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A highly efficient sulfonic acid resin for liquid-phase carbonylation of dimethoxymethane

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Methyl methoxyacetate (MMAc), which is an important fine chemical, can be used as an intermediate to produce ethylene glycol from syngas. For the reported vapor-phase carbonylation of dimethoxymethane (DMM), the reaction was conducted under a higher (>100) CO/DMM molar ratio with a lower CO conversion (<0.5%). This paper systematically studied the effects of different zeolites and sulfonic acid resin catalysts, reaction temperature, CO pressure, CO/DMM ratio, reaction time, drying temperature, as well as H_2O and methanol contents on DMM conversion and products selectivities, using a slurry phase reactor. A highly efficient sulfonic acid resin was selected without the assistance of a solvent and the DMM conversion reached nearly 100%, with 64.39% MMAc selectivity at 110 °C and 5.0 MPa for 6 h, with a CO/DMM ratio of only 1.67/1. The effects of H_2O (32 ppm–10 wt%) and methanol (0.5–10 wt%) content on the carbonylation efficiency were also systematically studied. After removing H_2O from the DMM and resin catalyst, the MMAc selectivity got as high as 74.14% under the same reaction conditions. According to these reaction results and a precise GC-MS analysis, DMM_2, MG, DMG, MA, and $MMAc_2$ were evidently produced, along with MMAc, DME, MF, and methanol. We propose reaction routes from these results, and anticipate that this direct carbonylation of DMM to produce an MMAc process is promising for industrial manufacturing.

1. Introduction

Methyl methoxyacetate (MMAc), an important and highly value-added fine chemical, can be used as an intermediate for the synthesis of medicines, pesticides, and dyes. For example, MMAc can be applied to synthesize vitamin B6 and sulfa-5-pyrimidine, for dynamic kinetic resolution of chiral amine substances, as a polymerization catalyst, and so on.[1] More importantly, it is readily converted to ethylene glycol (EG), a bulk commodity chemical widely used as antifreeze and a polyester monomer, *via* a hydrogenation process to produce 2-methoxyethanol and further a hydrolysis reaction. Currently EG is industrially manufactured by the epoxidation of ethylene, derived directly from naphtha cracking and subsequent hydration of ethylene oxide.[2–4] With the increasing depletion of crude oil resources, the development of non-oil routes to synthesize EG, a process which starts with syngas *via*

reforming of nature gas, the gasification of coal or biomass, has attracted extensive attention.[5–9]

Previously reported MMAc synthesis methods, including the reactions of methyl chloroacetate with sodium methoxide, oxidation of 2-methoxyethanol, and coupling of formaldehyde derivatives with methyl formate,[10,11] were all complicated, highly corrosive, and unsuitable for large-scale manufacture. In 2008, A. T. Bell *et al.*[6] reported liquid-phase carbonylation of dimethoxymethane (DMM) to MMAc using heteropoly acid catalysts, but the selectivity of MMAc was less than 30%. One year later, they first accomplished vapor-phase carbonylation of DMM with 79% selectivity and 20% yield of MMAc, using H-FAU zeolite.[12–14] The disproportionation of DMM was the only competing reaction, leading to the formation of methyl formate (MF) and dimethyl ether (DME).[15] S. D. Badmaev *et al.*[16] reported gas-phase carbonylation of DMM to MMAc over the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ with 54% selectivity and 40% yield of MMAc at 110 °C, 10 bar and GHSV = 6000 h^{−1} with the mole ratio of DMM/CO/Ar = 4/76/20. In our former work, an H-Nafion resin[17] without microporous structure was applied as the catalyst and the selectivity of MMAc was raised to 90%, but the price of H-Nafion resin was higher than $100 per g, making the entire process uneconomical.

Although the whole vapor-phase carbonylation of DMM process is easily operated and the MMAc selectivity is higher than

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70%,[12–14,17] the actual amount of DMM injected is only a thimbleful. The DMM-saturated vapor at a chilled temperature is carried by CO into the reactor, resulting in a high mole ratio of CO/DMM, generally greater than 100/1, but a low CO conversion rate, usually less than 0.5%. J. P. Wang *et al.*[18] achieved liquid-phase carbonylation of DMM with 99.1% conversion and 63.9% selectivity of MMAc using $H_3PW_{12}O_{40}$ (PW_{12}) as the catalyst and sulfolane as the solvent at 130 °C and 3.0 MPa for 3 h. The effects of solid acids catalysts as well as different solvents, reaction temperature, initial CO pressure, reaction time and recycle times were investigatived. In our previous study of the liquid-phase carbonylation of DMM where CO/DMM = 5/1, the DMM conversion reached nearly 100% with 74.32% MMAc selectivity, using sulfolane as the solvent and D-009B as the catalyst conducted at 110 °C and 5 MPa for 6 h.[19] The solubility of CO in the liquid phase is significantly promoted and the side reactions of DMM in the sulfolane solvent are obviously suppressed. In this work, we have identified a highly efficient sulfonic acid resin catalyst from commercial production, based on the acid strength, preparation methods, BET surface area, and pore structures, with which carbonylation can readily proceed without the assistance of the sulfolane solvent. The effects of sulfonic acid resin catalysts as well as different zeolites, reaction temperature, CO pressure, CO/DMM ratio, reaction time, drying temperature, as well as H_2O and methanol content on the DMM conversion, along with the selectivities of different products, were systematically studied using a slurry phase reactor. Many unreported and complicated side reactions from DMM were first observed during the carbonylation process, and the possible reaction routes in the liquid phase were proposed. The effects of H_2O and methanol content, which not only served as reactants but also acted as the products from esterification, significantly influenced the carbonylation efficiency and products distribution.

2. Experimental

2.1 Preparation of catalysts

The zeolites (H-Y, Si/Al = 2.7, Nankai Univ.; H-β, Si/Al = 40, Shentan Co. Ltd; H-ZSM-5, Si/Al = 50, Japan H_2O Chem.; Na-MOR, Si/Al = 6.7, Hongda Chem. Co. Ltd) were purchased commercially. Na-mordenite (Na-MOR) was converted into its NH_4^+ form by exchanging 30.0 g Na-MOR with 0.3 L NH_4NO_3 (1 mol L^{-1}) in an aqueous solution at 80 °C for 3 h, followed by filtration and washing with deionized H_2O. After repeating the above-mentioned process three times, the desired precursor was dried at 120 °C for 10 h, followed by calcination at 550 °C for another 6 h to obtain the H^+ form (H-MOR). Before application, all the H^+ form zeolites were calcined at 550 °C in air for 6 h to remove the adsorbed H_2O. Sulfonic acid resins DA330 (Dandong Mingzhu Special Resin Co. Ltd.), D-009B (Dandong Mingzhu Special Resin Co. Ltd.), DICP-001, and DICP-002 were also commercially obtained. Prior to use, all the resin catalysts were dried at 120 °C for 6 h in an air atmosphere.

2.2 Catalytic activity tests

A batch reactor with 120 mL inner volume and a stirrer was used to study the catalytic activity in the carbonylation of DMM. In a typical experiment, 10 g DMM and 1 g catalyst were first poured into the autoclave. The air inside was purged by 1.0 MPa CO for three times, then the pressure in the reactor was raised to 5.0 MPa at room temperature and the reaction took place at 110 °C for 6 h. After the reaction, 0.5 g methyl acetate was added into the products as an inner standard. The products were analyzed by GC-MS on an Agilent 7890A/5975C GC/MSD system, equipped with a bonded polyethylene glycol (HP-FFAP) capillary column connected to a flame ionization detector (FID). The conversion of DMM and the selectivity of MMAc were calculated according to the following equations:

$$\text{Conversion of DMM} = (M_{in} - M_{left})/M_{in}$$

$$\text{Selectivity of MMAc} = M_{MMAc}/M_{all}$$

where M_{in} is the initial weight of DMM fed; M_{left} is the mass of DMM identified in the products according to the internal standard; M_{MMAc} is the weight of MMAc formed in the products; M_{all} is the mass of all products.

3. Results and discussion

3.1 The influence of zeolites and sulfonic acid resin catalysts on DMM carbonylation

Dimethoxymethane (DMM) carbonylation was conducted at 110 °C for 6 h with an initial CO pressure of 5.0 MPa at room temperature, in a slurry phase reactor. For the vapor-phase carbonylation of DMM,[12] H-FAU exhibited the higher DMM conversion and methyl methoxyacetate (MMAc) selectivity. Therefore, zeolites (H-β, H-ZSM-5, H-Y, and H-MOR) with different framework types were used as references, while commercially obtained sulfonic acid resins (DA-330, D-009B, DICP-001, and DICP-002) were applied as the catalysts. In a typical experiment, 10 g DMM and 1 g catalyst were poured into a 120 mL autoclave. The mole ratio of CO/DMM was calculated as below:

$$n_{DMM} = m/M = 10/76.1 = 0.131 \text{ mol}$$

$$n_{CO} = PV/RT = 50 \times 101325 \times (120 - 10/0.8593 - 1) \times 10^{-6}/(8.314 \times 298) = 0.219 \text{ mol}$$

$$n_{CO}/n_{DMM} = 0.219/0.131 = 1.67/1$$

Unlike the previously reported vapor-phase carbonylation[17] of DMM with CO/DMM greater than 100/1 and liquid-phase carbonylation[19] under CO/DMM higher than 5/1, this reaction system used a much lower mole ratio of CO/DMM = 1.67/1, indicating that it is very difficult to proceed a carbonylation reaction under the studied conditions.

DMM conversion and product selectivities for different zeolites and sulfonic acid resins catalysts are shown in Table 1. All the zeolite catalysts displayed the lower MMAc selectivity and higher dimethyl ether (DME) selectivity. The highest MMAc selectivity was only 18.80%, but the lowest DME selectivity was 65.61%, illustrating that more than 65.61% of the product was DME when the zeolites were applied. This result indicated that the disproportionation rate was much higher than the carbonylation rate on the active sites with zeolites under the studied system. It also supported attributing the high rate of DMM disproportionation to the micropores of the zeolite,[12,13,15] which facilitated a critical initial step in the formation of DME and methyl formate (MF) (see reaction (1)). According to the stoichiometry of the disproportionation, the ratio of DME/MF is approximately two, but the DME/MF ratios in Table 1 does deviate far from the theoretical value across all zeolites (14, 24, 56, and 112 on H-β, H-ZSM-5, H-Y, and H-MOR, respectively). This phenomenon is derived from the decomposition of MF to produce methanol, and followed by the dehydration of methanol to form DME on the acid sites (see reactions (2) and (3)).

$$2CH_3OCH_2OCH_3 \rightarrow 2CH_3OCH_3 \ (DME) + HCOOCH_3 \ (MF) \quad (1)$$

$$HCOOCH_3 \rightarrow CH_3OH + CO \quad (2)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (3)$$
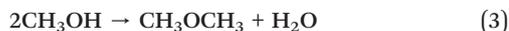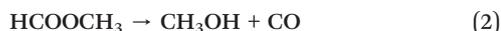
Four commercially obtained sulfonic acid resins, which were pretreated by different methods, were tested under the same conditions and noted as DA330, D-009B, DICP-001, and DICP-002, respectively. Compared to the zeolites, all the resin catalysts showed much higher catalytic activity and MMAc selectivity. The lowest MMAc selectivity among all the resins was 37.14%, which was about twofold larger than that of H-β. DICP-001 displayed about 100% DMM conversion and 64.39% MMAc selectivity. Methyl glycolate (MG), methyl methoxyacetate dimer (MMAc₂), methyl glycolate dimer (DMG), and methoxyacetic acid (MA), all of which are accurately measured by GC-MS, are all carbonylation products. The total mass ratios of the carbonylation products were about 80.47 wt% (64.39% + 1.17% + 2.01% + 11.76% + 1.14%), exhibiting excellent carbonylation capacity. In a formerly reported DMM carbonylation reaction with D-009B as the catalyst and sulfolane as the solvent, which significantly promoted the solubility of CO in the liquid phase, the mole ratio of CO/DMM was higher than 5/1; however, the CO/DMM ratio in this reaction system was only 1.67/1 without the help of a solvent. Therefore, the DICP-001 catalyst is promising for the industrial manufacture of MMAc.

We recognized that the excellent catalytic performance of DICP-001 was probably due to its structure and unique chemical properties. As discussed, the micropores of zeolites could promote DMM disproportionation, leading to an obvious decrease in MMAc selectivity. The DICP-001 resins had fewer small channels or cavities in which disproportionation mainly occurred. Therefore, the DMM disproportionation reaction over DICP-001 was effectively inhibited. Besides, it has been proven[17] that DMM carbonylation is a typical Bronsted acid-catalyzed process, and that the carbonylation efficiency is closely related to the acidity of the as-used catalyst. DICP-001 had higher acid strength than DA330, D-009B, and DICP-002, resulting in superior catalytic performance. So, DICP-001 was selected as the catalyst for the following investigation.

3.2 The influence of reaction temperature on DMM carbonylation

Fig. 1 shows the effect of reaction temperatures on DMM conversion and product selectivities in the range of 90 to 150 °C. At a low reaction temperature (90 °C), the conversion of DMM was as low as 56.27%. By gradually increasing the temperature from 90 to 110 °C, the conversion of DMM significantly increased to 99.18%. When the reaction temperature was higher than 110 °C, the conversion of DMM was maintained at above 99%.

With a reaction temperature of 90 °C, the selectivity of MMAc was only 31.93%, but the DME selectivity raised to 56.97%, illustrating that more than half of the product's weight was DME. By gradually increasing the temperature

Table 1 The effect of different catalysts on DMM carbonylation reaction

Catalysts	DMM Conv. (%)	Sel. (%)								
		DME	MF	MeOH	DMM₂	MMAc	MG	MMAc₂	DMG	MA
DA-330	64.06	46.41	1.95	0.63	1.25	40.18	0.33	3.41	2.80	3.03
D-009B	76.25	48.72	1.43	0.50	1.00	37.14	0.44	4.85	0.74	5.19
DICP-001	99.18	18.30	0.85	0.38	0.01	64.39	1.17	2.01	11.76	1.14
DICP-002	88.77	26.53	1.77	0.42	0.27	55.68	1.55	4.59	6.67	2.51
H-β	64.89	65.61	5.88	0.58	1.89	18.80	—	1.37	—	5.86
H-ZSM-5	57.78	76.80	4.12	0.71	—	15.41	—	2.22	—	0.74
H-Y	69.69	87.59	2.03	0.43	—	8.81	—	1.15	—	—
H-MOR	49.02	82.79	0.96	1.12	6.94	3.58	3.92	0.69	—	—

Reaction conditions: 10 g DMM, 1 g catalyst, reaction temperature: 110 °C, CO pressure: 5.0 MPa, reaction time: 6 h, the mole ratio of CO/DMM = 1.67/1.
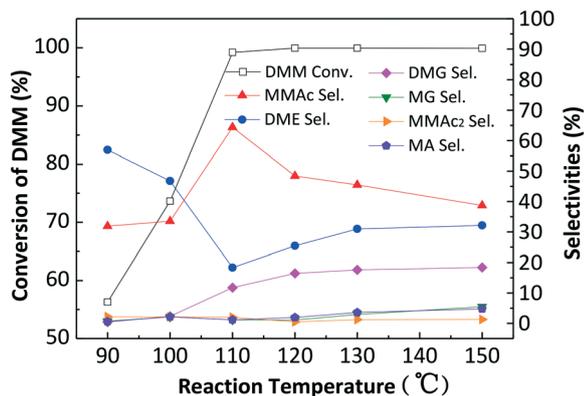
Fig. 1 The influence of reaction temperature on DMM carbonylation using a DICP-001 resin catalyst. Reaction conditions: 10 g DMM, 1 g catalyst, CO pressure: 5.0 MPa, reaction time: 6 h, the mole ratio of CO/DMM = 1.67/1.

from 90 to 110 °C, the selectivity of MMAc increased and exhibited a maximum value (64.39%) at 110 °C. However, DME selectivity obviously dropped and showed a minimum level (18.30%) at 110 °C. Further increasing the temperature (110–150 °C) led to a sharp decrease of MMAc selectivity from 64.39% to 38.76%, and a rapid increase in DME selectivity from 18.30% to 32.50%.

These phenomena could be explained by the fact that DMM carbonylation and DMM disproportionation are two competitive reactions. At low temperatures (90–100 °C), the rate of disproportionation was much higher than that of DMM carbonylation. Therefore, the selectivity of MMAc was low and the selectivity of DME was high. By slowly increasing the reaction temperature, both carbonylation and disproportionation reactions rates were promoted. Nevertheless, the enhanced rate of carbonylation was higher than that of DMM disproportionation. Accordingly, the selectivity of MMAc gradually increased while the DME selectivity gradually decreased. But a high reaction temperature led to the sulfonic acid resin catalyst's sintering inactivation, resulting in an obvious decrease of MMAc selectivity.

Polymethyldimethylether (DMM$_2$), methyl glycolate (MG), methyl glycolate dimer (DMG), methyl methoxyacetate dimer (MMAc$_2$), and methoxyacetic acid (MA) products are clearly identified by GC-MS on an Agilent 7890A/5975C GC/MSD system, equipped with a bonded polyethylene glycol (HP-FFAP) capillary column connected to a flame ionization detector (FID).

$$2CH_3OCH_2OCH_3 + H_2O \rightarrow CH_3OCH_2OCH_2OCH_3 + 2CH_3OH \quad (4)$$

$$HCHO + CO + H_2O \rightarrow HOCH_2COOH \text{ (GA)} \quad (5)$$

$$HOCH_2COOH + CH_3OH \rightarrow HOCH_2COOCH_3 \text{ (MG)} \quad (6)$$

$$2HOCH_2COOH + CH_3OH \rightarrow HOCH_2COOCH_2COOCH_3 + 2H_2O \quad (7)$$

$$CH_3OCH_2COOCH_3 + H_2O \rightarrow CH_3OCH_2COOH \text{ (MA)} + CH_3OH \quad (8)$$

$$CH_3OCH_2COOH + HOCH_2COOCH_3$$
$$\rightarrow CH_3OCH_2COOCH_2COOCH_3 \text{ (MMAc}_2) \quad (9)$$

In the presence of H$_2$O, dissociative-like formaldehyde and methanol were generated from the hydrolysis of DMM, which was a reversible reaction. Simultaneously, free formaldehyde could also be inserted into and react with DMM to form DMM$_2$ (ref. 20 and 21) (see reaction (4)). MG was derived from the carbonylation of formaldehyde to produce glycolic acid (GA)[22] and the subsequent esterification of GA with methanol (see reaction (5) and (6)). It had already proven[5] that MG could be produced following the above-mentioned routes, using heteropolyacids as catalysts under mild reaction conditions. Hence, it could be deduced that under the study system with a sulfonic acid resin catalyst at 110 °C, the esterification reaction was readily accomplished. DMG was probably produced from the esterification of GA with MG or the esterification of two molecules of GA and one molecule of methanol (see reaction (7)). Given the presence of H$_2$O, MA arose from the hydrolysis of MMAc[6] (see reaction (8)), because most of the product was MMAc and the reaction equilibrium spontaneously moved to reduce MMAc. MMAc$_2$ was not only derived from the carbonylation of DMM$_2$ (ref. 23) but also from the esterification of MA with MG (see reaction (9)).

As shown in Fig. 1, by gradually increasing the temperature from 90 to 150 °C, the selectivity of MG gradually increased and reached a maximum of 5.46% at 150 °C. The selectivity of DMG increased from 0.43% to 2.28% with the reaction temperature rising from 90 to 100 °C and sharply increased to 11.76% (110 °C), then continuously increased and reached its maximum (18.37%) at 150 °C. These phenomena demonstrated that the selectivities of MG and DMG, which are both formaldehyde carbonylation downstream products, were significantly influenced by the reaction temperature, and that the higher temperature was beneficial for the carbonylation of formaldehyde. Using an Amberlyst-15 resin catalyst, S. Y. Lee et al.[22] reported that the conversion of formaldehyde increased with the increased temperature and the maximum MG yield appeared near 135 °C, which is in good agreement with our reaction results. Under the studied system, the selectivities of MG and DMG were also influenced by esterification efficiency, which was obviously affected by the reaction temperature, as well as the content of H$_2$O and methanol. The MA selectivity increased from 0.59% to 4.77% as the temperature increased from 90 to 150 °C, because more H$_2$O content came from the esterification reaction and existed in the system, resulting in the hydrolysis of MMAc being more efficient at a higher temperature. The selectivity of MMAc$_2$ (about 2.20%), which could be considered as both carbonylation and esterification product, stayed nearly unchanged with the temperature variation.

3.3 The influence of CO pressure and CO/DMM ratios on DMM carbonylation

Fig. 2 exhibits the effect of a CO pressure increase from 0.625 to 5.0 MPa on the performance of DMM carbonylation over

the DICP-001 resin catalyst, with a mole ratio of CO/DMM = 1/1. It was clear that the conversion of DMM was dependent on CO pressure. At low CO pressure (0.625 MPa), DMM conversion was 85.06%. With gradually increasing CO pressure from 0.625 to 2.5 MPa, the DMM conversion increased to 91.31%. After further increasing the CO pressure from 2.5 to 5.0 MPa, the DMM conversion reached 95.81%, indicating that high CO pressure was beneficial for DMM conversion because high pressure significantly increased the collision efficiency of CO with the DMM molecules.

At 0.625 MPa CO and CO/DMM = 1/1, the selectivity of MMAc was only 1.15% but the DME selectivity was high, up to 95.70%, demonstrating that DMM was mainly converted to DME *via* a disproportionation route at low CO pressure. By gradually increasing CO pressure from 0.625 to 2.5 MPa, the MMAc selectivity exhibited a linear increase from 1.15% to 38.23% and the DME selectivity showed a linear decrease from 95.70% to 50.42%.

Further increasing the CO pressure (2.5–5.0 MPa) led to a rapid increase of MMAc selectivity from 38.23% to 55.98%, yet the DME selectivity obviously dropped from 50.42% to 27.12%. Under the study conditions, the mole ratio of CO/DMM was consistently kept at a constant (= 1/1). It could be deduced that the solubility of CO in the liquid phase increased with increasing CO pressure. Accordingly, the probability of simultaneous contact of the acid centers with DMM and CO was enhanced. Overall, the carbonylation of DMM was significantly promoted while the disproportionation of DMM was obviously suppressed, resulting in a rapid increase of MMAc selectivity and a sharp decrease of DME selectivity.

The selectivity variations of MG, DMG, MMAc$_2$, and MA are also displayed in Fig. 2. As discussed above, both MG and DMG were derived from the carbonylation of a dissociative-like formaldehyde. Hence, their selectivities also increased when increasing CO pressure from 0.625 to 5.0 MPa and reached maximum levels (1.04% and 8.76%, respectively) at 5.0 MPa. These experimental results illustrated that gradually increasing CO pressure not only promoted the carbonylation

of DMM but also facilitated the carbonylation of formaldehyde. S. Y. Lee *et al.*[22] reported a similar regular pattern for formaldehyde carbonylation by using an Amberlyst-36 resin catalyst. The selectivities of MMAc$_2$ and MA (about 1.54% and 1.17%), which were considered the products from esterification and hydrolysis reactions, remained essentially constant with CO pressure changes.

Fig. 3 shows the effect of different mole ratios of CO/DMM, from 1/1 to 4/1, on DMM conversion and products selectivities over a DICP-001 resin catalyst with a constant initial CO pressure (5.0 MPa). As stated, the DMM conversion was 95.81% with CO/DMM = 1/1, which is consistent with the exact stoichiometry of DMM carbonylation. By gradually increasing the mole ratio of CO/DMM from 1/1 to 1.67/1, the conversion of DMM increased to 99.18%. Thereafter, the DMM conversion was still higher than 99.90% when the CO/DMM ratio was greater than 2/1.

At CO/DMM = 1/1, the selectivities of MMAc and DME were 55.98% and 27.12%, respectively. By gradually increasing the mole ratio of CO/DMM from 1/1 to 2/1, the MMAc selectivity rapidly increased from 55.98% to 65.90%, and the DME selectivity obviously decreased from 27.12% to 16.48%. The partial pressure of CO increased with increasing CO/DMM ratios at a stable initial CO pressure (5.0 MPa). Therefore, the reaction of the DMM carbonylation was significantly promoted, which agrees with the results from previously reported vapor-phase carbonylations of DMM.[12,15,17] After further increasing the mole ratio of CO/DMM to 4/1, both the MMAc and DME selectivities were nearly consistent with those at CO/DMM = 2/1.

The effects of CO/DMM ratios on other products' selectivities are displayed in Fig. 3 as well. The MG and DMG selectivities, which probably arose from the carbonylation of formaldehyde and subsequent esterification of GA with methanol, increased when increasing the mole ratio of CO/DMM from 1/1 to 2/1 and exhibited maximum levels (1.60% and 11.77%, respectively). They remained constant when CO/DMM was further raised to 4/1, suggesting that the carbonylation of
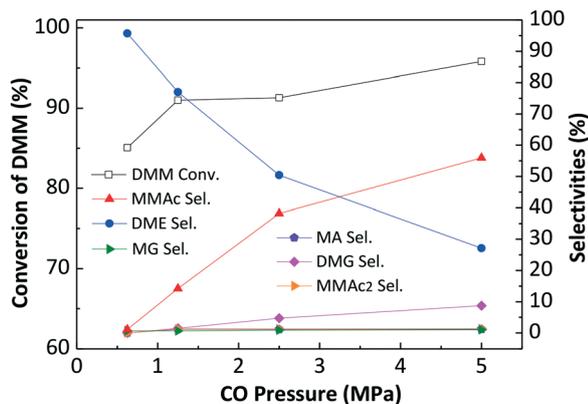
Fig. 2 The influence of CO pressure on DMM carbonylation using a DICP-001 resin catalyst. Reaction conditions: 10 g DMM, 1 g catalyst, reaction temperature: 110 °C, reaction time: 6 h, the mole ratio of CO/DMM = 1/1.
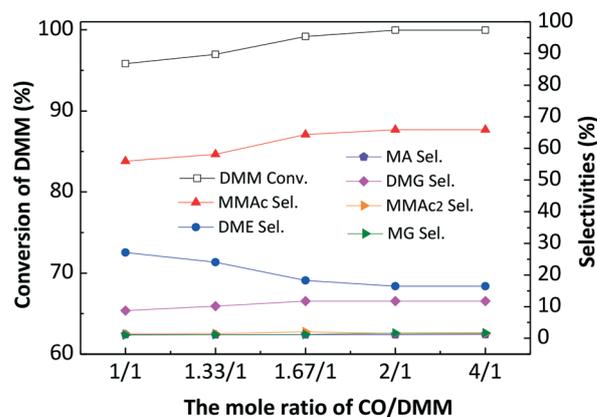
Fig. 3 The influence of CO/DMM ratios on DMM carbonylation using a DICP-001 resin catalyst. Reaction conditions: 10 g DMM, 1 g catalyst, reaction temperature: 110 °C, CO pressure: 5.0 MPa, reaction time: 6 h.

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formaldehyde was enhanced by the increased CO/DMM ratio. The selectivities of $MMAc_2$ derived from the esterification of MG with MA, and the MA produced by the hydrolysis of MMAc, were closely related to H_2O and methanol content in the system and maintained almost unchanged levels (about 1.54% and 1.17%) with given CO/DMM variations.

In conclusion, the initial CO pressure and the mole ratio of CO/DMM had an obvious impact on DMM carbonylation. The solubility of CO in a liquid phase and the concentration of CO were both enhanced with gradually increasing CO pressure and CO/DMM ratios. Thus, the carbonylation of DMM and formaldehyde were significantly promoted, resulting in increased MMAc, MG, and DMG selectivities and decreased DME selectivity. The $MMAc_2$ and MA selectivities were kept at a constant level with CO pressure and CO/DMM variations.

3.4 The influence of reaction time on DMM carbonylation

Fig. 4 exhibits the effect of reaction time, ranging from 0.5 h to 20 h, on the performance of DMM carbonylation with a DICP-001 resin catalyst. At the shorter reaction time (0.5 h), the conversion of DMM was as low as 63.32%. With gradually increasing reaction times from 1 h to 4 h, the conversion of DMM significantly increased from 71.15% to 97.38%. When the reaction time was longer than 6 h, the DMM conversion stayed above 99.50%.

The MMAc selectivity is also shown in Fig. 4, again with the influence of reaction time from 0.5 h to 20 h. At 0.5 h, the selectivity of MMAc was only 56.17% but the DME selectivity was high, up to 35.69%. One reason for the high DME selectivity was that the disproportionation reaction of DMM was carried out at a low temperature during the heating process, while the DMM carbonylation rate was very low in the meantime. Besides, it is much easier to produce a reversible reaction with DMM, using the residual H_2O left in the system to generate DMM_2 and MeOH. This could also produce DME on Bronsted acid sites, resulting in the formation of a large amount of MeOH (1.85%) and DME (see reactions (4) and
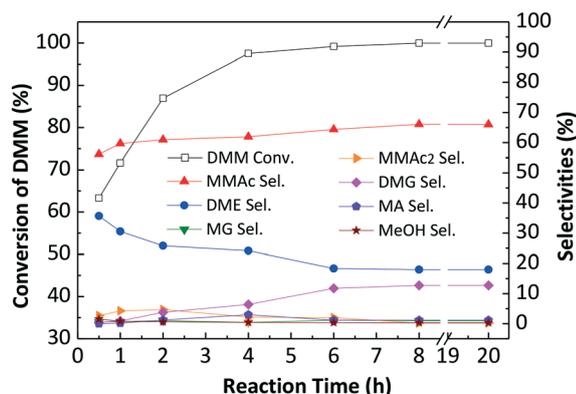
(3)). Given an increased reaction time from 1 h to 8 h, the MMAc selectivity gradually increased and reached its maximum (66.05%) at 8 h, but the DME selectivity decreased and reached a minimum (17.95%) at 8 h. These reaction results illustrated that the DMM carbonylation efficiency was higher than that of the DMM disproportionation at 110 °C, showing that more DMM tended to proceed the carbonylation reaction. This conclusion was also supported by the reaction results from the reaction temperature variations. When the reaction time was further increased to 20 h, both DME and MMAc selectivities were nearly consistent with those at 8 h, indicating that the carbonylation and disproportionation of DMM already reached the chemical equilibrium point at 8 h.

The influence of reaction time from 0.5 h to 20 h on other products' selectivities is also demonstrated in Fig. 4. MG selectivity, which arose from the carbonylation of dissociative-like formaldehyde and the esterification of GA with methanol, increased from 0.52% to 1.17% with gradually increasing reaction times (0.5–6 h), and stayed almost constant (about 1%) when the reaction time was raised to 20 h. The MG selectivity was influenced by the concentration of formaldehyde, H_2O, GA, DMG, and $MMAc_2$. The DMG selectivity, which probably came from the esterification of GA and MG, increased from 0.42% to 6.37% with increasing reaction times from 0.5 h to 4 h, and sharply increased to 11.76% at 6 h, before reaching its maximum (12.73%) at 8 h. This phenomenon could be explained by the fact that with the formation of DME, which is an irreversible process, more H_2O was produced and accumulated, leading to a higher ratio of H_2O/DMM in the reaction system. Therefore, both the hydrolysis of DMM and dissociation of formaldehyde were promoted with the extension of the reaction time, resulting in the additional formation of methanol and dissociative-like formaldehyde. GA was exactly derived from the carbonylation of formaldehyde, and MG clearly arose from the esterification of methanol with GA. Hence, the DMG selectivity was promoted by the increased reaction time. $MMAc_2$ selectivity, which was possibly produced from MA and MG, increased and reached its maximum (4.66%) at 2 h. Further increasing the reaction time (2–20 h) led to a slight decrease from 4.66% to 0.18%. MA selectivity, which was generated from the hydrolysis of MMAc to produce methanol, was too small to measure at 0.5 h, but it increased and reached a maximum value (2.99%) at 4 h, decreased to 1.14% at 8 h, and remained constant (1.14%) at 20 h. Actually, the selectivities of all the products were closely related to the concentrations of H_2O and methanol in the system, which simultaneously acted as reactants and products, taking part in multiple parallel or cascade reactions.

3.5 The influence of drying temperature on DMM carbonylation

The effect of varying the drying temperature from 90 to 130 °C on the performance of DMM carbonylation using a DICP-001 catalyst is shown in Fig. 5. At a low drying temperature

Fig. 4 The influence of reaction time on DMM carbonylation using a DICP-001 resin catalyst. Reaction conditions: 10 g DMM, 1 g catalyst, reaction temperature: 110 °C, CO pressure: 5.0 MPa, the mole ratio of CO/DMM = 1.67/1.

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(90 °C), the conversion of DMM was 73.20%. With gradually increasing drying temperatures from 90 to 120 °C, the conversion of DMM clearly increased from 73.20% to 99.18%. When the drying temperature was raised to 130 °C, the conversion of DMM remained almost unchanged.

The selectivity of MMAc was as low as 10.25% with DICP-001 dried at 90 °C, and the DME selectivity was as high as 27.60%, because the as-used resin catalyst still contained a large amount of moisture, including physically adsorbed water and chemically adsorbed crystal water, which significantly influenced the formation of multiple relevant products. For one reason, the residual moisture reliably interacted with H^+ and covered the Bronsted acid sites, leading to a reduced collision probability of DMM, CO, and active sites. Additionally, the reaction of DMM with H_2O producing DMM_2 and methanol, which was also a competitive reaction with DMM carbonylation, was promoted with more H_2O left in the system, resulting in the decreased MMAc selectivity and the enhanced methanol (14.28%) selectivity. Finally, the molecule numbers of free formaldehyde and hemiacetal, which contributed to the formation of MF, increased with the increased content of H_2O. Accordingly, DMM disproportionation to MF and DME was enhanced to a certain degree. In a word, the competitive reactions of DMM carbonylation were promoted when increasing the H_2O content in the study system, leading to the lower MMAc selectivity when DICP-001 was dried at 90 °C. By gradually increasing the drying temperature from 90 to 120 °C, the selectivity of MMAc rapidly increased and exhibited its maximum (64.39%) at 120 °C, because the content of the residual moisture was significantly reduced with a higher drying temperature. But the MMAc selectivity displayed a slight decrease (4.83%) with drying at 130 °C, although more chemically adsorbed water was removed. We recognized that the higher drying temperature led to the collapse of pores and surface sintering of the as-used catalyst, resulting in the decreased ability for DMM carbonylation.

The effects of drying temperature on other products' selectivities are also exhibited in Fig. 5. Both MG and DMG selectivities displayed maximums of 6.20% and 16.65%, respectively, when DICP-001 was dried at 90 °C. As stated, more residual moisture existed in the reaction system so the hydrolysis of DMM was promoted, resulting in the quantity of dissociative-like formaldehyde evidently increasing. Therefore, the carbonylation of formaldehyde reaction was easily conducted to form GA. Accordingly, the subsequent esterification of GA with methanol to generate MG and DMG was also promoted. After further increasing the drying temperature from 90 to 130 °C, the MG and DMG selectivities gradually decreased and displayed minimums of 1.05% and 11.57%, respectively. At low H_2O content, the hydrolysis of DMM was suppressed so less GA, MG, and DMG content was produced. Hence, the lower temperature at which the resin catalyst was dried, the greater H_2O content was left, and the higher selectivities of MG and DMG were realized. The selectivity of MA, which was derived from the hydrolysis of MMAc, exhibited its maximum (6.37%) with DICP-001 dried at 90 °C because of the maximum residual H_2O, and decreased from 6.37% to 0.98% as the drying temperatures gradually increased from 90 to 130 °C, due to the continuous decrease of H_2O content. The selectivity of $MMAc_2$ reached its maximum (2.59%) at 90 °C and its minimum (0.13%) at 130 °C, possibly because $MMAc_2$ came from the esterification of MG with MA. The variation law of $MMAc_2$ selectivity is in accordance with that of MG and MA.

3.6 The influence of H_2O content on DMM carbonylation

According to the former work[17] and the above-mentioned reaction results, we considered that DMM first reacted with the sulfonic acid groups to form methanol and methoxymethyl species. Thereafter, CO was inserted into methoxymethyl to form methoxyacetyl species, which could further react with DMM to produce MMAc and regenerate the methoxymethyl species. During the reaction cycle, H_2O interacted with H^+, which was the active center for DMM carbonylation. Therefore, the effect of H_2O content on DMM carbonylation was systematically studied. In typical experiments, 5A zeolites were implemented to remove H_2O from DMM and 1,4-dioxane was used to extract H_2O from resin catalysts; extra H_2O was also added to the system to obtain the target H_2O content, which was measured by a Karl Fischer method. As exhibited in Fig. 6, the conversion of DMM was as high as 99.98% with 32 ppm H_2O in the reaction system. With gradually increasing H_2O amounts from 32 to 2192 ppm, the conversion of DMM only had a slight decrease, from 99.98% to 98.31%. By further increasing the H_2O content from 2192 to 5×10^4 ppm, the conversion of DMM sharply decreased from 98.31% to 40.14%. At 10^5 ppm H_2O content (10 wt% of DMM), the DMM conversion was only 25.60%. These phenomena indicated that adding extra H_2O significantly decreased the activity of the sulfonic acid resin.

The MMAc selectivity, which was influenced by the content of H_2O from 32 to 10^5 ppm, is also shown in Fig. 6. At 32 ppm H_2O, the MMAc selectivity was as high as 74.14%, yet the

Fig. 5 The influence of drying temperature on DMM carbonylation using a DICP-001 resin catalyst. Reaction conditions: 10 g DMM, 1 g catalyst, reaction temperature: 110 °C, CO pressure: 5.0 MPa, reaction time: 6 h, the mole ratio of CO/DMM = 1.67/1.

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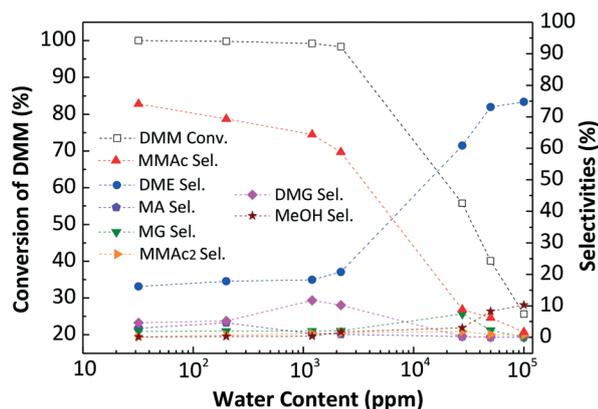
Fig. 6 The influence of H_2O content on DMM carbonylation using a DICP-001 resin catalyst. Notes: The solid symbols represent the real reaction data, while the dotted lines indicate the mutative trend of DMM conversion and product selectivities. Reaction conditions: 10 g DMM, 1 g catalyst, reaction temperature: 110 °C, CO pressure: 5.0 MPa, reaction time: 6 h, the mole ratio of CO/DMM = 1.67/1.

selectivity of DME was only 16.15%. By gradually increasing H_2O amounts from 32 to 2192 ppm, the MMAc selectivity exhibited a significant decrease from 73.14% to 58.77%, while the DME selectivity showed a gradual increase from 16.15% to 20.79%. Further increasing the H_2O content from 2192 to 10^5 ppm, the selectivity of MMAc sharply decreased and exhibited a minimum level of 1.67% at 10^5 ppm. Nevertheless, the selectivity of the DME rapidly increased and displayed a maximum of 74.76% at 10^5 ppm, illustrating that DMM carbonylation was obviously suppressed at higher H_2O content. The methanol selectivity evidently increased from 0.10% to 10.28% with increasing H_2O amounts from 32 to 10^5 ppm. It was deduced that the number of methoxymethyl groups, which were formed by the reaction of DMM with Bronsted acid sites and further reacted with CO to produce methoxyacetyl species, were reduced by competitive adsorption of H_2O through hydrogen-bond interaction, to form $-SO_3H_3O^+$ on acid sites. The dissociative H^+ was also surrounded by H_2O via hydrogen-bond interaction. Another reason was that the Bronsted acid sites, which were the active sites for CO insertion into methoxymethyl groups, might be covered by the $[(CH_3OCH_2)(H_2O)_n]^+$ clusters. The hydrolysis of DMM was promoted by increasing H_2O content to some extent, leading to an increased amount of methanol, free formaldehyde, and hemiacetal. Consequently, the more H_2O content there was, the lower the efficiency of DMM carbonylation was, resulting in lower MMAc selectivity and higher DME and methanol selectivity.

The selectivity of MG slowly increased from 0.2% by gradually increasing H_2O content from 32 to 2.77×10^4 ppm, and displayed a maximum of 1.85%. Further increasing the H_2O content (2.77×10^4 to 10^5 ppm) led to a slight decrease of MG selectivity from 1.85% to 0.65%. In fact, the dissociative formaldehyde content, which contributed to the production of GA, increased with increasing H_2O amounts. MG came from the esterification of GA and methanol. It was a combined effect in that the selectivity of MG was not only

influenced by the content of GA, methanol, and H_2O, but also affected by the carbonylation and esterification efficiency of the catalyst, which was reduced by continually increasing the H_2O amount. Therefore, the MG selectivity formed a volcano character. The DMG selectivity increased from 6.34% to 8.17% by increasing the H_2O content from 32 to 200 ppm, and displayed a maximum of 11.76% when the H_2O content reached 1200 ppm, and exhibited a sharp decrease from 11.76% to 0.27% when further elevating the H_2O content from 1200 to 2.77×10^4 ppm. Almost no DMG was observed at 10^5 ppm H_2O.

DMG selectivity was affected by the content of GA, which was influenced by the dissociative formaldehyde content and formaldehyde carbonylation activity; the content of methanol, which was directly impacted by the H_2O amount; and the esterification ability of the as-used catalyst. Hence, the DMG selectivity also exhibited a volcano shape and there was almost no DMG at a large amount of given H_2O, because the rate of DMG hydrolysis was much higher than that of esterification in high H_2O content. MA selectivity, which was closely related to MMAc and H_2O content, as well as the hydrolysis capacity, was 0.15% at 32 ppm H_2O, and gradually increased with increasing H_2O content before reaching a maximum of 8.89% at 2.77×10^4 ppm. It was nearly zero when the H_2O content was 10^5 ppm. More H_2O contributed to the higher MA selectivity, but plenty of H_2O led to almost no MA being produced, owing to very low upstream MMAc selectivity (1.67%). $MMAc_2$ selectivity, which mainly came from the esterification of MG with MA and was kept consistent with that of MG and MA, was 1.88% at 32 ppm H_2O amount, and gradually increased with increasing H_2O content, and reached a maximum of 7.42% at 2.77×10^4 ppm and was also nearly zero when the H_2O content was 10^5 ppm.

3.7 The influence of methanol content on DMM carbonylation

As known, DMM is industrially synthesized from the dehydration of methanol and formaldehyde. However, DMM cannot be completely separated through atmospheric distillation because DMM–methanol forms a minimum-boiling azeotrope with 94.06 wt% DMM.[24] Therefore, the influence of methanol content from 0.5–10 wt% on the performance of DMM carbonylation was systematically studied, and the experimental results are shown in Fig. 7. The conversion of DMM was as high as 97.06% when the methanol content was 0.5%. With gradually increasing methanol content from 0.5% to 5%, the DMM conversion had a slight decrease from 97.06% to 92.24%. When the methanol content reached 10%, the DMM conversion sharply decreased and displayed only 33.62%.

As displayed in Fig. 7, the selectivity of MMAc was 59.27% and the DME selectivity was 29.36% at 5% methanol content. With increasing the methanol content from 0.5% to 5%, the MMAc selectivity showed a linear decrease from 59.27% to 21.63%, while the selectivity of DME exhibited a linear

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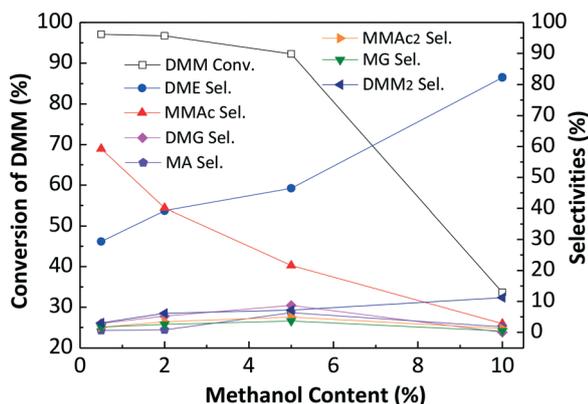
Fig. 7 The influence of methanol content on DMM carbonylation using a DICP-001 resin catalyst. Reaction conditions: 10 g DMM, 1 g catalyst, reaction temperature: 110 °C, CO pressure: 5.0 MPa, reaction time: 6 h, the mole ratio of CO/DMM = 1.67/1.

increase from 29.36% to 46.48%. After further increasing the methanol content from 5% to 10%, the MMAc selectivity sharply decreased and exhibited a minimum of 2.78%, while the DME selectivity significantly increased and showed a maximum of 82.28%. As a reference, an extra experiment by using 10 g methanol and 1 g DICP-001 was conducted at 110 °C and 5.0 MPa CO for 6 h. All the methanol was converted to DME with 100% selectivity, demonstrating that the dehydration reaction of methanol was readily carried out to produce DME and H_2O under the studied conditions. We concluded that the effect of methanol addition nearly equalled

the impact of simultaneous DME and H_2O addition. Namely, the influence of methanol on DMM carbonylation was more likely to resemble the effect of H_2O. Therefore, the MMAc selectivity clearly decreased, yet the DME selectivity obviously increased when gradually increasing the methanol. The hydrolysis of DMM was also promoted due to the produced H_2O, resulting in the DMM_2 selectivity significantly increasing from 3.05% to 11.18% as the methanol content increased from 0.5% to 10%. With gradual methanol adding, the variation trends of other products' selectivities are also consistent with that of H_2O increases.

In conclusion, different H_2O and methanol contents had a major influence on DMM carbonylation, which could be essentially ascribed to the impact of H_2O. H_2O interacted with Bronsted acid sites through hydrogen-bond to form $R\text{-}SO_3H_3O^+$, leading to a number of methoxymethyl groups, which were produced by the reaction of DMM with Bronsted acid sites, being significantly decreased because of the competitive adsorption of H_2O on acid sites. Likewise, the Bronsted acid sites, which were the active sites for the reaction of CO insertion into methoxymethyl groups to produce methoxyacetyl species, might be covered by the $[(CH_3OCH_2)(H_2O)_n]^+$ clusters. In contrast, the hydrolysis of DMM was conspicuously promoted, resulting in the increased amount of methanol, free formaldehyde, and hemiacetal. Hence, the efficiency of DMM carbonylation was evidently reduced when increasing H_2O or methanol content, resulting in obviously decreased MMAc selectivity, while the DME selectivity clearly increased. During the reaction cycle,

Fig. 8 The proposed reaction routes.

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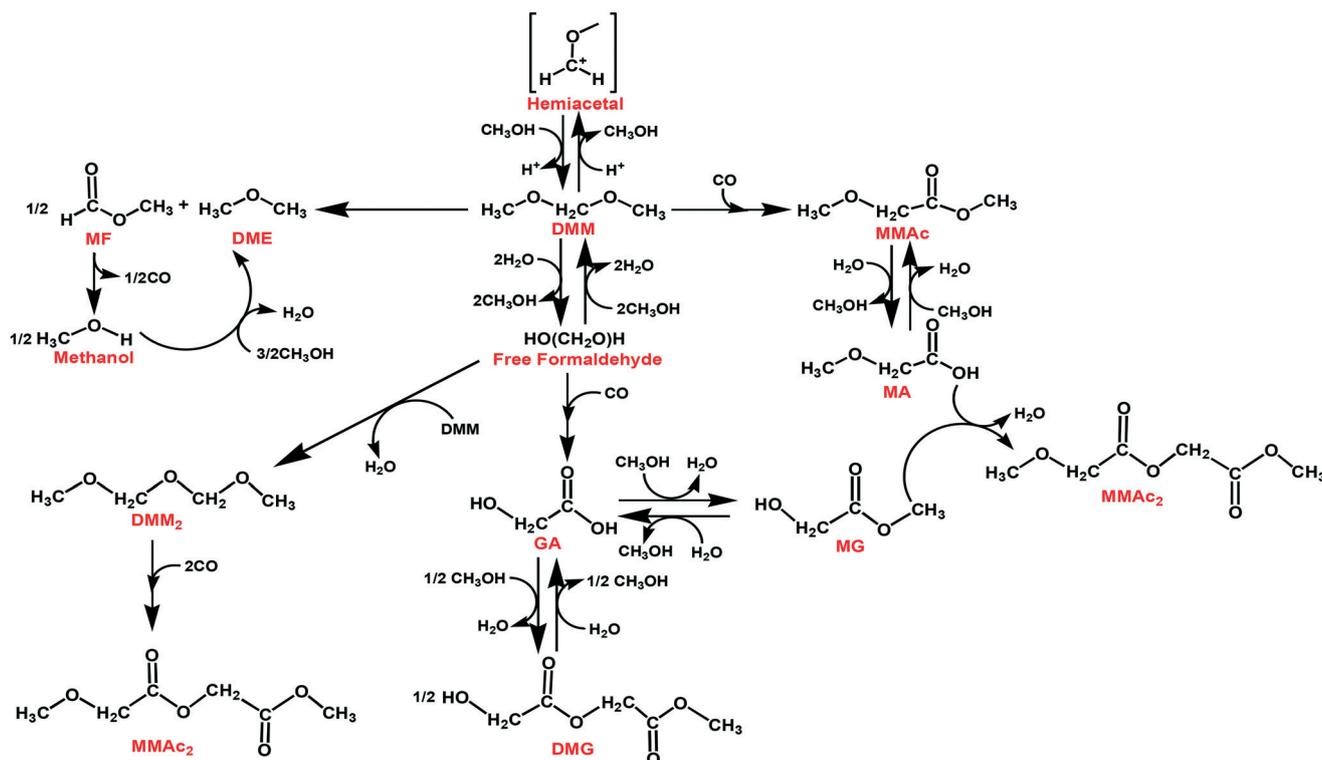
H_2O and methanol not only served as the reactants, but also acted as the products from esterification.

3.8 Discussion for the proposed reaction route

According to the reaction results and a precise GC-MS analysis of the products, as well as an understanding of the whole reaction processes,[17,19] several possible reaction routes are proposed and displayed in Fig. 8. The main reaction was the direct carbonylation of DMM with CO to produce MMAc. The disproportionation of DMM to yield DME and MF was one of the side reactions, which is in good agreement with the vapor-phase carbonylation of DMM to MMAc using zeolites with different framework structures.[12–15] According to the stoichiometry of disproportionation the mole ratio of DME/MF is approximately two, but we observed that the DME/MF ratio was much greater than the theoretical value with the DICP-001 resin catalyst. As a reference, an additional experiment was carried out by using 10 g MF and 1 g DICP-001 at 110 °C and 5.0 MPa CO for 6 h. All the MF was converted to DME with 100% selectivity, illustrating that the decomposition reaction of MF could first decompose to form methanol and CO, then the subsequent dehydration of methanol to generate DME and H_2O proceeded under the study system, which caused a significant increase in the DME/MF ratio.

Compared with vapor-phase carbonylation of DMM,[12–17] many complicated and unreported side reactions accompanied the liquid-phase carbonylation process. According to the analysis results (by GC-MS), DMM_2, MG, DMG, MA, and $MMAc_2$ were measured and produced, along with MMAc, DME, MF, and methanol. We considered that in the presence of H_2O and Bronsted acid sites, hemiacetal was produced by the protonation of DMM,[6] while free formaldehyde, which was in the form of $HO(CH_2O)H$ in an aqueous solution,[25] was yielded *via* the hydrolysis of DMM. GA could be generated through the carbonylation of free formaldehyde with CO, and DMM_2 was formed *via* the reaction of free formaldehyde with another molecule of DMM. Simultaneously, methanol was also produced from the hydrolysis of DMM. In this reaction system, DME was not only formed from the disproportionation of DMM, but also from the dehydration of methanol. MG was produced from the esterification of GA with methanol, and DMG was generated from the esterification of GA with MG, or from the esterification of one molecule of methanol and two molecules of GA, which was not easy to accomplish with the trimolecular reaction. MA was readily formed from the hydrolysis of MMAc because the main product (more than 50 wt%) in the system was MMAc. $MMAc_2$ probably came from not only the esterification of MG with MA, but also the carbonylation of DMM_2.[23] In the above-mentioned procedures, the H_2O and methanol content had significant effects on the formation of various products.

4. Conclusions

A highly efficient sulfonic acid resin was selected for the liquid-phase carbonylation of DMM to produce MMAc with-out the assistance of a solvent. The conversion of DMM reached nearly 100% with 64.39% MMAc selectivity, using the DICP-001 resin catalyst at 110 °C and 5.0 MPa CO for 6 h, with a CO/DMM ratio of only 1.67/1. The effects of reaction temperature, CO pressure, mole ratio of CO/DMM, reaction time, drying temperature, and H_2O and methanol content were systematically studied. The DMM conversion increased with increasing reaction temperature, CO pressure, the mole ratio of CO/DMM, reaction time, and drying temperature, while it decreased with increasing H_2O and methanol content. The MMAc selectivity exhibited a volcano shape with increasing the reaction temperature and drying temperature, and it increased with enhancing the CO pressure, the mole ratio of CO/DMM, and the reaction time, while it decreased with increasing the H_2O and methanol content. After removing H_2O from the DMM and resin catalyst, the MMAc selectivity was as high as 74.14% under the same reaction conditions. For liquid phase carbonylation of DMM, many complicated and unreported side reactions were observed. According to the analysis results, DMM_2, MG, $MMAc_2$, DMG, and MA were produced apart from MMAc, DME, MF, and methanol formation. The H_2O and methanol content had significant influences on the formation of these products. The reaction routes were first proposed to illustrate the relationships between reactants and products. This direct carbonylation of DMM to produce an MMAc process, which was more efficient and selective, exhibits enormous potential for industrial manufacturing.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 F. Balkenhohl, K. Ditrich, B. Hauer and W. Ladner, *J. Prakt. Chem.*, 1997, **339**, 381–384.
2 J. M. Berty, *Appl. Ind. Catal.*, 1983, **1**, 207–236.
3 H. R. Yue, Y. J. Zhao, X. B. Ma and J. L. Gong, *Chem. Soc. Rev.*, 2012, **41**, 4218–4244.
4 B. Li, S. Y. Bai, X. F. Wang, M. M. Zhong, Q. H. Yang and C. Li, *Angew. Chem., Int. Ed.*, 2012, **51**, 11517–11521.
5 Y. Sun, H. Wang, J. H. Shen, H. C. Liu and Z. M. Liu, *Catal. Commun.*, 2009, **10**, 678–681.
6 F. E. Celik, H. Lawrence and A. T. Bell, *J. Mol. Catal. A: Chem.*, 2008, **288**, 87–96.
7 Y. G. Kim, J. S. Lee and K. H. Lee, *Res. Chem. Intermed.*, 1998, **24**, 197–211.

This journal is © The Royal Society of Chemistry 2018

Catal. Sci. Technol., 2018, **8**, 580–590 | 589

8   A. T. Larson, Process for the preparation of glycolic acid, US 2153064, 1939.

9   S. A. I. Barri and D. Chadwick, *Catal. Lett.*, 2011, **141**, 749–753.

10 H. D. He, W. G. Huang, J. Y. Liu and Q. M. Zhu, *J. Mol. Catal. A: Chem.*, 1999, **145**, 335–338.

11 W. G. Huang, H. D. He, J. Y. Liu and Q. M. Zhu, *Appl. Catal., A*, 2000, **199**, 93–98.

12 F. E. Celik, T. J. Kim and A. T. Bell, *Angew. Chem., Int. Ed.*, 2009, **48**, 4813–4815.

13 F. E. Celik, T. J. Kim, A. N. Mlinar and A. T. Bell, *J. Catal.*, 2010, **274**, 150–162.

14 V. Shapovalov and A. T. Bell, *J. Phys. Chem. C*, 2010, **114**, 17753–17760.

15 F. E. Celik, T. J. Kim and A. T. Bell, *J. Catal.*, 2010, **270**, 185–195.

16 S. D. Badmaev, D. I. Potemkin, A. A. Pechenkin, G. G. Volkova, V. A. Sobyanin and V. N. Parmon, *Dokl. Phys. Chem.*, 2016, **468**, 85–88.

17 S. P. Liu, W. L. Zhu, L. Shi, H. C. Liu, Y. Liu, Y. M. Ni, L. Li, H. Zhou, S. T. Xu and Z. M. Liu, *RSC Adv.*, 2014, **4**, 40999–41002.

18 J. P. Wang, J. H. Liu, H. Y. Song and J. Chen, *Chem. Lett.*, 2015, **44**, 806–808.

19 L. Shi, J. Yao, W. L. Zhu and Z. M. Liu, *Huagong Xuebao*, 2017, **68**, 3739–3746.

20 J. Q. Zhang, D. Y. Fang and D. H. Liu, *Ind. Eng. Chem. Res.*, 2014, **53**, 13589–13597.

21 J. Q. Zhang, M. H. Shi, D. Y. Fang and D. H. Liu, *React. Kinet., Mech. Catal.*, 2014, **113**, 459–470.

22 S. Y. Lee, J. H. Kim, J. S. Lee and Y. G. Kim, *Ind. Eng. Chem. Res.*, 1993, **32**, 253–259.

23 Y. M. Li, W. L. Zhu, H. C. Liu, Y. Liu, Z. M. Liu, S. H. Meng, L. N. Li, S. P. Liu and H. Zhou, CN104725224B, 2017.

24 Q. Y. Wang, B. R. Yu and C. J. Xu, *Ind. Eng. Chem. Res.*, 2012, **51**, 1281–1292.

25 T. Grützner and H. Hasse, *J. Chem. Eng. Data*, 2004, **49**, 642–646.