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Gas-phase carbonylation of methanol to dimethyl carbonate on chloride-free Cu-precipitated zeolite Y at normal pressure

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Abstract

Chloride-free Cu/zeolite Y catalysts with Cu loading of 2–14% were prepared by precipitation from aqueous copper(II) acetate solutions and inert activation with an Ar flow at 700–750 °C for 15 h. This inert activation resulted in a considerable activity of the catalyst for the oxidative carbonylation of methanol (MeOH) to dimethyl carbonate (DMC) under normal pressure at 140–160 °C at 10–12 wt% Cu loading. Space-time yields (STY) of DMC up to 100 $g_{DMC}\,l_{Cat}^{-1}\,h^{-1}$ were achieved with a feed composed of 36% MeOH, 48% CO, 6% O_2, and balance He at a gaseous hourly space velocity (GHSV) of 3000 h^{-1}. A threshold of copper loading (5–6 wt%) was found to exist before catalysts became active. This is associated with the preferential location of copper at ion-exchange positions of the zeolite structure Y not accessible for the reactants. After saturation of these sites, the placement of copper ions within the supercage led to active catalysts. Characterization of samples at various stages of preparation by N_2 adsorption, XRD, XPS, ESR, ^{27}Al-MAS-NMR, and TPR analysis revealed that the solid-state ion exchange during inert activation is accompanied by reduction of Cu^{2+} to Cu^{+}. Copper ions exert a stabilizing effect on the crystallinity of the zeolite (in situ XRD, ^{27}Al-MAS-NMR). No crystalline metallic copper, cuprous oxide, or cupric oxide were formed (XRD), but melting occurred at 750 °C for catalysts with 14% copper loading, resulting in the formation of a glassy amorphous copper silicate/aluminate phase. The latter effect can be prevented by applying lower activation temperatures. The catalysts were prepared without using chloride, and the reaction did not require co-feeding of HCl for maintaining activity, as is needed for CuCl/zeolite catalyst formulations.

Keywords: Gas-phase carbonylation; MeOH; Dimethyl carbonate; Copper faujasite; Chloride-free

1. Introduction

Dimethyl carbonate (DMC) has increased in production volume because of its manifold applicability [1–4] as a monomer in phosgene-free polycarbonate processes, as an environmentally benign methylation agent, and as a possible gasoline-blending component due to its high oxygen content, low toxicity, and rapid biodegradability. The latter application may become attractive considering the current debate over potential groundwater contamination by the gasoline oxygenate methyl *tert*. butyl ether (MTBE).

Synthesis routes to DMC have been reviewed by Pacheco and Marshall [1] and by Delledonne et al. [2]. The conversion of MeOH by phosgene is the classic but obsolete route for DMC production,

$$COCl_2 + 2CH_3OH \rightarrow (CH_3O)_2CO + 2HCl. \qquad (1)$$

A phosgene-free route is the two-stage process via methylnitrite [5],

$$2CH_3OH + 2NO + (1/2)O_2 \rightarrow 2CH_3ONO + H_2O \qquad (2)$$

and

$$2CH_3ONO + CO \rightarrow (CH_3O)_2CO + 2NO. \qquad (3)$$

This process runs in either a continuous or a batch mode over a $PdCl_2/FeCl_3$ co-impregnated activated carbon (AC) catalyst. A major disadvantage is the loss of chloride in form of HCl, requiring regeneration steps and co-feeding of HCl.

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Alternatively, the direct oxidative carbonylation of MeOH,

$$2CH_3OH + CO + (1/2)O_2 \rightarrow (CH_3O)_2CO + H_2O, \quad (4)$$

over a CuCl/zeolite catalyst is commercialized by ENICHEM in a slurry phase process [1]. But again, loss of chloride is a drawback, causing corrosion and decrement of activity. Moreover, chlorinated byproducts may affect product quality.

Several attempts have been reported for grafting Cu^+ ions, which are considered the active species on suitable supports [6–11], for a continuous gas-phase process of DMC production. In 1996, King [6,7] reported a catalyst preparation route by solid-state ion exchange (SSIE) of Cu(I) into zeolite Y starting from a physical mixture of CuCl or Cu_2O and zeolite Y. The maximum STY of DMC during continuous oxidative gas-phase carbonylation of MeOH over 24% CuCl/zeolite HY after SSIE amounted to ca. 40 $g_{DMC}\,l_{Cat}^{-1}\,h^{-1}$ at 130 °C (GHSV, 829 h^{-1}). Using Cu_2O for SSIE resulted in less active catalysts with rapid deactivation during time on stream, and a sample made by liquid-phase ion exchange with $Cu(NO_3)_2$ solution had no activity at all under the reaction conditions applied.

Other proposals to get active and stable catalysts for this gas-phase process are numerous but do not convincingly improve the STY of DMC. Anderson and Root [8,9] used zeolites 13X and ZSM-5 to anchor Cu cations by SSIE starting with a physical mixture of CuCl and the zeolite. A CuCl catalyst heterogenized on diamide-immobilized copper on SBA-15 was reported by Cao et al. [10], and $CuCl_2$ immobilized on amino-functionalized MCM-41 and MCM-48 mesoporous structures was used by Yang et al. [12]. Drake et al. [11] proposed Cu/SiO_2 prepared by precursor grafting (using Cu alkoxides) or chemical vapor deposition (using CuCl) as a catalyst for DMC production through gas-phase oxidative carbonylation of MeOH. Yang et al. [12] proposed a $PdCl_2$–$CuCl_2$–CH_3COOK co-impregnated AC catalyst for the gas-phase oxidative carbonylation of MeOH with considerable STY of DMC (ca. 390 $g_{DMC}\,l_{Cat}^{-1}\,h^{-1}$). However, the catalyst suffered considerable deactivation already after a process time of 6 h. Obviously, chloride is essentially needed for stabilization of active copper sites. Preparation routes using other copper compounds (Cu_2O, $Cu(NO_3)_2$) did not lead to active catalysts.

Here we report a catalyst preparation route that does not use any halogenide but nevertheless leads to catalysts with appreciably high and stable STY of DMC under continuous-flow conditions at normal pressure. The principal novelty of the approach involves the use of copper(II) salt solutions (although Cu^+ is finally required for catalysis) for preparation of a precursor that is activated by autoreduction of Cu^{2+} to Cu^+ under inert conditions at elevated temperatures. The preparation is accomplished by removal of residual Brønsted acid sites, thus tuning the redox system Cu^{2+}/Cu^+.

The route applied for preparing appropriate precursors consists of precipitating copper hydroxide in the presence of NH_4-Y powder suspended in distilled water. The copper content was varied over a range of 2–14 wt%. Interpretation of the catalytic results is based on characterization data from N_2 adsorption measurements, XRD (in situ as well as ex situ), XPS, ESR, ^{27}Al-MAS-NMR spectroscopy, and temperature-programmed reduction (TPR).

2. Experimental

2.1. Catalyst preparation

Preparation started with a commercial zeolite Y in its NH_4 form (Aldrich, Germany). For precipitation of $Cu(OH)_2$, a specified amount of dried NH_4-Y powder was suspended in distilled water and, in quick succession, a $Cu(CH_3COO)_2$ solution (0.1 M) and a tetramethyl ammonium hydroxide solution (10 wt%, pH = 13) were added. Thus, contact of the NH_4-Y zeolite and $Cu(CH_3COO)_2$ solution for a longer time is avoided, to minimize ion exchange at the acidic conditions (pH ≈ 4). The use of inorganic strong bases for pH increase is not possible because of competitive exchange of Na^+ (in the case of NaOH) or K^+ (in the case of KOH) into the zeolite. Adding ammonium hydroxide solution would lead to formation of stable copper tetraammine complexes and prevent precipitation. $Cu(OH)_2$ precipitated after addition of the organic base up to pH values of 8–9. Subsequent heating of the slurry to 80 °C caused a color change from blue to brown, indicating conversion of $Cu(OH)_2$ to dispersed CuO. Afterward, the slurry was filtered, washed with distilled water three times, and dried at 120 °C overnight. There was no copper in the residual solution, so the copper content of the samples corresponded to the copper concentration of the acetate solution.

Samples are denoted as “synthesis forms” at this stage. After calcination at 400 °C in static air for 2 h, the catalysts are denoted as “precursors,” because all samples at this stage have only marginal activity for the carbonylation reaction.

The activation was carried out by conducting an argon stream (50 $cm^3\,min^{-1}$) through the catalyst bed at 700–750 °C for 15 h. The highest temperature required for activation depends on the Cu loading. In a first series, the activation temperature was kept constant at 750 °C (standard). A second series applied lower activation temperatures for selected samples with high Cu loading.

Samples are designated as $xxCu\text{-}Y_{zzz}$ with the copper content xx in front (in wt%) and the pretreatment or activation temperature zzz as subscript of the zeolite (in °C). The “synthesis” form (drying of the sample at 120 °C overnight), the “precursor” (calcination at 400 °C in air for 2 h or 24 h), and the “activated” form (inert dry treatment under flow conditions at 700–750 °C for 15 h) are differentiated. The overall exchange capacity of the parent zeolite Y was determined by decomposition of the ammonium form (see Section 2.2). Sample data are summarized in Table 1.

2.2. Characterization

Surface areas and pore volumes were determined from nitrogen adsorption isotherms at 77 K using the ASAP 2010M characterization unit (Micromeritics). Samples were outgassed at 400 °C for 2 h under vacuum; the surface area was calculated