

A Remarkable Effect of Alkali Addition in the Oxidative Carbonylation of Methanol to Dimethyl Carbonate Catalyzed by a Polymer-complexed Cu(II) Catalyst System

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The presence of a small amount of alkali additive in the polymer-complexed copper catalysts can lead to a remarkable increase in the reaction efficiency for the oxidative carbonylation of methanol to dimethyl carbonate.

The one-step methanol oxidative carbonylation process developed by Enichem is by far the most popular phosgene-free route for the industrial production of dimethyl carbonate (DMC), a highly attractive environmental benign chemical compound with versatile chemical reactivity.¹⁻⁴ In this well-established process, the direct synthesis of DMC is based on a simple CuCl catalyst system. One of the central problems of this process is the slurry nature of the CuCl catalyst system, which requires complex slurry reactors with specific reactor design.³ Thus, from the technological point of view, it would be highly desirable to develop new efficient homogeneous catalyst systems for DMC synthesis.⁵⁻¹²

We have recently reported a new inexpensive and readily available homogeneous polymer-complexed CuCl₂ catalyst system exhibiting good catalytic performance in the oxidative carbonylation of methanol to DMC,⁹ where poly(*N*-vinyl-2-pyrrolidone) (PVP) has been used as a unique polymeric ligand system to the copper(II) species. The promotion effect of PVP has been attributed to the formation of the PVP complex in the cation forms due to the coordination of the catalyst components to the pendant pyrrolidone groups in PVP. However, the overall methanol conversion rate over the PVP-CuCl₂ catalyst is still unfavorably slow. In the present work, we further report that the catalytic efficiency of the PVP-CuCl₂ catalyst system can

be dramatically enhanced by carrying out the reaction in the presence of a small amount of alkali additive, showing an attractive potential for practical application.

The catalytic oxidative carbonylation of methanol was carried out in an internal Teflon^R lined stainless steel autoclave of 135 mL.^{9,13} A typical procedure for the catalytic DMC synthesis was conducted as follows: into the autoclave, 10 mL of methanol, the powdered PVP-CuCl₂ catalyst and alkali additive (NaOAc, KOAc, LiOAc etc.) were charged ([Cu²⁺] = 180 mM).⁹ Then, O₂ (P_{O₂} = 0.24 MPa) and CO (P_{CO} = 2.76 MPa) were introduced. After carrying out the reaction at temperature around 120 °C for an assigned time under magnetic stirring, the liquid products were analysed by a GC equipped with FID and TCD detectors.^{9,13}

Table 1 shows the catalytic results as an average of three independent runs. It is shown that the CuCl₂ catalyst in the absence of PVP has exhibited a moderate catalytic activity. However, it is found that the DMC can be produced in a very high yield with nearly 100% selectivity based on methanol conversion from the oxidative carbonylation of methanol over the polymer-complexed PVP-CuCl₂ catalyst system. Upon the introduction of alkali additive, the methanol conversion is further greatly increased, showing a remarkable promotional effect of the alkali addition on the PVP-CuCl₂ catalyst in the DMC synthesis reaction. Table 1 shows the unique performance of NaOAc, which is much higher than other alkali additives at the same addition level in terms of the methanol conversion. It is seen that the conversion value of methanol for the PVP-CuCl₂ catalyst in the presence of 2 wt % NaOAc is more than four times of that for the catalyst in the absence of the alkali and as nearly ten times of that

Table 1. Catalytic performance of the alkali-promoted PVP-complexed CuCl₂ catalysts in the DMC synthesis^a

Catalyst	Alkali ^b /wt %	TOF ^c /h ⁻¹	CH ₃ OH ^d Conv/%	DMC Mass/%	DMC ^e Sel. (CH ₃ OH)/%	DMC ^f Yield(O ₂)/%	DMC ^g Sel.(O ₂)/%
CuCl ₂	/	1.4	2.1	2.8	95.8	10.1	97.3
CuCl ₂ -NaOAc	2.0	2.0	3.0	4.0	96.7	15.3	98.0
PVP-CuCl ₂	0.0	3.3	5.0	6.8	99.8	24.2	99.8
PVP-CuCl ₂ -NaOAc	0.5	10.4	15.6	19.7	99.4	72.5	100
PVP-CuCl ₂ -NaOAc	1.0	11.1	16.7	20.9	98.9	78.9	100
PVP-CuCl ₂ -NaOAc	2.0	14.0	21.0	25.3	97.6	98.6	100
PVP-CuCl ₂ -NaOAc	5.0	9.5	14.2	16.8	91.0	63.4	100
PVP-CuCl ₂ -KOAc	2.0	10.2	15.3	19.0	96.8	71.1	100
PVP-CuCl ₂ -LiOAc	2.0	11.8	17.7	21.9	98.6	82.7	100
PVP-CuCl ₂ -Mg(OAc) ₂	2.0	9.7	14.6	17.9	94.8	67.6	100
PVP-CuCl ₂ -NaOH	2.0	6.8	10.2	12.3	90.8	46.4	99.8

^aReaction conditions: Cu²⁺ = 180 mmol·L⁻¹, 0.24 mol of methanol, 120 °C, 2 h; ^bwt % of alkali = mass of alkali/mass of methanol; ^cTOF = converted methanol/(added Cu × reaction time). ^dMethanol conv. % = reacted methanol/introduced methanol; ^eDMC Sel. (CH₃OH)% = 2 produced DMC/reacted methanol; ^fYield of DMC (O₂)% = produced DMC/2 introduced O₂; ^gSelectivity of DMC (O₂)% = produced DMC/(produced DMC + produced CO₂)

for a pure CuCl_2 catalyst, also in sharp contrast to the case of the CuCl_2 - NaOAc system. In addition, the selectivity based on O_2 consumption is also slightly improved. However, a further increase in the amount of NaOAc to 5 wt % results in a sharp decrease of the TOF value for methanol conversion, suggesting the detrimental effect of the excess amount of alkali addition on the performance of the PVP-CuCl_2 catalyst.

The catalytic performance of the PVP-CuCl_2 catalyst in the presence of 2 wt % NaOAc in the reaction system as a function of time is plotted in Figure 1. As a direct comparison, the catalytic data obtained over the polymer-complexed catalyst in the absence of the base are also illustrated. It is seen that the methanol oxidative carbonylation reaction proceeds in a moderate rate over the catalyst in the absence of the alkali, whereas the methanol conversion approaches the maximum value only after the reaction is carried out for a time of 5 h. In sharp contrast, the conversion value of methanol increases much more steeply up to 21% in a reaction time of 2 h accompanied by a slight decrease in the overall selectivity based on methanol consumption. It is remarkable that a maximum DMC concentration of ca. 25.3 wt % can be attained after a reaction time of 2 h, demonstrating the superior performance of the alkali-modified PVP-CuCl_2 catalyst for DMC synthesis.

The promotional effect of alkali addition has also been reported for a heterogeneous catalyst system in vapor phase DMC synthesis, where the beneficial effect of alkali addition has been ascribed to the formation of catalytically active

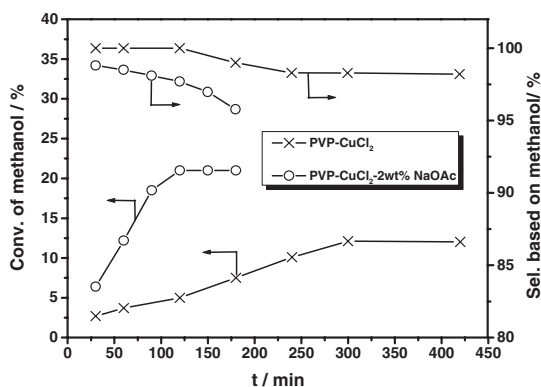


Figure 1. The catalytic activity of the PVP-CuCl_2 and PVP-CuCl_2 -2 wt % NaOAc catalysts in DMC synthesis as a function of reaction time.

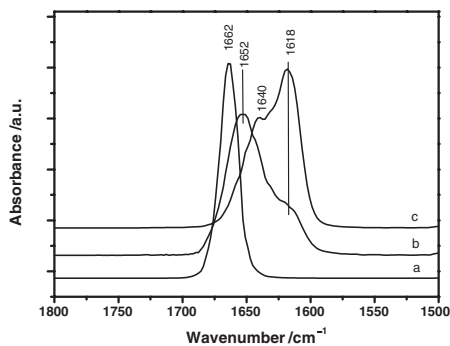


Figure 2. FTIR Spectra of (a) PVP, (b) PVP-CuCl_2 -2 wt % NaOAc , and (c) PVP-CuCl_2 , respectively.

$\text{Cu}_2(\text{OH})_3\text{Cl}$ intermediate species in $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts as a consequence of alkali addition.¹⁴ Figure 2 shows that the symmetric carbonyl band due to the amide carbonyl group of pure PVP appears at 1662 cm^{-1} . In comparison, a drastic red-shift of the carbonyl band to 1618 cm^{-1} with a well-resolved shoulder at 1640 cm^{-1} in the PVP-CuCl_2 complex is observed, demonstrating a strong ligand interaction between Cu(II) species and the polymeric ligands.⁹ However, a great attenuation of the carbonyl peaks at 1618 and 1640 cm^{-1} is identified for the PVP-CuCl_2 complex in the presence of NaOAc , accompanied by the appearance of an additional intense peak at 1652 cm^{-1} . Thus, the promotional effect of the alkali in the present reaction system is possibly due to a further modification of the ligand interaction between the Cu(II) species and the amide moieties in the PVP chains by facilitating the intrinsic Cu(II)/Cu(I) redox processes involved in the DMC synthesis reaction.^{9,15}

In summary, we have shown that the use of the simple and inexpensive alkali additive strongly modified the course of the PVP-CuCl_2 -catalyzed oxidative carbonylation of methanol. Under these novel conditions, methanol could be transformed more efficiently into DMC with a higher formation rate. Although the mechanism of the improvement of the PVP-CuCl_2 catalyst system with alkali addition needs to be further clarified, this work presents a highly efficient protocol for improving the synthesis of DMC under homogeneous conditions.

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