

Impact of preparation strategy on the properties of carbon-supported Wacker-type catalysts in vapor-phase dimethyl carbonate synthesis

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Abstract

Four supported Wacker-type catalysts were prepared by varying impregnation solvents and sequences of activated carbon. The catalysts were characterized by BET, XRD, SEM/EDXS, and TPR. They were tested for the dimethyl carbonate (DMC) synthesis from vapor-phase oxidative carbonylation of methanol. The results show that the preparation procedures have an impact on the reducibility, surface morphology as well as on the spatial distribution of the active-phase particles at the exterior of the carbon grains. Concerning the activity, the catalyst prepared by impregnating the carbon support with KOAc followed by PdCl₂/CuCl₂ employing ethanol as the impregnation solvent shows a higher performance in the oxidative carbonylation of methanol. The improved performance of the catalyst for methanol conversion to DMC can be attributed to the presence of a high surface concentration of an active phase comprising Pd and Cu species in close vicinity deposited on the external part of the carbon support.

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Keywords: Wacker-type catalysts; SEM; Activated carbon; Vapor-phase oxidative carbonylation; Dimethyl carbonate (DMC)

1. Introduction

Dimethyl carbonate (DMC) is an environmentally benign chemical compound and a unique intermediate with versatile chemical reactivity; it has attracted increasing interest from both practical and fundamental point of view in recent years [1–13]. The one-step liquid-phase methanol oxidative carbonylation process developed by Enichem is by far the most popular phosgene-free route for the industrial production of dimethyl carbonate. 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. Some additional disadvantages occurs, such as difficult separation of the products and corrosive effect of the catalyst on the reactor materials. Thus, from the tech-

nological point of view, it would be highly attractive to develop new efficient processes such as a vapor-phase process based on heterogeneous catalyst systems for DMC synthesis [2,3,6–10,13].

The copper catalyst systems supported on a number of catalytic supports such as SiO₂, Al₂O₃, zeolites as well as activated carbon have been extensively investigated as potential candidates for vapor-phase DMC synthesis [1–11,13]. Among them, the copper chloride-loaded carbon materials have been reported to be superior to any other catalysts in terms of activity, selectivity, and longevity for this reaction system. Recently, the potential of various carbon-supported Wacker-type catalysts comprising palladium and copper chlorides promoted by KOAc was evaluated in the DMC synthesis reaction [8,10]. It was observed that the vapor-phase DMC synthesis reaction is strongly dependent on the presence of the alkali promoters such as KOAc and is catalyzed by the active phase composed of well-defined Cu₂Cl(OH)₃ [7,10]. The essential role of the alkali promoter is suggested to be due to the electron-donating nature of the alkali metal K which has a strong impact on the electronic

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environment of the synergistic Pd–Cu active species in the catalyst [8].

On the other hand, we have recently demonstrated that the optimization of the surface nature of the carbon support is a prerequisite for the preparation of a catalyst with superior performance in the DMC synthesis reaction [13]. Moreover, it is found that the catalyst preparation processes involving the deposition of the active components onto the carbon support are far more difficult to control, since the conventional successive impregnation method may typically lead to a preferential deposition of the catalytic active phase on the interior or external surface of the catalytic support [14–16]. In addition, an uneven distribution of the active phase on the surface of the catalysts may also occur. When one considers that the impregnation order and solvent are very important preparation parameters to control the location and the distribution of the active phase and consequently the catalytic activity [16], it is therefore of vital importance to investigate the effect of the detailed impregnation procedures on the structure of the carbon-supported Wacker-type catalysts in DMC synthesis reaction. To the best of our knowledge, the effect of the detailed impregnation parameters such as impregnation order and solvent on the performance of the carbon-supported Wacker-type catalysts in DMC synthesis reaction has yet to be reported. In the present work, the influences of impregnation sequences and solvents for the active components on the catalytic performance of the PdCl₂–CuCl₂–KOAc/AC catalysts in the DMC synthesis have been investigated. The as-prepared samples were characterized by BET, XRD, SEM/EDX, and TPR measurements to establish a fundamental understanding of the relationship between the catalytic performance and the nature of the active sites in the carbon-supported Wacker-type catalysts.

2. Experimental

2.1. Catalyst preparation

The carbon-supported Wacker-type catalysts were prepared by a two-step impregnation of activated carbon (GH-1 type, 40/60 meshes; Beijing Guanghai) with aqueous or alcoholic solution of KOAc or palladium/copper chloride [13]. The metal precursors were PdCl₂ (Acros, 99.9%), CuCl₂·2H₂O (Aldrich, 99.9%) and CH₃COOK (Aldrich, 99.9%). The loadings of Pd and Cu were 0.45 and 3.2 wt.%, respectively, and the mole ratio of KOAc to PdCl₂ was 12:1 for all catalysts. The catalyst preparation procedures were carried out as follows.

2.1.1. CAT-A

Impregnation by alcoholic solution of KOAc, drying at 393 K for 2 h in air, followed by impregnation using alcoholic solution of palladium and copper, drying at 393 K for 12 h in air.

2.1.2. CAT-B

Impregnation by alcoholic solution of palladium and copper, drying at 393 K for 2 h in air, followed by impregnation using alcoholic solution of KOAc, drying at 393 K for 12 h in air.

2.1.3. CAT-C

Impregnation by aqueous solution of KOAc, drying at 393 K for 2 h in air, followed by impregnation using aqueous solution of palladium and copper, drying at 393 K for 12 h in air.

2.1.4. CAT-D

Impregnation by aqueous solution of palladium and copper, drying at 393 K for 2 h in air, followed by impregnation using aqueous solution of KOAc, drying at 393 K for 12 h in air.

2.2. Catalyst characterization

The BET surface area of the samples and the volume of microspores and mesopores were obtained by N₂ adsorption at 77 K, using a Micromeritics TriStar system. For these experiments, around 200 mg of sample was used, previously degasified at 350 °C for 3 h under nitrogen flow. The surface area data were calculated from the nitrogen adsorption data using the BET equation.

X-ray powder diffraction (XRD) patterns were obtained at room temperature using a D8 Advance X-ray diffractometer (Bruker Co., Germany) with nickel-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray tube was operated at 40 kV and 200 mA. Samples were finely ground and packed into a plastic holder having a 16 mm \times 16 mm \times 2 mm volume. No adhesive or binder was necessary. The 2θ angle was scanned at a rate of 4° min⁻¹.

Scanning electron microscopy (SEM) data were taken on a PHILIPS XL 30 instrument by placing the catalyst particles on the specimen holder and coating with gold. Surface species were checked by means of an electron probe. Elemental analysis was done with an energy-dispersive X-ray (EDX) instrument using this SEM apparatus.

Temperature-programmed reduction (TPR) was conducted in a mixture stream of H₂/Ar (5% H₂/Ar, 25 ml/min) heated from 25 to 750 °C at a rate of 5 °C/min. Samples (around 400 mg) were placed in a U-shaped quartz cell and pretreated with helium at room temperature for 3 h, the consumption of H₂ was monitored by GC with a TCD detector.

2.3. Vapor-phase oxidative carbonylation of methanol

The vapor-phase DMC synthesis reaction by oxidative carbonization 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 (~1.0 ml) of

catalyst sample was packed in the tubular reactor and this reactor was then 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. An electronic mass flow controller controlled the flow rate of carbon monoxide and oxygen. The reaction products leaving the reactor passed through an ice-water cooling trap and were separated by a gas–liquid separator. The liquid products were then 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 (MF), dimethoxy methane (DMM), and dimethyl ether (DME). The uncondensed gas products (O_2 , CO_2 and CO) were introduced to the GC through an on-line six-way valve and analyzed by TCD detection with a TDX-01 packed column.

3. Results and discussion

3.1. Catalytic activity of the carbon-supported Wacker-type catalysts

The catalysts prepared in different impregnation sequences and using different solvents were tested in the oxidative carbonylation of methanol to DMC over a range of reaction temperature: 90–160 °C. The results concerning the catalytic activity for the catalytic conversion of methanol to DMC are shown in Fig. 1. The catalytic activity is deeply affected by the impregnation solvent. The conversion values obtained with the catalysts prepared using ethanol as the impregnation solvent are always higher than the ones measured with the aqueous solution impregnated

samples. CAT-A displayed the best performance for DMC synthesis and a high conversion of 17.2% was achieved at the reaction temperature of 140 °C. However, the effect of the impregnation order is found to be dependent on the solvent used in the preparation procedures. For the samples prepared using ethanol as the impregnation solvent, the catalyst with the first impregnation of KOAc presents a much higher activity for methanol oxidative carbonylation than the one with the $PdCl_2/CuCl_2$ first. In comparison, a higher activity is observed on the catalyst with the first impregnation of $PdCl_2/CuCl_2$ for the catalysts prepared using water as the solvent.

The results concerning the product selectivity based on the conversion of methanol and carbon monoxide measured at temperature of 140 °C are shown in Fig. 2. The effects of the impregnation sequence and solvent on the product selectivity for the four catalysts are less important than the effects on the catalytic activity. The selectivity to DMC based on methanol conversion ($S_{DMC/MeOH}$) was observed to be much higher than the one ($S_{DMC/CO}$) based on CO conversion over all catalysts. A high $S_{DMC/MeOH}$ value of nearly 100% was obtained over CAT-A, CAT-C, and CAT-D. In sharp contrast, the $S_{DMC/CO}$ value measured on all catalysts was always lower than 50%. Irrespective of the impregnation solvent, a higher selectivity for both $S_{DMC/MeOH}$ and $S_{DMC/CO}$ was observed for the catalysts prepared by impregnation KOAc first. This observation suggests that the effect on the product selectivity for the impregnation order displayed is more important than the effect with the impregnation solvent.

Evidently, the results shown in Figs. 1 and 2 have demonstrated that the impregnation procedures do exert a remarkable influence on the catalytic performance of the carbon-supported Wacker-type catalysts in vapor-phase DMC synthesis reaction. On the other hand, it should be noted that the stability of the present catalyst system in

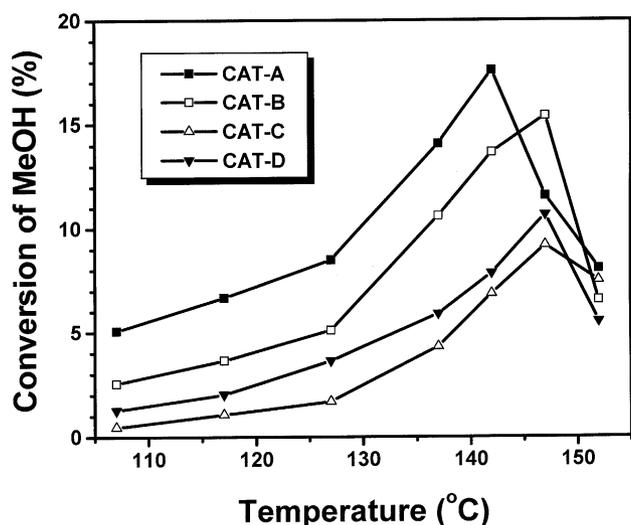


Fig. 1. The effect of reaction temperature on DMC synthesis reaction over $PdCl_2-CuCl_2-KOAc/AC$ catalysts prepared with different impregnation procedures. Reaction conditions: $CO/O_2 = 22/6$, GHSV = $1680 h^{-1}$, LHSV = $1.2 h^{-1}$.

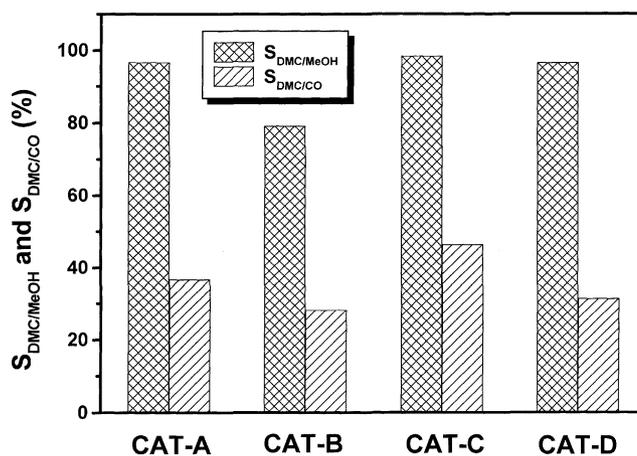


Fig. 2. The DMC selectivity based on methanol conversion ($S_{DMC/MeOH}$) and CO conversion ($S_{DMC/CO}$) over $PdCl_2-CuCl_2-KOAc/AC$ catalysts prepared with different impregnation procedures. Reaction conditions: $T = 140$ °C, $CO/O_2 = 22/6$, GHSV = $1680 h^{-1}$, LHSV = $1.2 h^{-1}$.

vapor-phase DMC synthesis was found to be poor, probably due to the loss of surface chloride with time on stream. It has been reported that the main reason of deactivation of supported copper chloride catalysts in DMC synthesis could be the loss of surface chloride [8,13]. In the present case, the catalytic performance of the as-prepared carbon-supported Wacker-type catalysts would achieve a steady state after 5 h on stream; however, the activity of the catalysts started to drop markedly after 11–15 h on stream. Nevertheless, it is notable that the selectivity for DMC production based on methanol conversion remained very high over all the time range of the reaction. A detailed investigation to elucidate the mechanism of the deactivation is currently under way and will be reported in another paper.

3.2. Characterization of the Wacker-type catalysts

The physicochemical properties were measured for the catalyst prepared by varying the impregnation sequence and solvent in the preparation procedure. Table 1 summarizes the textural results for the four Wacker-type catalysts obtained by varying the preparation procedures. Note that the data for the activated carbon support are also included. The carbon support and the four carbon-supported catalysts have almost the same pore size distribution (PSD) data, as shown in Table 1. Other N_2 adsorption data, such as BET surface area, the micropore surface area and the external surface area, were subjected to a dramatic decrease upon the introduction of the Wacker-type components. The results in Table 1 also demonstrate that the impregnation of the Wacker-type components would cause the loss of the pore volume of the carbon support. From a comparison of the micropore surface area and external surface area data of these catalyst samples, one can find that the loss in the total surface area of CAT-A is mainly due to the decrease in the external surface area of the carbon support. A more dramatic loss of the micropore surface area as compared to the external surface area were observed for CAT-B, CAT-C, and CAT-D. Hence, this observation indicates that the active component of CAT-A exist mainly on the external surface of the carbon support, whereas a much lower amount of the active component is present on the external surface of the carbon support for the other three catalysts.

Table 1

Physicochemical characterization of the Wacker-type catalysts prepared with different impregnation procedures

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{external} (m^2/g)	V (ml/g)	Pore size (nm)
AC	1282.6	804.3	478.3	0.64	2.00
CAT-A	1104.1	744.4	359.7	0.56	2.04
CAT-B	1075.6	651.4	424.2	0.54	2.04
CAT-C	1119.8	691.3	428.5	0.56	2.01
CAT-D	998.2	616.4	381.8	0.50	2.00

The data for the activated carbon support are also included.

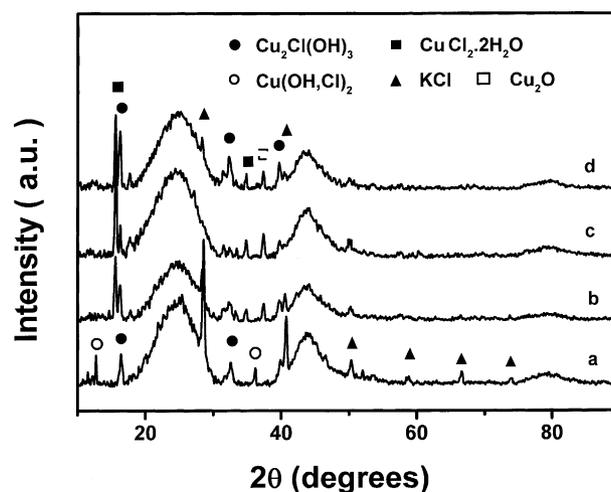


Fig. 3. X-ray diffractograms of the $\text{PdCl}_2\text{-CuCl}_2\text{-KOAc/AC}$ catalysts: (a) CAT-A, (b) CAT-B, (c) CAT-C, (d) CAT-D.

To establish a correlation between the catalytic performance and the active phase, we recorded the XRD patterns of the catalysts prepared with different impregnation order and solvents; they are shown in Fig. 3. No peaks related to Pd species can be observed, indicating a highly dispersed nature for palladium on the carbon support in all catalysts. In addition to the broad peaks due to the amorphous support, diffraction peaks with various intensities corresponding to $\text{Cu}_2\text{Cl(OH)}_3$, KCl, Cu(OH,Cl)_2 , $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ and Cu_2O were observed. One can see that the diffraction patterns attributed to $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, $\text{Cu}_2\text{Cl(OH)}_3$, KCl and Cu_2O phases were present on the samples CAT-B, CAT-C, and CAT-D, whereas the formation of $\text{Cu}_2\text{Cl(OH)}_3$, KCl and Cu(OH,Cl)_2 phases was observed on the sample of CAT-A. While all catalysts present the same copper phase corresponding to $\text{Cu}_2\text{Cl(OH)}_3$ species with similar intensity, the presence of additional copper phases such as Cu(OH,Cl)_2 or $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ demonstrates unambiguously the dramatic influence of the impregnation order and solvent on the phase compositions of the as-prepared Wacker-type catalysts. It has been previously suggested that $\text{Cu}_2\text{Cl(OH)}_3$ is the active phase for gas-phase DMC synthesis [7,10,13]. Hence, the present XRD results suggest that the dramatic difference in the catalytic performance for the present catalyst systems may be closely related to the presence of additional copper phases over the catalyst obtained by different procedures.

TPR experiments gave very useful information concerning the influence of the impregnation parameters on the reducibility of the Wacker-type active species supported on the activated carbon. Fig. 4 shows the results of TPR measurements of the parent carbon support as well as the reference monometallic catalysts of $\text{PdCl}_2\text{-KOAc/AC}$, and $\text{CuCl}_2\text{-KOAc/AC}$ in a temperature range from 25 to 750 °C. For the sake of comparison, the TPR profiles of pure CuCl_2 and CuCl reference compounds are also included. The presence of two-step reduction peaks attributed to the reduction of cupric species in the TPR profile of CuCl_2 and the

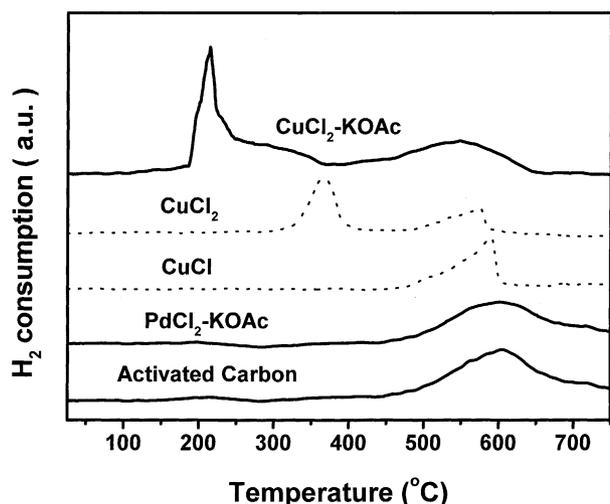


Fig. 4. TPR profiles of the $\text{PdCl}_2\text{-KOAc/AC}$ and $\text{CuCl}_2\text{-KOAc/AC}$ reference catalysts with those of pure CuCl_2 and CuCl as reference compounds.

presence of a single reduction peak due to the cuprous species in the TPR profile of CuCl are in accordance with the literature [17]. The broad peak at 600°C for the parent activated carbon was associated with the reduction of surface oxygen groups on the carbon support. The absence of any lower reduction peaks at temperatures lower than 600°C for reference sample $\text{PdCl}_2\text{-KOAc/AC}$ suggests the conversion of PdCl_2 compounds into metallic Pd species over the carbon support in the fresh catalyst. The formation of Pd metal particles in the present study is consistent with the findings in previous EXAFS studies on a carbon-supported $\text{PdCl}_2\text{-CuCl}_2$ system by Yamamoto et al. [18]. The fact that the two reduction peaks corresponding to cupric species are shifted to a lower temperature around 214°C with a shoulder at the higher temperature side for $\text{CuCl}_2\text{-KOAc/AC}$ as compared to CuCl_2 and CuCl suggests the presence of strong chemical interactions between Cu species and the carbon support.

The TPR results of all four Wacker-type catalysts prepared from different impregnation strategies are compared in Fig. 5. One can see that the reduction peaks for the Cu species are further shifted to low temperatures around 100°C with a broad shoulder at the higher temperature side in all catalysts as compared to $\text{CuCl}_2\text{-KOAc/AC}$ reference catalyst as shown in Fig. 4, suggesting that the presence of palladium species in the catalysts can significantly enhance the reducibility of the copper phases in all catalysts. Coupled with the TPR results reported in Fig. 4, the low temperature reduction peak located at around 100°C can be ascribed to the reduction of Cu^{2+} to Cu^+ species, whereas the broad peak at higher temperatures above 200°C could be due to the further reduction of Cu^+ species into metallic copper. Notice that the first reduction peak is observed to shift to a higher temperature in the TPR profiles for all four catalysts in the order of $\text{CAT-A} < \text{CAT-B} < \text{CAT-C} < \text{CAT-D}$, suggesting the important effect of the impregnation procedure

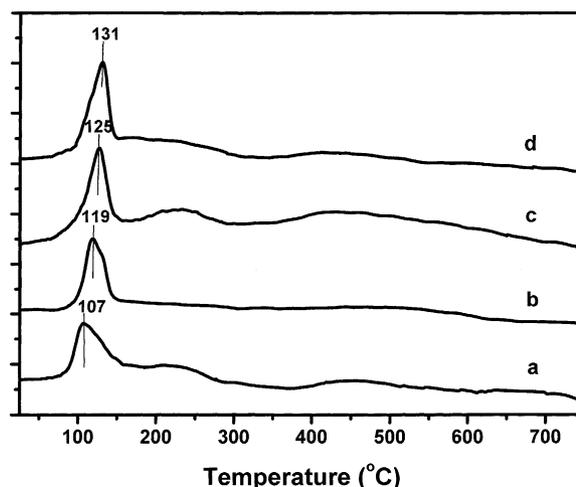


Fig. 5. TPR profiles of the $\text{PdCl}_2\text{-CuCl}_2\text{-KOAc/AC}$ catalysts: (a) CAT-A, (b) CAT-B, (c) CAT-C, (d) CAT-D.

on the reducibility of the Wacker-type catalysts. It is also interesting to note that an excellent correlation can be made between the temperature for the maximum activity and that for the first reduction peak for the catalysts derived from different impregnation conditions. This correlation may be understood by taking into account the fact that the catalytic performance for the present reaction system is closely related to the redox nature of the active phases.

Fig. 6 compares the surface morphology of the four Wacker-type catalysts prepared with different impregnation procedures. Distinct particles in the form of irregular aggregates of various shapes and sizes are observed in all four samples. The X-ray microprobe analysis (spot, line, and surface analysis) has been carried out in different surface points, indicating that white spots consist primarily of Cu, Pd, and Cl elements. Coupled with the XRD results, it can be supposed that the white spots in the SEM micrographs correspond to crystalline particles of various copper phases containing highly dispersed Pd species. In catalysts CAT-A, CAT-B, and CAT-D, the distribution of the main active particles seems to be practically uniform, with an average size less than $1\ \mu\text{m}$. It is notable that the small active particles in CAT-B and CAT-D tend to aggregate into larger agglomerates, while the active particles in CAT-A appear to be practically better distributed over the carbon support. An absolutely different surface morphology is observed for catalyst CAT-C prepared by the first impregnation of aqueous KOAc solution. The SEM micrographs show that the randomly distributed active particles in catalyst CAT-C are much larger, in the range of $5\text{--}8\ \mu\text{m}$, while their distribution density on the external surface of the carbon support is much lower and the exterior of the carbon support is only partially covered. Thus, the present SEM results suggest that the use of ethanol impregnation is more effective than that of water in preparation of the carbon-supported Wacker-type catalysts for the generation of more uniformly distributed active-phase particles on the exterior of the carbon support.

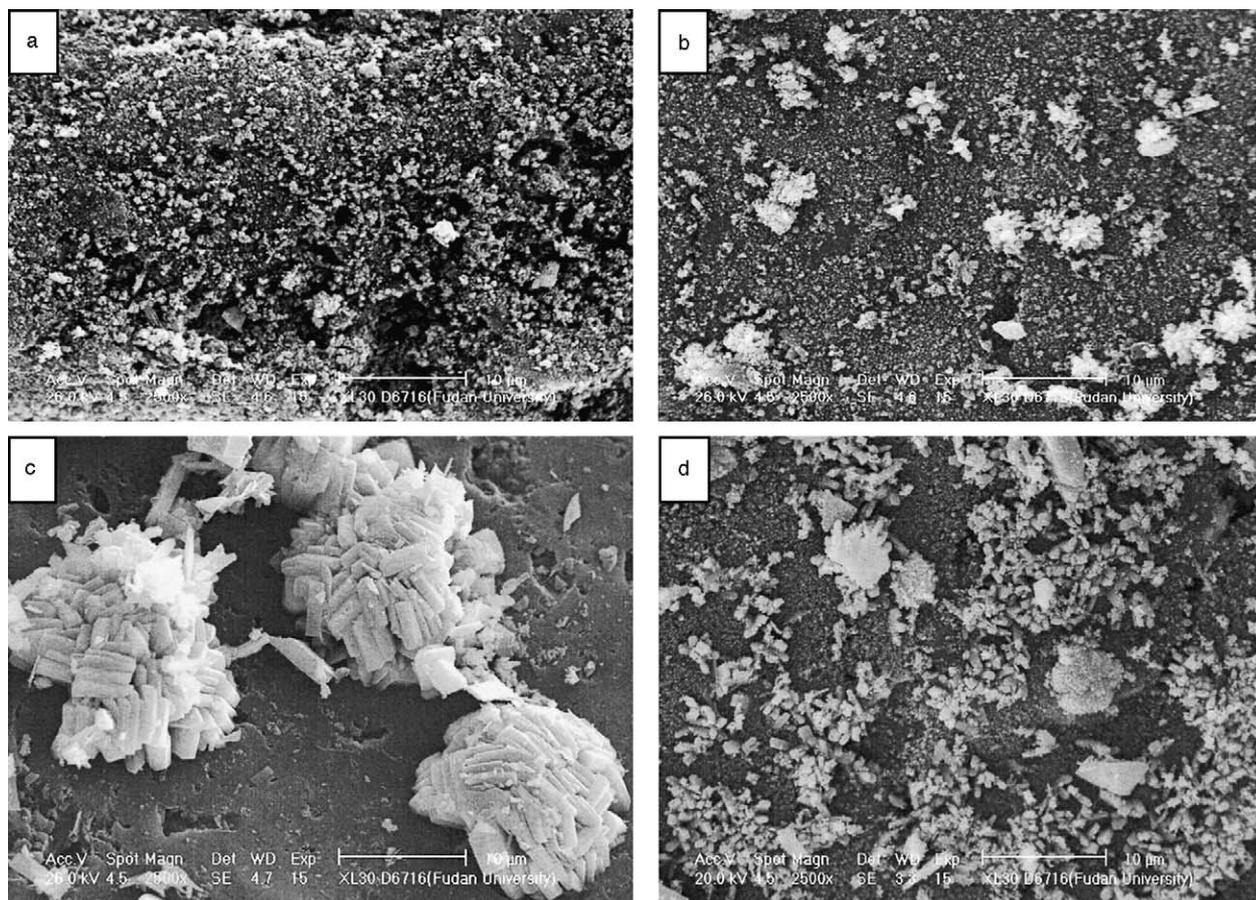


Fig. 6. SEM images of various $\text{PdCl}_2\text{-CuCl}_2\text{-KOAc/AC}$ catalysts: (a) CAT-A, (b) CAT-B, (c) CAT-C, (d) CAT-D.

EDX linescan analysis was used to determine the relative concentration of Pd, Cu, and Cl across the agglomerates of the catalyst crystallites. Typical elemental profiles for Pd, Cu, and Cl in CAT-A, CAT-B, CAT-C, and CAT-D with a linescan distance of $50\ \mu\text{m}$ are illustrated in Fig. 7. It can be seen that the Cu component profiles are almost the same as those for Pd and Cl components, confirming that the bright particles observed in Fig. 6 are composed of various copper phases containing Cu, Pd, and Cl species. This result provides direct evidence of the well-dispersed nature of Pd component in the well-defined copper phases located on the external surface of the carbon support; such evidence thus favors the catalytic synthesis of DMC through the oxidative carbonylation of methanol. The results presented in Fig. 7 also show pronounced differences in Pd, Cu, and Cl distribution for all the catalyst samples, reflecting clearly the influence of the preparation conditions on the spatial distribution of the active phases. The distribution of Pd, Cu, and Cl components across the surface of the catalyst is practically much more uniform in CAT-A than in CAT-B, CAT-C, and CAT-D. This may well explain the distinctive effect of investigated catalysts on the reaction performance in the oxidative carbonylation of methanol discussed above.

The $\text{PdCl}_2\text{-CuCl}_2$ catalysts supported on alumina, silica, and carbon supports have been used in a number of reac-

tions, such as the oxidation of CO, and synthesis of aldehydes, ketones, and ethyl dichloride [19–24]. In this study, the effect of impregnation procedures on the gas-phase DMC synthesis from oxidative carbonylation of methanol over carbon-supported $\text{PdCl}_2\text{-CuCl}_2\text{-KOAc}$ catalysts have been examined. The structural and redox properties as well as the surface morphology of the active species have also been studied using a combined characterization by BET, XRD, SEM/EDX, and TPR. The present XRD data provide evidence that at least four different types of copper phase, including $\text{Cu}_2\text{Cl}(\text{OH})_3$, $\text{Cu}(\text{OH},\text{Cl})_2$, $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, and Cu_2O species, can be formed on the carbon-supported Wacker-type catalysts by changing the preparation conditions. However, the most active and selective catalyst is CAT-A, which contains the $\text{Cu}_2\text{Cl}(\text{OH})_3$ and $\text{Cu}(\text{OH},\text{Cl})_2$ phases. This is in excellent accord with our previous results that the formation of well-defined copper solid phase, $\text{Cu}_2\text{Cl}(\text{OH})_3$, is essential for active and selective DMC synthesis [8]. In addition, the present SEM/EDX results have shown that the spatial distribution as well as the surface density of the active phase are another important aspect concerning the structural nature of the Wacker-type catalysts. Our results suggest that the high-performance catalyst is characteristic of the presence of practically uniformly distributed active-phase particles with a high surface coverage containing Pd, Cu, and Cl species.

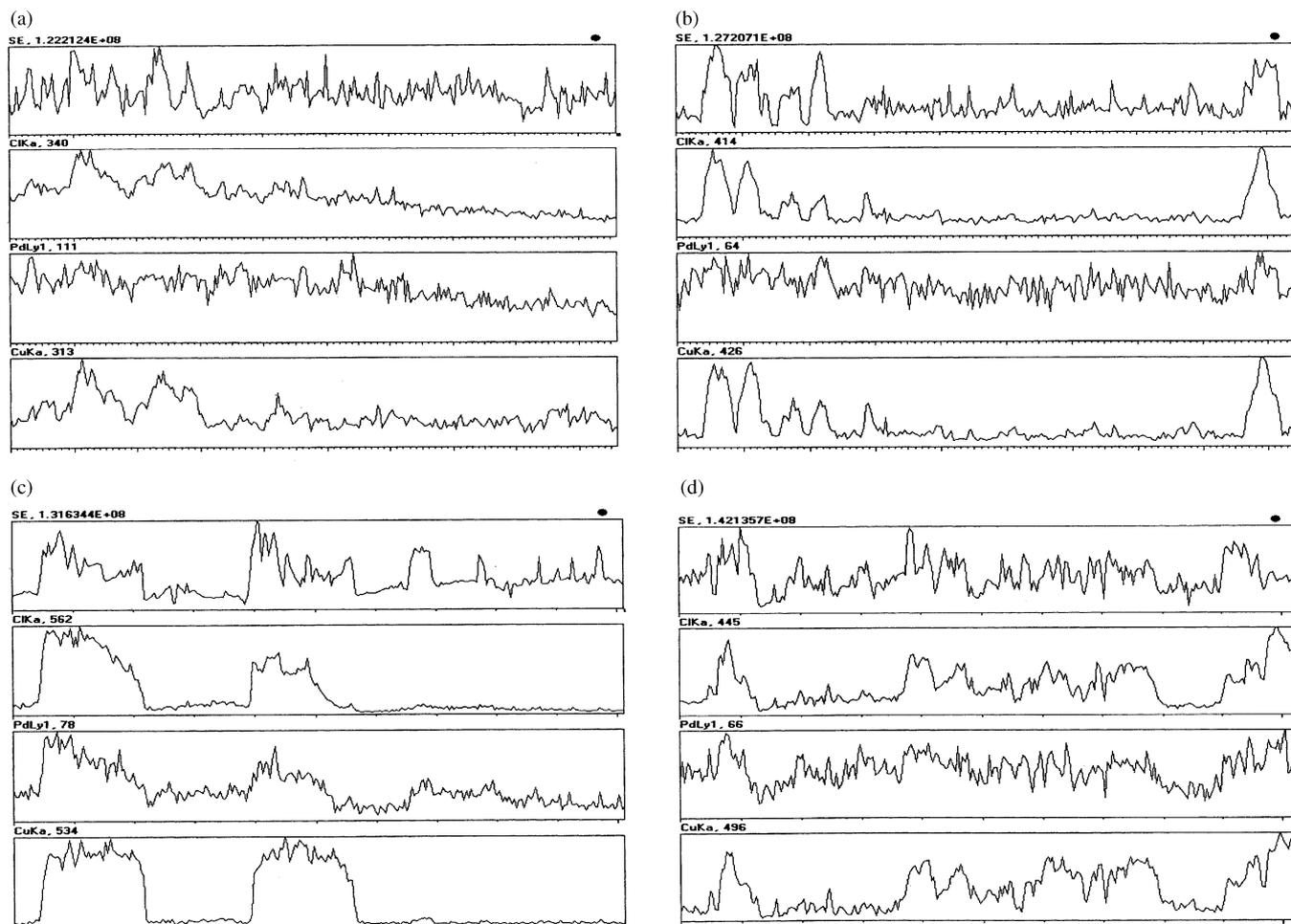


Fig. 7. Results of EDX line analysis of the $\text{PdCl}_2\text{-CuCl}_2\text{-KOAc/AC}$ catalysts: (a) CAT-A, (b) CAT-B, (c) CAT-C, (d) CAT-D.

On the other hand, most of the published reports have focused on the preparation and evaluation of the catalyst, while studies on the effects of promoters on the structure and performance of the supported Wacker-type catalyst systems are still very scarce. One recent report by Jiang et al. has investigated the effect of a series of alkali promoters including KOAc, NaOAc, and LiOAc on the performance of the carbon-supported $\text{PdCl}_2\text{-CuCl}_2$ catalysts [8], where KOAc has been claimed to be the best promoter in DMC synthesis reaction. Studies on the role of the alkali promoter have shown that KOAc plays an important role in the generation of active species during the preparation of the catalysts. It is suggested that the interaction between CH_3COOK and PdCl_2 or CuCl_2 that results in the formation of KCl can limit the loss of surface chlorine, thus leading to a prolonged lifetime of the catalyst in DMC synthesis reaction. In the present investigation, we have demonstrated that the catalyst prepared by impregnating the carbon support with KOAc followed by $\text{PdCl}_2/\text{CuCl}_2$ employing ethanol as the impregnation solvent shows a higher performance in the oxidative carbonylation of methanol. Thus the present results confirm that the use of KOAc in the present catalyst system is very

important for the effective generation of active species containing Pd, Cu, and Cl species over the carbon support. It is known that the presence of an appreciable amount of acidic functional groups on the surface of a carbon support would inhibit the formation of active $\text{Cu}_2\text{Cl}(\text{OH})_3$ phase over the carbon supports [13]. Considering that KOAc is an alkali promoter, we suggest that the main chemistry of the surface modification with KOAc in the catalyst preparation could be a neutralization of the acidic functional groups. Obviously, the interaction between the KOAc-modified carbon support and the PdCl_2 or CuCl_2 species could result in the effective formation of the well-defined active copper phase of $\text{Cu}_2\text{Cl}(\text{OH})_3$ during the catalyst preparation process.

In the conventional Wacker-type homogeneous redox system consisting of Pd and Cu for olefins oxidation, the Cu–Pd couple bridged by -Cl- species has been known to be highly reactive for the redox process of Cu(II)/Cu(I) and Pd(0)/Pd(II) at the same time [25]. Recently, the mechanism for CO oxidation in the presence of a heterogeneous $\text{PdCl}_2\text{-CuCl}_2$ catalyst is proposed to be similar to that of the homogeneous Wacker process. The overall chemistry of oxidation carbonylation of methanol has been suggested to

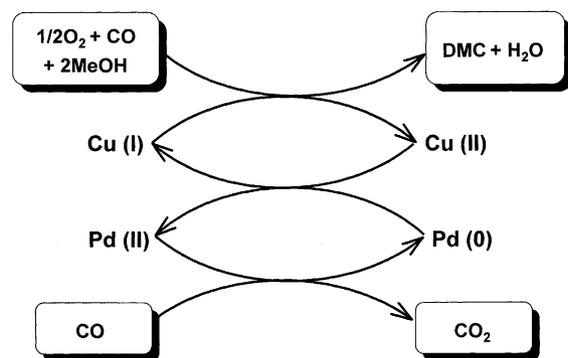


Fig. 8. Schematic presentation of the carbon-supported Wacker-type catalysis for the oxidative carbonylation of methanol.

be similar to the well-known CO oxidation Wacker process in the presence of a carbon-supported $\text{PdCl}_2\text{--CuCl}_2$ catalyst [9]. Therefore, it is highly possible that the oxidative carbonylation of methanol proceeds by a redox mechanism involving the Cu(II)/Cu(I) and Pd(0)/Pd(II) redox couples as illustrated in Fig. 8. For the present Wacker-type catalyst systems, the easier reducibility of the active copper phase compared to other Cu(II) species or copper phases as revealed by the appearance of the TPR peak at a lower temperature in the present TPR measurements is in good agreement with the TPR data reported by Rouco [26]. The high reducibility of the cupric species in the present Wacker-type catalysts can be attributed to the presence of palladium species in close vicinity of the copper species in the catalyst system, as supported by the SEM/EDXS data. As a result, the reaction can proceed more effectively on the surface of the palladium-doped copper hydroxychloride ($\text{Cu}_2\text{Cl(OH)}_3$) islands present on the carbon supports.

4. Conclusions

The catalysts prepared by varying impregnation solvents and sequences of the active components have been evaluated and characterized in the DMC synthesis reaction from oxidative carbonylation of methanol. It is found that the impregnation order and solvent is a very important parameter to control the location and the distribution of the active phase and consequently the catalytic activity. The carbon-supported Wacker-type catalyst (CAT-A) with copper and palladium chloride species mainly distributed on the exterior of the carbon support with a high surface concentration of active copper phases was prepared by procedures in which activated carbon was impregnated first by an alcoholic solution of potassium promoter. The presence of a high surface con-

centration of copper and palladium sites in close vicinity in the CAT-A sample results in the best catalytic performance in the catalytic oxidative carbonylation of methanol.

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