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Mesoporous bimetallic $PdCl_2$-$CuCl_2$ catalysts for dimethyl carbonate synthesis by vapor phase oxidative carbonylation of methanol

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Abstract

Dimethyl carbonate (DMC) synthesis reaction by oxidative carbonylation of methanol has been studied in a flow reaction system at atmospheric pressure in the presence of quaternary ammonium salt (QAS)-promoted bimetallic $PdCl_2$-$CuCl_2$ catalyst system supported on mesoporous HMS silica. The effects of the various QAS promoters, the promoter doping level and the Cu/Pd mole ratio were investigated, as well as the reaction conditions on the catalytic reactivates. The results showed that the tetrabutylammonium bromide (TBAB) promoted $PdCl_2$-$CuCl_2$/HMS catalyst system has the best catalytic performance. The characterization of $PdCl_2$-$CuCl_2$-TBAB/HMS catalysts was performed by means of BET, X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The essential role of TBAB promoter is to facilitate the Pd(0)/Pd(II) and Cu(II)/Cu(I) redox processes. The formation of substantial amounts of surface stabilized cuprous species on the bimetallic HMS catalysts may account for the significant enhancement of the catalytic performance in DMC synthesis.

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Keywords: Oxidative carbonylation; Dimethyl carbonate (DMC); Bimetallic catalyst; HMS silica

1. Introduction

Dimethyl carbonate (DMC) has recently attracted much attention as an important green chemical in relation to environmental problems [1]. DMC has a high oxygen content and can be used as a promising fuel additive in gasoline. DMC is also a novel reagent for methylation and carbonylation; it can replace toxic intermediates such as phosgene and dimethyl sulfate, which the chemical industry has been trying to ease out of use [2]. The best way to produce DMC is by oxidative carbonylation of methanol. Although a liquid slurry process employing a copper chloride catalyst has been commercialized [3], a gas phase process is more desirable because the copper chloride is highly corrosive in the liquid phase [4].

A number of investigations have been focused on the use of a supported copper catalyst to synthesis DMC via gas phase oxidative carbonylation of methanol [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. However, the active carbon is combustible and too brittle, so that a chemically inert support with improved

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mechanical strength and well-defined structure is desired. As a result, efforts dedicated to develop more suitable supports other than active carbon for more efficient gas phase oxidative carbonylation of methanol to DMC have been made [6,7]. Recently, the use of the mesoporous MCM-41 silica as a promising support for the gas phase oxidative carbonylation of methanol to DMC has been reported [8]. It is shown that the CuCl/MCM-41 catalyst prepared by a solid phase ion-exchange method had 100% selectivity of DMC based on methanol and thus a moderate conversion of methanol can be achieved. However, this method is quite elaborate and time-consuming. Moreover, the use of highly expensive high purity He as a purging gas is required. On the other hand, it is known that the well-known family of M41S molecular sieves offers a wide range of catalytically attractive mesoporous materials with varied structural and textural features. Hence, it would be highly interesting to further explore the possible application of the catalytically attractive mesoporous materials in this catalyst system.

HMS silica is another type of mesoporous material claimed to have larger pores, to be more stable and to have thicker pore walls than their MCM-41 counterparts [9]. We have recently demonstrated that HMS silica is a promising support for vanadia catalysts in the oxidative dehydrogenation of propane to propylene [10]. In the present work, we report a novel bimetallic $PdCl_2$-$CuCl_2$ catalytic system employing mesoporous HMS silica as support for gas phase oxidative carbonylation of methanol at atmospheric pressure. The characterization of $PdCl_2$-$CuCl_2$-tetrabutylammonium bromide (TBAB)/HMS catalysts has been performed by means of BET, X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. In addition, the essential role of TBAB in the $PdCl_2$-$CuCl_2$ catalyst system for the DMC production has been investigated.

2. Experimental

2.1. Catalyst preparation

Mesoporous HMS silica has been prepared by hydrolysis of TEOS in the presence of dodecylamine ($C_{12}H_{25}NH_2$), water, and ethanol as a cosolvent [11]. The use of a cosolvent improved template solubility. In a typical preparation, TEOS was added to a vigorously stirred solution of dodecylamine in ethanol and deionized water, affording a reaction mixture of the following molar composition: 1.0 TEOS:0.27 $C_{12}H_{25}NH_2$:9.09 EtOH:29.6 H_2O. The reaction mixture was aged at ambient temperature for 18 h in order to obtain the hexagonal mesoporous silica. The obtained crystalline products were recovered by filtration, washed with deionized water, air-dried, and finally calcined in air at 630 °C for 4 h.

The catalysts have been prepared by impregnating the 40–60-mesh HMS supports with an aqueous solution of mixed metal chlorides ($PdCl_2$-$CuCl_2$) with or without quaternary ammonium salt (QAS) at room temperature. Water was removed by heating, and drying was carried out at 120 °C for 12 h. The loading of Pd in all catalysts was kept at 0.45 wt.%. Three quaternary ammonium salts including tetraethylammonium chloride (TEAC), TBAB, and cetyltrimethylammonium bromide (CTAB) were investigated as the possible promoters.

2.2. Catalyst characterization

The textural parameters have been measured using the BET method by N_2 adsorption and desorption at 77 K in a Micromeritics TriStar system. The BET surface area, total pore volume and average pore radius were obtained from the adsorption isotherms. The XRD characterization of the catalysts was carried out on a Germany Bruker D8 Advance X-ray diffractometer using nickel filtered Cu Kα radiation ($\lambda = 1.5418$ Å) in the 2θ ranges from 10 to 80°. The XPS experiments were carried out on a Perkin-Elmer PHI 5000C ESCA system using Al Kα radiation (1486.6 eV). The spectrometer was operated at the resolution of about 1 eV. DRIFT characterization of the catalysts was performed using a Bruker Vector 22 instrument equipped with a DTGS detector and a KBr beam splitter. Powdered catalysts were placed in a sample cup inside a Harrick diffuse reflectance cell which was equipped with CaF_2 windows and a thermocouple mount that allowed direct measurement of the sample temperature [10]. All spectra were collected under 100 Torr CO at 100 °C in flowing N_2 by using the spectrum acquired under pure N_2 as background spectrum.

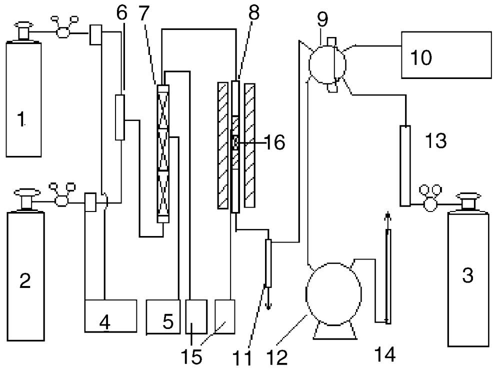

Fig. 1. Schematic diagram of the experimental apparatus. (1) CO cylinder; (2) air cylinder; (3) H_2 cylinder; (4) mass flow controller; (5) syringe pump; (6) gas mixture; (7) preheater; (8) reactor; (9) six-way valve; (10) gas chromatography.

2.3. Oxidative carbonylation of methanol

The 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. The reactor was made of stainless steel tube; it had an inner diameter of 10 mm and a length of 40 cm. The experimental apparatus is schematically illustrated in Fig. 1. About 1.0 g of catalyst sample (∼ 2 ml) was placed in the tubular reactor and positioned between two layers of glass beads. Methanol was introduced by using a syringe pump into the pre-heater, it was vaporized there and then entered the reactor together with carbon monoxide and air. The flow rates of carbon monoxide and air were controlled by a mass flow controller. The reaction products 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. It contained RSL 160 liquid phases for the separation of methanol, DMC, methyl formate $HCOOCH_3$ (MF), dimethoxy methane $CH_2(OCH_3)_2$ (DMM), and dimethyl ether CH_3OCH_3 (DME). The uncondensed gas products (N_2, O_2, CO_2 and CO) were introduced to the GC through an on-line six-way valve and analyzed by a TCD detector with a TDX-01 packed column.

3. Results and discussion

3.1. Oxidative carbonylation of methanol

3.1.1. Effect of various promoters on DMC synthesis

Fig. 2 shows the effect of QAS on the catalytic activities of $PdCl_2$-$CuCl_2$-QAS/HMS catalysts for the gas phase oxidative carbonylation of methanol to DMC at atmospheric pressure. The $PdCl_2$-$CuCl_2$/HMS catalyst in the absence of QAS can only afford formation of trace amounts of DMC in the oxidative carbonylation reaction. A similar result has been obtained

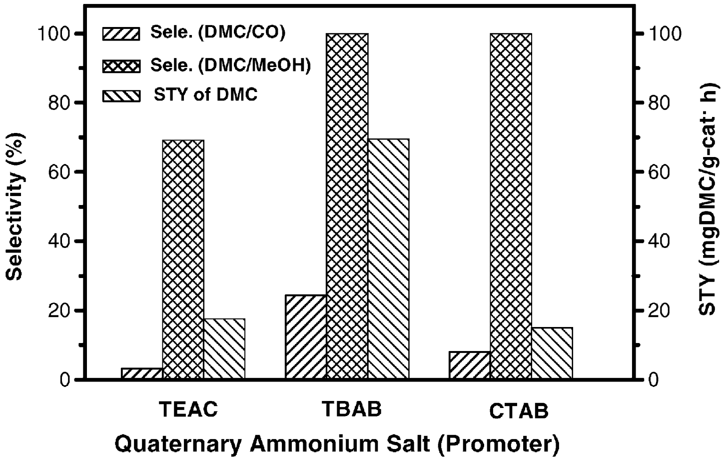

Fig. 2. Promotional effect of various quaternary ammonium salts (QASs) on the DMC synthesis reaction over $PdCl_2$-$CuCl_2$-QAS/HMS (0.11 wt.% Pd) catalysts at 393 K. Conditions: CO, 8 ml/ min; $CO/O_2 = 2$; GHSV $= 700\,h^{-1}$; molar ratio of Pd/Cu/QAS = 1/20/12.

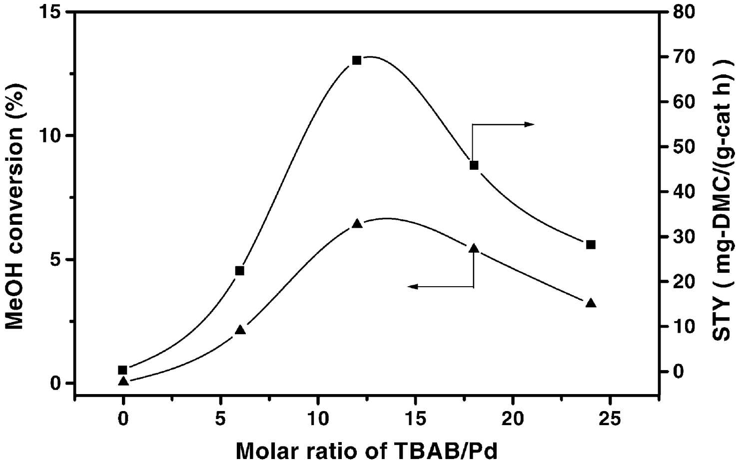

Fig. 3. The influence of TBAB addition on the catalytic performance of the $PdCl_2$-$CuCl_2$-TBAB/HMS (0.11 wt.% Pd) catalysts. Reaction conditions: CO, 8 ml/min; $CO/O_2 = 2$; GHSV = 700 h^{-1}; temperature ∼393 K.

on the active carbon-supported $PdCl_2$-$CuCl_2$ catalyst in gas phase DMC synthesis reaction by Wang et al. [12]. However, it is found that the poor catalytic performance of the $PdCl_2$-$CuCl_2$/HMS catalyst can be significantly enhanced by the addition of QAS into the catalyst system. Among the three QAS promoters investigated, the TBAB-promoted catalyst has shown the best catalytic performance, it provides the highest conversion of methanol equal to 6.4%. This catalyst can afford a high DMC productivity of about 69.5 mg DMC/(g cat h) in the DMC synthesis reaction. In comparison with the TBAB promoter, the catalysts promoted by TEAC and CTAB can only afford a STY of 17.5 and 14.9 mg DMC/(g cat h), respectively. Moreover, both TBAB- and CTAB-promoted catalysts give a high selectivity of 100% to DMC based on MeOH conversion, while the TEAC modified catalyst can only afford a low selectivity of 69.2% to DMC based on MeOH. It is also noticeable that all catalysts demonstrated a relatively low selectivity of DMC on CO, indicating the presence of a substantial combustion loss of CO in the present $PdCl_2$-$CuCl_2$-QAS/HMS catalyzed DMC synthesis reaction.

3.1.2. Effect of TBAB addition on DMC synthesis

To gain further insight into the influence of TBAB on the catalytic behavior of the $PdCl_2$-$CuCl_2$ bimetallic catalyst system, the catalytic activities of the DMC synthesis reaction over the TBAB-promoted $PdCl_2$-$CuCl_2$/HMS catalysts were investigated as a function of varying Pd/Cu/TBAB mole ratio. Fig. 3 shows the catalytic performance of the DMC synthesis reaction over the $PdCl_2$-$CuCl_2$-TBAB/HMS catalysts as a function of the mole ratio of TBAB/Pd in the range from 0 to ∼24/1, based on a fixed Pd/Cu ratio of 1/20. It is clear that the rate of the DMC formation over unmodified bimetallic HMS catalysts is much lower compared to those over the TBAB-modified bimetallic catalysts. Upon TBAB addition, the reaction activity is greatly enhanced over the bimetallic catalyst catalysts. There is a maximum in DMC formation with increasing TBAB content. The highest space–time yield (STY) of 69.5 mg DMC/(g cat h) is obtained at a 6.4% methanol conversion over the catalyst with a mole ratio of Pd/Cu/TBAB = 1/20/12. In all the above conditions, a high selectivity of up to 99% for DMC synthesis based on methanol conversion is obtained.

3.1.3. Effect of ratio of Cu/Pd mole ratio on DMC synthesis

The synthesis of DMC from MeOH, CO and O_2 mainly relies on the redox reactions between Cu^+/Cu^{2+} [3]. Therefore, the catalytic activities of the catalyst were further investigated as a function of Cu content based on a fixed Pd/TBAB mole ratio of 1/12. The catalytic performance of the DMC synthesis reaction over the $PdCl_2$-$CuCl_2$-TBAB/HMS

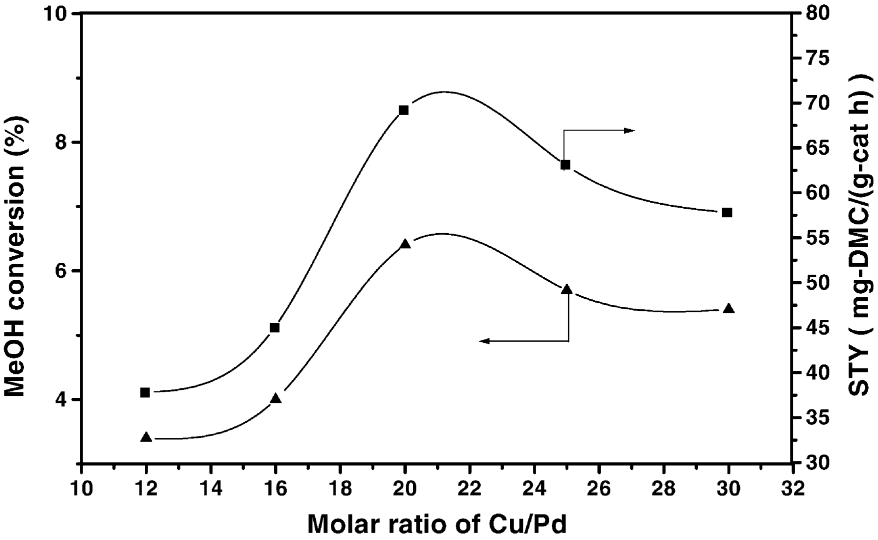

Fig. 4. The effect of copper concentration on the catalytic performance of the $PdCl_2$-$CuCl_2$-TBAB/HMS (0.11 wt.% Pd) catalysts for DMC synthesis at 393 K. Reaction conditions: CO, 8 ml/min; $CO/O_2 = 2$; $GHSV = 700\,h^{-1}$.

catalysts as a function of the mole ratio of Cu/Pd is shown in Fig. 4. When the Cu content is very low, the activity of the catalyst is poor. It is seen that a rapid increase of the rate of DMC formation over the $PdCl_2$-$CuCl_2$-TBAB/HMS catalysts can be achieved by increasing the Cu/Pd mole ratio up to 20/1. However, a further increasing of the Cu/Pd mole ratio would result in the decrease of the rate of the DMC formation over the HMS catalysts, suggesting the presence of a synergetic effect for the active components of palladium and copper on the catalytic performance in the present bimetallic catalyst system. The results demonstrate that the catalyst with Cu/Pd mole ratio of 20/1 shows the best catalytic performance.

3.1.4. *Effect of the reaction temperature on DMC synthesis*

The effect of the reaction temperature on the catalytic performance of the $PdCl_2$-$CuCl_2$-TBAB/HMS catalyst with a Pd/Cu/TBAB mole ratio of 1/20/12 is also investigated in this work. The methanol conversion as well as the STY of DMC as a function of the reaction temperature on the $PdCl_2$-$CuCl_2$-TBAB/HMS catalyst is shown in Fig. 5. For the sake of comparison, the catalytic data for the same catalytic system supported on active carbon are also presented. When the temperature was raised from 100 to 120 °C, both the methanol conversion and STY of DMC of the HMS-supported catalyst are sharply increased first at 110 °C, and then approach a maximum at 120 °C. A further increase in the reaction temperature results in the gradually decrease of the catalytic activity. In comparison, the reaction temperature has only displayed a moderate effect on the catalytic performance of the active carbon-supported catalyst. With increasing of the reaction temperature, there is a slow but continuous increase in the methanol conversion and STY of DMC on the carbon-supported catalyst. It should also be noted that, in all temperature ranges investigated, the HMS-supported catalyst exhibited considerably higher catalytic activity than the active carbon-supported one in terms of methanol conversion and STY of DMC, implying that the nature of the support may play a critical role in the DMC synthesis reaction.

3.2. *Catalyst characterization*

3.2.1. *Effect of TBAB introduction on the structural properties of the catalyst*

The specific surface area (S_{BET}) of the parent HMS has been measured to be 866 m^2/g and the cumulative pore volume is 0.67 cm^3/g. Table 1 summarizes the textural results for the $PdCl_2$-$CuCl_2$-TBAB loaded catalysts with various catalyst compositions.

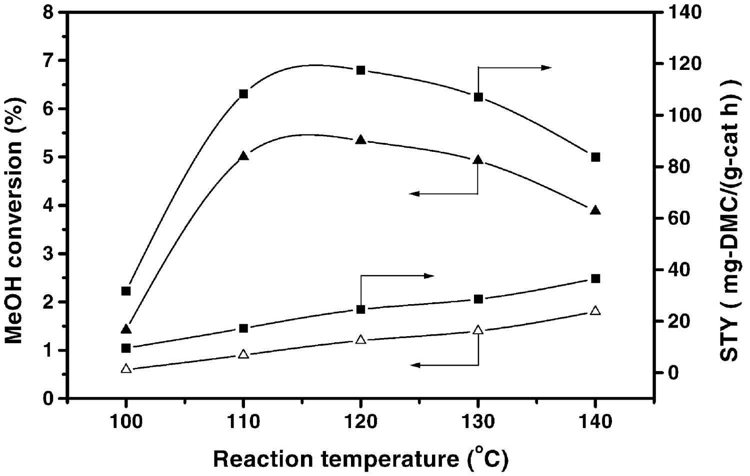

Fig. 5. Effect of reaction temperature on the catalytic performance over a HMS (■, ▲) and an active carbon (□, △) supported $PdCl_2$-$CuCl_2$-TBAB catalyst with a molar ratio of Pd/Cu/TBAB = 1/20/12 (0.11 wt.% Pd) for DMC synthesis. Reaction conditions: CO, 16 ml/min; $CO/O_2 = 2$; GHSV = 1400 h^{-1}.

It is seen that the S_{BET} of the catalysts prepared by the impregnation of catalytic components is lower than that of the unloaded supports and decreases with increasing $PdCl_2$-$CuCl_2$-TBAB content. The results in Table 1 also demonstrate that the introduction of $PdCl_2$-$CuCl_2$-TBAB would cause some loss of the pore volume of the HMS materials. When one keeps the loading of $PdCl_2$ and TBAB unchanged, there is a continuous decrease in the surface area and the cumulative pore volume of the catalysts with the increase of $CuCl_2$ loading. However, the introduction of TBAB appears to give rise to a more significant modification of the textural structure of the HMS catalysts. With the loading of $PdCl_2$ and $CuCl_2$ kept constant, an increase of TBAB would result in a more dramatic loss of the original surface area and pore volume of the HMS catalysts.

Table 1
Physico-chemical properties of the $PdCl_2$-$CuCl_2$-TBAB/HMS catalysts including various amounts of $CuCl_2$ and TBAB

$PdCl_2/CuCl_2$/TBAB	BET area (m^2/g)	Pore volume (cm^3/g)
Pure HMS	866	0.67
1/12/12	359	0.39
1/16/12	367	0.38
1/20/12	350	0.38
1/25/12	328	0.36
1/30/12	305	0.35
1/20/0	597	0.44
1/20/6	429	0.35
1/20/12	350	0.38
1/20/18	221	0.18
1/20/24	132	0.11

In order to get new insight into the effect of TBAB introduction on the structural properties of the $PdCl_2$-$CuCl_2$-TBAB/HMS catalysts, X-ray diffraction was conducted for the HMS-supported catalysts with various TBAB/Pd molar ratios. Fig. 6 presents the XRD profiles as a function of TBAB/Pd molar ratio obtained for $PdCl_2$-$CuCl_2$-TBAB/HMS catalysts. The powder X-ray diffraction patterns for the pure HMS samples show the characteristic low-angle diffraction peak attributable to the d_{100} reflection assuming a hexagonal lattice, typical of HMS solids. For the samples prepared by impregnating the $PdCl_2$-$CuCl_2$-TBAB, the gradual attenuation in intensity of the d_{100} peak is observed with the increase of TBAB loading. It is notable that the d_{100} peak is greatly attenuated on the $PdCl_2$-$CuCl_2$-TBAB/HMS catalysts upon the introduction of $PdCl_2$-$CuCl_2$-TBAB species. This phenomenon may be accounted for by considering that the blocking of the hexagonal pore walls of the HMS materials occurred upon TBAB introduction, especially when the TBAB content is very high [12]. In all cases,

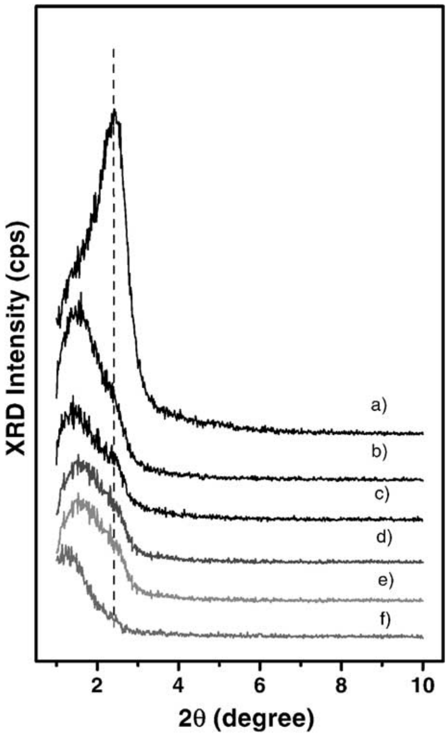

Fig. 6. XRD patterns of the $PdCl_2$-$CuCl_2$-TBAB/HMS catalysts (0.11 wt.% Pd, $n_{Cu/Pd} = 20$) as a function of TBAB/Pd mole ratio. (a) Parent HMS; (b) TBAB/Pd = 0; (c) TBAB/Pd = 6; (d) TBAB/Pd = 12; (e) TBAB/Pd = 18; and (f) TBAB/Pd = 24.

the absence of diffraction peaks at 2θ angles higher than 10° seems to exclude the presence of crystalline phase associated with Cu or Pd species, thus pointing to a highly dispersed nature of the Pd and Cu species.

3.2.2. Effect of TBAB introduction on the chemical properties of the catalyst

The chemical state of the catalyst components at the surface has been evaluated by XPS in $PdCl_2$-$CuCl_2$-TBAB/HMS samples with increasing TBAB addition. For the sake of clarity the Cu $2p_{3/2}$ core-level spectra of the $PdCl_2$-$CuCl_2$-TBAB/HMS samples as a function of TBAB/Pd ratio are displayed in Fig. 7. From these spectra it is clear that the Cu $2p_{3/2}$ profile changed drastically upon TBAB addition. The sample without TBAB promotion shows the principal Cu $2p_{3/2}$ line centered around 934.8 eV, which is characteristic of Cu^{2+} species [13–15]. The Cu^{2+} ions are also easily identified by the satellite peak, placed around 943.2 eV, whose origin is complex [16–18]. In marked contrast to the catalyst without TBAB addition, the disappearance of the satellite line and the simultaneous shift of the principal Cu $2p_{3/2}$ peak to a lower BE value of 932.9 eV upon TBAB addition show that the copper species are reduced to Cu^+ in all TBAB modified HMS catalysts.

The N 1s spectra of the samples with increasing TBAB containing are also presented in Fig. 7, this may allow a more clear insight into the effect of TBAB addition on the nature of the copper species. The BE of the N 1s peak is found to be located at 401.6 eV, which corresponds to the characteristic value of the typical N species in standard ammonium compounds [19]. This observation, however, suggests that the reduction of the Cu species may not be due to the presence of TBAB in the $PdCl_2$-$CuCl_2$/HMS catalyst system. On the other hand, it has been reported that some photoreduction of CuO phase in a series of sol–gel derived CuO-SiO_2 samples might occur during the XPS analysis [20]. Thus the present XPS analysis on the state of the Cu species present on the HMS catalysts provides evidence that a highly reducible nature of the copper species can be achieved for the bimetallic $CuCl_2$-$PdCl_2$ catalytic system with TBAB addition.

3.2.3. DRIFT analysis of the TBAB modified $PdCl_2$-$CuCl_2$/HMS catalyst systems

Further clarification is needed of the modification function of the TBAB on the $PdCl_2$-$CuCl_2$-TBAB/HMS catalyst system. So IR characterization using DRIFT technique has been applied to follow the surface nature of the catalytic system. Fig. 8 shows DRIFT spectra of the parent HMS support and the HMS-supported $PdCl_2$-$CuCl_2$-TBAB catalyst with a Pd/Cu/TBAB mole ratio of 1/20/12 under N_2 atmosphere in the 4000–400 cm^{-1} range. For the sake of convenience, the differential spectrum of the HMS-supported $PdCl_2$-$CuCl_2$-TBAB catalyst with respect to the HMS support and the spectrum of a pure TBAB salt are also included in Fig. 8c and d, respectively. It is shown in Fig. 8a that silanol groups having OH stretching vibrations at 3742 cm^{-1} (sharp band), 3715 cm^{-1} (shoulder band) and around 3550 cm^{-1} (broad band) are clearly identified on pure HMS. The sharp band at 3742 cm^{-1} is ascribed to the isolated terminal silanol groups present on the HMS; the bands at 3550 and 3715 cm^{-1} are assigned to

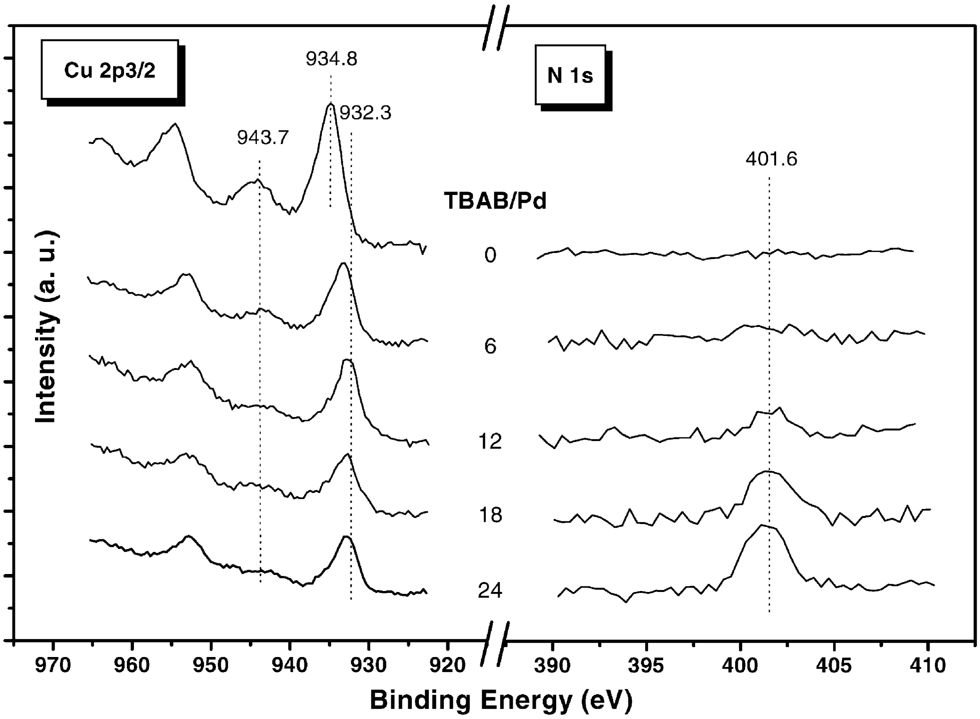

Fig. 7. Cu $2p_{3/2}$ and N 1s XPS patterns of the $PdCl_2$-$CuCl_2$-TBAB/HMS (0.11 wt.% Pd, $n_{Cu/Pd} = 20$) catalysts as a function of TBAB/Pd mole ratio.

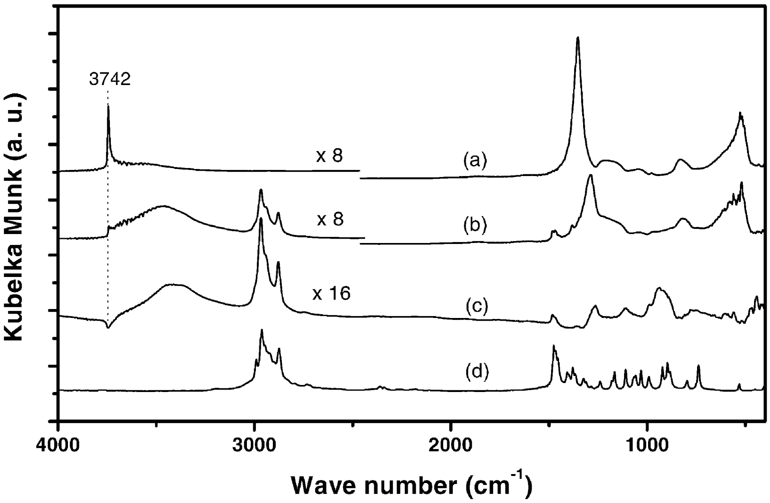

Fig. 8. DRIFT spectra of: (a) parent HMS; (b) $PdCl_2$-$CuCl_2$-TBAB/HMS (Pd/Cu/TBAB = 1/20/12, 0.11 wt.% Pd); (c) differential spectra between (b) and (a). The spectra were recorded on powder samples at 130 °C in N_2 atmosphere; and (d) pure TBAB.

silanol groups inside the channels of the HMS with and without strong hydrogen-bonding interactions [12]. The intensity of the 3742 cm^{-1} band is greatly attenuated as the $PdCl_2$-$CuCl_2$-TBAB catalyst system is loaded. The strong decrease in intensity of the isolated terminal silanol groups upon the loading of $PdCl_2$-$CuCl_2$-TBAB can be further identified in the differential spectrum shown in Fig. 8c, suggesting the involvement of surface hydroxyl groups in the formation of the catalytically active surface species on the $PdCl_2$-$CuCl_2$-TBAB/HMS catalyst.

Apart from the vibrational bands due to the HMS silica, new features at 2969, 2941, 2878, 1481 and 1383 cm^{-1} corresponding to characteristic vibrational peaks coming from molecular TBAB (Fig. 8d) can be observed in spectrum Fig. 8b and c for the HMS-supported $PdCl_2$-$CuCl_2$-TBAB catalysts. The fact that the TBAB moiety remains largely in its molecular state upon loading onto the bimetallic HMS catalysts can be further confirmed by a close comparison of the spectra in Fig. 8c and d, the result is consistent with the present results that are based on XPS analysis.

The in situ CO adsorption DRIFT spectra were recorded at 100 °C in the presence of 100 Torr CO diluted in a N_2 gas flow. DRIFT spectra in the range from 2300 to ~1800 cm^{-1} for CO adsorption on the $PdCl_2$-$CuCl_2$-TBAB/HMS catalysts with various TBAB/Pd mole ratio are shown in Fig. 9. There is one weak and broad band at a vibrational frequency of 2167 cm^{-1} for all catalysts investigated, suggesting the presence of vibrational features due to gas phase CO (2170 cm^{-1}) in present DRIFT spectra. For the catalysts without TBAB addition, there is one additional adsorption band at ca. 2140 cm^{-1} attributable to molecular CO adsorbed on Cu^{2+} [21,22], implying the presence of only a weak bond between the Cu species supported on HMS without TBAB modification. Upon TBAB addition, remarkable spectral changes have been identified. It is seen that there is an intense vibrational peak at 2131 cm^{-1} for the HMS catalyst with a TBAB/Pd ratio of 6/1. The band at 2131 cm^{-1} can be assigned to the CO adsorbed on Cu^+ species based on the literature data of the CO (2130 cm^{-1}) adsorbed on Cu_2O reported by Hierl et al. [23]. This observation thus suggests that the presence of TBAB can induce the reduction of Pd^{2+} and Cu^{2+} species over the TBAB modified bimetallic HMS catalysts under mild conditions. This conclusion is supported by the fact that with increasing TBAB addition there is a shift of the initial CO band at 2131–2117 cm^{-1}. Moreover, it is evidenced that a further increasing the amounts of the TBAB would result in a gradual decrease in peak intensity for the CO absorption, indicating the excess amount of TBAB would finally lead to the decrease of the concentration of Cu^+ species on the catalyst. Taking into account the fact that the Cu^+ species are catalytically active for the oxidative carbonylation reaction, we conclude that the present variation in CO peak intensity is in excellent agreement with the catalytic data, as shown in Fig. 4.

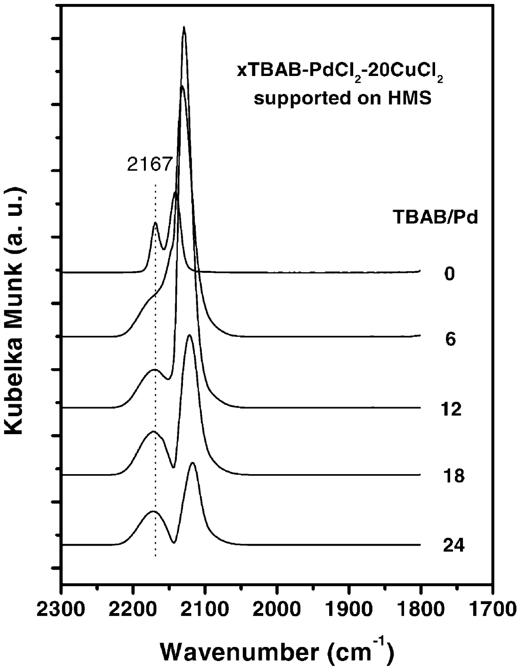

Fig. 9. DRIFT spectra for $PdCl_2$-$CuCl_2$-TBAB/HMS catalysts (0.11 wt.% Pd, $n_{Cu/Pd} = 20$) with increasing TBAB/Pd molar ratio in the presence of 100 Torr CO at 100 °C. Gas flow = 80 ml/min; total pressure = 760 Torr.

3.2.4. *The possible modification mechanism of TBAB*

In the present investigation, the effects of the presence of quaternary ammonium salts as promoters on gas phase DMC synthesis through oxidative carbonylation of methanol over bimetallic mesoporous HMS catalysts are reported. TBAB has been shown to be the most effective promoter for the remarkable enhancement of catalytic performance of the HMS-supported bimetallic $PdCl_2$-$CuCl_2$ catalyst for DMC synthesis. It is also demonstrated that the catalytic performance of the TBAB modified $PdCl_2$-$CuCl_2$/HMS catalyst is strongly dependent on the doping level of TBAB in the bimetallic catalyst system. Combined XPS and DRIFT characterization of the present bimetallic HMS catalyst systems has unambiguously shown that the introduction of TBAB can result in the substantial formation of surface stabilized Cu^+ species on the surface of the bimetallic catalysts. It has been well established that the cuprous compounds are the catalytically active species for DMC synthesis in the oxidative carbonylation of methanol; it is therefore understandable that the significant improvement of the $PdCl_2$-$CuCl_2$/HMS catalyst upon TBAB addition is due to the presence of a substantial amount of Cu^+ species on the surface of the bimetallic HMS catalysts.

It has been previously reported that the loading of an aqueous $PdCl_2$-$CuCl_2$ solution into the pores of the high-surface-area supports, which has been known as supported Wacker-type catalyst, can significantly accelerate the oxidation of carbon monoxide at low temperatures [24–26]. The overall chemistry of CO oxidation in the catalytic system is believed to be similar to that of the well-known Wacker processes in the presence of a homogeneous $PdCl_2$-$CuCl_2$ catalyst.

$$CO + PdCl_2 + H_2O \rightarrow CO_2 + Pd(0) + 2HCl \qquad (1)$$

$$Pd(0) + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl \qquad (2)$$

$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2CuCl_2 + H_2O \qquad (3)$$

It has been proposed that $PdCl_2$ is initially reduced to Pd(0) by carbon monoxide, and then Pd(0) is reoxidized to $PdCl_2$ by $CuCl_2$. CuCl formed in reaction (2) is reoxidized to $CuCl_2$ by molecular O_2, which is also included in the feed gas stream. The presence of water is found to be essential to sustain this catalytic cycle, as shown above for the supported Wacker-type catalysts [24,25,27] in the CO oxidation reaction.

In our case, we suggest that a similar catalytic cycle will be essential for the generation of catalytically active Cu(I) species for DMC synthesis. For the $PdCl_2$-$CuCl_2$/HMS catalyst without TBAB modification, the Pd and Cu species are randomly supported as well as separated on the HMS catalysts, which would make it difficult to sustain the catalytic cycle between the Cu(II)/Cu(I) and Pd(0)/Pd(II) redox processes. This can well explain the low reactivity of the $PdCl_2$-$CuCl_2$/HMS catalyst in DMC synthesis. However, the presence of TBAB can serve as a surfactant agent under reaction conditions to promote the formation of a thin-liquid film composed of methanol to dissolve $PdCl_2$ and $CuCl_2$ compounds, [28] which may result in the formation of substantial surface-stabilized cuprous species on the surface of the catalys by facilitating the redox capabilities of Cu(II)/Cu(I) and Pd(0)/Pd(II) on the HMS catalysts. As a result, it is easy to understand that the TBAB modified $PdCl_2$-$CuCl_2$/HMS catalysts have exhibited enhanced catalytic performance in the gas phase DMC synthesis.

4. Conclusions

In this work, DMC synthesis reaction by oxidative carbonylation of methanol has been studied using vapor phase flow reaction system in the presence of a series of mesoporous HMS silica-supported bimetallic $PdCl_2$-$CuCl_2$ catalysts at atmospheric pressure. The effects of various promoters and reaction conditions on the catalyst performance are evaluated in terms of methanol conversion and DMC selectivity. The $PdCl_2$-$CuCl_2$/HMS catalysts modified with TBAB have shown the best catalytic performance. X-ray diffraction, XPS and DRIFT analysis were also conducted in order to characterize the employed catalysts. The essential role of TBAB promoter is to facilitate the electron transfer between surface redox couples of Pd(0)/Pd(II) and Cu(II)/Cu(I) and the substantial formation of surface-stabilized cuprous species may account for the significant enhancement of the catalytic performance in DMC synthesis.

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