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Gas-phase oxycarbonylation of methanol for the synthesis of dimethyl carbonate using copper-based Supported Ionic Liquid Phase (SILP) catalysts

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ABSTRACT

Catalyst systems for the gas-phase oxycarbonylation of methanol often suffer from low catalyst activities and strong catalyst deactivation. In this work, the continuous gas-phase oxycarbonylation of methanol was realized by using Supported Ionic Liquid-Phase (SILP) catalysts. Copper(I) bromide dissolved in various ionic liquids and dispersed on Polymer-Based Spherical Activated Carbon (PBSAC) as supporting material was found to be an active catalyst. The poor activity and stability of copper halide catalysts reported in literature was substantially increased by the presence of ionic liquids. In particular, trioctylmethylammonium bromide in combination with a basic salt additive increased the activity of the CuBr catalyst and led to comparatively stable SILP catalyst operation reaching a total turnover number of 600 over 50 h time-on-stream.

1. Introduction

Dimethyl carbonate (DMC) is a potential alternative for phosgene in polycarbonate and isocyanate syntheses. Additional fields of application include the use of DMC as fuel additive [1], methylating agent [2], and green solvent [3]. The two major industrial production processes for DMC are the liquid-phase oxycarbonylation of methanol by Enichem [4] and the liquid-phase methylnitrite carbonylation by UBE [5,6]. Both processes suffer from safety aspects due to toxicity and explosion risks at high oxygen or nitric oxide contents [1]. Moreover, water as by-product leads to the formation of azeotropes and limits the overall selectivity of the industrial processes [7]. Current research in DMC production includes the direct synthesis from CO_2 [8], the transesterification of ethylene carbonate [9] or urea [3], and the vapor-phase methanol oxycarbonylation [10,11]. While synthesis from CO_2 suffers from very low activities (TON $\leqslant$ 3.2) [12], the transesterification reaction is associated with high feedstock costs. Due to recent developments, the vapor-phase methanol oxycarbonylation seems to be a more promising alternative [3]. This gas-phase production process is based on the same reaction as the liquid-phase Enichem process (see Fig. 1). Water is the only coupling product, while dimethyl ether (DME), dimethoxymethane (DMM), methylformate (MF), or methyl acetate (MA) are known by-products.

First work on gas-phase DMC synthesis was carried out at DOW Chemical with copper(II) chloride- and copper(II) methoxychloride-based pyridine catalysts on various supporting materials [13]. All catalysts with inorganic oxide supporting materials under investigation experienced very low activities (space time yield STY < 10 kg/m^3/h) and selectivity. Interestingly, activated charcoal (AC) as catalyst support yielded a more active and selective catalyst system producing 48 kg/m^3/h of DMC at 100 °C and 20 bar with $[(C_5H_5N)Cu(OCH_3)Cl]$ catalyst (2 wt.% Cu on activated charcoal) [13]. However, catalyst deactivation remained a serious issue for activated charcoal supported copper catalysts and chlorine loss has been assigned as a potential reason. DMC yields decreased by 50% after 50 h time-on-stream in the experiments of Itoh et al. [14], but the $CuCl_2$ catalyst was successfully reactivated by means of HCl treatment. Curnutt and Harley [13] limited the deactivation behavior by using $MgCl_2$ or KCl. Efforts to completely avoid deactivation and HCl loss through the application of different catalyst precursors revealed significantly lower catalyst activities for copper acetates or nitrates and emphasized the importance of chlorine catalyst species [15]. In the work of Ma et al. [16], basic treatment of the $CuCl_2$/AC catalysts by means of sodium hydroxide significantly

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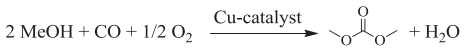

Fig. 1. Copper-catalyzed dimethyl carbonate synthesis.

promoted the catalyst activity yielding up to 5.6% conversion of methanol at 110 °C, 7 bar and a copper loading of 3 wt.% Cu. This positive influence of hydroxide solutions was attributed to the formation of Cu(OH)Cl and paratacamite $Cu_2Cl(OH)_3$ structures [17]. Additional promoting effects were found for alkali acetates [18] and palladium chloride [19]. Itoh et al. [14] studied the influence of the water content on the catalytic performance and found a strong limitation through the amount of water present in the methanol feed. A water content of only 5.5% significantly reduced the methanol conversion, which was attributed to the hydrolysis of DMC.

Ionic liquids on solid support were first applied for DMC synthesis by Wang et al. [20] who immobilized copper(I) and copper(II) halides on SBA-15 silica support and studied the influence of surface modification by means of silanization with the ionic liquid 3-trimethoxysilylpropyl-pyridinium chloride. $CuBr_2$ yielded the highest methanol conversion (17%) as well as the highest selectivity for DMC (97.5 %) on ionic liquid-modified SBA-15 reaching turnover frequencies of up to 7.09 h^{-1}. At the same time, Stricker et al. [21] reported on the use of task-specific catalytic ionic liquids containing copper(I) in the complex cation or anion or in both, anion and cation, for the liquid-phase dimethyl carbonate synthesis. Up to 62% conversion of methanol at 89% selectivity was obtained for copper(I)–bromide ionic liquid $[Cu(C_{12}\text{-imidazole})_2][CuBr_2]$ (5 mol% Cu with respect to MeOH, 120 °C, 50 bar CO, 3 bar O_2). In the current work, we want to take advantage of the negligible vapor pressure of ionic liquids and extend their application in DMC synthesis from the liquid phase to the continuous gas phase using the Supported Ionic Liquid-Phase (SILP) technology (see Fig. 2). In SILP systems, a well-defined catalyst complex is dissolved in an ionic liquid, which is dispersed as a thin film on the surface of a porous solid support with a large surface area. The resulting SILP catalyst powders are used as microscopically homogeneous, but macroscopically heterogeneous catalysts in the gas-phase oxycarbonylation of methanol in continuous operation mode.

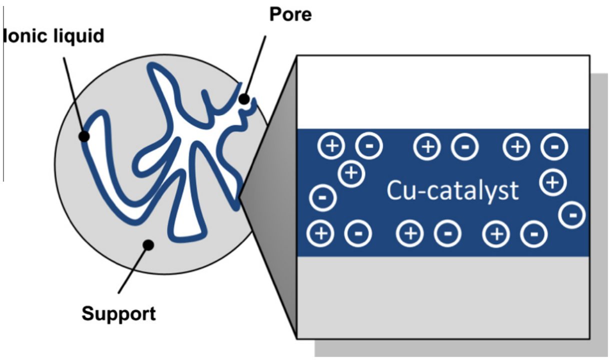

Fig. 2. Schematic view of the Supported Ionic Liquid-Phase (SILP) catalyst material applied in this work.

2. Materials and methods

2.1. Chemicals

The applied gases carbon monoxide (purity 3.7), synthetic air (purity 4.0), and helium (purity 4.6) were obtained from Linde AG. The copper precursors CuCl, $CuCl_2$, CuBr, $CuBr_2$, copper acetate, the organic base 4-(dimethylamino)pyridine, and methyl trifluoromethanesulfonate were purchased from Sigma–Aldrich. The precursor copper tris(pentafluoroethyl)trifluorophosphate and the ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[BMIM][NTf_2]$ (melting point: −2 °C), 1-butyl-3-methylimidazolium triflate [BMIM][OTf] (melting point: 16 °C), 1-butyl-3-methylimidazolium acetate [BMIM][OAc] (melting point: −20 °C), 1-butyl-3-methylimidazolium chloride [BMIM][Cl] (melting point: 70 °C), tetrabutylammonium chloride $[Bu_4N][Cl]$ (melting point: 83 °C), N-propylpyridinium chloride [PrPyr][Cl] (melting point: ∼ 110 °C), tetraethylammonium chloride tetrahydrate $[Et_4N][Cl]\ 4 \times H_2O$ (melting point: 37.5 °C), trioctylmethylammonium chloride [OMA][Cl] (melting point: ∼−20 °C), and trioctylmethylammonium bromide [OMA][Br] (melting point: <−20 °C) were obtained from Merck KGaA. The Polymer-Based Spherical Activated Carbon (PBSAC) was supplied by Blücher GmbH.

2.2. Synthesis of [DMMAP][OTf]

4.86 mL (43 mmol) of methyltriflate was slowly added to a cooled (−78 °C) solution of 5.0 g (40.9 mmol) 4-dimethylaminopyridine in dry dichloromethane. The resulting clear solution was stirred for 30 min, and subsequently, the cooling was stopped and the solution was stirred until ambient temperature was reached. Afterward, the solvent was removed in vacuo to yield 11.7 g (40.9 mmol; 99%) of the desired product 4-N,N-dimetylamino-N′-methylpyridinium triflate [DMMAP][OTf] as a white solid.

2.3. SILP preparation

SILP catalysts were prepared by impregnation under argon atmosphere using standard Schlenk techniques. 5 g of the PBSAC solid supporting material ($V_{pore} = 1.18$ mL/g; BET surface area = 2005 m^2/g) was stirred in 100 mL of a 1:1 mixture of water and methanol and the respective amounts of copper precursor (equal to 2–4 wt.% of Cu on PBSAC), the additive (KBr or organic base in equimolar amounts relative to copper) and the ionic liquid (equal to a pore-filling degree $\alpha_{IL} = V_{IL}/V_{pore}$ of 20–50%) were slowly added. The solution was stirred for 30 min. Finally, the solvent was slowly removed under reduced pressure at 50 °C.

2.4. Catalyst testing procedure

The MeOH oxycarbonylation experiments were conducted in continuous gas-phase operation mode at 110 °C and 10 bar using a fixed-bed reactor set-up (see Fig. 3). The gaseous feedstocks (CO 78.2 N mL/min) and synthetic air (36.5 N mL/min) were fed by El-Flow mass flow controllers (MFC) from Bronkhorst. Liquid methanol (0.05 mL/min) was pumped through a Knauer K-120 HPLC pump, evaporated and mixed with the feed streams of CO and synthetic air. The gaseous feed stream was led to a reactor where a fixed bed of 4 g SILP material catalyzed the reaction in a residence time of 14 s. The product feed stream was continuously analyzed by a Varian GC-3900 equipped with a FID-detector. All gas flow meters and the GC were calibrated prior to use.

2.5. Isolation and characterization of the catalytically active species

$[BMIM]_4[Cu_4(\mu^4\text{-}O)(\mu\text{-}Cl)_6Cl_4]$: [BMIM]Cl (2.24 g, 12.8 mmol) and CuCl (1.27 g, 12.8 mmol) were dissolved in 20 mL MeCN and placed in a glass liner of an stainless steel autoclave. Dry MeOH (4.11 g, 128 mmol) and water (230 mg, 12.8 mmol) were added; the mixture was pressurized with 0.5 bar O_2 and 4.5 bar N_2 and heated with stirring for 6 h at 110 °C. The autoclave was opened, and a dark green solution with some black finely suspended