Supplementary Information

Mechanistic investigations on dimethyl carbonate formation by oxidative carbonylation of methanol over CuY zeolite: An operando SSITKA/DRIFTS/MS study

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Experimental

For the SSITKA experiments with $^{16}$O$_2$/18O$_2$ and $^{12}$CO/$^{13}$CO different gas dosing systems were used the detailed flow diagrams of which are shown in Fig. S1a, and S1b. The following gases and gas mixtures were used: 5 vol.% $^{12}$CO/He, 5 vol.% $^{16}$O$_2$/He, and 1 vol. % Ne/He (Air Liquide), $^{13}$CO (pure) and 5 vol.% $^{18}$O$_2$/He (Linde). MeOH was dosed using a saturator (14°C) with He (cf. Fig. S1a, b).

The general feed composition was 5.1 vol.% MeOH / 2.5 vol.% CO / 1.2 vol.% O$_2$ balanced with He. In the experiments with Ne as marker the mixture additionally contained 0.2 vol.% Ne. The switching from the normal to the isotopic labelled gas mixture was done by a four-way valve realizing a constant flow rate of 25 ml min$^{-1}$.

Fig. S1a Scheme of gas dosing system applied for SSITKA/DRIFTS/MS with $^{16}$O$_2$/18O$_2$. 
Interaction of the CuY catalyst with $^{16}$O_2/$^{18}$O_2

It was checked if the oxygen of the zeolite lattice or the CuO_x agglomerates can be exchanged with gaseous oxygen at reaction temperature of 150°C. If $^{16}$O_2 is replaced by $^{18}$O_2 under steady state conditions a simultaneous increase of the MS signals of $^{18}$O_2 and the tracer Ne was observed 30 sec after switching whereas the MS signal intensity of $^{16}$O_2 decreases in parallel (Fig. S2). Because no $^{16}$O$^{18}$O was detected an exchange between lattice oxygen of both the zeolite and oxidic Cu species with gas phase oxygen can be excluded.

Fig. S2 MS signal intensities of $^{16/18}$O_2, $^{16/18}$O_2, $^{18/18}$O_2 and the tracer Ne versus time; switching from $^{16}$O_2 to $^{18}$O_2 at time = 0.
Interaction of the CuY catalyst with $^{12}$CO/$^{13}$CO

After switching from the $^{12}$CO/He to the $^{13}$CO/He gas mixture the DRIFT spectra shown in Fig. S3a were obtained. The bands at 2160/2144/2112 cm$^{-1}$ obtained after 30 min exposure to the $^{12}$CO/He feed are assigned to Cu(I)$^{−}$12CO modes of Cu(I) carbonyls at different sites. After switching to $^{13}$CO/He a rapid intensity decrease of these bands is observed accompanied by the appearance of new ones at 2110/2097/2062 cm$^{-1}$. The analysis of the respective integral band intensities (cf. Fig. S3a) in dependence on time demonstrates the quick $^{12}$CO/$^{13}$CO exchange (Fig. S3b).

Comparing the interaction of the CuY catalyst with MeOH/CO and MeOH/CO/O$_2$

Comparing the amounts of MF, DMC, and CO$_2$ formed during 120 min exposure the catalyst to 5.1 vol.% MeOH/2.5 vol.% $^{12}$CO/He and to 5.1 vol.% MeOH/2.5 vol.% $^{12}$CO/1.2 vol.% O$_2$/He at 150°C it is clearly seen that CO oxidation is preferred in the presence of oxygen (Fig. S4). The formation of DMC is lowered while the increased MF formation points to a higher extent of unselective MeOH oxidation. In the absence of oxygen (MeOH/CO/He feed) the MF formation proceeds by participation of lattice oxygen supplied by CuO$_x$. Because no additional oxygen is dosed the MF formation decreases with time.
**Fig. S4** MS signal intensities of MF, DMC, and CO$_2$ versus time measured during 120 min exposure the catalyst to a 5.1 vol.% MeOH/2.5 vol.% $^{12}$CO/He feed and to 5.1 vol.% MeOH/2.5 vol.% $^{12}$CO/1.2 vol.% O$_2$/He feed at 150°C, respectively.