Accepted Manuscript

Synthesis of dimethyl carbonate from methanol and urea over zinc-strontia mixed oxide catalysts



D. Dhana Lakshmi, B. Srinivasa Rao, N. Lingaiah

| PII: | \$1566-7367(19)30005-6 |
|----------------|--|
| DOI: | https://doi.org/10.1016/j.catcom.2019.01.005 |
| Reference: | CATCOM 5589 |
| To appear in: | Catalysis Communications |
| Received date: | 24 October 2018 |
| Revised date: | 3 January 2019 |
| Accepted date: | 7 January 2019 |

Please cite this article as: D. Dhana Lakshmi, B. Srinivasa Rao, N. Lingaiah, Synthesis of dimethyl carbonate from methanol and urea over zinc-strontia mixed oxide catalysts. Catcom (2018), https://doi.org/10.1016/j.catcom.2019.01.005

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Synthesis of dimethyl carbonate from methanol and urea over zinc-strontia mixed oxide catalysts[‡]

D. Dhana Lakshmi^{a,b}, B. Srinivasa Rao^{a,b}, N. Lingaiah^{a,b}*

^aCatalysis and Fine chemicals Division,

CSIR-Indian Institute of Chemical Technology, Hyderabad-500 007, India

^bCSIR-Academy of Scientific and Innovative Research (CSIR-AcSIR), New Delhi, India.

Abstract

A series of ZnO-SrO mixed oxide catalysts were prepared by co-precipitation with different compositions and tested for dimethyl carbonate synthesis from urea and methanol. The catalysts were characterized by BET surface area, XRD, NH₃-TPD and CO₂-TPD. The catalyst with 1:1 mole ratio exhibited high DMC yield of 35%. The uniform distributions of moderate to strong basic sites along with considerable number of acidic sites are accountable for high activity. Different reaction parameters were also screened and best possible conditions were established. The catalyst was easily recovered and reused with consistent activity.

Keywords: Dimethyl carbonate; Urea; Methanolysis; Zinc oxide; Strontium oxide.

*Corresponding author. Tel.: +91 40 27191722; fax: +91 40 27160921

E-mail address: nakkalingaiah@iict.res.in (N. Lingaiah)

[‡]Communication Number- IICT/Pubs./2018/367

1. Introduction

Dimethyl carbonate (DMC) an environmentally affable building block in chemical industry [1]. DMC have been received much attention in recent years [2], as this molecule contains active functional groups, negligible toxicity and good biodegradability. It can be utilized as a methylating and carbonylating agent to replace toxic substances such as methyl halides, phosgene and dimethyl sulphate [3]. Since it has elevated oxygen content (53%) and high octane value than methyl ter-butyl ether or ter-amyl methyl ether, it can be used as good additive of gasoline. Additionally, DMC can be used as an electrolyte in secondary lithium ion battery owing to its high dielectric constant [4-5]. Conventionally DMC is obtained majorly from phosgenation of methanol, carbonylation of methanol and transesterification of cyclic carbonate with methanol. All these processes have their own environmental disadvantages. Readily available carbon dioxide can be used as a raw material for DMC synthesis. However, there are some restrictions to use CO_2 as its activation is difficult [6-8].

In order to stay away from utilizing poisonous, corrosive and expensive raw materials, the production of DMC from alcoholysis of urea is considered as indirect synthesis of DMC from CO_2 and methanol since the released NH_3 can be recycled to produce urea by reaction with CO_2 [9-10]. This process has advantageous as it uses low cost urea and methanol. The DMC synthesis proceeds in two intermediate steps. Isocyanic acid forms as an intermediate molecule in the first step, which reacts with methanol to produce methyl carbamate. Then methyl carbamate and methanol yields DMC. It may further react with methyl carbamate (MC) to form N-methyl methylcarbamate (NMMC).

Different catalysts have been tested for the synthesis of DMC by methanolysis of urea. Yuhan Sun et. al. reported DMC synthesis over different metal oxides and among them ZnO showed superior yield [11]. Later many catalysts such as bases, organic tin, mixed metal oxides have been employed [12-15]. Among these, ZnO and its salts are highly active toward

DMC synthesis owing to its weak acidity/basicity, which is effectively helps for urea activation [16]. The key disadvantage of ZnO based catalysts related to its solubility in methanol [17]. The catalysts containing acidic and basic sites together are suitable for the synthesis of DMC. In this respect mixed oxide which potentially acidic oxide like ZnO and base oxide like SrO may suitable for urea methylation to DMC.

In this work, ZnO-SrO mixed oxide catalysts were prepared by varying the molar ratios of Zn to Sr and calcination temperatures. These catalysts were used for urea methylation to DMC. The activity results of the catalysts were supported with their characterization results. The catalysts were characterized by XRD, BET surface area, and TPD of NH₃, CO₂.

2. Experimental

2. 1. Catalyst preparation

The ZnO-SrO mixed oxide catalysts were synthesized by co-precipitation method with different molar ratios ranging from 3:1, 2:1, 1:1, 1:2, and 1:3. The samples were named as ZS 31, 21, 11, 12, 13, where the alphabets represented the metal ions and numbers represent the mole ratios. Details regarding catalysts synthesis procedure, their characterization and activity studies are reported in the supplementary data (Appendix A).

3. Results and discussion

3.1. Catalyst characterizations

BET surface areas of the catalysts are presented in Table 1. Surface areas of the catalysts varied from 3 to 11 m²/g depending on the ZnO and SrO molar ratio. The margin of error for these low surface area materials is ± 1 . The catalyst surface area is increased with raise in ZnO content. The catalyst with high SrO content (ZS13) showed low surface area (3 m²/g) due to the aggregation of crystals.

| Entry | Catalyst | $\mathbf{S}_{\mathrm{BET}}$ | Total basicity | | Total acidity | |
|-------|----------|-----------------------------|----------------|---------------------|---------------|---------------------|
| | | (m^2/g) | | | | |
| | | | (mmol/g) | (mmol/m^2) | (mmol/g) | (mmol/m^2) |
| 1 | ZS31 | 12.3 | 0.195 | 0.015 | 0.366 | 0.029 |
| 2 | ZS21 | 10.3 | 0.176 | 0.017 | 0.359 | 0.034 |
| 3 | ZS11 | 8.7 | 0.322 | 0.036 | 0.326 | 0.037 |
| 4 | ZS12 | 3.9 | 0.318 | 0.081 | 0.136 | 0.034 |
| 5 | ZS13 | 3.0 | 0.340 | 0.110 | 0.108 | 0.035 |

Table 1. Textural and surface properties of the catalysts.

Fig.1 shows the XRD patterns of the ZnO-SrO catalysts. ZnO exhibited peaks at 31.8° , 34.5° , 36.3° , 47.6° , 56.6° , 62.9° , 67.9° and 69.2° which are characteristic peaks of hexagonal wurtzite structure (JCPDS No. 36-1451). The diffraction lines at 2θ of 25.3° , 26° , 29.7° , 32.8° , 44.3° , 45.9° , and 48° were related to SrCO₃ (JCPDS 52-1526). The peaks at 31.6° , 37.6° , and 52.1° are corresponding to the diffractograms of SrO. The catalyst with ZnO and SrO with 1:1 molar ratio showed the diffractograms related to ZnO and SrO along with SrCO₃ phase. When SrO loading was increased in the catalysts, the intensities of diffractograms related to SrCO₃ also increased. The formation of SrCO₃ may be due the absorption of CO₂ by SrO as the basic sites of SrO attract the acidic CO₂. One can not eliminate the formation of it during the preparation of the catalysts from K₂CO₃, which is used as a precipitation agent.



Fig.1. Powder XRD patterns of the catalysts. SrCO₃ (•), SrO (\heartsuit), ZnO (\square).

Basicity of the catalysts was measured by TPD of CO₂ and the profiles are revealed in Fig. 2. All the synthesized catalysts showed an intense band around 600 °C, which indicates the presence of strong basic sites in the catalysts. Bulk SrO exhibited strong basic sites along with moderate sites, while pure ZnO did not show any considerable amount of basicity. The basicity of the catalyst varied with increase in SrO content. The high SrO containing catalyst (ZS13) showed high temperature desorption peak. This might be due to the presence of SrCO₃. The desorption peak relates strong basic sites shifted to low temperature with increase in the content of ZnO. This is mainly due to the acidic nature of ZnO. The ZS11 catalyst showed the presence of both moderate and strong basic sites compared other catalysts. The coprecipitation of SrO by the interaction with ZnO. The basicity values are calculated and shown in Table 2. The alkalinity of the catalysts increase in alkalinity for the catalyst with high Zn

content is due the acidic nature of ZnO. The alkalinity of ZS11 is slightly more than ZS12. This is may be due to well dispersion of SrO on ZnO at equimolar composition. In order to know if any desorption of CO₂ associated with SrCO₃ as the catalysts showed the presence of SrCO₃ diffraction peaks in XRD, a TPD of CO₂ experiment is carried without adsorption of CO₂. The TPD profile without CO₂ adsorption is also shown in Fig. 2. The ZS11catalyst without CO₂ adsorption showed two peaks in 600-700 °C range, indicating that CO₂ was desorbed from strontium carbonate present in the catalyst. Desorption peaks in the catalysts except the catalyst with high SrO (ZS13) are below 600 °C, which are related to basic sites associated to SrO, but not SrCO₃. The strong basic sites observed for the catalyst with high SrO (ZS13) mainly due to the presence of SrCO₃ phase.



Fig.2. CO₂-TPD profiles of the catalysts

The acidity of the catalysts was measured by ammonia TPD and the patterns are shown in Fig. S3. The acidity values of the catalysts are placed in Table 1. Fig. S3 indicates that the presence of more amount of ZnO in catalysts led to the generation of strong acidic sites.

3.2. Activity results

Alcoholysis of urea with methanol for the synthesis of DMC was carried over ZS catalysts and the results are summarized in Table 2. SrO a base catalyst exhibited lower DMC yield (15 %), while ZnO possessing predominantly acidic sites showed 21 % within 6 h of reaction time. The catalysts ZS11, ZS12 and ZS13 showed 35, 24 and 19 % of DMC yield respectively. High ZnO containing ZS21 and ZS31 catalysts exhibited about 18 and 16% of DMC yields respectively. Aforementioned results suggesting that the catalyst with high Sr content led to more NMMC yield and the one with high Zn content led to more MC yield.

The difference between the activities of various ZS catalysts was explained based on their acid and base properties. ZnO which contain both acidic and basic sites showed better activity than SrO which possess mainly basic sites. The ZnO-SrO mixed oxide catalysts showed high activity than single oxides. This indicates that alcoholysis reaction is favourable with the catalysts having both acid and base sites. ZS mixed oxide catalyst with high SrO content has strong basicity and showed low DMC yield. This is due to the easy decomposition of DMC that formed on strong basic sites and the decomposed DMC might react with MC to yield NMMC. High ZnO containing catalysts showed comparatively low DMC yield, as these catalysts have more acidity than basicity and these sites were not sufficient to convert initially formed MC to DMC. The catalyst with equi molar (ZS11) content of ZnO and SrO showed relatively high amount of DMC than other catalysts as it has both basic and acidic sites in relatively equal ratios. Therefore, the presences of both acidic and basic sites are responsible for the high catalytic activity of ZS11 catalyst towards DMC.

The basicity per unit surface area values of ZS catalysts calcined at 500 °C was increased with decrease in Zn/Sr mole ratio and there is no such variation was observed in case of acidity values. The high activity of ZS-11 catalyst is mainly due to the presence of acid/base sites per unit surface area.

| Catalyst | MC | DMC | NMMC | Total basicity | Total acidity |
|----------|-----------|-----------|-----------|----------------|---------------|
| | Yield (%) | Yield (%) | Yield (%) | (mmol/g) | (mmol/g) |
| ZS31 | 72 | 16 | 12 | 0.195 | 0.366 |
| ZS21 | 63 | 18 | 19 | 0.176 | 0.359 |
| ZS11 | 42 | 35 | 23 | 0.322 | 0.326 |
| | | | | | |
| ZS12 | 45 | 24 | 31 | 0.318 | 0.136 |
| ZS13 | 44 | 19 | 37 | 0.340 | 0.108 |

Table 2. Activity of ZS catalysts for the synthesis of DMC

Reaction conditions: methanol/urea mole ratio: 15, catalyst wt%: 2.6, time: 6h, temperature: 170 °C.

The present catalyst activity was compared with other reported catalysts and the details are shown in Table S1. M. Wang et al. studied DMC synthesis over ZnO with 29% DMC [11]. However, its reusability is very poor. In another study Zn(NO₃)₂-SiO₂ catalyst showed only 4.5% yield [18]. F. Xiao et. al. used ZnO-Al₂O₃ catalyst and they got about 36% DMC at relatively high methanol to urea ratio (20) in 10 h [19]. ZnO-CaO catalysts was showed maximum amount of 41% DMC yield with in 10 h of reaction at a high methanol to urea ratio of 20 [20]. The present reported catalyst is comparatively better than the other catalysts in the way of low methanol to urea mole ratio and high DMC yield in less reaction time.

3.3. Effect of calcination temperature

The catalyst activity is not only dependent on the molar ratio of the constituent elements but also on their surface, structural properties. These properties also depend on the calcination temperature of the catalysts. As the ZS11 catalyst showed high activity, this catalyst was subjected to different calcination temperatures varying from 400-800 °C. The effect of calcination temperature was studied and the results are mentioned in Table 3. The catalysts calcined at 400-600 °C showed more DMC yield compared to the catalysts calcined at 700 and 800 °C. Among these the catalyst calcined at 500 °C was shown high DMC yield. The high temperature calcined catalysts showed less activity towards DMC.

| Catalyst | MC | DMC | NMMC |
|----------|-----------|-----------|-----------|
| | Yield (%) | Yield (%) | Yield (%) |
| ZS11-400 | 55 | 28 | 17 |
| ZS11-500 | 42 | 35 | 23 |
| ZS11-600 | 38 | 29 | 33 |
| | | _, | |
| ZS11-700 | 80 | 12 | 8 |
| ZS11-800 | 85 | 9 | 7 |

Table 3. Activity of different calcined ZS11 catalyst.

Reaction conditions: methanol/urea mole ratio: 15, catalyst wt%: 2.6, time: 6h, temperature: 170 °C.

With the intention to know the alteration in activity of different calcined catalysts, these catalysts were characterized further by XRD and CO_2 -TPD techniques. The XRD patterns of different calcined temperatures (Fig. S1) indicates the decomposition of $SrCO_3$ to SrO at high calcination temperatures. CO_2 -TPD results as mentioned in Fig. S2 suggested that the basicity of the catalysts was increased with increase in calcination temperature from 400 to 600 °C and further increase in calcination temperature the strength of basicity was decreased sharply.

The decrease in basicity might be due to the absence of the $SrCO_3$ phase as it was stable up to 600 °C and decomposed to SrO when calcined at above 600 °C. The catalysts calcined at 700 and 800 °C showed less DMC yields as the basicity associated with $SrCO_3$ was absent. As a result of this, the activity towards DMC was decreased in case of ZS-11 catalyst calcined at high temperature. These results suggest the presence of $SrCO_3$ contribute to increase the DMC yield by facilitating the decomposition of urea on the basic sites.

The presence of basic sites along with acidic sites enhanced the catalytic activity of ZS-11 catalyst calcined at 500 °C.

3.4 Optimization of reaction conditions

The impact of reaction temperature on DMC yield was shown in Table S2. The DMC yield increased as the temperature increased in the range of 150-170 °C and then decreased beyond 170 °C. Nevertheless, it was known that urea begins to decompose into NH_3 and isocyanic acid (HNCO) at a temperature of 135 °C under ambient pressure. At an equivalent time, the speedy decomposition of urea at high temperature can lead to the reaction of methanol with isocyanic acid to generate intermediate MC and the formed DMC reacts with MC to produce NMMC. Thus, the rapid decline in the DMC yield was observed above 190 °C and this could be attributed to the formation of NMMC.

The effect of methanol/urea molar ratio on DMC synthesis is presented in Table S3. The results demonstrate that the DMC yield increased when methanol/urea molar ratio is in the range of 10 to 15. Further increase in the ratio up to 20 a decrease in activity was noticed. When the methanol/urea molar ratio was 15, the DMC yield reached a maximum of 35%. While the methanol/urea molar ratio was lower than 15, the urea concentration was high, the side reaction N-methylation of urea with DMC would occur easily resulting a lower DMC yield. Theoretically, higher methanol/urea molar ratio could promote the reaction equilibrium

towards DMC. Nevertheless, too high methanol/urea molar ratio would lead to the reduction of urea concentration. Consequently, some active sites of the catalyst for activating urea would be occupied by a larger amount of methanol. Thus, the reaction rate might decrease, resulting in a lower DMC yield. In the present case, from a practical point of view, the suitable methanol/urea molar ratio is 15.

The influence of catalyst quantity was investigated over ZS11 catalyst calcined at 500 °C. As shown in Fig. 3, the amount of DMC produced was elevated from 14 % to 35 % when catalyst amount varied from 0.6 to 3.9 wt%. The DMC yield was declined with further increment in catalyst amount, owning to the decomposition of DMC on available basic sites. The DMC yield reached maximum (35 %) at catalyst content of 2.6 wt%.



Fig.3. Effect of catalyst loading on reaction, Reaction conditions: methanol/urea mole ratio: 15, catalyst loading wt%: 0.6-3.9, time: 6h, temperature: 170 °C.

The was also studied Fig. 4 shows the profile of reaction time on DMC synthesis. The maximum DMC yield of 35% was achieved at 6 h of reaction time. Further elevation in reaction time led to decrease in DMC yield. When the reaction time exceeded 6 h, the yield was sharply decreased due to subsequent reaction of DMC with MC to produce NMMC as by

product. The optimum operational conditions based on above studies were obtained for ZS catalysts are; reaction temperature 170 $^{\circ}$ C, reaction time 6 h, CH₃OH/urea molar ratio 15 and the catalyst content of 2.6 wt%.



Fig.4. Influence of time on urea methanolysis, Reaction conditions: methanol/urea mole ratio: 15, catalyst wt%: 2.6, time: 2-8h, temperature: 170 °C.

3.4. Stability of catalyst

The stability and reusability of the catalyst was also studied. The catalyst was removed by centrifugation after reaction. After the separation, the catalyst was oven dried for 2 h and reused for the next run under the same conditions. The recycling was carried for four times and the results are shown in Fig. S4. The results indicate that the activity of the catalyst was almost similar even after fourth run. The used catalyst was characterized by XRD and the profiles are presented in Fig. S5. It was found that there is no much changes their structural features in used catalyst compared to the fresh catalyst. These results indicating that the catalyst was stable and active for repeated use.

4. Conclusions

The ZnO-SrO catalysts with both the acid and base properties were prepared by coprecipitation method. These are active catalysts for urea methanolysis to produce DMC. The catalyst with ZnO and SrO equimolar ratio and calcined at 500 °C showed high yield towards DMC. The catalyst with both acidic and basic sites is necessary to get high DMC yield. The surface characteristics of the catalysts are depends on the molar ratio of ZnO/SrO and treatment temperature. The presence of well dispersed ZnO and SrO/SrCO₃ phases were favours the urea alcoholysis to DMC. The catalyst is easy to separate and reusable with no substantial loss in activity.

Acknowledgement

D. Dhana Lakshmi thanks to University Grants Commission (UGC), New Delhi, India for the financial support in the form of junior research fellowship.

Appendix A. Supplementary data

Supplementary data to this article can be found online

5. References:

- [1] P.Tundo, Appl. Chem. 73 (2001) 1117-1124.
- [2] A. G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951-976.
- [3] P.Tundo, L. Rossi, A. Loris. 70 (2005) 2219-2224.
- [4] A.Dibenedetto, A. Angelini, Adv. Inorg. Chem. 66 (2014) 25-81.
- [5] P. Rounce, A. Tsolakis, P. Leung, A. York, Energy Fuels. 24 (2010) 4812-4819.
- [6] B. A. Santos, V. M. Silva, J. M. Loureiro, A. E. Rodrigues, ChemBioEng Rev. 1 (2014) 214-229.
- [7] M. Zhang, M. Xiao, Sh. Wang, D. Han, Y. Lu, Y. Meng, J. Cleaner Prod. 103 (2015) 847-853.

- [8] D. C. Stoian, E. Taboada, J. Llorca, E. Molins, F. Medina, A. M. Segarra, Chem. Commun. 49, (2013) 5489–5491.
- [9] W. B. Zhao, W. C. Peng, D. F. Wang, N. Zhao, J. P. Li, F. K. Xiao, W. Wei and Y. H. Sun, Catal. Commun. 10 (2009) 655-658.
- [10] W. Joe, H.J. Lee, U. G. Hong, Y. S. Ahn, C. J. Song, B. J. Kwon and I. K. Song, J. Ind.Eng. Chem. 18 (2012) 1018-1022.
- [11] M. Wang, N. Zhao, W. Wei, Y. Sun, Ind. Eng. Chem. Res. 44 (2005) 7596-7599.
- [12] X. M. Wu, M. Kang, N. Zhao, W. Wei, Y. H. Sun, Catal. Commun. 46 (2014) 46-50.
- [13] D. F. Wang, X. L. Zhang, W. B. Zhao, W. C. Peng, N. Zhao, F. K. Xiao, W. Wei, Y. H. Sun, J. Phys. Chem. Solids. 71 (2010) 427-430.
- [14] W. B. Zhao, W. C. Peng, N. Zhao, F. K. Xiao, W. Wei, Y. H. Sun. Petrochem.Technol. 38 (2009) 367-372.
- [15] M. H. Wang, H. Wang, N. Zhao, W. Wei, Y. H. Sun, Catal. Commun. 7 (2006) 6-10.
- [16] W. Zhao, F. Wang, W. Peng, N. Zhao, J. Li, F. Xiao, W. Wei, Y. Sun, Ind. Eng. Chem. Res. 47 (2008) 5913-5917.
- [17] W. B. Zhao, W. C. Peng, D. F. Wang, N. Zhao, J. P. Li, F. K. Xiao, W. Wei and Y. H. Sun, Catal. Commun. 10 (2009) 655-658.
- [18] Z. Z. Zhi, S. X. Lei, Z. X. Wen, F. X. Chen, J Fuel Chem Technol, 2015, 43(11), 1375-1379.
- [19] X. Wu, M. Kang, Y. Yin, F. Wang, N. Zhao, F. Xiao, W. Wei, Y. Sun, Appl. Catal. A: Gen., 473 (2014) 13–20.
- [20] X. Wu, M. Kang, N. Zhao, W. Wei, Y. Sun, Cat. Comm, 46 (2014) 46-50.

The research highlights:

- > Zn and Sr mixed oxide are active catalysts for synthesis of DMC with high yield
- The activity of the catalysts depends on the mole ratio and calcinations \triangleright temperature.
- > The presence of both acidity and basic sites directing the DMC yield.

the second secon