Elucidating the Mechanism of Dimethyl Carbonate Formation by Oxidative Carbonylation of Methanol over CuY Zeolite: An Operando SSITKA/DRIFTS/MS Study

Jana Engeldinger, Ursula Bentrup

Leibniz-Institut für Katalyse e. V. an der Universität Rostock (LIKAT), Rostock, Germany

Introduction and Objectives

Cu-containing zeolites, in particular CuY zeolites, have been found to be appropriate catalysts for the oxidative carbonylation of methanol (MeOH) to dimethyl carbonate (DMC) in the gas phase [1]. Such a process could be an attractive, and environmentally benign, alternative to the traditional synthetic route for DMC using highly hazardous and toxic phosgene as a reagent. However, to improve the catalytic performance of suitable catalysts knowledge about the reaction mechanism and kinetics is needed. Most of the studies published in literature are based upon *in situ* FTIR observations using Cu-exchanged zeolites [2-4] and higher loaded CuY samples [5]. Up to now, the nature of the catalytically active Cu species and reactive intermediates as well as the role of oxygen within the catalytic cycle is not satisfactorily elucidated.

To get more insight into the reaction mechanism a SSITKA/DRIFTS/MS setup was applied which enables to discriminate between active and spectator species by comparison of the isotopic exchange rate of the surface species, followed by DRIFTS, with the rate of exchange of gas phase species measured by MS. The aim was to elucidate the role of oxygen in the carbonylation reaction and its relevance concerning selective and unselective reaction pathways, and to follow the way of CO insertion. For this purpose the interaction of the catalyst with the different reactants and reactant mixtures (O_2, CO, CO/O_2, MeOH/O_2, MeOH/CO, and MeOH/CO/O_2) was studied in detail using $^{16}O_2/^{18}O_2$ as well as $^{12}CO/^{13}CO$ containing gas mixtures. For the experiments a CuY zeolite with a Cu content of 13 wt% Cu was selected which additionally contain CuO_x and crystalline CuO.

Results and Discussion

The available information from operando SSITKA/DRIFTS/MS experiments in terms of surface adsorbates and gas phase products are exemplarily displayed in Fig. 1. The Figure shows DRIFT spectra and MS signal intensities obtained after switching from MeOH/^{12}CO/He feed to the respective ^{13}CO-containing feed. Although the feed did not contain oxygen the formation of DMC as well as CO_2 was observed by MS. As can be seen from the DRIFT spectra besides CO adsorbed on Cu(I) methoxide, formate, monomethyl carbonate (MMC), and DMC species were detected.

Separate experiments showed that the formation of formate and CO_2 is attributed to the oxidation of MeOH and CO by lattice oxygen supplied by CuO_x species.

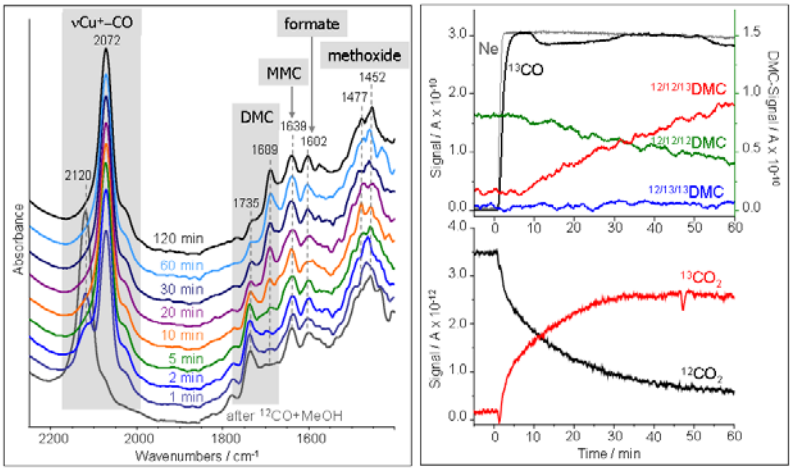

Fig. 1. DRIFT spectra (left) and MS signal intensities (right) obtained after 120 min reaction with MeOH/^{12}CO/He at 150°C and subsequent switching to MeOH/^{13}CO/He.

From the observed band shift of νCu(I)–CO (2120 → 2072 cm^{-1}) as well as adsorbed DMC (1735 → 1689 cm^{-1}) after switching from MeOH/^{12}CO/He to MeOH/^{13}CO/He follows that CO participates in DMC formation for which obviously no additional oxygen is needed. On the other hand position and intensity of the MMC band at 1639 cm^{-1} do not change. This suggests that the observed bidentate MMC species can not be an intermediate in DMC formation as discussed earlier. Further experiments showed that DMC is produced *via* a monodentate monomethyl carbonate (MMC) species as intermediate which is formed by the concerted action of adsorbed methoxide and CO with gas phase MeOH. The MMC formation, which requisites an oxidation step, proceeds under participation of lattice oxygen from CuO_x. Gas phase oxygen is needed to re-oxidize the catalyst (Mars-van-Krevelen mechanism) but favours also the oxidation of CO to CO_2 and unselective oxidation reactions of MeOH to methyl formate, dimethoxymethane, and CO_2. For this reason the appropriate choice of reaction temperature and oxygen content in the reactant gas mixture was found to be indispensable for reaching high DMC selectivities.

Conclusions

The *operando* DRIFTS/MS measurements under SSITKA conditions provide information on the transient progress of isotopic exchange in educts and products. Only in this manner it is possible to distinguish between active and spectator species which is essential for the elucidation of reaction mechanism especially in complex catalytic reaction systems.

References

[1] M. Richter, M. J. G. Fait, R. Eckelt, E. Schreier, M. Schneider, M.-M. Pohl, R. Fricke, *Appl. Catal. B: Environmental*, 2007, **73**, 269.
[2] S. T. King, *Catal.Today*, 1997, **33**, 173.
[3] S. A. Anderson, T. W. Root, *J. Mol. Catal. A: Chemical*, 2004, **220**, 247.
[4] Y. Zhang, A.T. Bell, *J. Catal.*, 2008, **255**, 153.
[5] J. Engeldinger, C. Domke, M. Richter, U. Bentrup, *Appl. Catal. A: General*, 2010, **382**, 303.