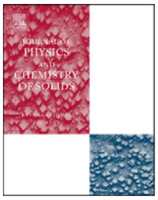
Journal of Physics and Chemistry of Solids 71 (2010) 427–430

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Synthesis of dimethyl carbonate from methyl carbamate and methanol catalyzed by mixed oxides from hydrotalcite-like compounds

Dengfeng Wang [a,b], Xuelan Zhang [a,b], Wenbo Zhao [a,b], Weicai Peng [a], Ning Zhao [a], Fukui Xiao [a], Wei Wei [a,*], Yuhan Sun [a,*]

[a] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, PR China
[b] Graduate University of Chinese Academy of Sciences, Beijing, 100049, PR China

ARTICLE INFO

Article history:
Received 17 May 2009
Received in revised form
24 September 2009
Accepted 26 September 2009

Keywords:
A. Multilayers
A. Oxides
B. Chemical synthesis
C. X-ray diffraction

ABSTRACT

A series of mixed oxides calcined from hydrotalcite-like compounds with different cations were prepared and their catalytic activities were studied by the synthesis of dimethyl carbonate (DMC) from methyl carbamate and methanol. Among them, ZnFe mixed oxide possessed the best catalytic ability. Furthermore, the zinc-based mixed oxides as well as the corresponding hydrotalcite-like compounds were characterized by using ICP, TGA, CO_2-TPD and N_2 adsorption/desorption techniques.

1. Introduction

Dimethyl carbonate (DMC) is attracting broad attentions in recent years from researchers owing to its use in replacing environmentally unfriendly compounds. It can be used as methylation and carbonylation reagents to replace dimethlsulfate, methyl halides, and phosgene [1]. It is also considered as an ideal additive for gasoline due to its high oxygen content [2]. Moreover, DMC is a promising electrolytic solution for the secondary lithium battery [3]. Up to now, several methods of DMC synthesis have been proposed [4,5]. Among them, urea methanolysis has drew extensive attentions because of low-cost and facile production separation. In this process, the intermediate methyl carbamate (MC) was produced first and further converted to DMC by consecutive reaction with methanol, which was the rate-control step [6–8]. So, detailed studies on the second step would be useful for the DMC synthesis via this new routine. As a precursor of homogeneous catalyst for urea methanolysis, ZnO could be used as a catalyst for the DMC preparation from MC and methanol, but the DMC yield was less than 5%. Zhao et al. reported that zinc compounds, especially $ZnCl_2$, presented high catalytic performance with the DMC yield of 33% [9–11]. However, these homogeneous catalysts suffered from the drawbacks of poor catalyst recovery and product separation. So, effective heterogeneous catalysts for this process are highly demanded.

As a type of layered solids, hydrotalcite-like compounds (HTlc), are also called as layered double hydrotalcites (LDHs) or anionic clays with a general formula, which could be determined as: $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A_{x/n})^{n-}\cdot mH_2O$, where M(II) is a divalent metal cation; M(III) represents a trivalent metal cation, A^{n-} is an anion, often carbonate in nature, m is the number of molars of co-intercalated water per formula weight of the compound, and x is the number of molars of M(III) per formula weight of the compounds [12]. They constitute a brucite-like net-work where the divalent cations are partially replaced by the trivalent ones. In other words, the HTlc are prepared by positive charged metal hydroxide layers, separated by interlayer regions containing anions and water molecules. Due to the character of the LDH compounds, the metal mixed oxides or spinel-like structures that obtained from thermal decomposition of LDHs usually present the advantages of thermal stability. Furthermore, highly dispersed metal clusters could also be obtained by dedicated activation treatments. Thus, calcined layered materials are often viewed as promising catalysts in many catalytic reactions.

The object of this work is to prepare and investigate the catalytic performance of mixed oxides derived from calcined hydrotalcite-like compounds for the DMC synthesis from MC and methanol. The results revealed that the zinc-containing composite oxides, especially zinc–iron mixed oxide, presented high catalytic activity.

---

* Corresponding authors. Tel.: +86 351 4049612; fax: +86 351 4041153.
E-mail addresses: weiwei@sxicc.ac.cn (W. Wei), yhsun@sxicc.ac.cn (Y. Sun).

0022-3697/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2009.12.005

2. Experimental

2.1. Synthesis of the samples

Preparation method of hydrotalcite-like compounds precursor has been described elsewhere [13]. Typically, solution A (100 mL) was obtained by mixing solution of metal nitrates with the divalent/trivalent atomic ratio of 3. Solution B was prepared by dissolving suitable amount sodium carbonate in 100 mL deionized water. Then the two solutions were added dropwise into a beaker containing 100 mL deionized water under constant stirring. And the pH of the solution was kept closed to 10.0 by addition of appropriate amounts of a 2 M sodium hydroxide. After that, the precipitates were aged in mother liquid at 343 K overnight. The solids were obtained separated by filtration and washed several times with deionized water until the filtrate showed no presence of Na^+. And the precipitates were dried at 353 K for about 12 h. A series mixed oxides were obtained by calcining the result hydroltalcite-like compounds in oven at 773 K for 5 h under a flowing stream of pure nitrogen. The hydrotalcite-like compounds synthesized here were referred as M(II) M(III)-*x*HT, where *x* standed for M(II)/ M(III) molar ratio. And the samples after calcined were labeled as M(II)M(III)O. For example, ZnFe-3HT and ZnFeO represented the ZnFe hydrotalcite-like sample and Zn/Fe mixed oxide, respectively.

2.2. Characterization

Power X-ray diffraction (XRD) experiments were carried out on a Rifaku D Max III VC instrument with Ni filtered Cu-Kα radiation (λ=1.5405 Å) at room temperature.

The specific surface area was obtained by N_2 adsorption–desorption method on a Micromeritics ASAP-2000 instrument (Norcross, GA).

The elemental chemical analysis was performed using the inductively coupled plasma-optical (ICP) emission spectroscopy on a Perkin Elemer 3000 equipment.

Thermogravimetric analysis (TGA) was conducted on TGA-92 instrument under nitrogen with the temperature range from 303 to 1073 K at the heating rate of 5 K/min.

The total basicity and base strength of the samples were determined by temperature-programmed desorption of absorbed CO_2 (CO_2-TPD). Catalysts (0.1 g, 40–60 mesh) were placed in the quartz reactor bed. After 5 h pretreatment at 873 K in Ar flow and cooled to room temperature, CO_2 was pulsed to the reactor using a 6-way valve until saturation was reached. The TPD procedure was started with a heating rate of 10 K/min under nitrogen flow. And the effluent was measured using a BALZAQ-mass spectrometer.

2.3. Catalytic test

The reaction of MC and methanol was carried out in a stainless steel autoclave of 300 mL with strong magnetic stirring and a reflux column. A typical experiment procedure was as follows: a desired amount of catalyst, MC and methanol were charged into the reactor, and then the bath was heated to the desired reaction temperature (controlling to a range of ± 2 K) in a desired time with stirring (revolving at a rate of 600 ± 50 rpm). After reaction, the reactor was cooled to room temperature. The liquid products were analyzed on a gas chromatography (GC) equipped with TCD after weighed and centrifugal separation from the catalyst.

3. Results and discussion

3.1. Texture and structure of zinc-containing mixed oxides and corresponding LDHs compounds

The results of chemical analysis revealed that the Zn/Al, Zn/Cr and Zn/Fe molar ratio in ZnAlO, ZnCrO and ZnFeO were all different from the corresponding divalent and trivalent metal molar ratio in mother solutions of 3.0 (Table 1). The molar ratio between divalent and trivalent cations in the mixed oxides

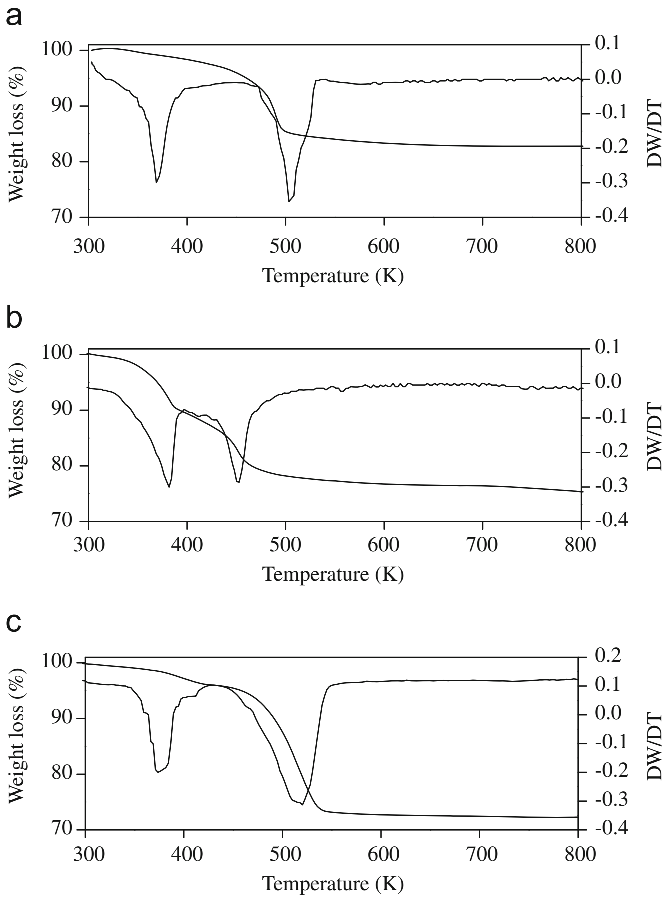


Fig. 1. TG-DTG curves of (a) ZnAl-3HT; (b) ZnFe-3HT; (c) ZnCr-3HT.

Table 1
Phisicochemical properties of the Zn-based mixed oxides and hydrotalcite-like compounds

Sample	Zn/M(III) in solids	Surface area (m^2/g)	CO_2 uptake (mmol/g)	Lattice parameters [a]	
				a (Å)	*c* (Å)
ZnAlO	2.82	50	1.72E−3	3.06	22.55
ZnFeO	2.81	52	1.03E−2	3.07	22.76
ZnCrO	2.86	72	1.18E−2	3.08	22.61

[a] The lattice parameters were belonged to corresponding hydrotalcite-like compounds

gradually decreased in the order of ZnCrO > ZnAlO > ZnFeO. Such a phenomenon might be ascribed to the different precipitation degrees for the three trivalent cations above-mentioned.

The thermal decomposition behaviors of the three samples were illustrated in Fig. 1. All the samples showed two typical weight-loss patterns. The first one, at low temperature (about 373 K), was due to the removal of the water in the interlayer without structure collapse, whereas the second one, at higher temperature (about 500 K), was assigned to the dehydroxylation of layers as well as decarbonation of anions leading to collapse of the layered network. It must be noted that for ZnCr-3HT material, Cr(III) ion can change to species with other chemical valencies due to the oxidation [14]. However, samples were all treated under an inert nitrogen condition in the present case. So, the second weight-loss peak of the ZnCr-3HT was also result in the decomposition of hydroxycarbonates to amorphous phases [15]. As a result, the three mixed oxides containing zinc were synthesized successfully by decomposition of corresponding HTls.

Fig. 2(a) showed the X-ray diffraction of as-synthesized hydrotalcite-like materials. The XRD patterns of all the samples revealed the peaks characteristic of LDH phases with the presence of sharp and intense lines at low angle values as well as less intense and asymmetric lines at higher values of 2θ[14–16]. It was well known that the hydrotalcite could be described by two important values, a and c. The parameter a decided by the (1 1 0) reflection (a=2d_{110}), was related to the unit cell dimension and depended on the divalent and trivalent metal element molar ratio. The peaks at 11.6° and 23.4° ascribed to the (0 0 3) and (0 0 6) reflections could be used to calculate the interlayer distance c, where c=3d_{003}, and further relied on the electrostatic force in the hydrotalcite interlayer [12,13,15,16]. The calculation results of the three hydrotalcite samples were given in Table 1. It should be noted that a steady increase of a was observed in the following order: ZnAl-3HT < ZnFe-3HT < ZnCr-3HT. This trend was in agreement with the ionic radii of the metal ions that in the follow of Al^{3+}(0.50 Å) > Fe^{3+}(0.64 Å) > Cr^{3+}(0.69 Å) [12]. Fig. 2(b) revealed the XRD patterns of HTls after calcination. It was found that all the hydrotalcite structure was destroyed and some new crystal phases were formed after calcination. According to Joint Committee on Powder Diffraction System (JCPDS), zinc oxide (ZnO) was the main content for the three mixed oxides, and new phases such as franklinite ($ZnFe_2O_4$), gahnite ($ZnAl_2O_4$) and picotite ($ZnCr_2O_4$) also appeared for ZnFeO, ZnAlO, and ZnCrO mixed oxides, respectively.

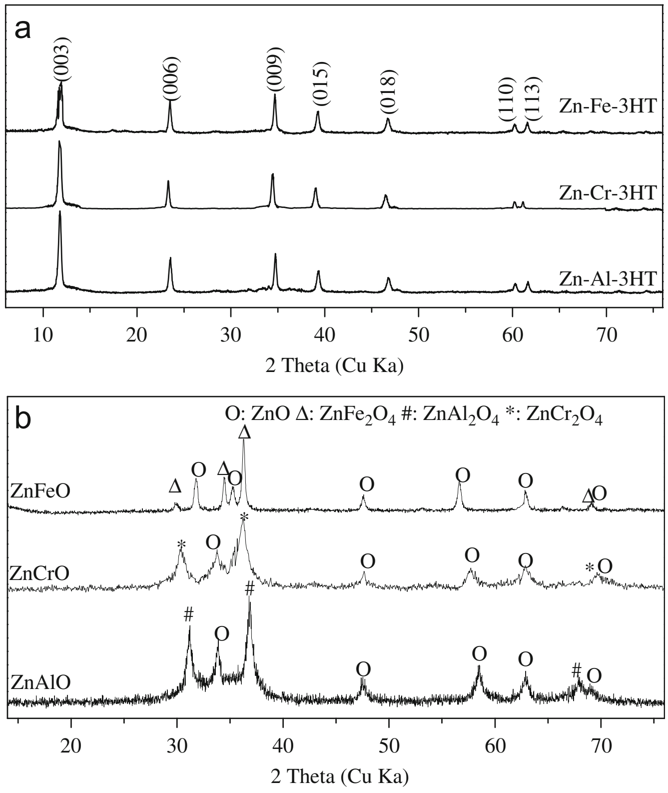


Fig. 2. XRD patterns of samples: (a) Before calcination (b) after calcination at 773 K for 5 h.

Fig. 3 illustrated the CO_2-TPD profiles of zinc-based mixed oxides prepared in this work. For the mixed oxide samples, basicity (basic sites amount per unit weight of catalysts) and basic strength were two important parameters that affected their catalytic performance. The baisicity of the three mixed oxides were listed in Table 1. Three desorption peaks were detected at 573, 533 and 463 K for ZnFeO, ZnCrO and ZnAlO, respectively (see Fig. 3). This implied that the basic strength of these catalysts decreased in the following sequence: ZnFeO > ZnCrO > ZnAlO.

3.2. Catalytic performance of mixed oxides

Usually, the synthesis of DMC from MC and methanol took place as follows: DMC was first produced as the methoxy group derived from methanol substituting the amino of MC. In order to improve the formation of DMC, ammonia should be removed in time. On the one hand, DMC could further react with MC to produce the by-product N-methyl methyl carbamate (NMMC). On the other hand, it also decomposed into dimethyl ether and carbon dioxide over solid basic and acidic oxides at high temperature [17,18]. Therefore, high temperature, long reaction time and excessive catalysts would have negative effects on the DMC synthesis. because It should be noted that dimethyl ether cannot be detected by gas chromatography, because it was easy to volatilize when the autoclave was opened. Therefore, all the catalysts were evaluated based on MC conversion, DMC and NMMC yield in the present work.

Table 2 showed typical results of MC methanolysis over various catalysts. It was observed that the DMC yield was only 2.58% in the absence of catalyst (Entry 1). ZnO, as an ideal catalyst for production of DMC from urea methanolysis, exhibited low

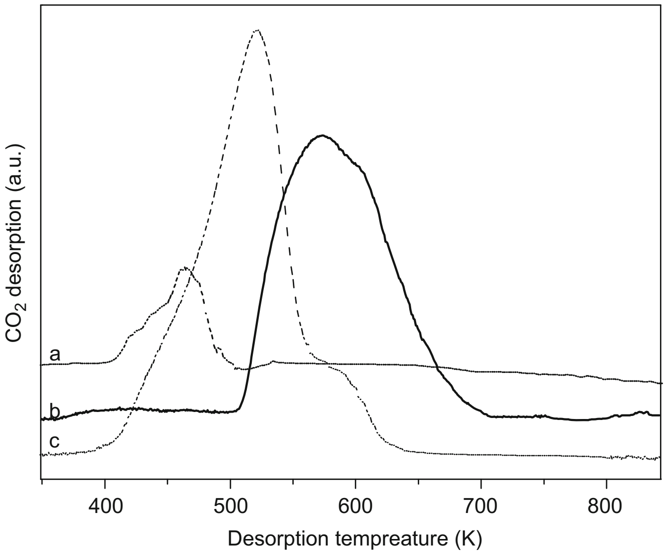


Fig. 3. CO_2-TPD profiles of (a) ZnAlO; (b) ZnFeO; (c) ZnCrO catalysts.

Table 2
Catalytic performance of catalysts

Entry	Catalyst	MC conversion (%)	DM Cyield (%)	NMM Cyield (%)
1	–	4.06	2.58	0
2	ZnO	7.29	4.52	0
3	Fe_2O_3	9.04	2.62	0
4	Al_2O_3	10.58	4.38	0
5	Cr_2O_3	9.46	3.70	0
6	ZnO–Fe_2O_3[a]	5.62	3.25	0
7	MgFeO	24.07	7.82	0
8	NiFeO	23.69	3.21	0
9	CuFeO	31.81	2.66	0
10	ZnAlO	24.87	13.91	3.64
11	ZnCrO	27.64	17.04	4.01
12	ZnFeO	66.58	31.48	9.53

Reaction conditions: MC, 7.5 g; methanol, 64 g; reaction temperature, 463 K; reaction time 10 h; catalyst amount, 1.0 g.

[a] The metal oxides were mixed and the molar ratio of ZnO/Fe_2O_3 was 4.

activity for the reaction. This was consistent with the results reported previously (Entry 2) [9,10]. Moreover, iron-based mixed oxides, such as MgFeO and NiFeO were also found to be less activity, with the DMC yield of 7.82% and 3.21%, respectively (Entries 7, 8). Under the same reaction conditions, the zinc-based mixed oxides, especially ZnFeO, presented the best catalytic ability, yielding 31.48% DMC (Entry 12). Based on these as well as the characterization results, zinc showed a positive effect on the catalytic performance of these mixed oxide. This further confirmed by comparing the catalytic behavior of ZnO/Fe_2O_3 physically mixture (Entry 6). Surprisingly, the activity of ZnCrO was poor despite its larger surface area compared with that of ZnFeO, which might suggest that surface area of catalyst is not the decisive factor for this reaction. It was considered that the appearance of the new component, especially zinc ferrite could promote the DMC synthesis. In other words, the activity of catalysts must be owing to the synergistic effect between the zinc ferrite and zinc oxide.

In addition, as shown in CO_2-TPD profile figure, ZnFeO also presented the highest basic strength among the three zinc-based samples. In the previous report, the basic strength of the catalyst was considered as an important factor for the DMC synthesis from MC and methanol. The reason was that methanol could be activated by base sites via abstraction of $H^{\delta+}$ to form $CH_3O^{\delta-}$ followed by nucleophilic attack of carbon atom of MC to produce DMC [6]. It could also explain why ZnFeO has the best catalytic ability in the present case.

4. Conclusions

Among the calcined hydrotalcite-like compounds, zinc/iron mixed oxide was an effective catalyst for the synthesis DMC from MC and methanol. XRD patterns showed that this catalyst showed both zinc oxide and zinc ferrite phases and they produced a synergistic effect on its catalytic performance. In addition, the basic strength of the catalyst was an important factor to activate methanol and further promoted the reaction between MC and methanol through the abstraction of $H^{\delta+}$ by base sites.

Acknowledgement

This work was supported by the State Key Program for Development and Research of China (No. 2006BAC02A08).

References

[1] Y. Ono, Appl. Catal. A 155 (1997) 133–136.
[2] M.A. Pacheco, C.L. Marshall, Energy Fuel 11 (1997) 2–29.
[3] S. Megahed, W. Ebner, J. Power Sources 54 (1995) 155–162.
[4] U. Romano, R. Twesel, C.L. Marshall, Ind. Eng. Chem. Proc. Res. Dev. 19 (1980) 396–403.
[5] H. Itoh, Y. Watanabe, K. Moric, H. Umino, Green Chem. 5 (2003) 558–562.
[6] M. Wang, H. Wang, N. Zhao, W. Wei, Y. Sun, Catal. Commun. 7 (2006) 6–10.
[7] J. Sun, B. Yang, H. Lin, Chem. Eng. Technol. 27 (2004) 435–439.
[8] N.V. Kaminskaia, N.M. Kostic, Inorg. Chem. 37 (1998) 4302–4312.
[9] M. Wang, H. Wang, N. Zhao, W. Wei, Y. Sun, Ind. Eng. Chem. Res. 44 (2005) 7596–7599.
[10] W. Zhao, W. Peng, D. Wang, N. Zhao, J. Li, F. Xiao, W. Wei, Y. Sun, Catal. Commun. 10 (2009) 655–658.
[11] W. Zhao, F. Wang, W. Peng, N. Zhao, J. Li, F. Xiao, W. Wei, Y. Sun, Ind. Eng. Chem. Res. 47 (2008) 5913–5917.
[12] F. Cavani, F. Trifiro, A. Vaccari, Catal. Today 11 (1991) 173–301.
[13] G. Wu, X. Wang, B. Chen, J. Li, N. Zhao, W. Wei, Y. Sun, Appl. Catal. A 329 (2007) 106–111.
[14] K. Fuda, K. Suda, T. Matsunaga, Chem. Lett. 22 (1993) 1479–1482.
[15] J.M. Fernadez, M.A. Ulibarri, F.M. Labajos, V. Rives, J. Mater. Chem. 8 (1998) 2507–2514.
[16] F.M. Labajos, V. Rives, Inorg. Chem. 35 (1996) 1154–1160.
[17] Y. Fu, H. Zhu, J. Shen, Thermochim. Acta 434 (2005) 88–92.
[18] S.A. Anderson, S. Manthata, T.W. Root, Appl. Catal. A 280 (2005) 117–124.