS 4A [e,g]	0.20	70.69	91.58	58.91

[a] Reaction conditions: DMC(0.1 mol), DEC(0.1 mol), 100 °C and 12 h, [b] the amount of ZIF or MgO, [c] Determined by GC, [d] Moles converted, [e] MS 4A (10.000 g). [f] n(DMC)/n(DEC)=2:1, [g] n(DMC)/n(DEC)=1:2

The activity of different catalysts were investigated in Table 1, while molecular sieves was evaluated as co-catalyst. No EMC was detected (Entry 1) in the blank test. Bare ZIF-8 or molecular sieves showed weak activity (Entry 2 and Entry 3). However, the addition of molecular sieves to ZIF-8 resulted in dramatic increases from 50.3% to 84.7% in the yield of EMC (Entry 5). Besides, we studied the effects of catalyst amount (Entry 4 - Entry 7). The EMC yield was from 58.68% to 84.72% when the catalyst amount was from 0.05 g to 0.2 g. And the ratios of reactant were researched (Entry 5, Entry 8 - Entry 9) , and the results indicated that the EMC yield was the most when the ratio was 1. Therefore, we chose the ratio of 1:1 as the optimum ratio of DMC to DEC.

Previously, Shen et al[8] revealed that the moderately basic sites on MgO play a crucial role in the transesterification for synthesis of EMC, while La_2O_3 with strong basic sites and CeO_2 with weak basic sites both performed relatively poorly. The results also indicated that ZIF-8 with moderately acid and basic sites was the most active solid catalyst. These results also imply that the strength of the acid and basic sites of catalysts is one of the most important factors for the synthesis of EMC. Thus, it can be concluded that the moderately acid and basic sites are mainly responsible for the synthesis of EMC. Meanwhile, the surface areas of the solid catalysts exhibit some effects on their activities in this reaction.

We also test the leaching of the catalyst system. The yield was from 0.28% to 84.72% when the reaction time was from 1 h to 24 h with ZIF-8 and molecular sieves catalysts at 100 °C. For comparation, in another test run, we removed ZIF-8 and molecular sieves catalysts at 18 h, and found that the yield remain unchanged. If any catalyst whether ZIF-8 or molecular sieves is leaching in the reaction system, the reaction will continue after removal of catalyst, and a rise of EMC yield will be observed.

The reusability of ZIF-8 and molecular sieves were carried out. ZIF-8 and molecular sieves were recovered by filtration, and washed, then dried, respectively, for the next reaction. The yields only drop slightly, indicating that the catalyst system of ZIF-8 and molecular sieves has good reusability. In other hands, the XRD patterns of recycled ZIF-8 are same to that of fresh one, so ZIF-8 shows good stability.

4. Conclusion

In this work, ZIF-8 and molecular sieves, a new heterogeneous catalyst system, exhibited good activities. The yield of 84.72% was obtained over ZIF-8 and co-catalyst of molecular sieves under mild conditions. And the molecular sieves was important for promoting the synthesis of EMC.

Acknowledgments

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