OXIDATIVE CARBONYLATION OF METHANOL TO DIMETHYL CARBONATE BY CHLORINE-FREE HOMOGENEOUS AND IMMOBILIZED 2,2′-BIPYRIMIDINE MODIFIED COPPER CATALYST

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Received May 19, 2007
Accepted June 15, 2007

This paper is dedicated to Professor Štefan Toma on the occasion of his 70th birthday.

A chlorine-free catalyst, prepared in situ from Cu(II) acetate and 2,2′-bipyrimidine, can be used for the oxidative carbonylation of methanol to dimethyl carbonate. In situ high pressure IR and NMR spectroscopic studies suggest the formation of [Cu(2,2′-bipyrimidine)(CO)(OMe)] as one of the key intermediates. The catalytic performance of the 2,2′-bipyrimidine-modified Cu-catalyst is similar to the CuCl-based system. The chlorine free catalyst can be immobilized by using the copolymer of 5-vinyl-2,2′-bipyrimidine and styrene.

Keywords: Homogeneous catalysis; Oxidative carbonylation; Methanol; Dimethyl carbonate; Copper; 2,2′-Bipyrimidine; Immobilized catalysts.

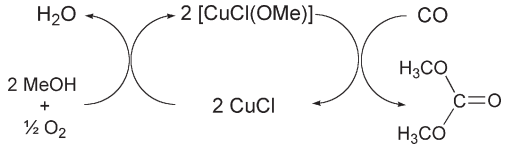
Dimethyl carbonate (DMC) is a safe, non-corrosive, and environmentally friendly alternative to the carbonylating, carboxymethylating and methylating agents phosgene, metoxycarbonyl chloride, dimethyl sulfate, and methyl halides, respectively[1,2]. DMC can also be used as solvent, octane booster in gasoline, and oxygenate to reduce CO and NO_x emissions from automobiles. The conventional DMC process is based on the reaction of methanol with the highly toxic phosgene using chlorinated solvent[3].

The first alternative process was based on the oxidative carbonylation of methanol in the presence of CuCl at 2–3 MPa and 100–130 °C [4]. Although the exact mechanism of the process has not been established, it has been proposed, that the reaction of CuCl, methanol and oxygen leads to the formation of the key intermediate Cu(OMe)Cl, which reacts with CO to yield

Collect. Czech. Chem. Commun. 2007, Vol. 72, No. 8, pp. 1094–1106

doi:10.1135/cccc20071094

DMC and CuCl (Scheme 1). Due to the formation of wet HCl by the hydrolysis of chloride containing copper species, the process is extremely corrosive and all commercial equipment, exposed to the CuCl–MeOH–H_2O–HCl mixture, must be glass lined. In addition, the formation of chlorinated organic side-products could be an environmental issue for subsequent, presumably green applications of DMC.



SCHEME 1
Oxidative carbonylation of methanol

An alternative non-corrosive process was published by EniChem using cobalt catalysts with oxygen and nitrogen donor ligands such as carboxylates, acetylacetonates, picolinates, and Schiff bases[5]. The performance of the Schiff base-modified cobalt(II) complexes was the best; the conversion of methanol was in the range of 10–30% with 96–99% selectivity to DMC. Palladium[6a–6c] and selenium[6d] based systems have been also reported for liquid phase oxidative carbonylation of methanol to DMC. An alternative approach is the conversion of carbon dioxide and methanol to DMC, although the by-product water could lower the catalytic activity by the decomposition of the organotin catalysts[7a,7b]. It should be noted that supercritical carbon dioxide can be also used as the reaction medium[7c] for DMC synthesis from acetals[7d]. Finally, heterogeneous copper-based catalysts[7e,7f] and zeolites[7g] have been used succesfully for the oxidative carbonylation of methanol.

We report here the development of a chlorine-free homogeneous catalytic system based on Cu(II) acetate and 2,2′-bipyrimidine and its heterogenized version using the co-polymer of 5-vinyl-2,2′-bipyrimidine and styrene.

EXPERIMENTAL

CuCl, Cu(II) acetate, coumalic acid, piperidine, 2-chloropyrimidine, and AIBN were purchased from Aldrich Chemical and used as received. 2,2′-Bipyrimidine was synthesized according to literature method[8]. Carbon monoxide (purity > 99.9%, Linde AG.) and air (purity > 99.9%, Linde AG.) were used without further purification. Other chemicals and solvents were obtained from Reanal Chemical Co., Hungary. All high-pressure NMR experiments were performed in 10-mm single crystal sapphire tube equipped with a titanium

head[9] using a 250 MHz Bruker NMR instrument. Chemical shifts are given in ppm (δ-scale). Infrared spectra were collected on a Mettler-Toledo AutoChem ReactIR™ 1000 instrument using a SiComp™ high-pressure probe. High-pressure experiments were conducted in stainless steel reactors (100, 300 and 1000 ml). The reaction products were analyzed by GC using a capillary HP-1 column with H_2 as carrier gas on a HP 5890 Seies II gas chromatograph equipped with a flame ionization detector using cyclohexane or acetone as the internal standard.

2-Oxo-2*H*-pyran-5-carbonyl Chloride (**2**)

12.5 g (90 mmol) of 2-oxo-2*H*-pyran-5-carboxylic acid (**1**) and 25 ml (344.5 mmol) of $SOCl_2$ were placed in a two-necked flask fitted with a reflux condenser, a N_2 inlet, and a magnetic stirrer. The reaction mixture was heated to 100 °C for 8 h, during which the brown solution turned to a reddish-brown solid. The precipitate was dissolved in a mixture of 50 ml CH_2Cl_2 and 200 ml of *n*-hexane and crystallized to give an off-white solid. Yield 84%. M.p. 68–70 °C. ^{1}H NMR (250 MHz, $CDCl_3$): 6.38 d, 1 H; 7.56 d, 1 H; 8.6 s, 1 H. ^{13}C NMR (250 MHz, $CDCl_3$): 162.8, 162.7, 158.1, 140.2, 116.5, 115.3.

2-Oxo-2*H*-pyran-5-carbaldehyde (**3**)

6.152 g (38.8 mmol) of 2-oxo-2H-pyran-5-carbonyl chloride (**2**) was added to a mixture of 30 ml xylene and 0.3 g of $Pd/BaSO_4$ (10%) as the catalyst in a round-bottomed flask equipped with reflux condenser and gas inlet. The reaction mixture was stirred at 110 °C and hydrogen was slowly bubbled through for 12 h. After the removal of the catalyst at the reaction temperature by filtration under N_2, 6 ml of *n*-hexane were added. The solution was kept in a refrigerator overnight to get white crystals. It should be noted that the product becomes yellow in air at room temperature. Yield 41.5%. ^{1}H NMR (250 MHz, $CDCl_3$): 9.7 s, 1 H; 8.8 dd, 1 H; 7.8 dd, 1 H; 6.4 d, 1 H. ^{13}C NMR (250 MHz, $CDCl_3$): 185.0, 162.6, 159.2, 138.1, 119.7, 116.5.

Pyrimidine-2-carbonitrile (**7**)

The preparation of **7** was done in two steps. 6.94 g (61 mmol) of 2-chloropyrimidine (**5**) was dissolved in a mixture of 120 ml benzene and 0.27 mol of Me_3N at 0 °C to form *N*,*N*,*N*-trimethylpyrimidin-2-aminium chloride. The solution was allowed to warm slowly to room temperature and stirred overnight. The precipitate was filtered under inert atmosphere and washed with dried diethyl ether. **6** was dried under vacuum. Yield 4.55 g (91%). 60 ml of CH_2Cl_2 and 5.6 g (35.88 mmol) of tetraethylammonium cyanide were placed in a round-bottomed flask with a magnetic stirrer. 5.66 g (32.62 mmol) of **6** was slowly added to the mixture, stirred at room temperature for 30 min, and washed with ice-water (3 × 60 ml). The organic phase was dried with anhydrous $MgSO_4$ and the solvent was evaporated. **7** was distilled at 100 °C at 0.5 mm Hg. Yield 93%. M.p. 39–41 °C. ^{1}H NMR (250 MHz, $CDCl_3$): 8.8 d, 2 H; 7.5 t, 1 H. ^{13}C NMR (250 MHz, $CDCl_3$): 158.1, 145.3, 123.6, 115.6.

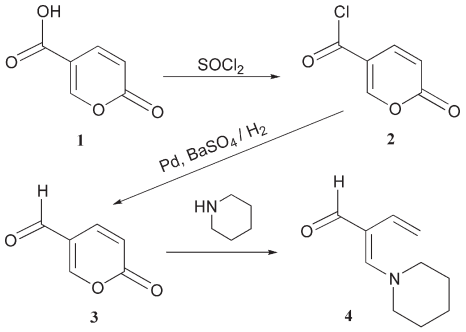
Pyrimidine-2-carboximidamide Hydrochloride (**9**)

2.6 g (25 mmol) of **7** was added to 0.67 g (12.4 mmol) of CH_3ONa in 45 ml of methanol in a round-bottomed flask and the mixture was stirred at room temperature overnight. After

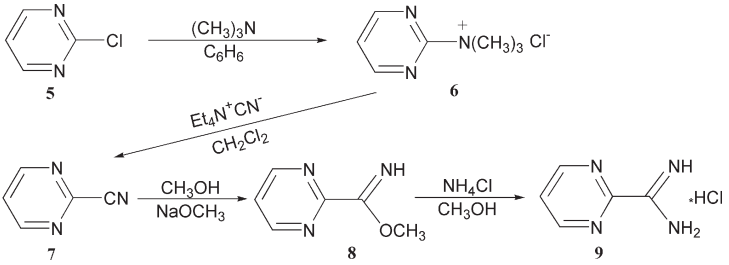
the addition of 2 g (37.4 mmol) NH_4Cl, the reaction mixture was stirred until the inorganic salt dissolved (3 h). After filtration, the methanol was evaporated and the product washed with diethyl ether. Yield 90%. ^{1}H NMR (250 MHz, $CDCl_3$): 9.2 d, 2 H; 7.8 t, 1 H. ^{13}C NMR (250 MHz, $CDCl_3$): 125.7, 159.2.7, 153.6, 161.

5-Vinyl-2,2′-bipyrimidine (**10**)

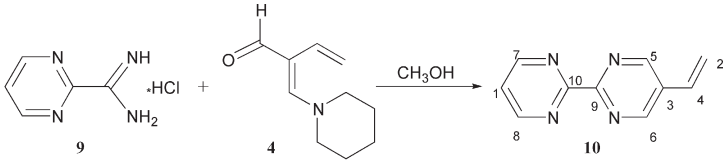
5-Vinyl-2,2′-bipyrimidine (**10**) was synthesized by the reaction of 3-piperidino-2-vinylpropenal (**4**) (for synthesis see Scheme 2) and pyrimidine-2-carboximidamide hydrochloride (**9**) by modified literature methods shown in Schemes 3 and 4. 0.637 g (7.5 mmol) of piperidine in 0.75 ml of acetonitrile was stirred with a solution of 0.93 g (7.5 mmol) freshly distilled **3** in 7.5 ml of acetonitrile at 0 °C for 5 min. The formation of **4** and the concomitant evolution of CO_2 was complete in 3 h, and the orange-yellow solution became red. The solution of **4** was added to a 1.25 M methanolic solution of **9** (6 ml) and stirred at 80 °C for 3 h. The solution was filtered at room temperature and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica using $CHCl_3$·MeOH 19:1 as eluent. The first yellow fraction was sublimed at 100 °C at pressure of 10 mm Hg. Yield 42%. ^{13}C NMR (250 MHz, $CDCl_3$): 119.0 (C 1), 121.2 (C 2), 130 (C 3), 130.6 (C 4), 155.0 (C 5,6), 157.7 (C 7,8), 161.5 (C 9), 162.6 (C 10).



SCHEME 2
Synthesis of 3-piperidino-2-vinylpropenal (**4**)[10,11]



SCHEME 3
Synthesis of pyrimidine-2-carboximidamide hydrochloride (**9**)[12,13]



SCHEME 4
Synthesis of 5-vinyl-2,2′-bipyrimidine (**10**)[14]

Preparation of Copper-Modified 5-Vinyl-2,2′-bipyrimidine–Styrene Copolymer (Cu-VBS)

A mixture of 0.184 g (1 mmol) 5-vinyl-2,2′-bipyrimidine and 3.120 g (30 mmol) styrene was placed into a Schlenk flask with 25 mg (0.155 mmol, 0.5 mole %) AIBN. The flask was degassed five times and sealed under vacuo. The flask was placed in a 60 °C bath for 24 h. The polymer formed was dissolved in 130 ml toluene and mixed with 0.2 g (1 mmol) of $Cu(OOCCH_3)_2 \cdot H_2O$ in 20 ml of methanol. The solvents were evaporated, the polymer was dissolved in 20 ml of toluene and washed with water. The Cu-VBS was precipitated with 300 ml of methanol to give 3.18 g (90%) of pale-blue solid. Analysis: 87.43% C, 7.03% H, 1.48% N.

General Procedure for Oxidative Carbonylation of Methanol in a Batch Reactor

CAUTION: The oxidative carbonylation experiments are extremely hazardous, must be approached with care, and a thorough safety assessment must be made.

A 1000-ml stainless steel autoclave equipped with a safety relief, manometer, temperature controller (Parr 4842 PID), sampling line, and direct hollow shaft stirrer was used. The autoclave was filled with methanol and the catalyst components, and pressurized with CO. The desired pressure was set with O_2, followed by heating the reaction mixture to reaction temperature. These reactions were carried out under non-isobaric conditions, and the reaction progress was followed by measuring the pressure drop in the autoclave. In all experiments the oxygen concentration was not higher than 4%. When the pressure decreased to a constant value, the reactor was refilled from an O_2 cylinder.

Preparation of DMC with Copper Cu-VBS in a High-Pressure NMR Tube

0.225 g of Cu-VBS was dissolved in 5 ml of toluene and placed into a high-pressure NMR tube. The solvent was removed in vacuo and 1 ml of methanol was added to the pale-blue solid. The tube was first pressurized with 5.5 MPa CO and then with O_2 to give a total pressure of 6.2 MPa. The tube was heated at 100 °C. The color of the solid changed to brown. After 1 h the tube was cooled to room temperature and re-pressurized with 5.5 MPa CO and then with O_2 to give a total pressure of 6.0 MPa. The tube was heated up to 100 °C. This procedure was repeated three times (thus the tube was totally re-pressurized five times). After cooling the tube to room temperature, the pressure was released and the colorless liquid was poured into a vial. 10 wt.% of acetone was added as internal standard. The reaction mixture was analyzed by GC. The concentration of DMC was 0.028 mol/l in the reaction mixture (0.025 mmol).

General Procedure for Oxidative Carbonylation of Methanol in a Continuous Reactor

In a typical experiment, the continuous high-pressure autoclave was charged with the catalyst and methanol (Fig. 1). The mixture was pressurized at room temperature with CO/air (150/400 ml/min) to adjust the desired pressure. The reactor was heated to the reaction temperature and the flow rates were reduced to 15/40 ml/min CO/air, respectively. The temperature was controlled by Parr 4842 PID controller. Samples were collected for off-line GC analysis by taking a small amount of samples with a dip-leg into a sample holder, cooled with dry ice.

RESULTS AND DISCUSSION

The oxidative carbonylation of methanol in the presence of CuCl results in the formation of DMC and water. Unfortunately, the hydrolysis of chloride containing copper species leads to aqueous HCl, which could cause significant corrosion and the formation of chlorinated organic by-products. Therefore, we have tried to overcome these problems by the addition of 2,2′-bipyrimidine, which has successfully been used as a ligand in hot sulfu-

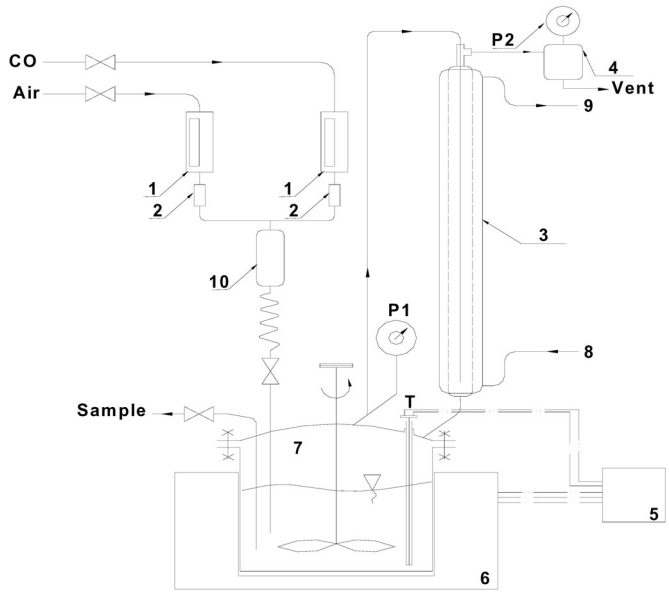


FIG. 1
Flowchart of the continuous reactor. 1 Mass flow controller, Brooks 5850 E; 2 safety relief, Nupro SS-4C-1/3; 3 high-pressure condenser; 4 MityMite, Grove S-91XV; 5 electronic module, Parr 4842; 6 electronic heater; 7 high-pressure reactor; 8 cooling in; 9 cooling out; 10 gas mixer; T thermocouple; P1 and P2 manometers

ric acid even at high temperatures by Periana[15a], to remove the by-product HCl via protonation of the two non-coordinating N atoms. It should be noted that the beneficial addition of various pyridines and bipyridines has been demonstrated for the stoichiometric carbonylation of Cu(OMe)Cl in MeOH [15b]. In order to develop a novel chlorine-free catalyst system, we have next tested combinations of $Cu(OOCCH_3)_2 \cdot H_2O$ with pyridine, 2,2′-bipyridine, and 2,2′-bipyrimidine (Table I).

Since the total amount of oxygen in the reactor is limited for safety reasons, the batch reactor had to be recharged several times. While the reaction took place in the presence of pyridine, the stability of the catalyst was limited as evidenced by the formation of metallic copper during the reaction. Furthermore, the lower catalytic activity at higher Cu concentrations indicated the formation of polynuclear copper complexes. The catalyst stability was improved by using bidentate N-heterocyclic ligands, among which 2,2′-bipyrimidine has shown higher catalytic activity than that of 2,2′-bipyridine. The best DMC production was achieved using the 2,2′-bipyrimidine-$Cu(OOCCH_3)$ catalyst (Table I, runs 6 and 7), which could be reused without losing catalytic activity (Table I, run 8), similarly to the activity of Co-based systems[5]. In order to evaluate and compare the chloride-free and CuCl-based catalysts, we have also studied their performance in a continuous reactor in which volatile gases can be separated from methanol, DMC, water, and the catalysts (Fig. 1). While the maximum and steady-state concentration of DMC (~1.2 mol/l at 100 °C, 2.5 MPa total pressure, and 15/40 ml/min CO/air flow rates) was reached after 12 h using the 2,2′-bipyrimidine modified copper catalyst, it took about 22 h for the CuCl-based system and it appeared that the reaction is equilibrium-limited in both cases (Fig. 2).

In order to confirm that the oxidative carbonylation of methanol is equilibrium-limited, we have monitored the reaction of 4.9 mmol (0.415 ml) $CH_3OCOOCH_3$, 4.9 mmol (0.090 ml) D_2O, 24.6 mmol (1.0 ml) CD_3OD in the presence of 0.060 mmol $Cu(OOCCH_3)_2 \cdot H_2O$ and 0.060 mmol bipyrimidine in a high-pressure NMR tube. The solution was first pressurized with 3.0 MPa CO and then with O_2 giving a total pressure of 3.3 MPa. The tube was heated at 100 °C for 16 h, cooled to room temperature, and the pressure was released. Indeed, ^{13}C NMR has shown the formation of CH_3OH from $CH_3OCOOCH_3$ and $CD_3OCOOCD_3$ from CD_3OD, simultaneously[16]. It should be emphasized, that the formation of DMC-d_6 in the absence of Cu catalyst could not be detected.

We have also studied the reaction mechanism using $Cu(OOCCH_3)_2 \cdot H_2O$ and 2,2′-bipyrimidine as the catalyst in methanol by in situ IR. A solution

TABLE I
Preparation of dimethyl carbonate in batch reactor

Run	Ligand, (mmol)	$Cu(OOCCH_3)_2 \cdot H_2O$ mmol	P_{total} MPa	O_2 number of recharge	V_{MeOH} ml	Time h	DMC mmol	TON[a]	TOF[b] h^{-1}
1	Pyridine, (1200)	300	5.5	3.8% (10)	300	3.5	36[c]	0.12	0.034
2	Pyridine, (1200)	300	5.5	3.8% (10)	300	7	78[c]	0.26	0.037
3	Pyridine, (120)	30	7.6	2.9% (10)	300	7.5	72[c]	2.4	0.32
4	Pyridine, (24)	8	7.0	2.7% (5)	300	8	84	10.37	1.3
5	2,2′-Bipyridine, (16)	8	7.6	2.7% (5)	300	6.5	39	4.81	0.74
6	2,2′-Bipyrimidine, (8)	8	7.6	2.7% (9)	300	10.5	216[d]	26.73	2.54
7	2,2′-Bipyrimidine, (8)	8	7.5	2.7% (7)	300	13.5	160	19.75	1.46
8	Recycled from run 7[e]		7.9	2.7% (6)	300	10.5	138	17.03	1.62

[a] TON, turnover number. [b] TOF, turnover frequency. [c] The formation of metallic Cu was observed. [d] 3.16 v/v% CO_2 formed. [e] All liquids from run 7 were removed in vacuo and the residue was dissolved in 300 ml of methanol.

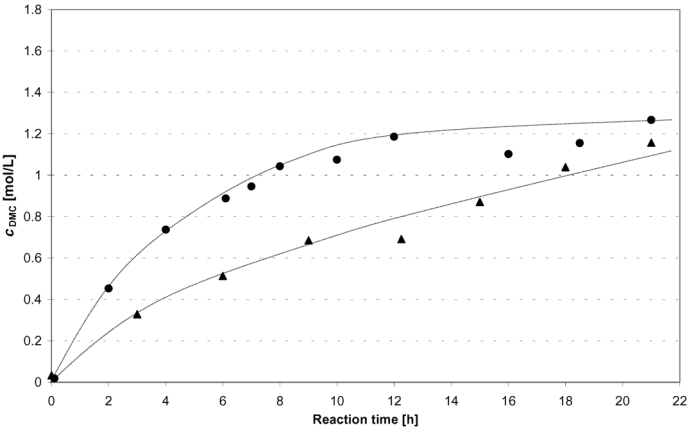


FIG. 2

Formation of DMC with $Cu(OOCCH_3)_2 \cdot H_2O$-2,2′-bipyrimidine (●, 6.1 mmol) and CuCl (▲, 6.1 mmol) catalysts in 80 ml of MeOH (2.47 mol) at 2.5 MPa total pressure and 15/40 ml/min CO/air flow rates

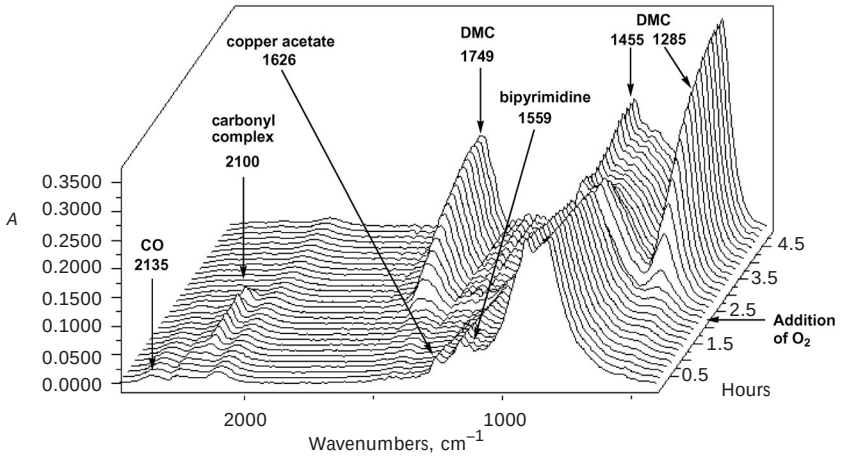


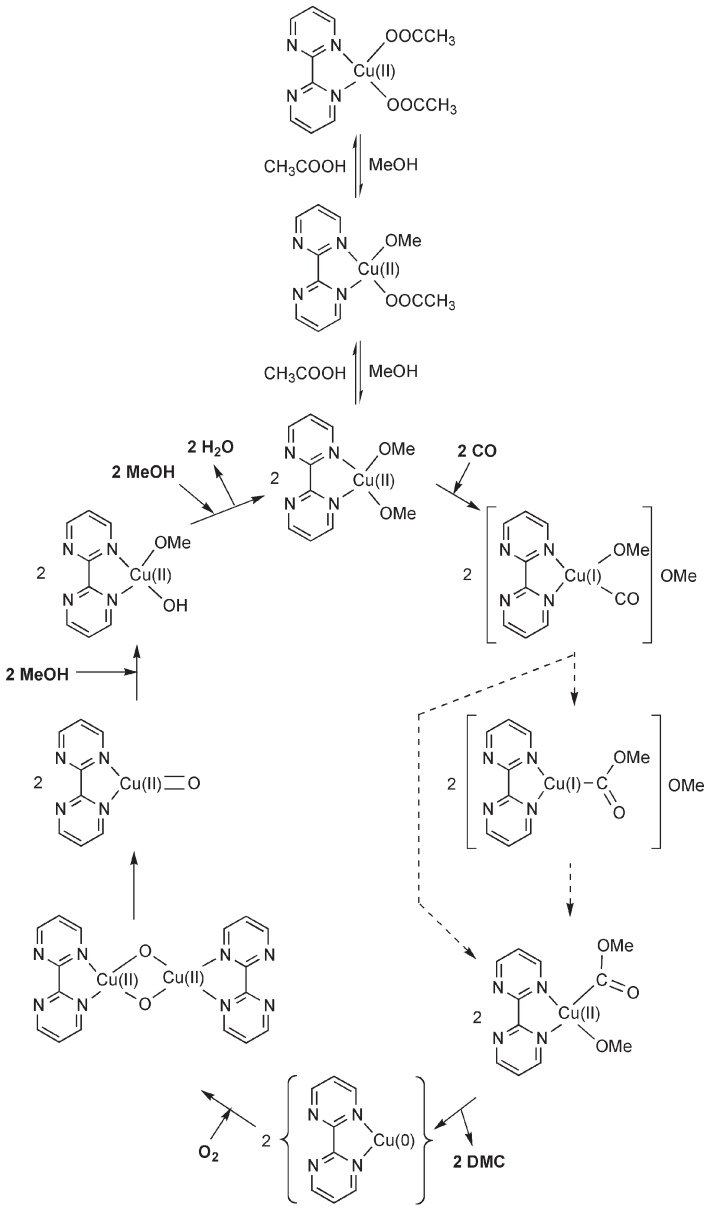
FIG. 3

In situ IR spectra of the oxidative carbonylation of MeOH in the presence of 2,2′-bipyrimidine-modified Cu(II) acetate catalyst

of 1 mmol $Cu(OOCCH_3)_2 \cdot H_2O$ and 1 mmol 2,2′-bipyrimidine in 10 ml of methanol was placed in a high-pressure reactor, charged with 6.0 MPa CO, and heated to 100 °C resulting in a total pressure of 7.3 MPa. The characteristic IR bands of $Cu(OOCCH_3)_2$ and free 2,2′-bipyrimidine at 1626 and 1559 cm^{-1}, respectively, have disappeared and a new band appeared at 2100 cm^{-1} which is probably due to the formation of [Cu(2,2′-bipyrimidine)-(CO)(OMe)] (Fig. 3). The formation of a similar $[CuCl(CO)L_2]$ ($L = H_2O$) species has been reported[17], which is stable only under CO. Furthermore, the appearance of the same band at 2100 cm^{-1} could be observed when $Cu(OMe)_2$ was used as the catalyst precursors[18]. The new species reached a maximum concentration after two hours. When the reactor was charged with O_2 to give a total pressure of 7.3 MPa, the peak at 2100 cm^{-1} disappeared and the IR bands for DMC at 1749, 1455, and 1285 cm^{-1} started to increase reaching a maximum value after two hours when all the O_2 was consumed. The formation of the new species was also investigated by high-pressure NMR. When a solution of a regenerated Cu-2,2′-bipyrimidine catalyst (isolated from run 8 in Table I) in CD_3OD was charged with 4.0 MPa ^{13}CO, a broad peak was observed at 184.3 ppm, next to the dissolved CO at 184.7 ppm, indicating the presence of a carbonyl group. The broadening of the new peak is probably due to the exchange process with free CD_3OD. Thus, we propose the formation of [Cu(2,2′-bipyrimidine)(CO)(OMe)] as the key intermediate.

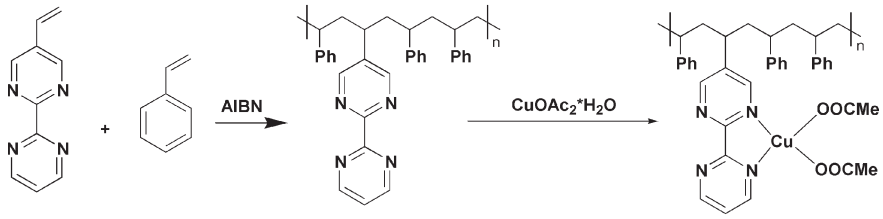
The proposed reaction mechanism based on the literature[19,20] and our data is shown on Scheme 5. Since a terminal carbonyl group containing intermediate was observed starting from both $Cu(OOCCH_3)_2 \cdot H_2O$ and $Cu(OCH_3)_2$, the formation of [Cu(2,2′-bipyrimidine)(CO)(OMe)] was proposed. The facile insertion of CO into the copper–oxygen bond followed by the coordination of methoxide or the nucleophilic attack of OCH_3 on the coordinated carbonyl group will result in a methoxy–methoxycarbonyl–copper(II) intermediate, which, in turn, could reductively eliminate the product, DMC, and a copper(0) species. In the absence of stabilizing ligand(s) this could explain the formation of metallic copper. The oxidation of Cu(0) species probably goes through a mononuclear copper–oxygen complex to form a dimeric intermediate, which could generate a copper(II) oxo complex which could react with methanol to form the dimethoxy-copper(II) and restart the catalytic cycle. The nature of the ligands has of course a very important role in controlling the overall catalytic activity and catalyst stability.

Finally, the immobilization of the chlorine-free 2,2′-bipyrimidine-modified Cu catalyst was achieved by adding 0.06 wt.% copper(II) acetate to a co-



SCHEME 5
Proposed catalytic cycle of oxidative carbonylation of methanol

polymer prepared from 1 equivalent of 5-vinyl-2,2′-bipyrimidine (**10**) and 32 equivalents of styrene (Scheme 6).



SCHEME 6
Supported catalyst

The formation of 10% of DMC was observed when 0.12 mol methanol was treated with 6.2 MPa CO and 1.0 MPa O_2 at 104 °C in the presence of 300 mg copper(II)-modified copolymer of 5-vinyl-2,2′-bipyrimidine and styrene.

CONCLUSIONS

We have developed a chlorine-free catalyst for the oxidative carbonylation of methanol to produce dimethyl carbonate. Isotope labeling study has established that the reaction is reversible and therefore equilibrium-limited. The chlorine-free catalyst can be prepared in situ from copper(II) acetate and 2,2′-bipyrimidine. High-pressure IR and NMR spectroscopic studies suggest the formation of [Cu(2,2′-bipyrimidine)(CO)(OMe)] as one of the key intermediates. The catalytic performance of the 2,2′-bipyrimidine-modified Cu catalyst is similar to the CuCl-based system. The chlorine-free catalyst can be immobilized by co-polymerizing 5-vinyl-2,2′-bipyrimidine with styrene.

This work was partially supported by the ExxonMobil Research and Engineering Company and the Hungarian National Scientific Research Fund (OTKA-T032850). The donation of the ReactIR 1000 instrument by Applied Systems Inc, a Mettler-Toledo Company is greatly appreciated.

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