

Excellent foreground in methyl methoxyacetate synthesis with highly active and reusable sulfonic acid resin catalyst

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Supplementary Information

1. The effect of H₂O content on the carbonylation of DMM

For the vapour-phase DMM carbonylation, a Koch mechanism had been put forward [1-2]. Based on our previous work [3], and the earlier stated results, we deduced that the liquid-phase carbonylation over resin catalyst proceeds through the same mechanism. First, DMM reacted with the -SO₃H to generate methoxymethyl species and methanol. Then, the former product was attacked by CO to produce the methoxyacetyl species. After that, the obtained species could react with DMM to yield MMAc and regenerate the methoxymethyl species. During the reaction cycle, H₂O could interact with H⁺ as the active site for the carbonylation of DMM. Hence, the effect of H₂O content on the carbonylation reaction was investigated. In representative experiments, 5A molecular sieves were used to eliminate H₂O from DMM by physical adsorption. The H₂O content was counted by a Karl-Fischer method as shown in Table S1. When using DMM-1 industrial raw material, the conversion of DMM was 99.93%, and the selectivity for MMAc was 50.66% while that of DME was 23.70% with 2887 ppm H₂O in the system. Decreasing the H₂O content from 2887 to 325 ppm, the DMM conversion had a slight increase from 99.93% to 99.95%, MMAc selectivity shot up to 60.89%, and the DME selectivity dropped from 23.70% to 19.14%. DMM conversion rose to 99.98% when the H₂O amount was further reduced to 100 ppm, the

MMAc selectivity rapidly reached a maximum of 68.83%, while that of DME decreased to a minimum of 14.11%. Conversely, the selectivity for methanol dropped from 0.53% to 0.11% with decreasing H₂O measures from 2887 to 100 ppm. Meanwhile, the DMM conversion improved from 97.80% to 99.92% with H₂O content dropped from 2893 to 152 ppm, using DMM-2 industrial raw material. As for DMM-3 industrial raw material, the DMM conversion was only 71.59% with 4759 ppm H₂O content, which increased to 99.95% as H₂O content decreased to 158 ppm. It was practically clear that the higher the H₂O content, the lower the activity of the sulfonic acid resin catalyst.

Table S1 The effect of water content on DMM carbonylation reaction

Industrial raw materials	Water Content (ppm)	DMM Conv. (%)	Sel. (%)							
			DME	MF	MeOH	MMAc	MG	MMAc ₂	DMG	MA
DMM-1	2887	99.93	23.70	3.24	0.53	50.66	4.26	0.58	14.77	2.26
	325	99.95	19.14	0.35	0.25	60.89	3.10	0.23	13.80	2.24
	100	99.98	14.11	0.71	0.11	68.83	2.47	0.34	11.79	1.65
DMM-2	2893	97.80	27.15	1.59	0.59	44.85	3.80	0.30	16.85	4.87
	461	99.87	19.31	1.28	0.24	54.90	2.56	2.45	16.68	2.59
	152	99.92	14.77	0.73	0.14	68.59	1.94	0.40	12.39	1.04
DMM-3	4759	71.59	41.85	2.39	2.00	28.20	5.13	2.36	12.22	5.84
	158	99.95	26.62	1.11	0.63	56.00	2.28	1.76	9.77	1.84

Notes: DMM-1 (2.5 wt% methanol), DMM-2 (9.68 wt% methanol), DMM-3 (10 wt% methanol).

Reaction conditions: 3 g DICP-001 resin catalyst, 10 g DMM, temperature: 393 K, initial pressure of CO: 6.0 MPa, CO to DMM ratio = 1.97/1, reaction time: 6 h.

Using DMM-2 and DMM-3 industrial raw materials, the variation pattern of MMAc, DME and methanol selectivity was consistent with that of DMM-1 industrial raw material. The reason may be that the amount of methoxymethyl species were dropped by hydrogen bond interaction with the competitive adsorption of H₂O to generate -SO₃H₃O⁺ on acid centers. Besides, the dissociative H⁺ was encircled by H₂O by means of hydrogen bond interaction. The DMM hydrolysis was significantly inhibited by decreasing H₂O content to some extent, resulting in a lower quantity of methanol. The less H₂O content there was, the higher the DMM carbonylation efficiency, leading to higher selectivity of MMAc and lower selectivity of methanol and DME.

The influence of H₂O content on other products' selectivity when using DMM-1 industrial raw material is also displayed in Table 1. The MG formation dropped from 4.26% to 2.47% as H₂O content decreases from 2887 to 100 ppm. The selectivity for MG and DMG was affected by the dissociation and carbonylation activity of formaldehyde. Therefore, the MG and DMG selectivities decreased upon decreasing H₂O content. The selectivity of MA was closely related to the MMAc and H₂O content, as well as the capacity of hydrolysis, was 2.26% at 2887 ppm H₂O, and slowly decreased to 1.65% at 100 ppm of H₂O. More H₂O contributed to the hydrolysis of MMAc, owing to the high MA selectivity. MMAc₂ selectivity was 0.58% at 2887 ppm H₂O content and slowly decreased to 0.34% at 100 ppm of H₂O. Using DMM-2 and DMM-3 industrial raw material, the change of other products' selectivity was in a similar pattern as that of DMM-1 industrial raw material.

Different contents of H₂O had an important influence on the carbonylation of DMM. The DMM carbonylation efficiency was significantly promoted when decreasing H₂O content, leading to an increase in the selectivity of MMAc, while the selectivity of DME dropped drastically. During the loop of reaction, H₂O not only acted as a reactant but was also one of the products from esterification.

2. The effect of pretreatment temperature of as-used catalyst on DMM carbonylation

As shown in Fig. S1, when the pretreatment temperature was 363 K, the conversion of DMM was 76.60%. Upon improving the pretreatment temperature from 363 to 393 K, the DMM conversion risen from 76.60% to 99.80%. The DMM conversion kept practically unchanged at a high drying temperature of 403 K.

At 363 K of pretreatment temperature, the MMAc selectivity was merely 9.27%, while that of DME was 40.38%. The as-used catalyst still contained lots of physically and chemically adsorbed water at a low pretreatment temperature. As described earlier, H₂O had an important influence on the production of numerous products. The competitive reactions resulted in a lower MMAc selectivity at a pretreatment temperature of 363 K. Improving the pretreatment temperature from 363 to 393 K, the selectivity of MMAc rapidly enhanced to a maximum value of 50.66% due to the

lower moisture content at a higher pretreatment temperature. However, MMAc experienced a trifling decrease (4.40%) in selectivity when catalyst was pretreated at 403 K. We acquainted the higher pretreatment temperature resulted in pore breakage and surface sintering of catalyst, leading to the reduced DMM carbonylation ability.

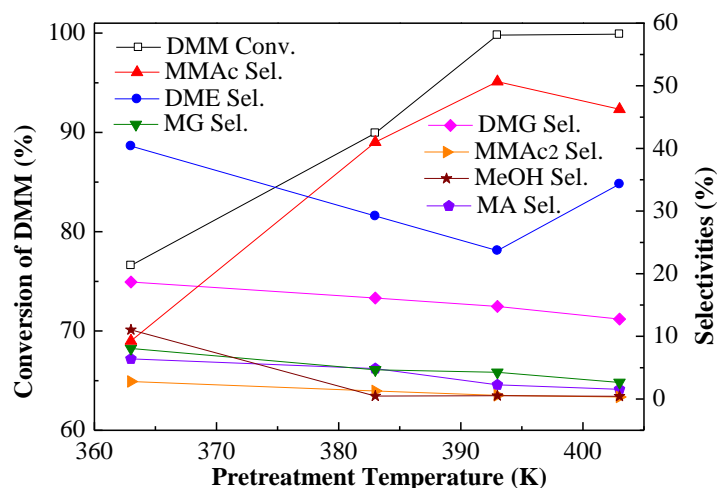


Fig. S1 The effect of pretreatment temperature on DMM carbonylation. Reaction conditions: 3 g DICP-001 resin catalyst, 10 g DMM-1 industrial raw material (2.5 wt% methanol and 2887 ppm water), reaction temperature: 393 K, reaction pressure: 6.0 MPa, CO to DMM ratio = 1.97/1, reaction time: 6 h.

When the pretreatment temperature was 363 K, MG and DMG selectivities were 8.07% and 18.68%, respectively. Due to residual H₂O in the research system, DMM hydrolysis was prevalent, leading to the formation of dissociative-like formaldehyde. Hence, the formaldehyde carbonylation reaction was readily carried out to yield glycolic acid (GA). Consequently, the follow-up esterification of methanol with GA to produce DMG and MG also prevailed. Further elevating the pretreatment temperature to 403 K, the DMG and MG selectivities dropped to 12.76% and 2.63%, respectively. Higher pretreatment temperature resulted in low H₂O content in the catalyst thereby, inhibiting the hydrolysis of DMM to yield GA, MG, DMG and vice-versa. MA selectivity was 6.40% at 363 K pretreatment temperature due to high H₂O content and then dropped to 1.54% as the pretreatment temperature was elevated to 403 K. The MMAc₂ attained its maximum selectivity (2.79%) at 363 K, and decreased to 0.31% at 403 K, perhaps because MMAc₂ arose from MA and MG both of which were in short supply at 403 K. The change in MMAc₂ selectivity was dependent on that of

MA and MG.

3. The effect of reaction pressure and CO to DMM ratio on the carbonylation of DMM

As displayed in Fig. S2, when reaction pressure was 0.75 MPa, the conversion of DMM was only 80.78%. The conversion of DMM improved to 98.63% with slowly enhancing reaction pressure from 0.75 to 3.0 MPa. Further improving the reaction pressure to 6.0 MPa, the conversion of DMM achieved 99.80%, showing that the DMM conversion evidently enhanced at a higher reaction pressure as it clearly increased the rate of collision of CO gas molecules with that of DMM.

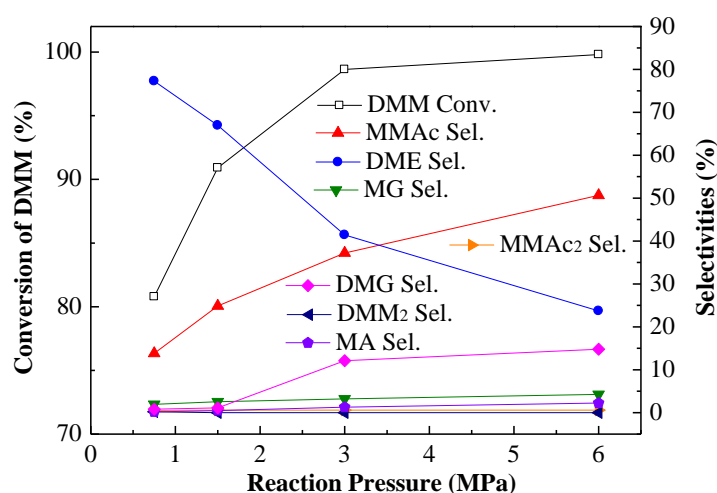


Fig. S2 The effect of reaction pressure on DMM carbonylation. Reaction conditions: 3 g DICP-001 resin catalyst, 10 g DMM-1 industrial raw material (2.5 wt% methanol and 2887 ppm water), reaction temperature: 393 K, CO to DMM ratio = 1.97/1, reaction time: 6 h.

At reaction pressure of 0.75 MPa, MMAc selectivity was as low as 13.82%, while DME selectivity reached up to 77.28%, denoting that the DMM disproportionation to produce DME was predominant at lower reaction pressure. With improving reaction pressure from 0.75 to 3.0 MPa, the MMAc selectivity showed a linear rise from 13.82% to 37.21%, while the selectivity of DME decreases similarly from 77.28% to 41.43%. When the reaction pressure increased from 3.0 to 6.0 MPa, the selectivity of MMAc rapidly improved from 37.21% to 50.66%, while the DME selectivity goes the opposite direction from 41.43% to 23.70%. Meanwhile, the CO to DMM ratio was consistently maintained at 1/1. The higher the reaction pressure, the higher the CO solubility. Hence, the possibility of mutual contact of CO and DMM

with the active sites was improved. In summary, the carbonylation was obviously improved, yet the disproportionation was evidently inhibited, leading to a rapid improve in the MMAc selectivity and a drastic decrease in the DME selectivity.

As mentioned above, the carbonylation of formaldehyde to form DMG and MG. Accordingly, both selectivities were also enhanced with improving reaction pressure and achieved maximum values (4.26% and 14.77%, respectively) at 6.0 MPa. These phenomena highlighted that not only the DMM carbonylation but also the formaldehyde carbonylation were promoted with enhancing initial CO pressure. By using sulfonic acid resin catalyst, J.S. Lee et al. [4] made known the similar trend for the carbonylation of formaldehyde. MMAc₂ and MA selectivities (about 0.60% and 1.05%), which were derived from the hydrolysis and esterification reactions, kept virtually constant with the variation of reaction pressure.

As exhibited in Fig. S3, at the CO to DMM ratio was 1/1, the DMM conversion was 93.36%. Enhancing the CO to DMM ratio from 1/1 to 1.97/1, the DMM conversion rose from 93.36% to 99.80%. At the CO to DMM ratio was greater than 3/1, the conversion of DMM kept above 99.90%.

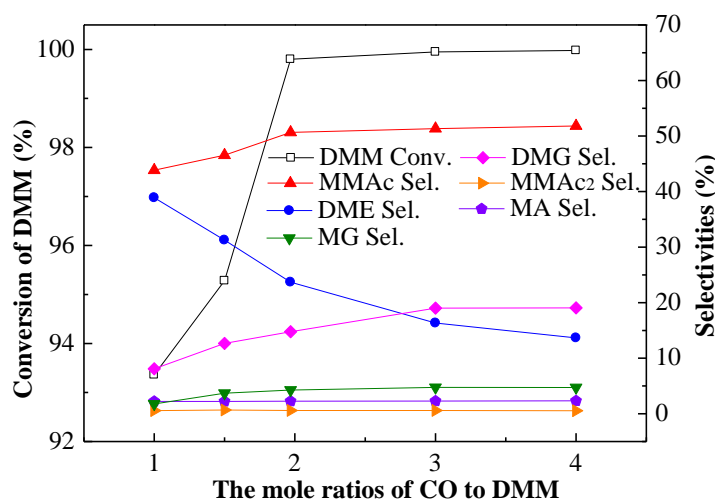


Fig. S3 The effect of CO to DMM ratio on DMM carbonylation. Reaction conditions: 3 g DICP-001 resin catalyst, 10 g DMM-1 industrial raw material (2.5 wt% methanol and 2887 ppm water), reaction temperature: 393 K, reaction pressure: 6.0 MPa, reaction time: 6 h.

DME and MMAc selectivities were 38.89% and 43.86% respectively, at the CO/DMM ratio was 1/1. With slowly improving the ratio from 1/1 to 3/1, the selectivity of MMAc rose from 43.86% to 51.33%, while that of DME decreased from

38.89% to 16.33%. When the reaction pressure is constant, the partial pressure of CO increased as the CO / DMM ratio improved. Hence, the carbonylation of DMM was clearly elevated, and this is also in agreement with reported results on vapor-phase DMM carbonylation [1,5-6]. Further increasing the CO to DMM ratio to 4/1, MMAc and DME selectivities kept almost unchanged.

As above discussed, both DMG and MG probably came from the formaldehyde carbonylation and the esterification of methanol with GA. Their selectivities improved with the increase in CO to DMM ratio and showed maximum levels (4.75% and 19.02%, respectively) when the mole ratio was 3/1. They kept almost unchanged when CO to DMM ratio was hoisted to 4/1, demonstrating that the formaldehyde carbonylation was improved with increasing CO to DMM ratio. Whereas, MMAc₂ and MA selectivities of 0.59% and 2.26% were unaffected with the variation of CO to DMM ratio.

4. The effect of reaction time on the carbonylation of DMM

As shown in Fig. S4, when the reaction time was 0.5 h, the DMM conversion was only 66.50%. Improving reaction time from 1 h to 4 h, the DMM conversion rose from 84.16% to 98.35%. At a longer reaction time (6-20 h), the DMM conversion maintained above 99.80%.

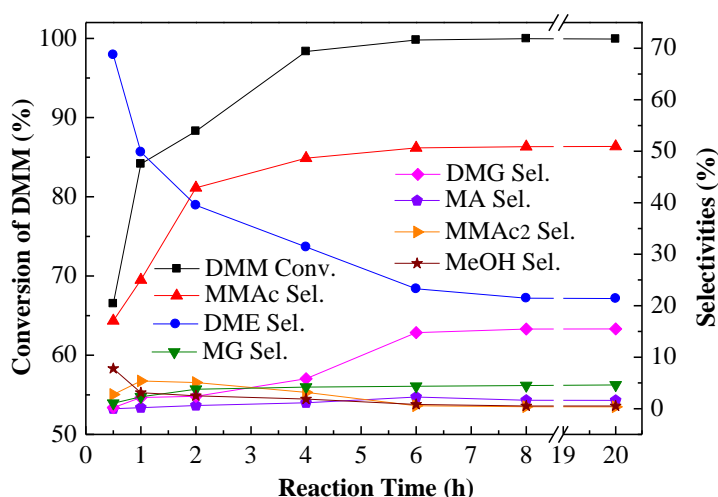


Fig. S4 The effect of reaction time on DMM carbonylation. Reaction conditions: 3 g DICP-001 resin catalyst, 10 g DMM-1 industrial raw material (2.5 wt% methanol and 2887 ppm water), reaction temperature: 393 K, reaction pressure: 6.0 MPa, CO to DMM ratio = 1.97/1.

At 0.5 h, MMAc selectivity was 17.07%, while that of DME was 68.74%. During the heating process, the rate of DMM disproportionation reaction being more favored to DMM carbonylation reaction at low temperature. Besides, the residual H₂O left in the system makes it extremely easier to carry out the hydrolysis of DMM to generate MeOH and DMM₂. This may also generate DME on active sites, leading to the production of lots of DME and MeOH (7.79%). Gradually increasing reaction time, the MMAc selectivity slowly improved and attained its maximum (50.89%) at 8 h, whereas, the selectivity of DME dropped to a minimum (21.46%) value at same time. These consequences showed that the carbonylation rate was greater than disproportionation rate at 393 K. Further increasing the reaction time to 20 h, the selectivity for MMAc and DME kept nearly unchanged, showing that the disproportionation and carbonylation already achieved chemical equilibrium at 8 h.

The selectivity to MG increased from 1.06% to 4.50% from a period of 0.5 to 8 h into the reaction and kept almost constant (about 4.60%) when the reaction continued to a duration of 20 h. MG selectivity was affected by the density of dissociative-like formaldehyde, H₂O, GA, DMG as well as MMAc₂. DMG selectivity rose from 0.20% to 5.82% when the reaction time proceeded from 0.5 h to 4 h, which rapidly improved to 14.77% at 6 h, and then finally reached its maximum value of 15.47% at 8 h. Above mentioned phenomenon could be illustrated by the tangible that more H₂O was generated and accumulated with the DME formation, resulting in a higher ratio H₂O/DMM in the studied system. Hence, as the reaction time is prolonged, both the DMM hydrolysis and formaldehyde dissociation were facilitated, leading to the additional formation of formaldehyde and methanol. MMAc₂ selectivity increased and attained its maximum (5.07%) value at 2 h. Extending the reaction time from 2 to 20 h caused a drop from 5.07% to 0.36%. The selectivity for MA, which evolves from the MMAc hydrolysis, increased and attained a maximum (2.26%) at 6 h. However, it dropped to 1.64% as the reaction time was further extended to 8 h, then kept constant (1.62%) at 20 h.

The ^1H NMR and ^{13}C NMR data of the target product MMAc were collected on a Bruker Ascend 500 III instrument, using CDCl_3 as solvent. The spectra were as follows:

^1H NMR (500 MHz, CDCl_3) δ (ppm): 3.92 (s, 2H), 3.64 (s, 3H), 3.32 (s, 3H).

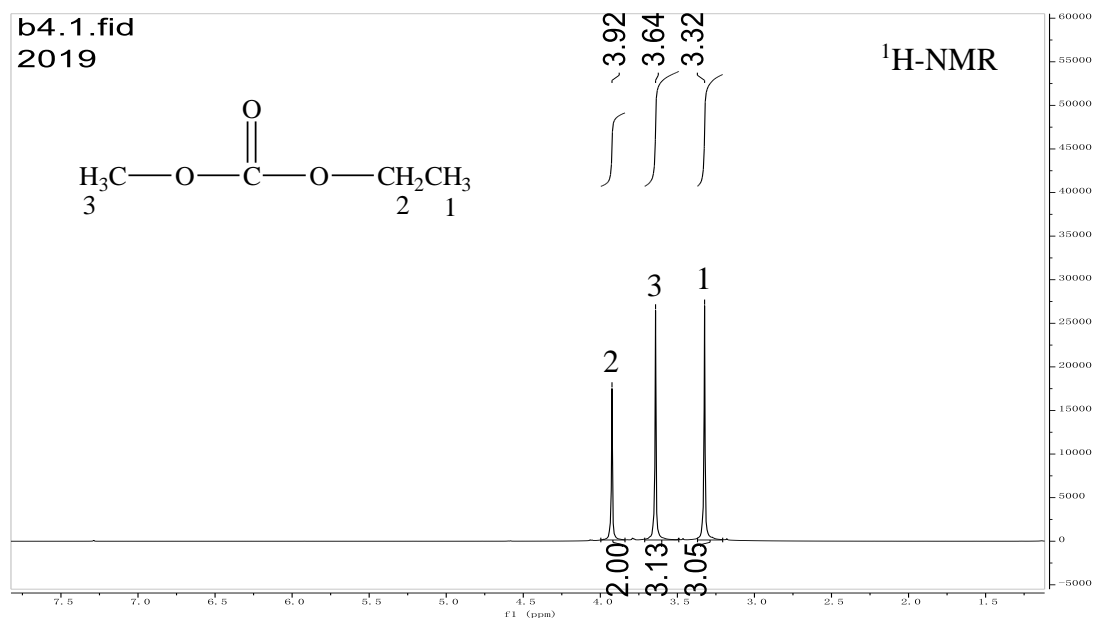


Fig. S5 ^1H NMR spectrum of MMAc

^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 169.68, 68.65, 58.28, 50.77.

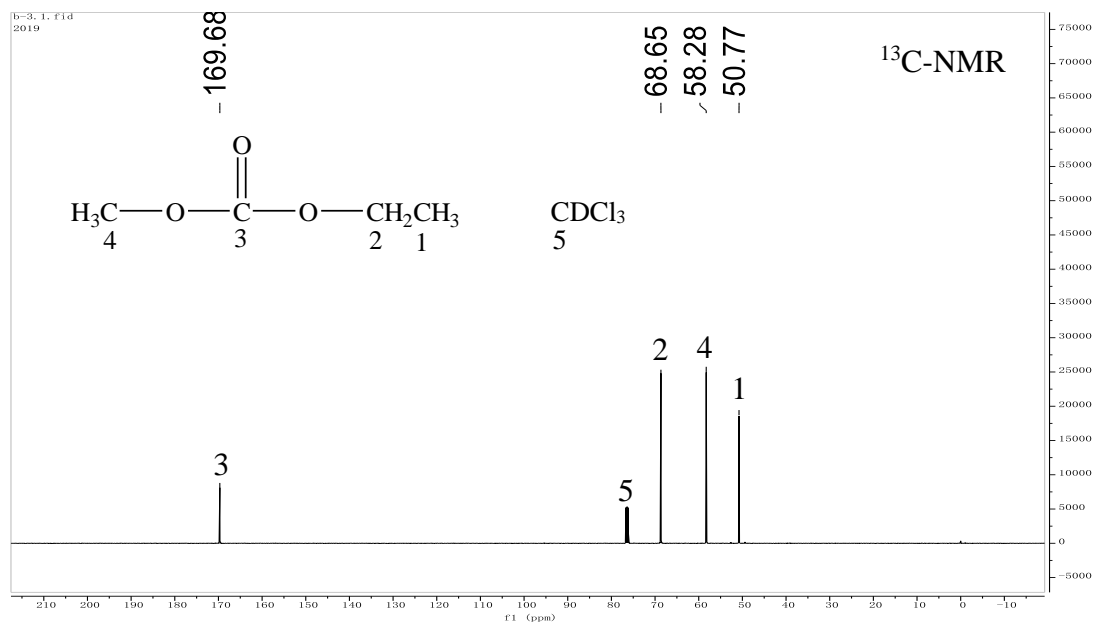


Fig. S6 ^{13}C NMR spectrum of MMAc

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