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# Driving dimethyl carbonate synthesis from CO<sub>2</sub> and methanol and production of acetylene simultaneously using CaC<sub>2</sub>†

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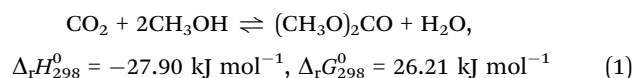
**The synthesis of dimethyl carbonate (DMC) from CO<sub>2</sub> and methanol is a very interesting reaction, but is thermodynamically limited. In this work, CaC<sub>2</sub> was used to consume the water produced in the reaction to shift the reaction equilibrium, and C<sub>2</sub>H<sub>2</sub> was produced at the same time. This is the first work on the combination of driving a thermodynamically unfavorable reaction and producing C<sub>2</sub>H<sub>2</sub> using CaC<sub>2</sub>.**

Carbon dioxide (CO<sub>2</sub>) is the major greenhouse gas, it is also a renewable, abundant, nontoxic, non-flammable and easily available carbon resource, and its utilization has attracted extensive attention. Various chemicals have been synthesized using CO<sub>2</sub> as a feedstock,<sup>1</sup> such as cyclic carbonates,<sup>2</sup> methanol,<sup>3</sup> formic acid,<sup>4</sup> nitrogen containing chemicals,<sup>5</sup> and polymers.<sup>6</sup>

Dimethyl carbonate (DMC) has negligible toxicity and good biodegradability, and has been used as a green solvent, a gasoline octane enhancer,<sup>7</sup> a precursor of polycarbonate resins, and a methylating and carbonylating agent to replace some toxic substances such as dimethyl sulphate, phosgene, and methyl chloroformate.<sup>8</sup> DMC can be produced from the reaction of phosgene with methanol,<sup>9</sup> oxidative carbonylation of methanol,<sup>10</sup> oxidative reaction of carbon monoxide and methyl nitrite,<sup>11</sup> and transesterification of methanol with cyclic carbonates.<sup>12</sup> However, obvious shortcomings exist in these routes, such as toxic, corrosive, and expansive reactants.

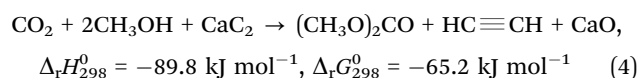
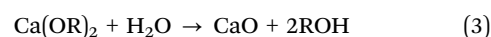
DMC can be synthesized from CO<sub>2</sub> and methanol as shown in eqn (1). This reaction is very attractive and has been studied extensively.<sup>13</sup> The standard Gibbs free energy of the reaction is 26.21 kJ mol<sup>−1</sup>, indicating that the reaction is thermodynamically unfavourable.<sup>14</sup> Removing water from the reaction system can

enhance the yield of DMC, as can be known from eqn (1). A 3 Å molecular sieve has been used in an outline dehydrating system of this reaction to promote the yield of DMC,<sup>15</sup> but this process is highly energy-consuming. Various organic dehydrating reagents have been used for this reaction, including dicyclohexyl carbodiimide, trimethyl phosphate,<sup>16</sup> orthoester,<sup>17</sup> ketals<sup>18</sup> and various nitriles,<sup>19</sup> and this topic has been reviewed.<sup>20</sup> These routes have some disadvantages, such as consumption of dehydrating agents, yielding of byproducts, and energy intensive nature. So finding suitable substances to substitute these dehydrating agents is highly desirable.



Calcium carbide (CaC<sub>2</sub>) is a fundamental chemical in industry. The main application of CaC<sub>2</sub> is in the production of acetylene *via* a reaction with water, in which a large amount of heat is released.<sup>21,22</sup> CaC<sub>2</sub> has been used in some reactions<sup>23,24</sup> as a substitute for acetylene, with the risk of explosion and requiring complex equipment. CaC<sub>2</sub> has also been used in other purposes, such as carbon sources for preparing carbon nanostructures,<sup>23</sup> as a reducing agent,<sup>25</sup> and for absorbing water.<sup>26</sup>

CaC<sub>2</sub> can react with alcohols to produce calcium alkoxide and acetylene<sup>27</sup> at certain temperature as shown in eqn (2). Calcium alkoxide can react with water and form calcium oxide and the corresponding alcohol as shown in eqn (3). Combining eqn (1)–(3), we can get eqn (4), *i.e.*, the reaction of CO<sub>2</sub> with methanol and CaC<sub>2</sub> can generate DMC, acetylene and calcium oxide. The standard Gibbs free energy of eqn (4) is −65.2 kJ mol<sup>−1</sup>;<sup>22</sup> this means that CaC<sub>2</sub> can be used as a drying agent to remove water formed in the DMC producing process and enhance the yield of DMC.



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In this work,  $\text{CaC}_2$  was used as a dehydrating agent in DMC synthesis from  $\text{CO}_2$  and methanol, and acetylene was produced at the same time. In this way, the water generated in the synthesis of DMC from methanol and  $\text{CO}_2$  was consumed by the reaction with  $\text{CaC}_2$  to produce acetylene, and thus the reaction equilibrium is enhanced. As far as we know, this is the first work on the combination of driving a thermodynamically unfavorable reaction and producing acetylene using  $\text{CaC}_2$ .

The purity of  $\text{CaC}_2$  was 77%, which was determined in this work by the amount of acetylene formed from the reaction of  $\text{CaC}_2$  with water. The reaction of  $\text{CaC}_2$  and methanol (eqn (2)) was first studied in this work.  $\text{CaC}_2$  powder reacted with methanol at  $60^\circ\text{C}$  and acetylene was released smoothly, and the reaction could finish in one hour. The amount of acetylene generated from the reaction of  $\text{CaC}_2$  and methanol was the same as that obtained from the reaction of  $\text{CaC}_2$  with water. This indicates that  $\text{CaC}_2$  could react with methanol completely and yield equimolar acetylene and calcium methoxide.

The influence of reaction conditions on DMC synthesis from  $\text{CO}_2$  and methanol using calcium methoxide (formed from  $\text{CaC}_2$  and methanol, eqn (2)) as the drying agent was studied in this work. Some simple and commonly used catalysts for the synthesis of DMC from  $\text{CO}_2$  and methanol were tested, including  $\text{ZnCl}_2$ ,  $\text{ZnO}$ ,  $\text{Bu}_2\text{SnO}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{SnCl}_2$ ,  $\text{CuCl}$ ,  $\text{CuI}$ ,  $\text{KI}$ , and  $\text{ZnI}_2$ .<sup>20,28</sup> It can be seen from Fig. 1a that catalysts influenced the formation of DMC greatly.  $\text{Bu}_2\text{SnO}$ ,  $\text{ZnCl}_2$  and  $\text{CuI}$  showed satisfactory activities, and  $\text{Bu}_2\text{SnO}$  had the best performance. Therefore, the reaction conditions were further optimized using  $\text{Bu}_2\text{SnO}$  as the catalyst.

The effect of the  $\text{Bu}_2\text{SnO}$  amount on the reaction is shown in Fig. 1b. The yield of DMC increased with increasing amount of the catalyst, and was independent of the  $\text{Bu}_2\text{SnO}$  amount after 5 wt% (methanol basis). Therefore, the reaction conditions were further optimized using 5 wt%  $\text{Bu}_2\text{SnO}$  as the catalyst.

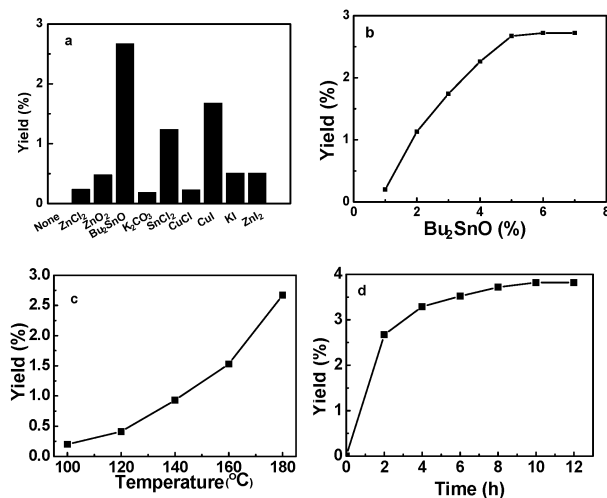


Fig. 1 Effect of reaction conditions on DMC synthesis from  $\text{CO}_2$  and methanol in the presence of  $\text{CaC}_2$ . Common conditions: methanol 2.0 g,  $\text{CaC}_2$  0.22 g, catalyst 0.1 g,  $\text{CO}_2$  15 MPa,  $180^\circ\text{C}$ , 2 h; DMC yields are based on methanol. (a) Performance of various catalysts (none: without  $\text{CaC}_2$  and catalyst); (b) effect of  $\text{Bu}_2\text{SnO}$  amount; (c) effect of temperature; and (d) effect of reaction time.

The effect of temperature on DMC synthesis is demonstrated in Fig. 1c. It can be known that the yield of DMC was very low at lower temperature, and increased significantly with the increase of temperature.

The effect of reaction time on DMC synthesis at  $180^\circ\text{C}$  is illustrated in Fig. 1d. The yield of DMC increased rapidly with time at the beginning, and then increased slowly with increasing reaction time. The reaction reached equilibrium at about 10 h, which was known from the fact that the yield was unchanged with time over 10 h.

The effect of the  $\text{CaC}_2$  amount on the yield of DMC was also investigated and the results are given in Fig. 2. The yield of DMC was only 0.9% without adding  $\text{CaC}_2$ . As discussed above, the direct synthesis of DMC by the reaction of  $\text{CO}_2$  and methanol (eqn (1)) is thermodynamically limited, so the conversion of methanol was very low. The yield increased linearly with the amount of  $\text{CaC}_2$  added, and the yield reached 11.3% when 12.3 mol%  $\text{CaC}_2$  (based on methanol) was added, and the reason will be discussed in the following.

As discussed above,  $\text{CaC}_2$  reacted with alcohols to produce  $\text{Ca}(\text{OCH}_3)_2$ , which may react with  $\text{CO}_2$  to form DMC without the catalyst considering that  $\text{Ca}(\text{OCH}_3)_2$  has stronger nucleophilicity than  $\text{CH}_3\text{OH}$ . To clarify this, we also studied the effect of the  $\text{CaC}_2$  amount on the reaction without a catalyst, and the results are shown in Fig. 2. Trace amount of DMC was formed and the yield increased with increasing amount of  $\text{CaC}_2$ , but the yield of DMC was extremely low without the catalyst ( $\text{Bu}_2\text{SnO}$ ). This indicates that the efficiency of the reaction of  $\text{Ca}(\text{OCH}_3)_2$  and  $\text{CO}_2$  was very low, and the catalyst was necessary for the reaction.

On the basis of the results above and knowledge in the literature, we can discuss the possible reaction pathway and the reason for the enhancement of the equilibrium yield, as shown in Scheme 1. Initially,  $\text{CaC}_2$  reacts with methanol and generates acetylene and  $\text{Ca}(\text{OCH}_3)_2$  (eqn (2)). As  $\text{CO}_2$  reacts with methanol and generates DMC and water (eqn (1)),  $\text{Ca}(\text{OCH}_3)_2$  reacts with the water to form  $\text{CaO}$  and methanol (eqn (3)). As water is consumed, the equilibrium of the reaction (eqn (1)) is shifted towards the right side and the equilibrium yield is increased.

In summary, the route to simultaneously producing acetylene and enhancing reaction equilibrium using  $\text{CaC}_2$  as a dehydrating agent has been proposed. The method has been used to shift the reaction equilibrium for the synthesis of DMC from  $\text{CO}_2$  and methanol efficiently and produce acetylene simultaneously.

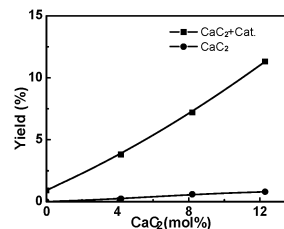
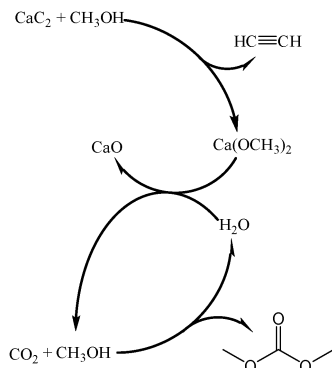


Fig. 2 Effects of the  $\text{CaC}_2$  amount on DMC synthesis from  $\text{CO}_2$  and methanol with and without  $\text{Bu}_2\text{SnO}$ . Methanol 2.0 g,  $\text{Bu}_2\text{SnO}$  0.1 g,  $\text{CO}_2$  15 MPa,  $180^\circ\text{C}$ , 10 h.



**Scheme 1** The possible reaction pathway for  $\text{CaC}_2$  driving DMC synthesis from  $\text{CO}_2$  and methanol and producing acetylene simultaneously.

This work is appealing because the water generated in the synthesis of DMC is consumed by the reaction with  $\text{CaC}_2$  to produce acetylene, and thus the reaction equilibrium is shifted. We believe that this idea can also be used to enhance the reaction equilibrium of the other thermodynamically limited reactions that generate water.

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## Conflicts of interest

There are no conflicts to declare.

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