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Thermal decomposition of dimethoxymethane and dimethyl carbonate catalyzed by solid acids and bases

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Abstract

The thermal decomposition of dimethoxymethane (DMM) and dimethyl carbonate (DMC) on MgO, H-ZSM-5, SiO_2, γ-Al_2O_3 and ZnO was studied using a fixed bed isothermal reactor equipped with an online gas chromatograph. It was found that DMM was stable on MgO at temperatures up to 623 K, while it was decomposed over the acidic H-ZSM-5 with 99% conversion at 423 K. On the other hand, DMC was easily decomposed on the strong solid base and acid. The conversion of DMC was 76% on MgO at 473 K, and 98% on H-ZSM-5 at 423 K. It was even easier decomposed on the amphoteric γ-Al_2O_3. Both DMM and DMC were relatively stable on SiO_2 possessing little surface acidity and basicity. They were even more stable on ZnO with the conversion of DMM and DMC of about 1.5% at 573 K. Thus, metal oxides with either strong acidity or basicity are not suitable for the selective oxidation of DMM to DMC, while ZnO may be used as a component for the reaction.

Keywords: Thermal decomposition; Dimethoxymethane; Dimethyl carbonate; Metal oxides; Solid acid; Solid base

1. Introduction

Dimethyl carbonate (DMC) is a versatile environmental benign chemical used in many reactions. In recent years, DMC has been tested as an effective gasoline additive because it contains rich oxygen and is of high octane value. A large potential DMC supply is supposed to be fulfilled for the refinery need if the MTBE (methyl tertiary-butyl ether) is phased out from the gasoline additive list in the near future [1]. In the present, two processes are employed to manufacture DMC in large scale, one was developed by ENIChem (Italy) and was characterized by oxidative carbonylation of methanol using a CuCl catalyst while the other was developed by UBE (Japan) using a nitric oxidation catalyst and was operated at much higher conversion. There are many other processes in the patent literature for DMC synthesis; some are close to application, but not commercially practiced yet. Recently, studies have been focused on the DMC synthesis from CO_2, which is thermodynamically unfavorable under normal conditions. Therefore, the process in which reaction was carried out under CO_2 critical state and the *trans*-esterification method were developed in order to add driving force to achieve reasonable CO_2 conversion level [2]. Dimethoxymethane (DMM) may be another potential oil additive drawing much attention in recent years [3–5]. Because of its low octane value, DMM cannot be used as a gasoline additive, but it may be used as a diesel additive, which may effectively decrease the emissions of NO_x and carbon particles [6].

By comparing the molecular structure of DMM and DMC as shown in Fig. 1, it is easily seen that DMM can be converted into DMC if the two hydrogen atoms on the central carbon are replaced by an oxygen atom. Such replacement may occur through the selective oxidation of DMM, similar to the selective oxidation of methane to formaldehyde. Thus, the selective oxidation of DMM to DMC may become a new route for the synthesis of DMC.

$$CH_3OCH_2OCH_3 + O_2 \rightarrow (CH_3O)_2CO + H_2O \qquad (1)$$

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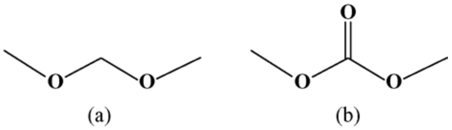

Fig. 1. The molecular structure of DMM (a) and DMC (b).

A thermodynamic calculation of reaction (1) revealed that the change in Gibbs free energy at standard state is a large negative value, $\Delta G^\circ = -466.2\,\mathrm{kJ\,mol^{-1}}$. The primary thermodynamic data of DMC were quoted from Zhao et al. [7], while the data of DMM and H_2O were obtained from Ref. [8]. The large negative value of ΔG° indicates that the reaction (1) is highly favored thermodynamically. A suitable catalyst must be essential for the reaction. The selective oxidation of methane to formaldehyde has been extensively studied by using different metal oxide catalysts. Similar metal oxide catalysts may be employed for the selective oxidation of DMM to DMC. However, before trying any catalysts for the selective oxidation of DMM, it must be confirmed that both DMM and DMC are thermally stable under the reaction conditions. In addition, since the oxidation ability and selectivity of any metal oxide catalysts depend strongly on the surface acidity and basicity, the influence of surface acidity and basicity on the thermal decomposition of DMM and DMC must be considered. The purpose of this work was to examine the thermal stability of DMM and DMC over some solid oxides possessing different surface acidity and basicity. Only when DMM and DMC are stable enough at high temperatures, there may be a possibility for the conversion of DMM to DMC through the catalytic oxidation. In this work, MgO, H-ZSM-5, SiO_2, γ-Al_2O_3 and ZnO were chosen as the basic, acidic, neutral and amphoteric oxides for the thermal decomposition of DMM and DMC. γ-Al_2O_3 is usually taken as a solid acid, but actually it is amphoteric and possesses both acidity and basicity [9]. In addition, it is usually believed that the surface acidity is stronger than basicity over γ-Al_2O_3. SiO_2 is usually taken as a neutral oxide. At most, it possesses only very weak surface acidity owing to its surface hydroxide groups. MgO is known to be a strong solid base while H-ZSM-5 is a strong solid acid. ZnO has been found to be amphoteric [10]. Its surface acidity is weaker than that of γ-Al_2O_3 while its surface basicity is stronger than that of γ-Al_2O_3 [11].

2. Experimental

The oxides used were all commercial products with surface areas of 79, 450, 350, 290 and 6 m^2/g for MgO, H-ZSM-5, SiO_2, γ-Al_2O_3 and ZnO, respectively. The samples were pressed, crushed and sieved to 20–40 meshes for catalytic tests. They were calcined in air at 573 K for 3 h before used for the decomposition reactions and BET surface area measurements.

The stability evaluation of DMM and DMC on the oxides was carried out in a fixed bed glass reactor with an inner diameter of 6 mm. An 80-mesh stainless steel sieve plug was used in the reactor to sustain a catalyst in the reaction zone. About 0.2 g sample was loaded for each test. The sample was heated in a N_2 (99.999%, 15 ml/min) flow at 573 K for 1.0 h and then cooled to room temperature. At the reaction temperature, the sample was purged for 0.5 h with N_2 flow (15 ml/min) before the vapor of DMM (Aldrich, 99%, with H_2O and CH_3OH as main impurities) or DMC (Fluka, 99%, with H_2O and CH_3OH as main impurities) was introduced into the catalyst bed by bubbling N_2 (99.999%, 15 ml/min) through a glass saturator filled with DMM or DMC maintained at a given temperature (273 K for DMM and 285 K for DMC). The feed composition was DMM:N_2 = 17:83 with a gas hourly space velocity (GHSV) of $5400\,\mathrm{ml\,g^{-1}\,h^{-1}}$, and DMC:$N_2$ = 4:96 with a GHSV of $4700\,\mathrm{ml\,g^{-1}\,h^{-1}}$. The reactants and products were analyzed on-line by a gas chromatograph (GC) with FID and TCD detectors. One column was packed with Porapack N for separating dimethyl ether (DME), CH_3OH, methyl formate (MF), DMM, DMC, CH_4, C_2H_4 and other light hydrocarbons, and the other two columns connected to TCDs were packed with TDX-01 for the analysis of CO and CO_2. In some cases, another GC equipped with TCDs was employed to analyze formaldehyde (FA).

Blank tests were performed for the thermal decomposition of DMM and DMC using an empty reactor tube or using the reactor tube with a porous glass or a stainless steel sieve support.

The decomposition reactions were performed under atmospheric pressure. The products of decompositions were identified as CO_2, DME, CH_3OH, MF, FA, CH_4 and C_2H_4. Some unidentified organic products were reported as 'etc.' here. The stability was expressed in terms of conversion and selectivity at a given temperature.

3. Results and discussion

The blank tests showed that DMM was quite stable. No decomposition was observed at temperatures up to 623 K. Even at 723 K, the decomposition of DMM was negligible. In contrast, DMC is apt to decompose upon heat treatment. At 473 K, the decomposition products from DMC were observed. At 573 K, about 2.6% DMC were decomposed and the products identified were methanol, DME and CO_2. The different thermal stability for DMM and DMC may be due to that the replacement of the two H atoms in DMM by an oxygen atom in DMC weakens the C–OCH_3 bonds.

The porous glass frit possessed some acidity. Thus, both DMM and DMC exhibited certain decomposition at 573 K. Fig. 2 shows that the decomposition of DMM increased slowly with the increase of temperature, while the conversion of DMC increased drastically when the temperature increased to higher than 473 K. This result implies that the activation energy of decomposition may be higher for DMC than for

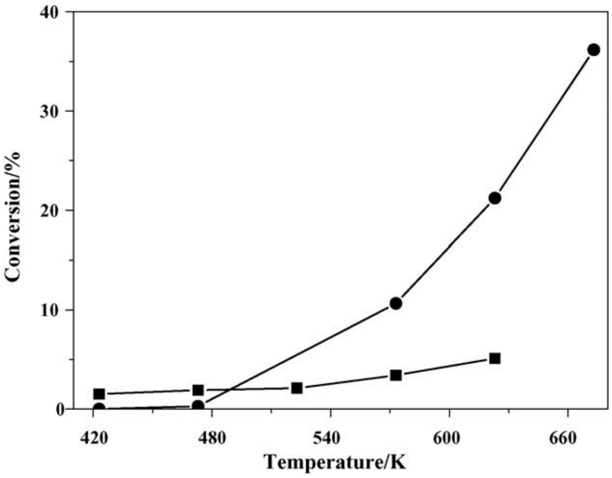

Fig. 2. Decomposition of DMM (■) and DMC (●) on porous glass frit.

DMM on the porous glass frit. On the other hand, both DMM and DMC exhibited good stability on the stainless steel sieve support. The decomposition of DMM on the stainless steel sieve was negligible up to 623 K, while the decomposition of DMC on it was about 2.8% at 573 K, which was similar to the rate of decomposition with the empty tube (2.6%). Thus, the stainless steel sieve support was used to sustain the oxides in the reactor tube for the catalytic decomposition of DMM and DMC.

Table 1 presents the results for the decomposition of DMM and DMC over MgO. It was shown that DMM was stable on the basic oxide, MgO. The decomposition was negligible at the temperature up to 623 K. In contrast, DMC was decomposed easily on MgO. Even at the temperature as low as 323 K, the decomposition product was detected. The predominant decomposition product was methanol at 323 K, indicating that DMC might undergo hydrolysis with water that might exist in small quantity in DMC and/or in the N_2 flow. The conversion of DMC increased greatly when the temperature was increased from 373 to 473 K. At 523 K, the conversion of DMC reached 96% with the formation of mainly DME and CO_2. The surface basicity may play the important role for the decomposition of DMC due to the formation of surface carbonates. Apparently, the abstraction of CO_2 from DMC by MgO leads to the formation of DME.

Table 2 gives the results for the decomposition of DMM and DMC over H-ZSM-5. The decompositions occurred at the temperature as low as 325 K, and the conversion increased rapidly with the increase of temperature in the range from 373 to 423 K. DMM and DMC were nearly completely converted on H-ZSM-5 at 423 K.

Both DMM and DMC were decomposed readily on γ-Al_2O_3 at relatively low temperatures. Table 3 shows that 98.2% of DMC was decomposed at 423 K and the main product was DME and CO_2 along with small amount of other organic products such as methane, methanol and some unidentified organic compounds. The amount of unidentified products formed was comparable to that of DME at 373 K. The thermal decomposition of DMM reached 47.7% conversion at 473 K and 100% conversion at 553 K on γ-Al_2O_3. The organic products were DME, methanol, formaldehyde and methyl formate. The methyl formate might be formed through the dimerization of formaldehyde in the absence of gas-phase oxygen [12]. The decomposition of DMM may undergo two steps. DMM may react with water to produce methanol and formaldehyde, and methanol formed undergoes dehydration to DME and water over γ-Al_2O_3. The

Table 1
Thermal decomposition of DMM and DMC on MgO

	Temperature (K)	Conversion (%)	Main organic products
DMM	573	0	
	623	0.2	DME, FA and methanol
DMC	323	0.6	Methanol
	373	2.1	DME (80.9%), methanol, etc.
	473	76.4	DME (99.3%), methanol, etc.
	523	96.0	DME (99.8%), methanol, etc.
	553	98.7	DME (98.4%), methanol, etc.

Table 2
Thermal decomposition of DMM and DMC over H-ZSM-5

	Temperature (K)	Conversion (%)	Main organic products
DMM	323	1.5	DME (4.7%), FA, methanol, etc.
	373	29.2	DME (87.8%), FA, MF, methanol, etc.
	423[a]	99.6	DME (96.5%), FA, MF, methanol, etc.
DMC	323	1.0	DME (33.0%), methanol, etc.
	348	6.8	DME (37.8%), methanol, etc.
	373	32.9	DME (79.2%), methanol, etc.
	423[a]	98.4	DME (98.4%), methanol, etc.

[a] Coke was found for the decomposition of DMM and DMC at 423 K.

Table 3
Thermal decomposition of DMM and DMC over γ-Al_2O_3

	Temperature (K)	Conversion (%)	Main organic products
DMM	473	47.7	DME (75.6%), FA, MF, methanol, etc.
	523	88.4	DME (75.8%), FA, MF, methanol, etc.
	553	100	DME (91.5%), FA, MF, methanol, etc.
DMC	323	8.8	DME (2.2%), methanol, etc.
	348	12.9	DME (33.3%), methanol, etc.
	373	53.0	DME (77.7%), methanol, etc.
	423	98.2	DME (86.7%), methanol, etc.

Table 4
Thermal decomposition of DMM and DMC over SiO_2

	Temperature (K)	Conversion (%)	Main organic products
DMM	373	1.0	DME, FA, methanol, etc.
	423	2.7	DME, FA, methanol, etc.
	573	6.3	DME, FA, methanol, etc.
DMC	473	1.0	DME (2.0%), methanol, etc.
	523	2.9	DME (50.0%), methanol, etc.
	573	9.3	DME (72.0%), methanol, etc.

Table 5
Thermal decomposition of DMM and DMC over ZnO

	Temperature (K)	Conversion (%)	Main organic products
DMM	373	0.7	DME, FA, methanol, etc.
	473	1.0	DME, FA, methanol, etc.
	573	1.3	DME, FA, methanol, etc.
DMC	573	1.5	DME, methanol, etc.
	623	3.0	DME, methane, methanol, etc.

water formed through the dehydration of methanol was used for the hydrolysis of DMM to produce methanol. In this way, the conversion of DMM to DME continued, as catalyzed by the surface acidic sites. On the other hand, the decomposition of DMC was catalyzed by the surface basicity of γ-Al_2O_3. In this case, DMC might be decomposed directly into DME and CO_2, which were enhanced through the formation of surface carbonates due to the interaction of CO_2 with surface basic sites on γ-Al_2O_3. The surface acidity of γ-Al_2O_3 might play a role in the decomposition of DMC, as evidenced by the decomposition of DMC on H-ZSM-5. However, the conversion of DMC was higher on γ-Al_2O_3 than on H-ZSM-5 at 373 K, indicating a synergic effect might exist between the surface acidity and basicity for the decomposition of DMC.

The results of decomposition of DMM and DMC over SiO_2 are shown in Table 4. At 573 K, 6.3% of DMM and 9.3% DMC were decomposed on SiO_2. The decomposition of DMC on SiO_2 at temperatures below 473 K was negligible.

Table 5 presents the results for the thermal decomposition of DMM and DMC over ZnO at different temperatures. It is seen that both DMM and DMC on ZnO were quite stable upon thermal treatments. The conversion of the two compounds was about 1.5% over ZnO at 573 K. It is interesting to note that DMM and DMC were more stable over ZnO than over SiO_2 although ZnO is usually taken as an amphoteric oxide that exhibits surface acidity and basicity stronger than those of SiO_2. The higher surface area of SiO_2 might explain why the decomposition of DMM and DMC were more serious over SiO_2 than over ZnO. However, the decomposition activity of DMC was so different on MgO and ZnO although both the oxides exhibited basicity. The difference in surface areas between MgO and ZnO was not enough to explain such a great difference in activity. For example, the surface area of MgO was 13 times greater than that of ZnO, while the conversion of DMC on MgO at 473 K was 50 times higher than the conversion of DMC on ZnO at 573 K. This comparison for the decomposition of DMC over MgO and ZnO clearly demonstrated that the surface basicity mainly determined the decomposition of DMC. The surface basicity of ZnO does not seem to be strong enough to catalyze the decomposition of DMC. With the same reason, the surface acidity of ZnO does not seem to be strong enough either to catalyze the decomposition of DMM and DMC. Thus, ZnO with a low surface area may be a promising candidate used as a component for the selective oxidation of DMM to DMC.

4. Conclusions

We demonstrated in this work that DMM was stable over the basic oxide such as MgO, but it was easily decomposed over the acidic oxide such as H-ZSM-5 and γ-Al_2O_3. Specifically, DMM was stable on MgO up to 623 K, while it was decomposed on H-ZSM-5 with 99.6% conversion at 423 K. On the other hand, DMC was found to be easily decomposed over both basic and acidic oxides. It was decomposed with 76.4% conversion on MgO at 473 K while with 98.4% conversion on H-ZSM-5 at 423 K. It was even easier to be decomposed on γ-Al_2O_3, an amphoteric oxide, at the temperatures lower than 423 K. Thus, the co-existence of basic and acidic sites on the surface of γ-Al_2O_3 might enhance the decomposition of DMC (the synergic effect). Both DMM and DMC were quite stable over SiO_2 with little surface acidity and basicity (the conversion of DMM and DMC were 6.3% and 9.3% on SiO_2 at 573 K). Both DMM and DMC were even more stable over the ZnO used in this work. The conversions were about 1.5% on the ZnO at 573 K for the decomposition of both DMM and DMC. Although ZnO is an amphoteric oxide, its surface acidity was weaker than that of γ-Al_2O_3 while its surface basicity was weaker than that of MgO. It seems that no synergic effect occurred over the ZnO, which might account for the low activity of ZnO for the decomposition of DMM and DMC. Thus, ZnO may be a promising oxide that can be used as a component for the selective oxidation of DMM to DMC up to the temperature of 623 K.

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