Electronic Supplementary Material (ESI) for RSC Advances

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.

	ρ_b	$\nabla^2\rho_b$	ε	H_b	G_b	V_b	$\lvert V_b \rvert / G_b$	$\lvert \lambda_1 \rvert / \lambda_3$
CH_3O-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	01674
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_3OCOOH								
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.

	ρ_b	$\nabla^2\rho_b$	ε	H_b	G_b	V_b	$\lvert V_b \rvert / G_b$	$\lvert \lambda_1 \rvert / \lambda_3$
MMC-CH_3OH								
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	0.0254	0.0907	0.3718	0.0009	0.0217	-0.0207	0.9539	0.1719
C1-O4	0.2827	-0.6052	0.0597	-0.3852	0.2339	-0.6190	2.6464	1.0511
C1-O6	0.3024	-0.6791	0.0753	-0.4296	0.2598	-0.6895	2.6540	1.0690
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_2O								
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.

	ρ_b	$\nabla^2\rho_b$	ε	H_b	G_b	V_b	$\lvert V_b \rvert / G_b$	$\lvert \lambda_1 \rvert / \lambda_3$
CH_3O-OH-CH_3OH								
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	-0.2006	0.0713	-0.2719	3.8135	0.9066
CH_3O-CH_3O-H_2O								
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.

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.

	ρ_b	$\nabla^2\rho_b$	ε	H_b	G_b	V_b	$\lvert V_b \rvert / G_b$	$\lvert \lambda_1 \rvert / \lambda_3$
CH_3O-CH_3O-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