



# Effect of chemical treatment of activated carbon as a support for promoted dimethyl carbonate synthesis by vapor phase oxidative carbonylation of methanol over Wacker-type catalysts

Ping Yang, Yong Cao, Wei-Lin Dai, Jing-Fa Deng, Kang-Nian Fan\*

*Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, PR China*

Received 7 June 2002; received in revised form 5 September 2002; accepted 16 October 2002

## Abstract

The effects of chemical treatment of the support on the dimethyl carbonate (DMC) synthesis by vapor phase oxidative carbonylation of methanol over carbon-supported Wacker-type catalysts promoted by  $\text{CH}_3\text{COOK}$  are reported.  $\text{N}_2$  adsorption, X-ray photoelectron spectroscopy (XPS) and FT-IR were used to characterize the textural and surface characteristics of carbon support. XRD patterns and XP spectra of the catalysts were measured to determine the structure, the chemical environment and the dispersion of palladium and copper species. Although acidic functional groups were found to be enriched on the carbon support pretreated with  $\text{HNO}_3$  or air oxidation, the results show that the support pretreated with  $\text{H}_2\text{O}$  and  $\text{KOH}$  or  $\text{H}_2$  reduction promoted the formation of the active  $\text{Cu}_2\text{Cl}(\text{OH})_3$  phase over the catalysts. An excellent correlation was observed between the XRD peak intensity of  $\text{Cu}_2\text{Cl}(\text{OH})_3$  and the space–time yield (STY) for DMC production. The formation of active copper phase by chemical pretreatment of activated carbon appears to be responsible for the variation of the performance for DMC synthesis over the carbon-supported Wacker-type catalysts.

© 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Carbon support; Surface pretreatment;  $\text{CH}_3\text{COOK}$  promoter; Vapor phase oxidative carbonylation; Dimethyl carbonate (DMC)

## 1. Introduction

Dimethyl carbonate (DMC) is a nontoxic compound that has recently attracted much attention as an important green chemical in relation to environmental problems [1]. DMC has been proposed for use as a methylating reagent in place of methyl halides and dimethyl sulfate, which are both toxic and

corrosive, and as an intermediate in the synthesis of polycarbonates and isocyanates, thereby avoiding the need to use phosgene [2]. DMC is also a candidate for replacing methyl *tert*-butyl ether (MTBE) as an oxygen-containing additive for gasoline, due to its high oxygen content [3].

Several routes have been developed for the possible production of DMC: (1) the phosgene–methanol process, in which  $\text{COCl}_2$  is reacted with methanol, obviously involving dangerous phosgene gas; (2) the methyl nitrite route, in which methanol is first converted into methyl nitrite ( $\text{CH}_3\text{-ONO}$ ) and then into

\* Corresponding author. Tel.: +86-21-65643977;

fax: +86-21-65641740.

E-mail address: [kxfan@fudan.edu.cn](mailto:kxfan@fudan.edu.cn) (K.-N. Fan).

DMC via reaction with CO. While this second scheme is promising, it involves the use of two separate reactors with two separate reaction schemes; (3) the liquid phase oxidative carbonylation of methanol over a slurry of CuCl produces significant amounts of DMC [4], but this process is known to have technical drawbacks of severe corrosivity and a short service life; (4) the vapor phase oxidative carbonylation of methanol using a heterogeneous supported catalyst [5–8]. Although a commercial oxidative carbonylation process utilizing the vapor phase approach has yet to be established, this new process has recently been considered as the most promising way for DMC production by offering advantages to overcome the shortcomings associated with the commercial liquid process.

A number of catalytic supports, such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and zeolites as well as activated carbon, have been extensively investigated in an effort to develop more efficient heterogeneous catalyst systems for vapor phase oxidative carbonylation of methanol to DMC [5–8]. Carbon supports have been reported to be superior to any other supports in terms of activity, selectivity, and longevity for this catalyst system. Recently, a new type of Wacker-type PdCl<sub>2</sub>-CuCl<sub>2</sub> catalyst supported on activated carbon, proposed by Wang et al. [9], has been shown to be effective for the gas phase DMC synthesis from oxidative carbonylation of methanol at atmospheric pressure. The effect of alkali metal promoters on the catalytic performance of the carbon-supported Wacker-type catalysts has been investigated. Results demonstrated that the use of CH<sub>3</sub>COOK as promoter of the carbon-supported Wacker-type catalyst allows an efficient production of DMC at a high space–time yield (STY) of 217 g-DMC/(l-cat h).

On the other hand, it is well known that the carbon-supported Wacker-type catalysts are highly active for oxidation of carbon monoxide [10–18]. Previous studies have shown that pretreatment of the support can significantly affect the interaction between the active phase and the support as well as the dispersion of the active species on the Wacker-type catalysts for CO oxidation [18]. In the present study, the carbon-supported PdCl<sub>2</sub>-CuCl<sub>2</sub>-CH<sub>3</sub>COOK catalyst system has been investigated by the chemical pretreatment of the carbon support. The purposes are to improve the catalytic activities of the heterogeneous Wacker-type catalysts for DMC synthesis by

oxidative carbonylation of methanol and CO and to gain insight into the active forms of the metal species supported on activated carbon.

## 2. Experimental

### 2.1. Preparation of support and catalyst

Five kinds of carbon supports were used to determine the effect of surface functional groups on DMC synthesis from oxidative carbonylation of methanol. Activated carbon (AC) was obtained from Beijing Guanghua Co.; its particulate size was 40–60 mesh. Surface-modified activated carbons were prepared by chemical treatment with water, 5N HNO<sub>3</sub> and 1N KOH at 373 K for 3 h, followed by washing with distilled water and drying at 393 K for 12 h. These were denoted as AC-1, AC-2, and AC-3, respectively, and the carbons treated by H<sub>2</sub> reduction or air oxidation at 723 K for 3 h were labeled as AC-4 and AC-5, respectively.

The catalysts were prepared by a wet impregnation method to impregnate CH<sub>3</sub>COOK-premodified support with an alcoholic solution of palladium and copper. The CH<sub>3</sub>COOK-premodified support was obtained by impregnation with aqueous CH<sub>3</sub>COOK solution, followed by drying at 393 K for 2 h in an oven before PdCl<sub>2</sub>-CuCl<sub>2</sub> impregnation. The metal precursors were PdCl<sub>2</sub> (Acros, 99.9%), CuCl<sub>2</sub>·2H<sub>2</sub>O (Aldrich, 99.9%) and CH<sub>3</sub>COOK (Aldrich, 99.9%). Five kinds of supported Wacker-type catalysts (catalyst WA-*x* represents a PdCl<sub>2</sub>-CuCl<sub>2</sub>-CH<sub>3</sub>COOK catalyst system loaded on carbon support of AC-*x*) were prepared, as described in Table 1. The loadings of Pd and Cu for all catalysts were 0.45 and 3.2 wt.%, respectively, and the mole ratio of CH<sub>3</sub>COOK: PdCl<sub>2</sub> was 12:1 for all catalysts. All catalysts were stored under ambient conditions before the reaction.

### 2.2. Characterization of catalysts

The textural parameters have been measured using the BET method by N<sub>2</sub> adsorption and desorption at 77 K in a Micromeritics TriStar system. The X-ray powder diffraction (XRD) characterization of the catalysts was carried out on a Germany Bruker D8 Advance X-ray diffractometer using nickel-filtered

Table 1  
Effect of support pretreatment on the catalytic performance of vapor phase DMC synthesis over carbon-supported Wacker-type catalysts

Catalyst	Treated with	$X_{\text{MeOH}}$ (%)	$S_{\text{DMC/MeOH}}$ (%)	$S_{(\text{MF}+\text{DMM})/\text{MeOH}}$ (%)	$S_{\text{DMC/CO}}$ (%)	$S_{\text{CO}_2/\text{CO}}$ (%)	STY (g-DMC/(l-cat h))
WA-1	H <sub>2</sub> O	7.3	97.7	2.3	28.5	71.5	389.7
WA-2	HNO <sub>3</sub>	3.3	63.4	36.6	3.8	96.2	109.8
WA-3	KOH	6.0	99.4	0.6	40.7	59.3	325.6
WA-4	H <sub>2</sub>	6.6	98.7	1.3	33.2	66.8	346.0
WA-5	Air	2.9	98.1	1.9	18.4	81.6	110.9

Reaction conditions: time on stream = 8 h,  $T = 403$  K,  $\text{CO/O}_2/\text{MeOH} = 22/6/44$ ,  $\text{GHSV} = 4300$  h<sup>-1</sup>.

Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) in the  $2\theta$  ranges from 10 to 80°. The X-ray Photoelectron Spectroscopy (XPS) experiments were carried out on a Perkin-Elmer PHI 5000C ESCA system using Al K $\alpha$  radiation (1486.6 eV). The spectrometer was operated at a resolution of about 1 eV. Fourier transform infrared spectroscopy (FT-IR) spectra of the catalysts were acquired in the 4000–400 cm<sup>-1</sup> wavenumber range, 100 scans being taken at 4 cm<sup>-1</sup> resolution using a Bruker Vector 22 instrument equipped with a DTGS detector and a KBr beam splitter. Pellets were prepared by mixing powdered sample and KBr (Merck, for spectroscopy) at a sample/KBr weight ratio of 1:100 [18]. The spectrum of a similar mass pellet, which was made with pure KBr and prepared in the same way as the sample pellets, was recorded and used as the background spectrum.

### 2.3. Gas phase oxidative carbonylation of methanol to dimethyl carbonate

The gas phase DMC synthesis reaction by oxidative carbonylation of methanol with carbon monoxide and oxygen was investigated in a continuous flow system with a fixed bed reactor at atmospheric pressure. The reactor was made of a stainless steel tube having an inner diameter of 10 mm and a length of 40 cm. About 0.5 g of catalyst sample of 40/60 meshes was packed in the tubular reactor and positioned between two layers of glass bead beds. Methanol was introduced by using a syringe pump into the pre-heater, where it was vaporized and then entered the reactor together with carbon monoxide and oxygen. The flow rates of carbon monoxide and oxygen were controlled by a mass flow controller. The reaction products on leaving the reactor passed through a cooling trap and were separated by a gas–liquid separator. The

liquid products were weighted and measured with a flame ionization detector (FID) equipped with a 30 m capillary column of fused silica containing RSL 160 liquid phases for the separation of methanol, DMC, methyl formate HCOOCH<sub>3</sub> (MF), dimethoxy methane CH<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub> (DMM), and dimethyl ether CH<sub>3</sub>OCH<sub>3</sub> (DME). The uncondensed gas products (O<sub>2</sub>, CO<sub>2</sub> and CO) were introduced to the GC through an on-line six-way valve and were analyzed with a TCD detector with a TDX-01 packed column.

## 3. Results and discussion

### 3.1. Catalytic activity of PdCl<sub>2</sub>-CuCl<sub>2</sub>-CH<sub>3</sub>COOK/AC catalysts

The effect of surface treatment of carbon supports on DMC synthesis via vapor phase oxidative carbonylation of methanol over carbon-supported Wacker-type catalysts promoted by CH<sub>3</sub>COOK has been investigated. Table 1 compiles the catalytic data for methanol oxidative carbonylation at 130 °C and the selectivity to DMC. The table also shows the main by-products (MF, DMM in liquid, CO<sub>2</sub> in gas phase) based on methanol and CO conversion for the catalysts obtained from the carbon supports pretreated by various methods. The selectivity to methanol for DMC production is much higher than the selectivity to CO over these five carbon-supported Wacker catalysts. In addition, the conversion values of methanol over the WA-1, WA-3, and WA-4 catalysts were observed to be much higher than the other two counterparts. As can be expected from the results of DMC yields, the catalysts of WA-1, W-3 and WA-4 display a much higher space–time yield (STY) for DMC synthesis than that over WA-2 and WA-5 catalysts. Particularly, the best

catalytic performance has been attained over a sample of WA-1 with a 7.3% methanol conversion at a 97.7% selectivity to methanol and the highest STY value of 389.7 g-DMC/(l-cat h) for DMC synthesis. To our knowledge, this value is remarkably higher than any previously reported value for DMC production via vapor phase direct oxidative carbonylation of methanol [8,9].

The significant variations of the methanol conversion and selectivity as well as the STY for DMC production demonstrate that the catalytic performance of the carbon-supported Wacker-type catalysts depends strongly on the surface pretreatment method of the carbon supports. The present results clearly indicate that the catalysts supported on carbon pretreated with gas or liquid oxidants exhibit much lower catalytic activity and selectivity for oxidative carbonylation of methanol to DMC. However, the catalytic performance of the catalyst can be significantly improved by a simple pretreatment of carbon support by  $H_2$  reduction or by exposure to boiling water and alkali solution.

The carbon-supported Wacker-type catalysts promoted by  $CH_3COOK$  have been shown to be active as a catalyst in the oxidative carbonylation of methanol, but their stability was found to be poor. As shown in Fig. 1, the STY for DMC production increased significantly in the initial 4 h along with the reaction,

suggesting the presence of induction period for the oxidative carbonylation reaction over catalyst of WA-1. The catalytic performance of WA-1 achieved a steady-state after 5 h on stream, however, the activity of WA-1 started to drop markedly after 11 h on stream. It is notable that the selectivity for DMC production based on methanol conversion remained very high over all the time range of the reaction. It has been reported that the main reason of deactivation of supported Wacker-type catalysts could be attributed to loss of surface chlorine [19]. The detailed investigation for the reason of deactivation is being carried out and will be reported in another paper.

### 3.2. Characterization of supports and catalysts

The physical properties were measured for the surface modified activated carbon prepared by various chemical pretreatments. Table 2 summarizes the textural results for the five carbon supports as well as for the corresponding Wacker-type catalysts. The five carbon supports have almost the same pore size distribution (PSD) and cumulative pore volume data, as shown in Table 2. Other  $N_2$  adsorption data, such as BET surface area and the shape of the adsorption–desorption isotherms, were also quite similar. Hence, this observation indicates that surface modification of the

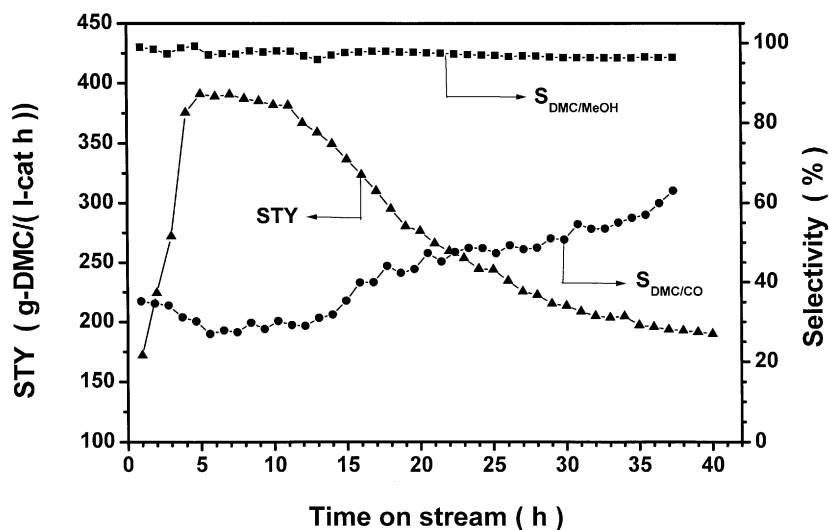


Fig. 1. The catalytic performance of catalyst WA-1 as a function of time on stream. Reaction conditions:  $T = 403$  K,  $CO/O_2/MeOH = 22/6/44$ ,  $GHSV = 4300$  h $^{-1}$ .

Table 2

N<sub>2</sub> adsorption data for activated carbons and supported Wacker-type catalysts obtained by various chemical pretreatments

Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$S_{\text{m}}$ (m <sup>2</sup> /g)	$S_{\text{e}}$ (m <sup>2</sup> /g)	$V_{\text{t}}$ (ml/g)	$V_{\text{m}}$ (ml/g)	$R$ (Å)
AC-1	1299.7	806.8	492.9	0.65	0.37	20.1
AC-2	1321.3	780.9	540.3	0.67	0.35	20.2
AC-3	1329.7	917.2	412.4	0.67	0.41	20.1
AC-4	1240.6	861.1	379.5	0.62	0.39	19.9
AC-5	1354.8	838.2	516.6	0.69	0.37	20.3
WA-1	1084.3	663.6	420.7	0.55	0.30	20.4
WA-2	1076.2	656.8	419.4	0.54	0.30	20.4
WA-3	1036.2	640.8	395.4	0.52	0.29	20.2
WA-4	1029.4	694.7	334.6	0.52	0.31	20.2
WA-5	1063.8	605.7	458.1	0.54	0.27	20.5

$S_{\text{BET}}$ ,  $S_{\text{m}}$  and  $S_{\text{e}}$  represent BET, micro, and external area, respectively;  $V_{\text{t}}$  and  $V_{\text{m}}$  are total and micro pore volume;  $R$  denotes the average pore diameter.

carbon supports has been successfully made without disrupting the original textural structures of AC [18].

Upon the introduction of the Wacker-type active components, a dramatic decrease in the total BET surface area and micro pore surface area over the carbon-supported catalysts has been identified. The results in Table 2 also demonstrate that the impregnation of the PdCl<sub>2</sub>-CuCl<sub>2</sub>-CH<sub>3</sub>COOK would cause the loss of the pore volume of the carbon materials. In contrast, the average pore diameter of the catalysts is similar to that of the unloaded supports. This result suggests that the introduced PdCl<sub>2</sub>-CuCl<sub>2</sub>-CH<sub>3</sub>COOK species would be preferentially deposited onto the wall of the micro pore of the carbon supports, which results in a more dramatic loss of the micro pore area as compared to other N<sub>2</sub> adsorption data, as shown in Table 2.

FT-IR spectra were obtained to observe the differences in the surface functional groups of activated carbon supports subjected to different chemical pretreatments. The activated carbon pretreated with boiling water (AC-1) has a broad envelope band over 1000–1300 cm<sup>-1</sup>, a broad asymmetric band over 1400–1600 cm<sup>-1</sup> and a small band at 1385 cm<sup>-1</sup>, as shown in Fig. 2. Upon oxidation pretreatment with HNO<sub>3</sub> and air at elevated temperatures, the intensity of bands observed in AC-1 was strengthened and a new band at 1717 cm<sup>-1</sup> appeared in AC-2 and AC-5. Upon reduction treatment with H<sub>2</sub>, the small band at 1385 cm<sup>-1</sup> disappeared in AC-4 as compared to the AC-1 sample. For AC-3 treated with KOH, the intensity of bands observed in AC-4 was intensified. It was previously reported [18,20] that bands at 1100–1450,

1580, and 1550–2050 cm<sup>-1</sup> could be related to C–O stretching, polyaromatic C=C stretching, and C=O stretching modes, respectively. The band at 1717 cm<sup>-1</sup> that appeared in samples AC-2 and AC-5 can be attributed to the stretching vibrations of C=O moieties in carboxylic, ester, lactone and in quinone and/or ion–radical structures [21]. The present FT-IR data demonstrate that acidic surface oxygen groups are enriched and diversified over activated carbon upon oxidizing treatment with HNO<sub>3</sub> and air. On the other

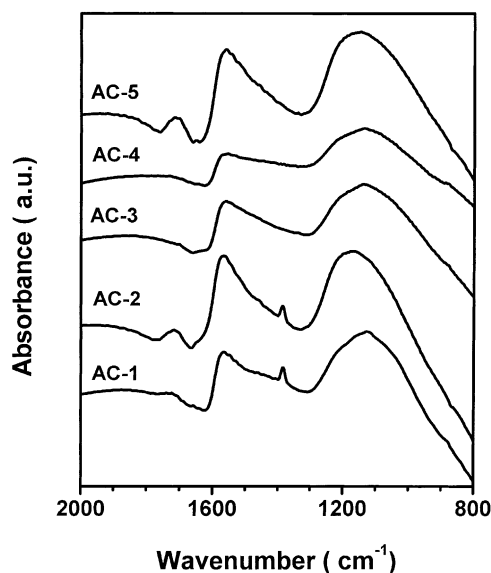


Fig. 2. FT-IR spectra of carbon supports with various chemical pretreatments.

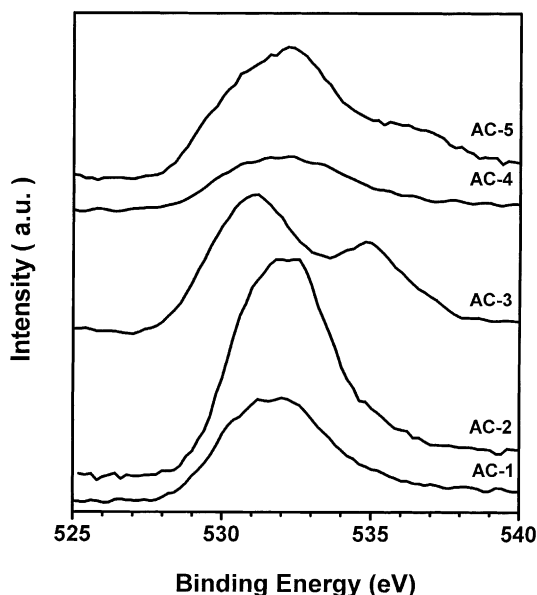


Fig. 3. XP O 1s core level spectra of the chemically pretreated activated carbons.

hand, basic surface oxygen groups such as quinoidic groups are formed over sample AC-3 treated with KOH, and surface oxygen groups are dramatically reduced over sample AC-4 treated with H<sub>2</sub> reduction.

The surface concentration as well as the types of the oxygen groups on the carbon supports has been directly measured using XPS. Fig. 3 depicts the XP O 1s spectra of the carbon supports treated with different methods. The high-resolution O 1s spectra of sample AC-1 shows a symmetrical broad peak centered around 531.7 eV and AC-2 shows a more intense symmetrical peak centered at 532.3 eV, whereas AC-5 show asymmetric peaks centered at 532.4 eV with a shoulder at 536.2 eV. AC-3 shows two peaks

centered at 531.0 and 534.8 eV, respectively, and sample AC-4 has a O 1s signal centered at 531.8 eV. The O 1s spectra for all carbon supports have been resolved into two or three individual component peaks representing basic surface oxygen groups corresponding to quinoidic C=O groups (Peak 1, BE = 530.4–530.8 eV), C–OH and/or C–O–C groups (Peak 2, BE = 532.4–533.1 eV), and chemisorbed oxygen and/or water (Peak 3, BE = 534.8–535.6 eV) [21,22].

Table 3 compares the O/C mole ratio and the type of oxygen species in the O 1s region of carbon supports. The O/C ratios of AC-2, AC-3, AC-5 samples are much higher than those for samples of AC-1 and AC-4. The results demonstrate that the treatment with oxidation and KOH results in the enrichment of the surface oxygen groups, whereas treatment with surface reduction leads to a notable decrease of the surface oxygen concentration, in excellent agreement with the above FT-IR data. The ratio of three O 1s peaks representing different surface oxygen groups is observed to be substantially different for carbon supports treated with different methods. The increase in O 1s peak intensity at BE around 534.8–535.6 eV on carbon supports treated with HNO<sub>3</sub>, air and KOH could be explained in terms of increasing of the surface chemisorbed oxygen and/or water [21]. The remarkable decrease in the concentration of the oxygen species with BE located at 534.8–535.6 eV for H<sub>2</sub>-treated carbon supports as compared to all other samples suggests that the chemisorbed oxygen can be easily removed by H<sub>2</sub> reduction. It should be noted that the O 1s signal in sample AC-3 has a much higher oxygen component at BE of 530.4–530.8 eV. This finding shows that the remarkable increase in surface concentration of the basic surface oxygen groups such as quinoidic groups has been achieved on the KOH-treated carbon support [22].

Table 3  
Results of XPS analysis for chemically pretreated activated carbons

Sample	O/C mole ratio	O 1s peaks (%)		
		Peak 1 (530.4–530.8 eV)	Peak 2 (532.4–533.1 eV)	Peak 3 (534.8–535.6 eV)
AC-1	0.10	27.7	56.9	15.4
AC-2	0.22	12.4	65.3	22.3
AC-3	0.17	62.2	–	37.2
AC-4	0.09	17.7	72.5	9.8
AC-5	0.19	14.4	64.2	21.4



Table 4  
Surface compositional results for carbon-supported catalysts obtained from XPS analysis

Catalyst	Cu (%)	Pd (%)	K (%)	Cl (%)	Cl/(Cu + Pd)
WA-1	22.1	0.08	1.80	7.31	0.33
WA-2	1.65	0.07	1.53	1.87	1.09
WA-3	18.7	0.30	0.71	7.47	0.39
WA-4	28.2	0.19	0.77	7.67	0.27
WA-5	1.40	0.12	3.44	1.58	1.04

In order to obtain information on the location and distribution of the active components on the supports, XPS analysis of the catalysts supported on activated carbons has been carried out. An illustration of the XPS results is shown in Table 4. The surface concentration and distribution of Cu, Pd and K species obtained from XPS characterization were quite different for these five samples, though the same amounts of catalytic components have been employed in the catalyst preparation procedure. The active Cu and Cl components are enriched on the surface of the catalysts upon the pretreatment using water, H<sub>2</sub> and KOH, whereas the treatment with HNO<sub>3</sub>, in air gives the opposite result. On the other hand, the K component is enriched on air-treated carbon-supported catalyst as compared to the catalysts treated with other methods. This observation can be well understood by taking into account the fact that the HNO<sub>3</sub>-treated carbon support has a much higher population of acidic oxygen functional

groups than the other supports. It should also be noted that the mole ratio of Cl/(Cu + Pd) on all five catalysts was much <2, suggesting that a substantial part of the Cl<sup>-</sup> anions are lost during the procedure of catalyst preparation. This phenomenon has been reported earlier [23].

To gain an insight into the relation between the catalytic performance and the active phase, XRD patterns of the carbon-supported catalysts were recorded and are shown in Fig. 4. No peaks related to Pd species can be observed, indicating a highly dispersed nature for palladium on the carbon support. In addition to the broad peaks due to the amorphous support, only peaks with different intensities corresponding to Cu<sub>2</sub>Cl(OH)<sub>3</sub>, KCl and Cu(OHCl)<sub>2</sub>·2H<sub>2</sub>O are observed. Supported catalysts WA-2 and WA-5 show very weak intensity of Cu<sub>2</sub>Cl(OH)<sub>3</sub> phase. This indicates that the acidic surface functional groups do not effectively promote the formation of an active copper phase, Cu<sub>2</sub>Cl(OH)<sub>3</sub>, for these two catalysts. However, the strong diffraction peaks representing the Cu<sub>2</sub>Cl(OH)<sub>3</sub> and KCl phases are observed over WA-1, WA-3 and WA-4. Hence, the present XRD results suggest that a carbon support with basic surface functional groups favors the formation of active Cu<sub>2</sub>Cl(OH)<sub>3</sub> phases, in excellent accord with the results obtained from XPS and FT-IR characterization.

The effect of the copper phase on CO oxidation over supported Wacker-type catalysts was previously

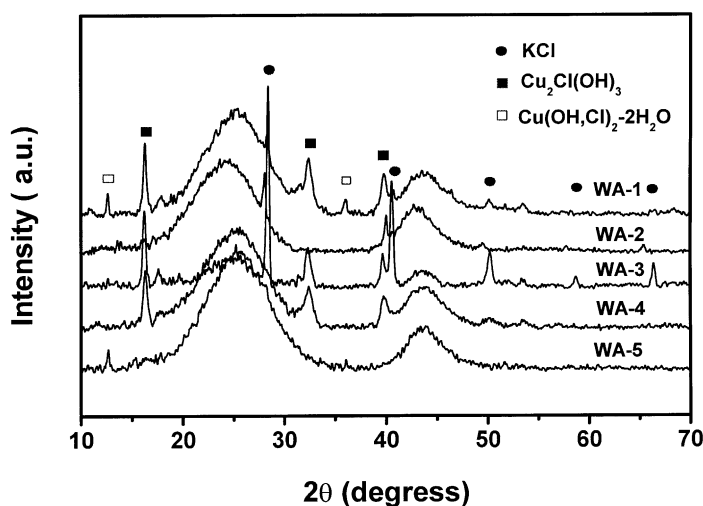


Fig. 4. X-ray diffractogram of the carbon-supported Wacker-type catalysts: (a) WA-1, (b) WA-2, (c) WA-3, (d) WA-4 and (e) WA-5.

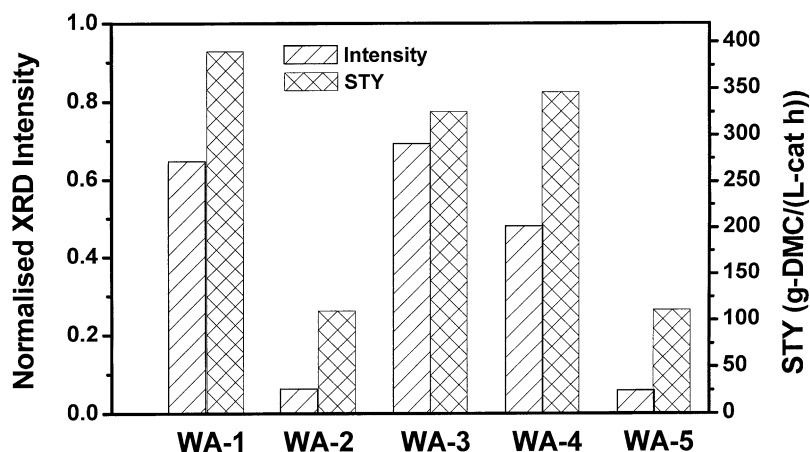
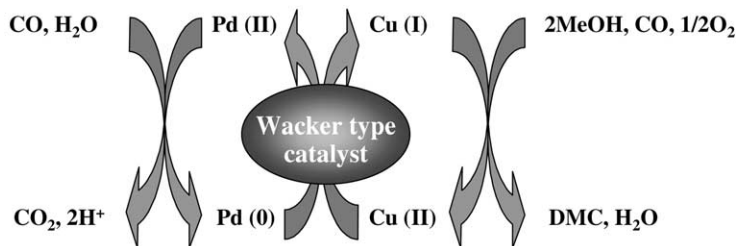


Fig. 5. Comparison between the normalized XRD intensity of  $\text{Cu}_2\text{Cl}(\text{OH})_3$  peak at  $2\theta \approx 16^\circ$  and the STY for DMC production over the carbon-supported catalysts after various chemical pretreatments.

studied by Park et al. [15,17,18], who reported that the XRD intensity of the  $\text{Cu}_2\text{Cl}(\text{OH})_3$  phase of a catalyst was closely correlated with its catalytic activity. A recent XRD characterization of the diethyl carbonate (DEC) synthesis catalysts by Punnoose et al. has also shown an excellent correlation between the  $\text{Cu}_2\text{Cl}(\text{OH})_3$  phase concentration and the yield for DEC production over activated carbon-supported  $\text{CuCl}_2\text{-PdCl}_2$  catalysts [24]. It is therefore highly interesting to make a comparison between the catalytic activity of the carbon-supported catalysts and the results obtained from XRD analysis. Fig. 5 shows the comparison between the relative changes in the intensity of the main  $\text{Cu}_2\text{Cl}(\text{OH})_3$  Bragg peak near  $2\theta \approx 16^\circ$  and STY for DMC production over the catalysts supported on activated carbons with various surface pretreatments. An excellent correlation is obtained for the five catalysts, suggesting the key role

played by  $\text{Cu}_2\text{Cl}(\text{OH})_3$  phase in the production of DMC.

In this study, the effects of surface oxygen groups of carbon on the vapor phase DMC synthesis by oxidative carbonylation of methanol over carbon-supported Wacker-type catalysts have been examined and the phase and the chemical distribution of the active species have been studied. We have experimentally demonstrated the formation of a well-defined copper solid phase,  $\text{Cu}_2\text{Cl}(\text{OH})_3$ , in XRD patterns for highly active catalysts such as WA-1, WA-3 and WA-4. This observation indicates clearly that the active copper phase is formed by an interaction between the copper precursor and the surface functional groups, which can be selectively produced by surface pretreatment of the carbon supports using various convenient chemical methods. We suggest that the overall chemistry of oxidative carbonylation of methanol is somewhat similar



Scheme 1. The redox cycles of the carbon-supported Wacker-type catalyst system involved in oxidative carbonylation of methanol to dimethyl carbonate (DMC).



to the well-known CO oxidation Wacker process in the presence of a heterogeneous PdCl<sub>2</sub>-CuCl<sub>2</sub> catalyst. The reaction scheme is illustrated in [Scheme 1](#), based on the present experimental observations as well as some results from the literature [18]. Thus, initially the Pd(II) species is reduced to Pd(0) by carbon monoxide, and then the Pd(0) is reoxidized to Pd(II) species by a Cu(II) compound which is reduced during this process into Cu(I) species. The formation of catalytically active Cu(I) species is important for oxidative carbonylation of methanol to DMC. In this process, the Cu<sub>2</sub>Cl(OH)<sub>3</sub> phase is believed to perform better than other copper phases for the accomplishment of the surface redox cycles to maintain the presence of catalytically active Cu(I) species over the catalysts.

#### 4. Conclusion

The surface nature of activated carbon used to prepare supported Wacker-type catalysts can be effectively improved by chemical pretreatment with HNO<sub>3</sub>, water and KOH or by air oxidation and H<sub>2</sub> reduction. It was found that acid carboxylic and carbonyl groups are enriched on the carbon support pretreated with HNO<sub>3</sub> or air oxidation. Meanwhile, treatment of the carbon supports with KOH, water or H<sub>2</sub> reduction enriches the basic surface oxygen groups and promotes the formation of an active copper phase, Cu<sub>2</sub>Cl(OH)<sub>3</sub>. The enhanced basic surface nature and the formation of the active copper phase appear to be responsible for the improved catalytic performance for DMC synthesis by vapor phase oxidative carbonylation of methanol over a heterogeneous Wacker-type catalyst supported on activated carbon.

#### Acknowledgements

The financial supports from National Natural Science Foundation of China (Grant No. 20203003,

20073009) and the Committee of Shanghai Science and Technology (Grant No. 0112NM076, 02QA14006, 02DJ14021) are gratefully acknowledged.

#### References

- [1] M.A. Pacheco, C.L. Marshall, *Energy Fuels* 11 (1997) 2.
- [2] M. Mass, U. Romano, F. Rivetti, *Ind. Chim. Ital.* 21 (1985) 6.
- [3] J. Haggin, *Chem. Eng. News* 65 (1987) 26.
- [4] G.L. Curuntt, D.C. Harley, *Oxygen Complexes and Oxygen Activation by Transition Metals*, Plenum Press, New York, 1988, pp. 215–232.
- [5] Y. Ono, *Catal. Today* 35 (1997) 15.
- [6] S.T. King, *J. Catal.* 161 (1996) 530.
- [7] D.W. Smith, S.D. Landau, US Patent 5,171,874 (1992), to Quantum Chemical Company.
- [8] L. Zhong, K.C. Xie, R.C.T. Slade, *Appl. Catal. A* 205 (2001) 85.
- [9] Y.J. Wang, X.Q. Zhao, B.G. Yuan, B.C. Zhang, J.S. Cong, *Appl. Catal. A* 171 (1998) 255.
- [10] K.I. Choi, M.A. Vannice, *J. Catal.* 127 (1991) 465.
- [11] K.I. Choi, M.A. Vannice, *J. Catal.* 127 (1991) 489.
- [12] K.I. Choi, M.A. Vannice, *J. Catal.* 131 (1991) 22.
- [13] K.I. Choi, M.A. Vannice, *J. Catal.* 131 (1991) 36.
- [14] Y. Yamamoto, T. Matsuzaki, K. Ohdan, Y. Okamoto, *J. Catal.* 161 (1996) 577.
- [15] E.D. Park, J.S. Lee, *J. Catal.* 180 (1998) 123.
- [16] J.S. Lee, E.D. Park, B.J. Song, *Catal. Today* 54 (1999) 57.
- [17] E.D. Park, S.H. Choi, J.S. Lee, *J. Phys. Chem.* 104 (2000) 5586.
- [18] E.D. Park, J.S. Lee, *J. Catal.* 193 (2000) 5.
- [19] R.X. Jiang, Y.J. Wang, X.Q. Zhao, S.F. Wang, C.Q. Jin, C.F. Zhang, *J. Mol. Catal.* 185 (2002) 159.
- [20] A. Dandekar, R.T.K. Baker, M.A. Vannice, *Carbon* 36 (1998) 1821.
- [21] S. Biniak, G. Szymański, J. Siedlewski, A. Świątkowski, *Carbon* 35 (1997) 1799.
- [22] G. Mestl, N.I. Maksimova, N. Keller, V.V. Roddatis, R. Schlögl, *Angew. Chem. Int. Ed.* 40 (2001) 2066.
- [23] K. Tomishige, T. Sakai, S. Sakai, K. Fujimoto, *Appl. Catal. A* 181 (1999) 95.
- [24] A. Punnoose, M.S. Seehra, B.C. Dunn, E.M. Eyring, *Energy Fuels* 16 (2002) 182.