

Synthesis of DMC from CH₃OH and CO₂ over Ce_{0.5}Zr_{0.5}O₂ Catalysts

Zhi-Fang Zhang^{1,2}, Zhong-Wen Liu^{1,2}, Jian Lu¹, Zhao-Tie Liu^{1,2,*}

¹Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education, Xi'an 710062 (China); ²School of Chemistry & Materials Science, Shaanxi Normal University, Xi'an 710062 (China)
*ztliu@snnu.edu.cn

Introduction

As an environmentally benign chemical product, dimethyl carbonate (DMC) has many potential applications, and is achieving increasing importance in the chemical industry [1]. Among the investigation methods, the direct synthesis of DMC from CO₂ and CH₃OH is the more preferred route as it follows the viewpoint of "Sustainable Society" and "Green Chemistry".

Among the catalysts investigated, Ce_xZr_{1-x}O₂ solid solutions showed potentially high catalytic performance [2,3]. In this work, we used different complex agents of salicylic acid, tartaric acid, adipic acid and citric acid to synthesize the Ce_{0.5}Zr_{0.5}O₂ solid solutions with significantly varied physical and structural properties, and applied them for the titled reaction. The catalytic performance of Ce_{0.5}Zr_{0.5}O₂ was well correlated with its physical and structural properties.

Materials and Methods

The solid solution of Ce_{0.5}Zr_{0.5}O₂ was prepared by complex-decomposition method using Ce(NO₃)₃·6H₂O and Zr(NO₃)₄·4H₂O as the cerium and zirconium precursors, respectively. The solid solutions of Ce_{0.5}Zr_{0.5}O₂ calcined at 773 or 1273 K prepared by using salicylic acid, tartaric acid, adipic acid, and citric acid as a complex agent were designated as S, T, A and C, respectively. The titled reaction was performed in an autoclave with an inner volume of 100 ml, and the products were analyzed on a GC equipped with FID and TCD detectors.

Characterizations of catalysts were performed by XRD, SEM, N₂ adsorption-desorption at 77 K, CO₂ pulse chemisorption, and TPR.

Results and Discussion

The morphology of Ce_{0.5}Zr_{0.5}O₂ calcined at 773 K was different depending on the complex agents used. For sample S, a clear layered structure with irregular layered spaces was observed. However, the sample T showed the slit-shaped holes. Similar to sample T, sample A was composed mainly of the partly ordered slit-shaped holes. It is interesting that well distributed round pores with average pore size of about 400 nm were appeared for sample C as shown in Fig. 1. The sample A showed a remarkably higher BET surface area and total pore volume than the other samples. Moreover, the BET surface area was decreased obviously in the order of sample T, S and C. The H₂-TPR profiles for different Ce_{0.5}Zr_{0.5}O₂ solid solutions show that there was only one peak for samples S, T, A, and C-1273, but there were two peaks observed for sample C. These results indicated that TPR patters in the lower temperature

region were basically the same for the samples S, T, A, and C, irrespective of the complexants used. In the case of sample C, we speculated that the appearance of higher temperature peak was a result of the structure and porous framework of the material. The amount of DMC formed under the same reaction conditions was significantly changed with the solid solutions of Ce_{0.5}Zr_{0.5}O₂ as given in Table 1. The sample C gave the lowest amount of DMC while sample C-1273 produced the highest. By comparing the results of CO₂ adsorption with the activity of DMC synthesis, it can be concluded that the crystal structure is more important than the acid-base property of the solid solution in determining the catalytic activity. Based on the above result and reasoning, it is expected a *t*-phase Ce_{0.5}Zr_{0.5}O₂ (Fig. 2) with high surface area and reducible oxygen capacity is a desirable catalyst for DMC synthesis.

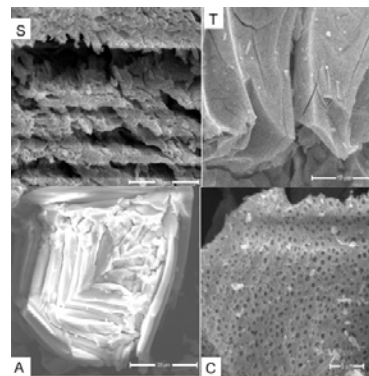


Fig. 1 The SEM micrographs of different Ce_{0.5}Zr_{0.5}O₂ solid solutions.

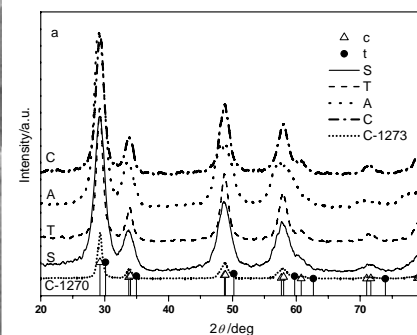


Fig. 2 XRD patterns of Ce_{0.5}Zr_{0.5}O₂ catalysts.

Table 1. Effect of complex agent and calcination temperatures on DMC formation over Ce_{0.5}Zr_{0.5}O₂*

Catalysts		S	T	A	C
DMC /mmol	Calcined at 773 K	0.16	0.20	0.33	0.11
	Calcined at 1273 K	1.75	0.00	0.33	1.80

* Conditions: 24 h, 20 MPa and 373 K; CH₃OH: 8 g, catalyst: 0.5 g

Significance

Relationships between DMC formation and crystal structure and BET surface area were observed. The crystal structure is a key factor in determining the catalytic activity. A significantly increase in methanol conversion was achieved after adding different amounts of 1, 1, 1-trimethoxy methane.

References

- Selva, M., Marquez, C. A., Tundo, P. *J. Chem. Soc., Perkin Trans. 1*, 1323 (1994).
- Fang, S., Fujimoto, K. *Appl. Catal. A: General*. 142, L1 (1996).
- Choi, J.C., Sakakura, T., Sako, T. *J. Am. Chem. Soc.* 121, 3793 (1999).