Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

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

Jana Engeldinger, Manfred Richter and Ursula Bentrup*

Experimental

For the SSITKA experiments with $^{16}O_2$/$^{18}O_2$ 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}.

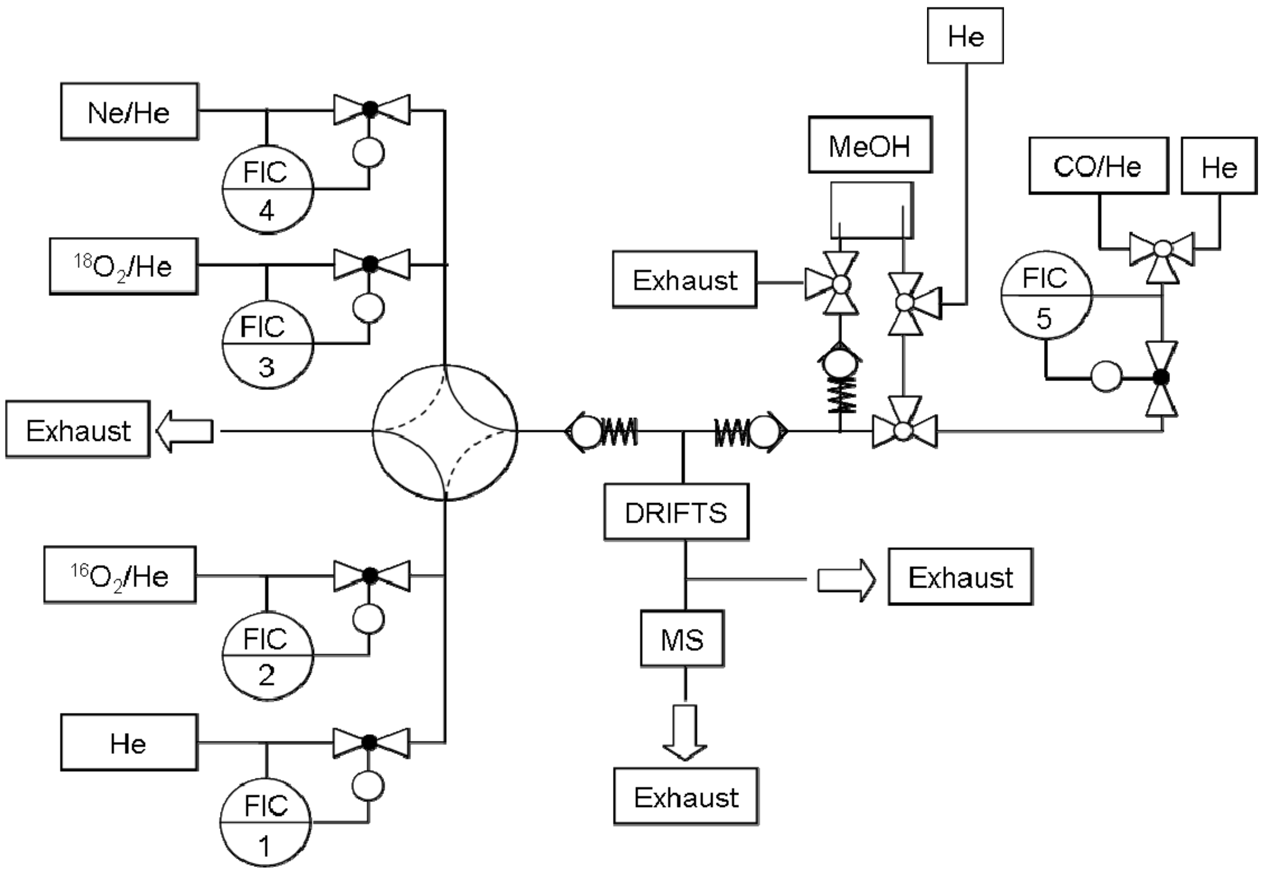

Fig. S1a Scheme of gas dosing system applied for SSITKA/DRIFTS/MS with $^{16}O_2$/$^{18}O_2$.

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
This journal is © The Owner Societies 2011

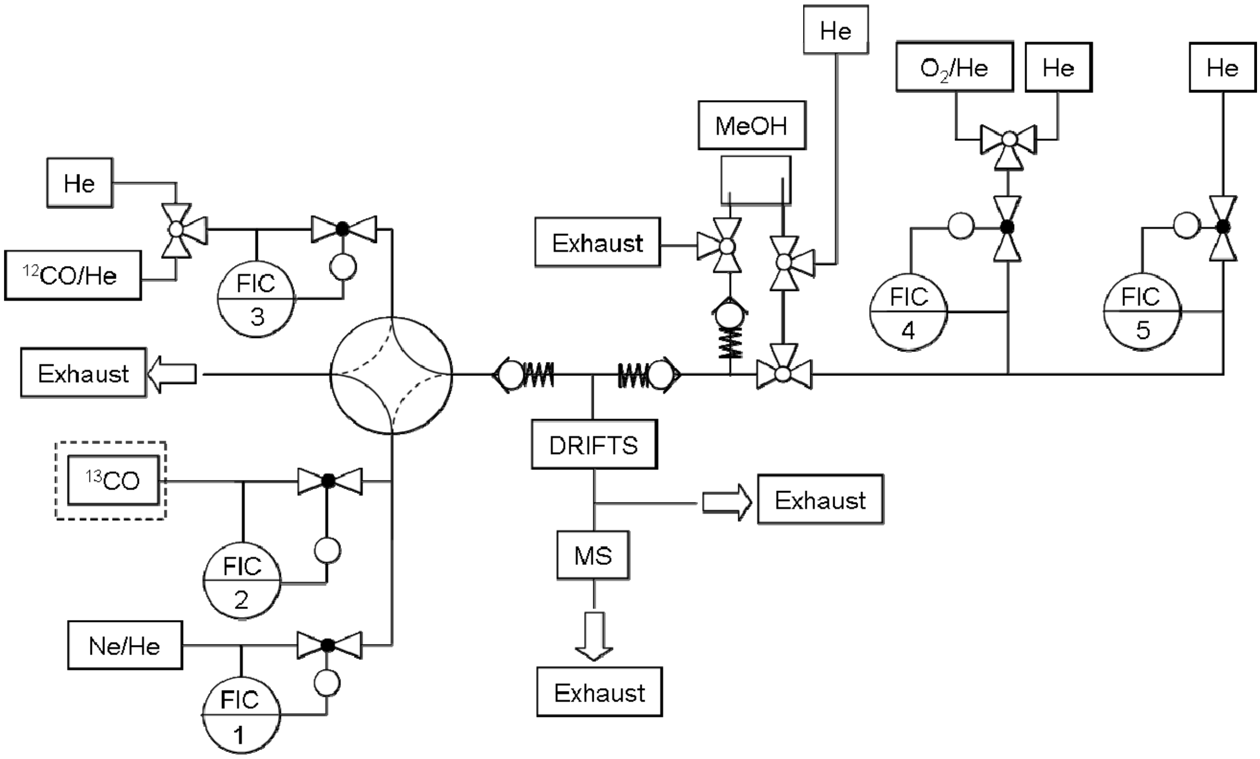

Fig. S1b Scheme of gas dosing system applied for SSITKA/DRIFTS/MS with ^{12}CO / ^{13}CO.

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.

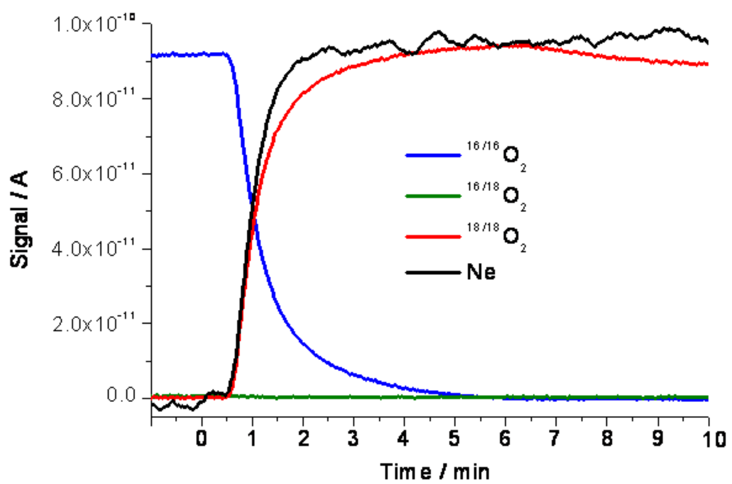

Fig. S2 MS signal intensities of $^{16/16}O_2$, $^{16/18}O_2$, $^{18/18}O_2$ and the tracer Ne versus time; switching from $^{16}O_2$ to $^{18}O_2$ at time = 0.

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)–^{12}CO 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).

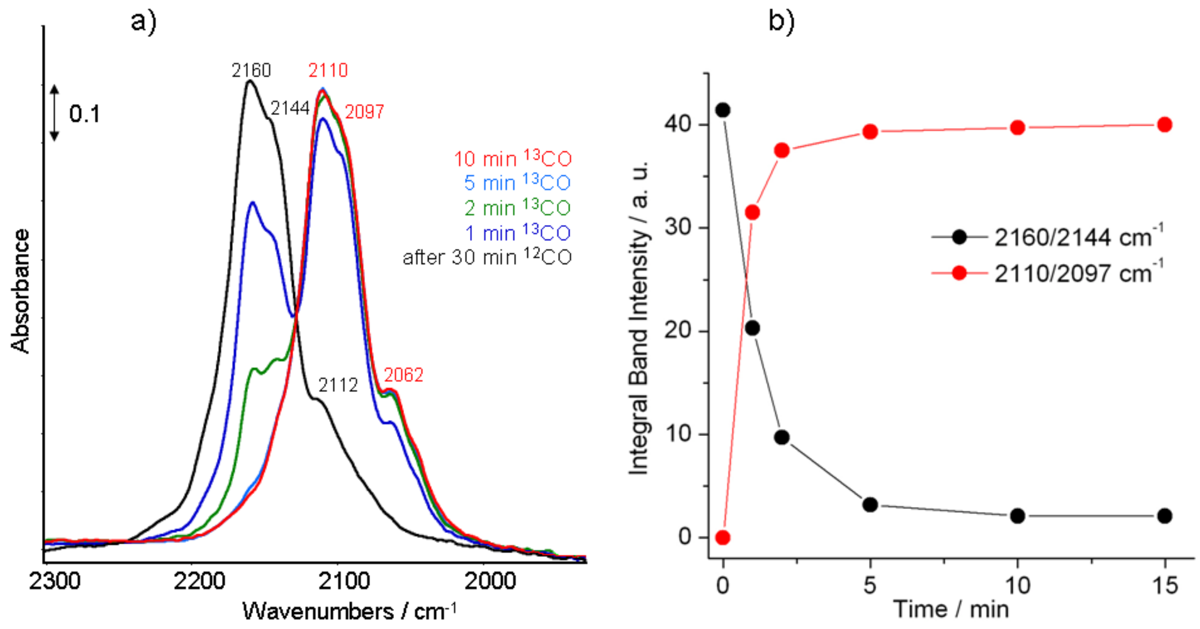

Fig. S3 a) DRIFT spectra of adsorbed CO on 13CuY at 150°C after 30 min exposure to 2.5 vol.% ^{12}CO/He and subsequent switching to 2.5 vol.% ^{13}CO/He; b) Integral intensities of the Cu(I)–^{12}CO (2160/2144 cm^{-1}) and Cu(I)–^{13}CO (2110/2097 cm^{-1}) bands versus time calculated from the measured DRIFT spectra.

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.

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

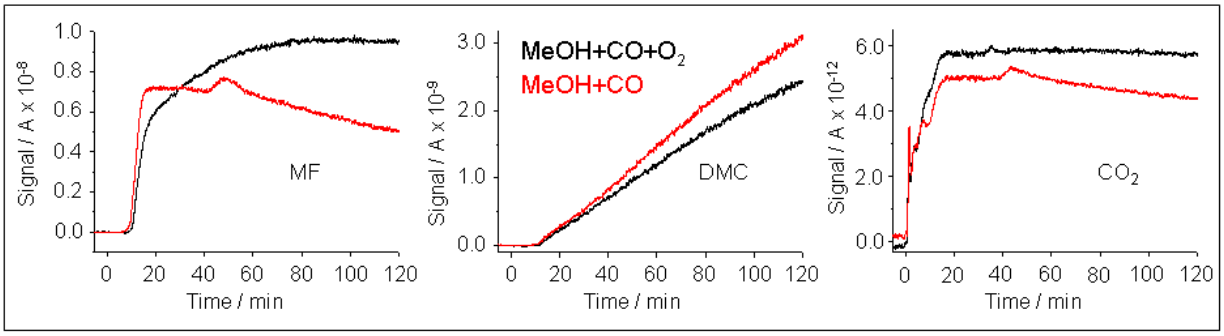

Fig. S4 MS signal intensities of MF, DMC, and CO_2 versus time measured during 120 min exposure the catalyst to a 5.1 vol.% MeOH/2.5 vol.% ^{12}CO/He feed and to 5.1 vol.% MeOH/2.5 vol.% ^{12}CO/1.2 vol.% O_2/He feed at 150°C, respectively.