Supporting Information for

Reaction Mechanism of Dimethyl Carbonate Synthesis on Cu-β
Zeolites: DFT and AIM Investigations

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Table S1. Local topological properties (in au.) of the electronic charge density distribution calculated at the position of the bond critical points of selected bond paths for energy minima and transition state of the MMC formation reaction from B3PW91/6-31++G** calculations.

|         | $\rho_b$ | $\nabla^2 \rho_b$ | $\epsilon$ | $H_b$  | $G_b$  | $V_b$ | $\left| V_b \right|/G_b$ | $\left| \lambda_1 \right|/\lambda_3$ |
|---------|----------|-------------------|------------|--------|--------|------|------------------------|------------------------|
| CH$_3$O-OH-CO |          |                   |            |        |        |      |                        |                        |
| Cu-O1   | 0.0673   | 0.3360            | 0.0433     | -0.0052| 0.0892 | -0.0945| 1.0594                 | 0.1594                 |
| Cu-O2   | 0.0536   | 0.2961            | 0.0224     | -0.0053| 0.0649 | -0.0703| 1.0832                 | 0.1641                 |
| Cu-O3   | 0.1184   | 0.5050            | 0.0547     | -0.0206| 0.1469 | -0.1675| 1.1402                 | 0.2203                 |
| Cu-O4   | 0.1151   | 0.6943            | 0.0692     | -0.0183| 0.1436 | -0.1619| 1.1274                 | 0.2209                 |
| Cu-C1   | 0.0184   | 0.0546            | 0.0243     | -0.0006| 0.0142 | -0.0148| 1.0423                 | 0.1800                 |
| C1-O5   | 0.4732   | 0.5600            | 0.0023     | -0.8283| 0.9683 | -1.7965| 1.8553                 | 0.4228                 |
| C1-O3   | n.a.     | n.a.              | n.a.       | n.a.   | n.a.   | n.a.   | n.a.                   | n.a.                   |
| C1-O4   | n.a.     | n.a.              | n.a.       | n.a.   | n.a.   | n.a.   | n.a.                   | n.a.                   |
| O3-H1   | 0.3488   | -0.6735           | 0.0253     | -0.6573| 0.0705 | -0.7278| 10.3234                | 1.7456                 |
| TS      |          |                   |            |        |        |      |                        |                        |
| Cu-O1   | 0.0637   | 0.3028            | 0.0372     | -0.0062| 0.0819 | -0.0882| 1.0769                 | 0.1674                 |
| Cu-O2   | 0.0211   | 0.0696            | 0.2918     | -0.0017| 0.0192 | -0.0210| 1.0938                 | 0.1863                 |
| Cu-O3   | 0.0540   | 0.2610            | 0.9483     | -0.0056| 0.0708 | -0.0764| 1.0791                 | 0.1678                 |
| Cu-O4   | 0.0833   | 0.3877            | 0.0211     | -0.0082| 0.1052 | -0.1134| 1.0779                 | 0.1866                 |
| Cu-C1   | 0.1084   | 0.2416            | 0.0307     | -0.0350| 0.0954 | -0.1303| 1.3658                 | 0.2791                 |
| C1-O5   | 0.4512   | 0.4400            | 0.0302     | -0.7862| 0.8962 | -1.6824| 1.8773                 | 0.4314                 |
| C1-O3   | 0.1085   | 0.1338            | 0.1510     | -0.0302| 0.0636 | -0.0938| 1.4748                 | 0.3778                 |
| C1-O4   | n.a.     | n.a.              | n.a.       | n.a.   | n.a.   | n.a.   | n.a.                   | n.a.                   |
| O3-H1   | 0.3337   | -2.1733           | 0.0205     | -0.6100| 0.0667 | -0.6768| 10.1469                | 1.7130                 |
| CH$_3$OOCOOH |        |                   |            |        |        |      |                        |                        |
| Cu-O1   | 0.0929   | 0.5582            | 0.0117     | -0.0099| 0.1494 | -0.1593| 1.0663                 | 0.1609                 |
| Cu-O2   | 0.0261   | 0.0900            | 0.1712     | -0.0029| 0.0254 | -0.0283| 1.1142                 | 0.1742                 |
| Cu-O3   | n.a.     | n.a.              | n.a.       | n.a.   | n.a.   | n.a.   | n.a.                   | n.a.                   |
| Cu-O4   | 0.0758   | 0.4803            | 0.0467     | -0.0042| 0.1243 | -0.1286| 1.0346                 | 0.1525                 |
| Cu-C1   | n.a.     | n.a.              | n.a.       | n.a.   | n.a.   | n.a.   | n.a.                   | n.a.                   |
| C1-O5   | 0.4231   | -0.2506           | 0.1299     | -0.7291| 0.6665 | -1.3956| 2.0939                 | 0.6033                 |
| C1-O3   | 0.3137   | -0.6192           | 0.0856     | -0.4622| 0.3074 | -0.7696| 2.5036                 | 0.9345                 |
| C1-O4   | 0.2829   | -0.5844           | 0.0686     | -0.3880| 0.2419 | -0.6298| 2.6036                 | 1.0209                 |
| O3-H1   | 0.3488   | -2.4756           | 0.0175     | -0.6792| 0.0602 | -0.7395| 12.2841                | 1.7378                 |
Table S2. Local topological properties (in au.) of the electronic charge density distribution calculated at the position of the bond critical points of selected bond paths for energy minima and transition state of the DMC formation reaction from B3PW91/6-31++G** calculations.

|             | \( \rho_b \) | \( \nabla^2 \rho_b \) | \( \varepsilon \) | \( \mathcal{H}_b \) | \( \mathcal{G}_b \) | \( \mathcal{V}_b \) | \( \left| \frac{\mathcal{V}_b}{\mathcal{G}_b} \right| \) | \( \left| \frac{\lambda_1}{\lambda_3} \right| \) |
|-------------|--------------|----------------|-------------|----------------|----------------|----------------|-----------------|-----------------|
| **MMC-CH$_3$OH** |
| Cu-O1       | 0.0797       | 0.4569         | 0.0099      | -0.0078       | 0.1220         | -0.1298        | 1.0639          | 0.1585          |
| Cu-O2       | 0.0225       | 0.0773         | 0.1930      | -0.0019       | 0.0212         | -0.0231        | 1.0896          | 0.1706          |
| Cu-O4       | 0.0649       | 0.3772         | 0.0392      | -0.0047       | 0.0990         | -0.1036        | 1.0465          | 0.1560          |
| Cu-O6       | 0.0348       | 0.1197         | 0.0234      | -0.0058       | 0.0357         | -0.0415        | 1.1625          | 0.1843          |
| C1-O5       | 0.4208       | -0.2669        | 0.1262      | -0.7232       | 0.6564         | -1.3795        | 2.1016          | 0.6083          |
| C1-O3       | 0.3101       | -0.6227        | 0.0804      | -0.4537       | 0.2980         | -0.7518        | 2.5228          | 0.9509          |
| C1-O4       | 0.2905       | -0.5939        | 0.0714      | -0.4061       | 0.2576         | -0.6638        | 2.5769          | 0.9971          |
| C1-O6       | n.a.         | n.a.           | n.a.        | n.a.           | n.a.           | n.a.           | n.a.            | n.a.            |
| O3-H1       | 0.3505       | -2.4763        | 0.0183      | -0.6806       | 0.0615         | -0.7422        | 12.0683         | 1.7430          |
| O3-H2       | n/a          | n/a            | n/a         | n/a            | n/a            | n/a            | n/a             | n/a             |
| O6-H2       | 0.3434       | -2.3683        | 0.0226      | -0.6592       | 0.0671         | -0.7263        | 10.8241         | 1.7344          |
| **TS**      |
| Cu-O1       | 0.0959       | 0.5799         | 0.0155      | -0.0106       | 0.1556         | -0.1663        | 1.0688          | 0.1623          |
| Cu-O2       | 0.0198       | 0.0676         | 0.3761      | -0.0009       | 0.0178         | -0.0187        | 1.0506          | 0.1723          |
| Cu-O4       | 0.0780       | 0.4901         | 0.0603      | -0.0048       | 0.1274         | -0.1322        | 1.0377          | 0.1560          |
| Cu-O6       | n.a.         | n.a.           | n.a.        | n.a.           | n.a.           | n.a.           | n.a.            | n.a.            |
| C1-O5       | 0.4251       | -0.1981        | 0.1169      | -0.7338       | 0.6843         | -1.4181        | 2.0723          | 0.5824          |
| C1-O3       | 0.2827       | 0.0907         | 0.3718      | 0.0009        | 0.0217         | -0.0207        | 0.9539          | 0.1719          |
| C1-O4       | 0.3024       | -0.6791        | 0.0753      | -0.4296       | 0.2598         | -0.6895        | 2.6540          | 1.0690          |
| C1-O6       | n.a.         | n.a.           | n.a.        | n.a.           | n.a.           | n.a.           | n.a.            | n.a.            |
| O3-H1       | 0.3527       | -2.3817        | 0.0240      | -0.6647       | 0.0692         | -0.7339        | 10.6055         | 1.6737          |
| O3-H2       | 0.3652       | -2.5222        | 0.0237      | -0.7032       | 0.0727         | -0.7760        | 10.6740         | 1.7537          |
| O6-H2       | n/a          | n/a            | n/a         | n/a            | n/a            | n/a            | n/a             | n/a             |
| **DMC-H$_2$O** |
| Cu-O1       | 0.0961       | 0.5776         | 0.0168      | -0.0108       | 0.1552         | -0.1660        | 1.0696          | 0.1630          |
| Cu-O2       | 0.0216       | 0.0749         | 0.2857      | -0.0013       | 0.0200         | -0.0213        | 1.0800          | 0.1709          |
| Cu-O4       | 0.0821       | 0.5259         | 0.0544      | -0.0052       | 0.1366         | -0.1418        | 1.0381          | 0.1556          |
| Cu-O6       | n.a.         | n.a.           | n.a.        | n.a.           | n.a.           | n.a.           | n.a.            | n.a.            |
| C1-O5       | 0.4220       | -0.2726        | 0.1221      | -0.7248       | 0.6567         | -1.3815        | 2.1037          | 0.6082          |
| C1-O3       | n.a.         | n.a.           | n.a.        | n.a.           | n.a.           | n.a.           | n.a.            | n.a.            |
| C1-O4       | 0.2755       | -0.5879        | 0.0657      | -0.3661       | 0.2191         | -0.5852        | 2.6709          | 1.0618          |
| C1-O6       | 0.3234       | -0.6601        | 0.1067      | -0.4803       | 0.3153         | -0.7956        | 2.5233          | 0.9547          |
| O3-H1       | 0.3514       | -2.3753        | 0.0223      | -0.6651       | 0.0713         | -0.7364        | 10.3282         | 1.7464          |
| O3-H2       | 0.3494       | -2.3800        | 0.0218      | -0.6647       | 0.0697         | -0.7344        | 10.5366         | 1.7470          |
| O6-H2       | n.a.         | n.a.           | n.a.        | n.a.           | n.a.           | n.a.           | n.a.            | n.a.            |
Table S3. Local topological properties (in au.) of the electronic charge density distribution calculated at the position of the bond critical points of selected bond paths for energy minima and transition state of the dimethoxide formation reaction from B3PW91/6-31++G** calculations.

| Bond                | ρ_b  | V^2ρ_b | ε   | H_b  | G_b  | V_b  | |V_b| / |G_b| |λ_1| / |λ_3|
|---------------------|------|--------|-----|------|------|------|-----|-----|-----|-----|-----|-----|
| CH₃O-OH-CH₂OH       |      |        |     |      |      |      |     |     |     |     |     |     |
| Cu-O1               | 0.0750 | 0.3008 | 0.0633 | -0.0231 | 0.0983 | -0.1215 | 1.2360 | 0.1851 |
| Cu-O2               | 0.0656 | 0.2519 | 0.0324 | -0.0195 | 0.0825 | -0.1019 | 1.2352 | 0.1870 |
| Cu-O3               | 0.1314 | 0.4550 | 0.0500 | -0.0520 | 0.1657 | -0.2177 | 1.3138 | 0.2444 |
| Cu-O4               | 0.1304 | 0.4614 | 0.0609 | -0.0506 | 0.1660 | -0.2166 | 1.3048 | 0.2446 |
| Cu-O5               | 0.0221 | 0.0849 | 0.0260 | 0.0003  | 0.0209 | -0.0206 | 0.9856 | 0.1617 |
| O3-H1               | 0.3487 | -1.9587 | 0.0242 | -0.5631 | 0.0734 | -0.6365 | 8.6717 | 1.1738 |
| O3-H2               | n.a.  | n.a.   | n.a. | n.a.  | n.a.  | n.a.  | n.a. | n.a. |
| O5-H2               | 0.3599 | -2.0278 | 0.0260 | -0.5826 | 0.0756 | -0.6582 | 8.7063 | 1.1836 |
| TS                  |      |        |     |      |      |      |     |     |     |     |     |     |
| Cu-O1               | 0.0794 | 0.3336 | 0.0287 | -0.0237 | 0.1071 | -0.1307 | 1.2204 | 0.1763 |
| Cu-O2               | 0.0391 | 0.1449 | 0.0891 | -0.0056 | 0.0418 | -0.0473 | 1.1316 | 0.1855 |
| Cu-O3               | 0.0768 | 0.2389 | 0.0450 | -0.0265 | 0.0863 | -0.1129 | 1.3082 | 0.2405 |
| Cu-O4               | 0.1358 | 0.4961 | 0.0448 | -0.0521 | 0.1761 | -0.2282 | 1.2959 | 0.2294 |
| Cu-O5               | 0.0603 | 0.2108 | 0.0525 | -0.0159 | 0.0686 | -0.0846 | 1.2332 | 0.2076 |
| O3-H1               | 0.3260 | -1.7440 | 0.0048 | -0.5012 | 0.0652 | -0.5663 | 8.6856 | 1.1650 |
| O3-H2               | 0.1129 | -0.0280 | 0.0455 | -0.0699 | 0.0629 | -0.1327 | 2.1097 | 0.5369 |
| O5-H2               | 0.1718 | -0.5169 | 0.0101 | -0.2060 | 0.0713 | -0.2719 | 3.8135 | 0.9066 |
| CH₃O-CH₃O-H₂O        |      |        |     |      |      |      |     |     |     |     |     |     |
| Cu-O1               | 0.0850 | 0.3695 | 0.0488 | -0.0264 | 0.1187 | -0.1451 | 1.2224 | 0.1831 |
| Cu-O2               | 0.0243 | 0.0976 | 0.2315 | 0.0003  | 0.0241 | -0.0238 | 0.9876 | 0.1666 |
| Cu-O3               | 0.0245 | 0.0966 | 0.0272 | 0.0001  | 0.0241 | -0.0240 | 0.9959 | 0.1675 |
| Cu-O4               | 0.1432 | 0.5970 | 0.0423 | -0.0541 | 0.2034 | -0.2575 | 1.2660 | 0.2244 |
| Cu-O5               | 0.1198 | 0.3920 | 0.0309 | -0.0477 | 0.1457 | -0.1935 | 1.3281 | 0.2455 |
| O3-H1               | 0.3550 | -2.0379 | 0.0234 | -0.5816 | 0.0721 | -0.6537 | 9.0666 | 1.1790 |
| O3-H2               | 0.3529 | -2.0422 | 0.0234 | -0.5810 | 0.0704 | -0.6514 | 9.2528 | 1.1811 |
| O5-H2               | n.a.  | n.a.   | n.a. | n.a.  | n.a.  | n.a.  | n.a. | n.a. |

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Table S4. Local topological properties (in au.) of the electronic charge density distribution calculated at the position of the bond critical points of selected bond paths for energy minima and transition state of the CO insertion reaction from B3PW91/6-31++G** calculations.

|        | $\rho_b$ | $\nabla^2 \rho_b$ | $\varepsilon$ | $H_b$  | $G_b$  | $V_b$  | $|V_b|/G_b$ | $|\lambda_1|/\lambda_3$ |
|--------|----------|-------------------|---------------|--------|--------|--------|-------------|------------------|
| **CH$_3$O-CH$_3$O-CO** |          |                   |               |        |        |        |             |                  |
| Cu-O1  | 0.0590   | 0.2759            | 0.0227        | -0.0056 | 0.0745 | -0.0801| 1.0752     | 0.1607           |
| Cu-O2  | 0.0608   | 0.2920            | 0.0448        | -0.0051 | 0.0781 | -0.0833| 1.0666     | 0.1599           |
| Cu-O3  | 0.1141   | 0.4898            | 0.0656        | -0.0183 | 0.1408 | -0.1591| 1.1300     | 0.2205           |
| Cu-O4  | 0.1143   | 0.4888            | -0.0430       | -0.0185 | 0.1407 | -0.1592| 1.1315     | 0.2178           |
| Cu-C1  | 0.0232   | 0.0641            | 0.3786        | -0.0022 | 0.0182 | -0.0204| 1.1209     | 0.1978           |
| C1-O5  | 0.4719   | 0.5799            | 0.0020        | -0.8241 | 0.9691 | -1.7932| 1.8504     | 0.4203           |
| C1-O3  | n.a.     | n.a.              | n.a.          | n.a.   | n.a.   | n.a.   | n.a.       | n.a.             |
| C1-O4  | n.a.     | n.a.              | n.a.          | n.a.   | n.a.   | n.a.   | n.a.       | n.a.             |
| **TS** |          |                   |               |        |        |        |             |                  |
| Cu-O1  | 0.0622   | 0.2988            | 0.0349        | -0.0053 | 0.0800 | -0.0853| 1.0663     | 0.1628           |
| Cu-O2  | 0.0321   | 0.1077            | 0.0986        | -0.0048 | 0.0317 | -0.0365| 1.1515     | 0.1860           |
| Cu-O3  | 0.0421   | 0.1800            | 1.8199        | -0.0049 | 0.0499 | -0.0548| 1.0982     | 0.1780           |
| Cu-O4  | 0.1108   | 0.5106            | 0.0463        | -0.0166 | 0.1444 | -0.1610| 1.1150     | 0.2064           |
| Cu-C1  | 0.0933   | 0.2176            | 0.0177        | -0.0275 | 0.0819 | -0.1093| 1.3346     | 0.2639           |
| C1-O5  | 0.4555   | 0.4870            | 0.0165        | -0.7931 | 0.9148 | -1.7079| 1.8670     | 0.4252           |
| C1-O3  | 0.0868   | 0.1531            | 0.1345        | -0.0150 | 0.0532 | -0.0682| 1.2820     | 0.3234           |
| C1-O4  | n.a.     | n.a.              | n.a.          | n.a.   | n.a.   | n.a.   | n.a.       | n.a.             |
| **DMC** |         |                   |               |        |        |        |             |                  |
| Cu-O1  | 0.0946   | 0.5703            | 0.0135        | -0.0103 | 0.1528 | -0.1632| 1.0681     | 0.1617           |
| Cu-O2  | 0.0232   | 0.0792            | 0.2372        | -0.0020 | 0.0218 | -0.0237| 1.0872     | 0.1733           |
| Cu-O3  | n.a.     | n.a.              | n.a.          | n.a.   | n.a.   | n.a.   | n.a.       | n.a.             |
| Cu-O4  | 0.0784   | 0.4994            | 0.0485        | -0.0046 | 0.1294 | -0.1340| 1.0355     | 0.1535           |
| Cu-C1  | n.a.     | n.a.              | n.a.          | n.a.   | n.a.   | n.a.   | n.a.       | n.a.             |
| C1-O5  | 0.4211   | -0.2430           | 0.1257        | -0.7235 | 0.6628 | -1.3863| 2.0916     | 0.6004           |
| C1-O3  | 0.3191   | -0.6110           | 0.1033        | -0.4735 | 0.3207 | -0.7942| 2.4764     | 0.9190           |
| C1-O4  | 0.2788   | -0.5779           | 0.0688        | -0.3777 | 0.2333 | -0.6110| 2.6189     | 1.0369           |