Zn/Fe mixed oxide: Heterogeneous catalyst for the synthesis of dimethyl carbonate from methyl carbamate and methanol

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ABSTRACT

A series of Zn–Fe–O mixed oxides were prepared for the synthesis of dimethyl carbonate (DMC) from methyl carbamate and methanol. X-ray diffraction revealed that zinc ferrite crystal phase appeared and changed with different Zn/Fe molar ratio. The DMC yield could reach 30.7% under suitable conditions. In addition, elemental chemical analysis and the reusability test indicated that these catalysts presented good stability.

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1. Introduction

As an environmental benign chemical product, dimethyl carbonate (DMC) has been used widely in fields of chemical industry. It is mainly used as methylation and carbonylation reagent to replace dimethyl sulphate, chloromethane, and phosgene without environmental pollution [1–4]. Besides, because of its versatile chemical properties, it is also used as electrolyte, foodstuff flavoring agent, and potential additive for gasoline [5,6]. Since DMC was first produced from methanol and phosgene in 1910s [7], there are several environmentally compatible DMC synthesis routines including oxidative carbonylation of methanol, ester exchange, and esterification of carbon dioxide with methanol. However, all these techniques suffer some corresponding drawbacks such as explosion hazards, reaction routine complex and low conversation, respectively [8–10].

Thus, in order to avoid all shortcomings mentioned above, a new process for synthesis of DMC from methanol and urea has been investigated [11]. It can be divided into two steps as follows:

$$NH_2CONH_2 + CH_3OH \rightarrow NH_2COOCH_3 + NH_3 \qquad (1)$$
$$NH_2COOCH_3 + CH_3OH \rightarrow CH_3OCOOCH_3 + NH_3 \qquad (2)$$

The intermediate methyl carbamate (MC) is first formed, and further converted to DMC by reaction with methanol. Generally speaking, urea can be easily converted to ammonia and isocyanic acid, and the latter can react with methanol to produce MC with high selectivity and yield even without catalysts. Nevertheless, MC to DMC is more difficult than the first step. This is because the ammonia produced in the first step can restrict the reaction shift to the DMC preparation. Consequently, the second step is the key and rate-control step for this approach [12–14]. Thus, the key to improve the DMC synthesis by urea methanolysis is to develop a catalyst with high activity towards the reaction of MC and methanol.

ZnO presented high catalytic performance for the reaction between urea and methanol [15]. Unfortunately, for the reaction of MC and methanol, it didn't exhibit satisfactory property. In fact, ZnO was a precursor of homogeneous catalyst for the DMC synthesis from urea and methanol [16]. As to the isolated second reaction, solid bases were tested in a batch reactor, but the DMC yield was still far from satisfaction [12]. Our group reported that using $ZnCl_2$ as catalyst, the DMC yield could reach 33.6% [17]. However, it was famous that the catalyst recovery was a great inconvenience for industry production using homogeneous catalyst. Therefore, it was of significance to explore highly efficient heterogeneous catalytic materials for the DMC production from MC and methanol.

Here, a series of zinc/iron mixed oxides were prepared and tested by the DMC synthesis from MC and methanol. The effect of Zn/Fe molar ratio was also discussed in detail on their catalytic performance. Based on the results of element analysis and reusability test, a heterogeneous catalyst was successfully explored.

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2. Experimental

2.1. Catalysts preparation

Zinc/iron catalyst precursors were prepared by co-precipitation method as following: according to desired metals proportion (Zn/Fe = 2, 4, 8, 10), a 100 mL aqueous solution containing x mol $Zn(NO_3)_3$ and y mol $Fe(NO_3)_3$ ($x + y = 0.1$) and another 100 mL aqueous solution containing 0.15 mol $(NH_4)_2CO_3$ was prepared separately. Then, these two solutions were added dropwise with stirring to 100 mL deionized water simultaneously. During this process, pH value of the mixed solution was maintained close to 8.0 using ammonia solution. After that, the mother liquid was aged at 65 °C with stirring overnight. The as-prepared products were obtained after being filtered and washed with deionized water until pH was 7.0. After being dried at 80 °C for 12 h, all samples were calcined at 600 °C for 5 h. They were called ZFO-X, in which X was corresponding to the initial zinc/iron atomic ratio. Besides, zinc oxide was obtained via the same procedure and method as that of the zinc/iron mixed oxides in the present case.

Zinc ferrite material was prepared as the description in the literature elsewhere [18]. In brief, zinc and iron nitrates were dissolved with a Zn:Fe ratio = 2. Under vigorous stirring, aqueous ammonia solution was added slowly to the mixed solution until the pH was 8.0. Then the resulting sol obtained was aged at 60 °C for 24 h. The powers were separated by centrifugation, washed repeatedly with deionized water, further filtered and dried at 100 °C overnight. Finally, the $ZnFe_2O_4$ sample was obtained by calcining at 600 °C for 5 h.

Other chemicals were analytic reagent from chemical products corporation without any purification.

2.2. Characterization

Power X-ray diffraction (XRD) experiments were performed on a Rifaku D max III VC instrument with $\lambda = 0.1541$ nm, Cu-Kα radiation in the 2θ range of 5–70°.

Elemental chemical analysis of solid catalysts and the methanol solution after reaction was carried out using the inductively coupled plasma-optical (ICP) emission spectroscopy on a Perkin Elemer 3000 equipment.

The surface area of catalysts was determined with the BET method using N_2 on a Micromeritics ASAP-2000 instrument.

2.3. Catalytic test

Reaction of MC and methanol was carried out in a stainless steel autoclave of 300 mL with a magnetic stirrer and a reflux column. In a typical experiment, 7.5 g MC, 64 g methanol and 1.0 g catalyst were put into the reactor. Then the reactor was heated to 190 °C and kept for 10 h with stirring. After the reaction, the reactor was cooled down to room temperature. Products in liquid phase after centrifugal separation were analyzed by a gas chromatography (GC) equipped with TCD. It should be mentioned that the by-product dimethyl ether could not be detected by chromatography because it was easy to volatilize when the autoclave was opened.

2.4. Calculations

The MC conversion, DMC and NMMC yield were calculated by the following formulas, respectively:

$$MC\ conversion = \frac{(starting\ MC-MC)\ (mol)}{starting\ MC\ (mol)} \times 100\%$$

$$DMC\ yield = \frac{DMC\ (mol)}{starting\ MC\ (mol)} \times 100\%$$

$$NMMC\ yield = \frac{NMMC \times 2\ (mol)}{starting\ MC\ (mol)} \times 100\%$$

3. Results and discussion

3.1. Catalysts structure

The chemical analysis revealed that the Zn/Fe molar ratio in mixed oxide samples deviated from that in mother solutions. Besides, the deviation gradually increased with the rise of the Zn/Fe molar ratio. It was well known that the low pH value disfavored the incorporation of Zn^{2+} into precipitation due to the relatively high solubility of $Zn(OH)_2$ ($K_{sp} = 6.8 \times 10^{-17}$) in comparison of $Fe(OH)_3$ ($K_{sp} = 2.8 \times 10^{-39}$) [18].

XRD patterns of solid catalysts with different Zn/Fe molar ratio were given in Fig. 1. Each phase was identified by its characteristic diffraction peak using JCPDS. All of the mixed oxides prepared displayed two phases, $ZnFe_2O_4$ and ZnO. It should be mentioned that diffraction peaks of the two crystal phases presented obvious change with different Zn/Fe molar ratio. ZFO-2 exhibited almost all peaks ascribed to $ZnFe_2O_4$, for there were peaks existed at 2θ of 18.2°, 30.5°, 35.4°, 36.9°, 43.1°, 53.4°, 56.9° and 62.6°. Only one $ZnFe_2O_4$ peak at 35.5° was observed for ZFO-10. Interestingly, all peak intensity attributed to ZnO became stronger and stronger
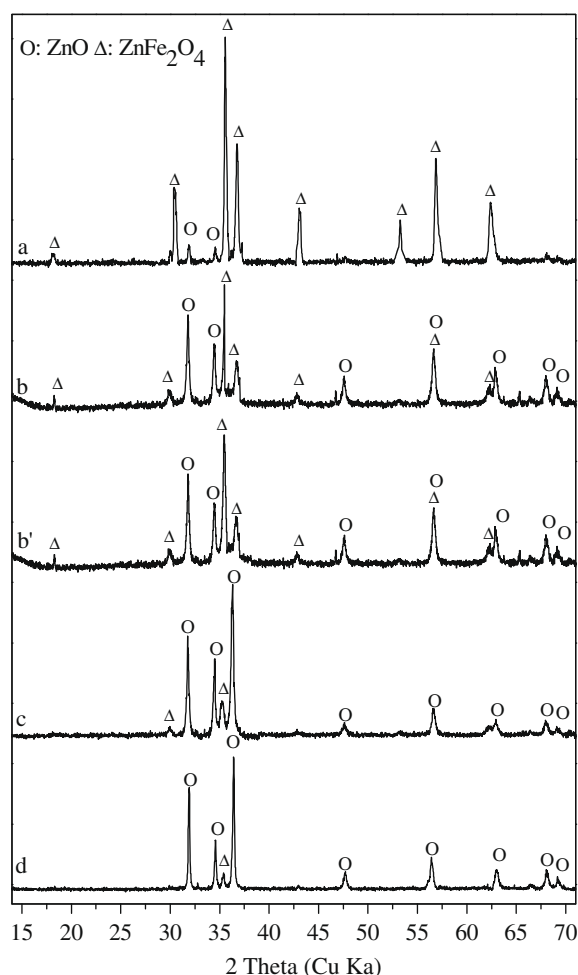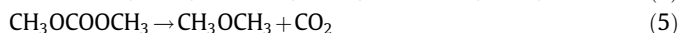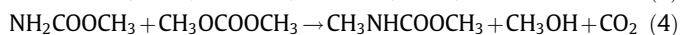

Fig. 1. XRD patterns of zinc/iron mixed oxides: (a) ZFO-2, (b) ZFO-4 before reaction, (b′) ZFO-4 after reaction, (c) ZFO-8 and (d) ZFO-10.

with increase of Zn/Fe molar ratio. While, that of zinc ferrite tended to weaker and weaker. As a result, the formation of crystal phase of catalysts was correlated with Zn/Fe molar ratio, and might further display influence on the catalytic performance of the catalysts. More important, Fig. 1 illustrated that when Zn/Fe atomic ratio was 4, not only the number of characteristic peaks for both ZnO and $ZnFe_2O_4$, but also the peak intensity was in a temperate degree among these catalysts.

Typical XRD patterns of the as-synthesized $ZnFe_2O_4$ and ZnO materials were shown in Fig. 2. It could be observed that the characteristic crystallographic peaks such as (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) of the spinal structure were well-assigned to these of standard $ZnFe_2O_4$ (Franklinite, JCPDS 22-1012) [19,20]. Thus, the zinc ferrite was successfully synthesized in the present case.

3.2. Performance of catalysts

As a multiple system, synthesis of DMC from MC and methanol could be proposed as follows:

$$NH_2COOCH_3 + CH_3OH \rightarrow CH_3OCOOCH_3 + NH_3 \quad (3)$$
$$NH_2COOCH_3 + CH_3OCOOCH_3 \rightarrow CH_3NHCOOCH_3 + CH_3OH + CO_2 \quad (4)$$
$$CH_3OCOOCH_3 \rightarrow CH_3OCH_3 + CO_2 \quad (5)$$

First, methoxy group in methanol substituted amino group of MC to produce DMC. Moreover, the by-product N-methyl methyl carbamate (NMMC) produced from the reaction of MC and DMC when the concentration of DMC reached a certain extent [17]. Besides, DMC could decompose into dimethyl ether and carbon dioxide at high temperature [17,21].

The catalytic results of different catalysts were showed in Table 1. It was found that the yield of DMC was only 2.6% without any catalysts (Entry 1). As an ideal catalyst for the DMC synthesis from urea methanolysis, ZnO was inactive for this reaction (Entry 2). This was consistent with the results reported previously [15,16]. For Fe_2O_3, the catalytic activity was also very low (Entry 3). Among mixed oxides, ZFO-4 exhibited the best catalytic performance and the DMC yield could reach 30.7% (Entry 5). Obviously, it was more active than base catalyst and its activity was even as the same as that of $ZnCl_2$, a typical homogeneous catalyst for this reaction
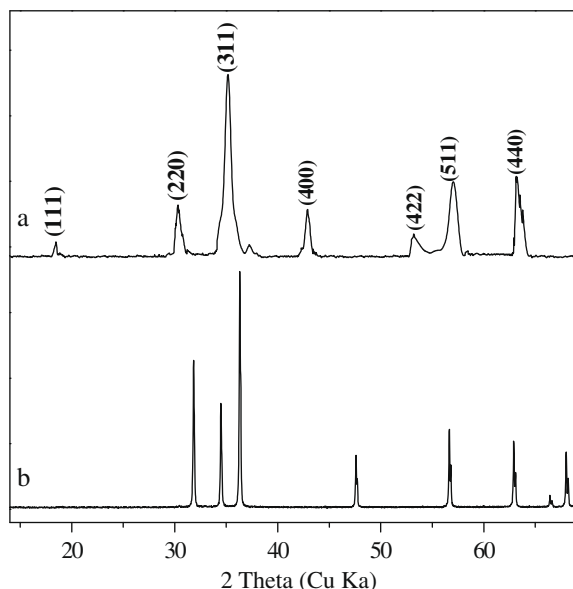
Table 1
Catalytic performance of catalysts[a].

Entry	Catalyst	MC conversion (%)	DMC yield (%)	NMMC yield (%)
1	None	4.1	2.6	0
2	ZnO	7.1	3.8	0
3	Fe_2O_3	9.1	2.6	0
4	$ZnO-Fe_2O_3$[b]	4.3	3.0	0
5	ZFO-4	46.1	30.7	7.1
6	ZFO-2	28.8	16.0	5.9
7	ZFO-8	29.9	15.5	5.4
8	ZFO-10	24.7	7.9	0
9	$ZnFe_2O_4$	10.86	6.4	0

[a] Reaction conditions: reaction temperature, 190 °C; reaction time, 10 h; catalyst amount, 1.0 g; MC, 7.5 g; methanol, 64 g.
[b] Metal oxides were physically mixed and molar ratio of ZnO/Fe_2O_3 was 4.

[12,17]. Furthermore, the surface areas of the Zn/Fe mixed oxides are listed in Table 2. It could be seen that their surface areas decreased in the order of ZFO-10 > ZFO-4 > ZFO-8 > ZFO-2. However, their catalytic activity followed this order: ZFO-4 > ZFO-2 > ZFO-8 > ZFO-10. Thus, surface area of catalysts was not a decisive factor for their catalytic ability in the present work. Interestingly, according to the discussions mentioned above, both ZnO and $ZnFe_2O_4$ proportion of ZFO-4 were in a temperate state among these catalysts. Therefore, Zn/Fe molar ratio was a crucial factor for their catalytic performance. More important, such obviously high catalytic ability of Zn–Fe–O catalyst compared ZnO could be attributed to the appearance of $ZnFe_2O_4$.

In order to eliminate that the catalytic ability of ZFO-4 originated from ZnO and Fe_2O_3 interaction, a mixture of the two oxides with molar ratio of 4 was evaluated and it did not presented good performance (Entry 4). Besides, a further investigation on the performance of $ZnFe_2O_4$ was conducted. Obviously, it showed a little catalytic activity (Entry 9). This also confirmed the role of interaction between $ZnFe_2O_4$ and ZnO for catalyzing this reaction.

3.3. Stability of Zn/Fe mixed oxides

According to former studies reported, Zn^{2+} could activate MC via coordination with the nitrogen atom in MC molecule [17]. Therefore, $ZnCl_2$ exhibited the best catalytic performance, just because it could solve in methanol completely even at room temperature. Wu et al., proposed Zn-based catalyst to catalyze urea alcoholysis. Unfortunately, its catalytic ability was very low compared to that of ZnO [15,22]. Therefore, on the one hand, a model heterogeneous catalyst preparing DMC during this routine should be insoluble in methanol solution at certain temperature. On the other hand, the catalytic ability of the heterogeneous catalyst was similar to that of the homogenous one.

Table 2 showed element analysis results of methanol solutions after reaction in different systems. It could be found that divalent zinc ion concentration was very low, when catalysts were ZnO and Zn/Fe mixed oxides. Because there was lack of Zn^{2+} in the reaction system, ZnO presented no significant activity for the DMC production from MC and methanol. However, the high catalytic performance of mixed oxides, especially ZFO-4, was obviously not related to the metallic ions that dissolved in solution. In other words, there was no species that could dissolve in methanol. It also provided evidence that the excellent performance of these mixed oxides originated from the interaction of ZnO with $ZnFe_2O_4$.

A further study on the catalytic reusability of ZFO-4 was carried out. After the first run, used ZFO-4 sample was separated by filtrating, and washed with methanol several times, dried and reused in another two catalytic cycles. Fig. 3 presented that it still showed high catalytic performance after used three times. Additionally,

Fig. 2. XRD pattern of (a) zinc ferrite, and (b) zinc oxide.

Table 2
Composition, BET surface area of the catalysts and the content of cations in solution after the reaction[a].

Catalyst	Zn/Fe in solids	BET surface area (m^2/g)	Zn content (mg/L)	Fe content (mg/L)
ZnO	–	17.6	2.0	–
ZFO-2	1.86	16.90	0.3	0.2
ZFO-4	3.77	21.76	0.2	<0.1
ZFO-8	7.70	20.16	<0.1	<0.1
ZFO-10	9.59	26.95	<0.1	<0.1

[a] Reaction conditions: reaction temperature, 190 °C; reaction time, 10 h; catalyst amount, 1.0 g; MC, 7.5 g; methanol, 64 g.
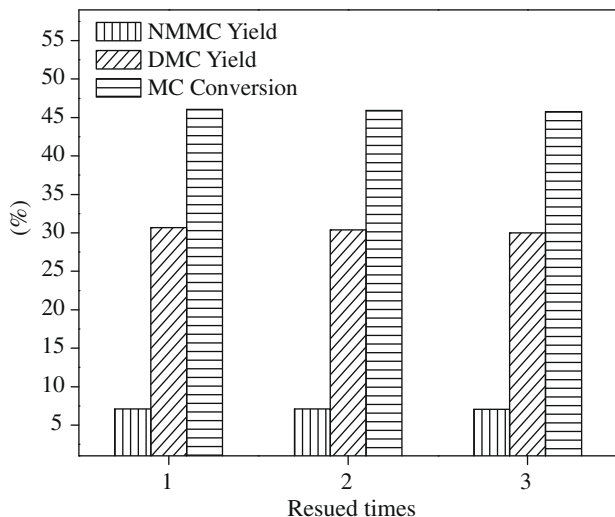

Fig. 3. Catalytic reusability of ZFO-4.

the recovered catalyst after reused three times was analyzed using XRD technique (see Fig. 1b′). Diffraction peak number was as the same as the fresh one, and the peak intensity didn't show any significant change. This demonstrated that a heterogeneous catalyst with high catalytic performance and stability for this reaction was successfully developed.

4. Conclusions

Zinc/iron mixed oxide showed the best catalytic performance for DMC synthesis from MC and methanol when the Zn/Fe molar ratio was 4. The MC conversion and DMC yield at the optimal reaction conditions were 46.1% and 30.7%, respectively. Elemental chemical analysis revealed that metal elements in methanol solution after reaction could be neglected. In addition, based on results of XRD experiment and the reusability test, its high catalytic performance and stability originated from the interaction of ZnO with $ZnFe_2O_4$.

Acknowledgement

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