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The effects of promoters over $PdCl_2$-$CuCl_2$/HMS catalysts for the synthesis of diethyl carbonate by oxidative carbonylation of ethanol

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ABSTRACT

Diethyl carbonate (DEC) has been produced by the oxidative carbonylation of ethanol in the gas phase over a heterogeneous $PdCl_2$-$CuCl_2$ catalyst supported on hexagonal mesoporous silica (HMS). The various quaternary ammonium salt (QAS) promoters have a great effect on the performance of the catalyst, which was due to the high dispersal of the active species on the film composed of nonpolar groups. The catalytic performance of the $PdCl_2$-$CuCl_2$/HMS catalyst was greatly improved by the addition of promoter tetraethyl ammonium bromide (TEAB). Under the $PdCl_2$-$CuCl_2$-TEAB/HMS catalyst system, space time yield (STY) of DEC was 210.9 g DEC/(L-cat h), and conversion of EtOH was 13.6%. An optimized TEAB/Pd mole ratio existed for catalytic activity, which was about 12/1. From X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), low-temperature electron spin resonance (ESR) spectroscopy, and infrared resonance (IR) spectroscopy, it could be concluded that the essential role of TEAB not only promoted the formation of surface-stabilized copper species but also improved a high dispersal of the active species, which enhanced catalytic performance in the gas phase DEC synthesis.

1. Introduction

Diethyl carbonate (DEC), an environmentally benign chemical, represents a viable alternative to phosgene in the chemical industry and in the motor fuel industry. The presence of two ethyl groups and one carbonyl group in its molecule makes DEC a promising alternative to both ethyl halides and phosgene for ethylation and carbonylation processes. Because of its high oxygen content (40.6 wt%), DEC has been proposed as a replacement for *tert*-butyl ether (MTBE) as an attractive oxygen-containing fuel additive, and the gasoline/water distribution coefficients for DEC are more favorable than for dimethyl carbonate and ethanol [1]. When released into the environment, DEC slowly biodegrades to carbon dioxide and ethanol [2].

There are several methods for the DEC synthesis, such as a phosgene process [3], oxidative carbonylation of ethanol [4–7], carbonylation of ethyl nitrite [8], and an ester exchange process [9]. Among them, the vapor phase oxidative carbonylation of ethanol represents one of the proposed favorable processes. In the case of synthesis of DEC by oxidative carbonylation, $CuCl_2$-$PdCl_2$/AC catalysts have previously been shown better catalytic performances. So efforts have been dedicated to gain the attractive materials supported $CuCl_2$-$PdCl_2$ catalyst.

Mesoporous silicates such as MCM-41 [10], MCM-48 [11], HMS [12], and FSM-16 [13] have recently attracted much attention, because they consist of a regular array of uniform one or three-dimensional pores with diameters of 1.5–10 nm and high surface area (more than 1000 m^2/g), and the features of these mesoporous materials are suitable for the chemical reaction of larger molecules. Among these mesoporous materials, HMS has been reported to demonstrate more advantages than other supports, such as HMS possesses thicker framework walls, small crystallite size of primary particles and complementary textural porosity, which may provide better transport channels for reactants to the active sites [14,15].

In the present work, mesoporous HMS supported $PdCl_2$-$CuCl_2$ catalysts were synthesized effectively and the effects of the various quaternary ammonium salt (QAS) promoters were investigated. The possible modification mechanism of promoters for the surface structure of catalysts was proposed to explain that the promoter facilitate the better dispersal of active species on the surface of the catalysts. In addition, the catalysts were characterized by IR, XRD, XPS and ESR spectra.

2. Experimental

2.1. Catalyst preparation

HMS was synthesized following the procedures similar to those proposed by Tanev et al. via neutral templating pathway using

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dodecylamine (DDA) as the surfactant [12,16]. 3.85 g DDA was dissolved in 130 ml of water, and 32.5 ml of ethanol was then added to afford a 40:10 H_2O/EtOH solution of the surfactant. The surfactant solution was stirred for 15 min and then was added in the mixture of 20 ml ethanol and 23 ml tetraethyl orthosilicate (TEOS). Then the mixture was slowly added to the surfactant solution, stirred for about 2 h. The resultant solution was aged for 18 h at room temperature (25 °C) to obtain crystalline product. The solid precipitates were filtered out, dried at 120 °C over night, and calcined at 600 °C for 4 h. Finally, HMS was obtained for further experiments.

A Pd-Cu-containing solution with or without QAS was prepared by heat-dissolving palladium chloride ($PdCl_2$) and copper chloride ($CuCl_2$) in methanol solution at a temperature of 65 °C. With this solution, a fully dried HMS was mixed and the resultant mixture was stirred for about 3 h to impregnate the HMS with Pd-Cu-containing solution. Thereafter, methanol was evaporated away from the mixture at a temperature of 65 °C under a reduced pressure. The residual mixture was heat-treated at 120 °C for one hour to prepare a solid catalyst. The total content of the metal compound in terms of metallic palladium was 0.25% by weight based on the weight of carrier, and the atomic ratio of Pd/Cu in the catalysts was 1/20.

2.2. Characterization of catalysts

Catalytic activity was measured by a computer-controlled continuous micro reactor system (MRCS-8004B) with a stainless steel tubular reactor of 8 mm inner diameter. The reaction products collected in the cooling trap were taken out and sampled every hour, and were analyzed by a gas chromatograph (GC) (4890D, Agilent) with an FID detector. The uncondensed gas products were introduced to the gas chromatograph (GC-8A, Shimadzu) through an on-line six-way valve and analyzed by a TCD detector with a TDX-01 and Propak-Q packed column. Similar to the previous work [17], the reaction conditions were steadily kept at a reaction temperature of 150 °C and a reaction pressure of 0.64 MPa.

The characterization of catalysts was conducted by X-ray powder diffraction (XRD) using a Rigaku C/max-2500 diffractometer using graphite filtered Cu Kα radiation ($\lambda = 1.54056$ Å) at 40 kV and 200 mA with a scanning rate of $4^\circ\ \mathrm{min}^{-1}$ from $2\theta = 1^\circ$ to $2\theta = 10^\circ$. The XPS analysis of the catalysts was carried out on a PerkinElmer PHI 1600 ESCA system operated at a pass energy of 187.85 eV for survey spectra with a Al Kα X-ray source ($E = 1486.6$ eV). The IR spectroscopic measurements were carried out on a Nicolet, 5DX spectrometer with 4 cm^{-1} resolution and 400–3000 cm^{-1} scanning range. The ESR measurements were carried out using a standard reflection-type x-band (9.56 GHz) spectrometer equipped with a Varian microwave cavity and a variable temperature (4–300 K) cryostat system obtained from Oxford instruments.

3. Results and discussion

3.1. Effect of various promoters on DEC synthesis

The introduction of QAS as surfactant appears to have a more significant influence on the modification of the textural structures of silica supports [18]. At this point, four QAS including cetyltrimethylammonium briomide (CTAB), tetrabutylammonium bromide (TBAB), cetyltrimethylammonium chloride (CTAC) and TEAB were investigated as the possible promoters on the catalytic activity of $PdCl_2$-$CuCl_2$/HMS catalysts for synthesis of DEC in the first place. As shown in Fig. 1, the catalytic performance of $PdCl_2$-$CuCl_2$/HMS catalyst could be enhanced in a certain extent by the addition of QAS into the catalyst system. The TEAB-promoted catalyst has shown favorable catalytic properties, and the conversion of EtOH was about 13.6%, the STY of DEC was 210.9 g DEC/(L-cat h).

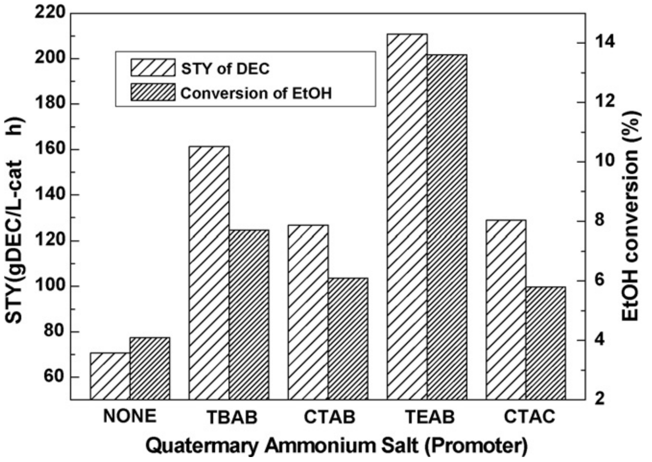
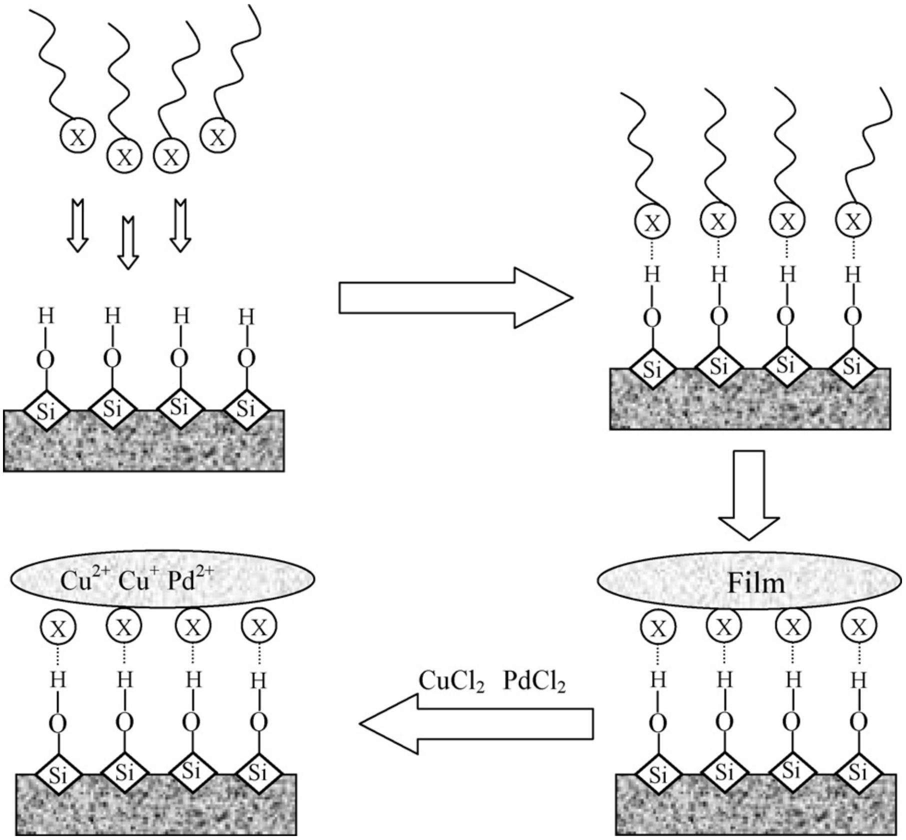


Fig. 1. Results obtained from promoter test over $PdCl_2$-$CuCl_2$/HMS. Reaction condition: T = 423 K, P = 0.64 MPa, O_2 = 10 sccm, CO = 80 sccm, N_2 = 50 sccm.

QAS as promoters on gas phase DEC synthesis through oxidative carbonylation of ethanol facilitated the improvement of the performance of the catalysts supported on HMS. Scheme 1 shows a possible modification mechanism of promoters for the surface structure of catalysts. First, the hydrophilic polar groups X of QAS (where X is the halogen on the QAS) approach the polar OH groups on the support after the adding of promoters. During this process, an effect like the covalent bond was produced between the hydrophilic polar groups of the promoter and those on the support surface. Further, the presence of the hydrophobic nonpolar groups of the surfactant under reaction conditions promotes the formation of a thin film composed of alkyl. Finally, the active species was highly dispersed on the film due to the loading of $PdCl_2$ and $CuCl_2$. In our case, for the $PdCl_2$-$CuCl_2$/HMS catalyst without promoter modification, the Pd and Cu species are randomly loaded 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. The presence of the film composed of hydrophobic nonpolar groups not only facilitates the high dispersal of active species but also promotes the formation of substantial surface-stabilized copper species, which avoids the strong interaction between active species and the supports. As a result, it is easy to understand that the promoters modified $PdCl_2$-$CuCl_2$/HMS catalysts have enhanced catalytic performance in the gas phase DEC synthesis.

3.2. Effect of TEAB promoter addition on DEC synthesis

The result indicated that QAS promoters played an important role in modifying HMS support, so TEAB was selected as the most effective promoter for $PdCl_2$-$CuCl_2$/HMS catalysts in the following work. In order to gain further insight into the influence of TEAB promoter, the catalytic performance of $PdCl_2$-$CuCl_2$-TEAB/HMS catalyst was investigated as a function of TEAB/Pd mole ratio in Fig. 2. The catalytic performance of DEC formation gradually increased at a low TEAB/Pd mole ratio, following by a steep dropping at TEAB/Pd>12/1. The conversion of EtOH followed the same law as STY of DEC, and the selectivity based on EtOH to DEC holded the level of up to 90%. An optimum TEAB/Pd mole ratio existed for catalytic activity, which was about 12/1.



Scheme 1. The possible modification mechanism of promoters for the surface structure of catalysts.

3.3. Characterization of mesoporous HMS supported $PdCl_2$-$CuCl_2$ catalysts

The infrared spectrum of HMS and $CuCl_2$-$PdCl_2$-TEAB/HMS samples was shown in Fig. 3. From Fig. 3, the characteristic bands of two samples were almost coincident. The bands at 450 cm^{-1} could be interpreted as the tetrahedral vibration of zeolites, and the intensity of that could be confirmed the crystal degree of mesoporous structure [19]. It was supposed that weakening of the intensity of the bands at 450 cm^{-1} of the catalyst was the result of the interaction between active components and the support surface and blockage of the pore mouths by loading active species. The band at 1080 and 1250 cm^{-1} which was attributed to the Si-O-Si stretching vibration [19] was found to be significantly higher for pure HMS than for $CuCl_2$-$PdCl_2$-TEAB/HMS sample. It was inferred that the relative weakening of the 1080 and 1250 cm^{-1} band might be attributed to the coverage of some Si-O-Si brands, which was due to the presence of the film composed of hydrophobic nonpolar groups. It could be seen from the previous modification mechanism of promoters.

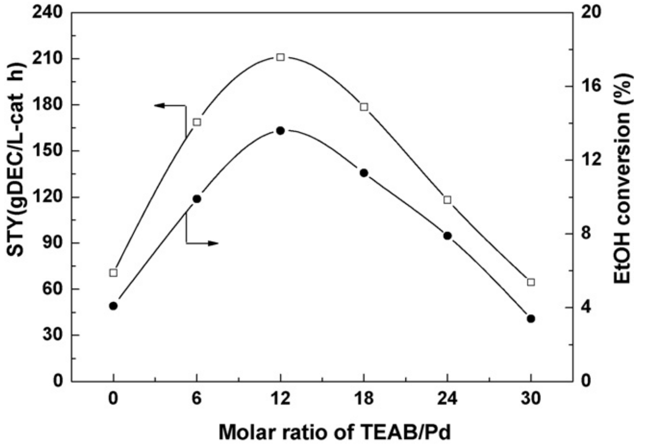


Fig. 2. Influence of TEAB addition on the catalytic performance of the $CuCl_2$-$PdCl_2$/HMS catalysts. Reaction condition: T = 423 K, P = 0.64 MPa, O_2 = 10 sccm, CO = 80 sccm, N_2 = 50 sccm.

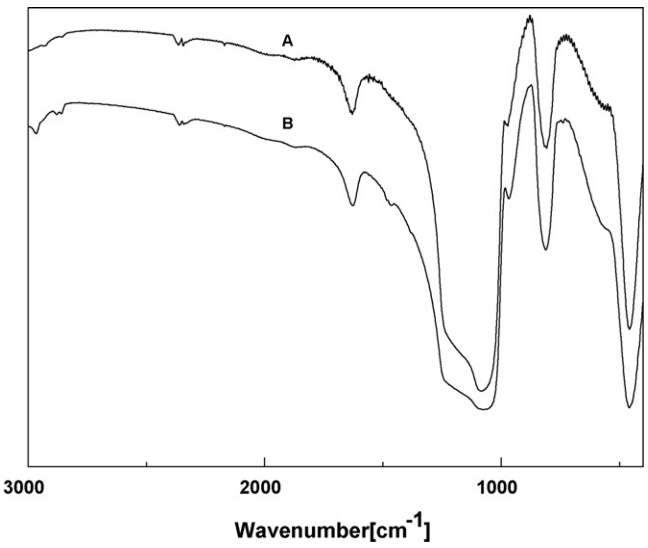


Fig. 3. Infrared spectra of HMS and $CuCl_2$-$PdCl_2$-TEAB/HMS samples (A: HMS; B: $CuCl_2$-$PdCl_2$-TEAB/HMS).

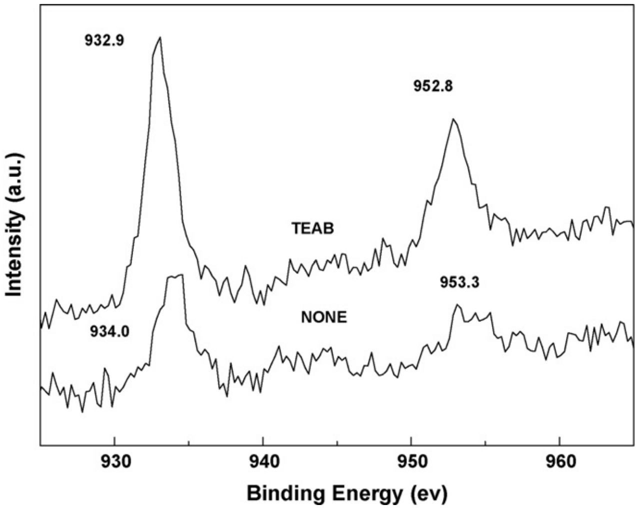


Fig. 4. Cu 2p XPS spectra of $PdCl_2$-$CuCl_2$/HMS catalyst and $PdCl_2$-$CuCl_2$-TEAB/HMS catalyst.

In order to gain an insight into the chemical state of the active components on the $CuCl_2$-$PdCl_2$/HMS catalysts and $PdCl_2$-$CuCl_2$-TEAB/HMS catalyst, Cu 2p3/2 XPS analysis has been carried out. As shown in Fig. 4, the sample without TEAB promotion showed the principal Cu 2p3/2 line centered around 934.0 eV, which was assigned to Cu^{2+} cations [6,20,21]. The Cu 2p3/2 peak of the catalyst with TEAB located at 932.9 eV, which shifted towards lower binding energy. The lower binding energies at 932.9 eV suggested the presence of reduced Cu^{+} species, which was in agreement with that TEAB loading promoted the formation of surface-stabilized copper species in the previous modification mechanism of promoters. Because the existence of Cu^{+} is related to the better catalytic activity [22,23], it could be easily explained that the promoter improved the catalytic performances in our work.

$CuCl_2$-$PdCl_2$/HMS catalysts with various QAS promoters were characterized by XRD for establishing structure. The XRD patterns of $CuCl_2$-$PdCl_2$/HMS catalysts were shown in Fig. 5. Obviously, all XRD patterns of the samples were dominated by a peak at $2\theta < 3^\circ$ corresponding to the [1 0 0] diffraction. $CuCl_2$-$PdCl_2$/HMS catalysts with various QAS promoters exhibited only the [1 0 0] diffraction peak, which were agreement with that literature reported by Tanev and Pinnavaia [16]. It could be noted that the intensities of the reflection peak [1 0 0] for the samples showed different with the introduction of different QAS promoters. This might be due to that the QAS promoters loaded on HMS samples resulted in a partial collapse of the HMS framework and reduction of hexagonal order during the preparation of the catalysts. Among XRD patterns of the four QAS promoters investigated, the TEAB-promoted catalyst has shown the preferable order degree of mesoporous structure, which could be due to a higher dispersal of the active species. And this result was consistent with the catalytic performances of various promoters on DEC synthesis. In all cases, the absence of diffraction peaks at 2θ angles higher than 10° seemed to exclude the presence of crystalline phase associated with Cu or Pd species, thus pointing to a highly dispersed nature of the Cu and Pd species.

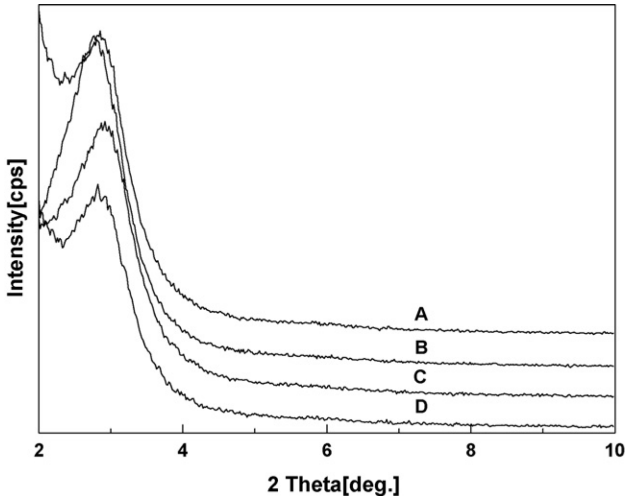


Fig. 5. XRD patterns of $CuCl_2$-$PdCl_2$/HMS catalysts with various QAS promoters (A: TBAB; B: TEAB; C: CTAB; D: CTAC).

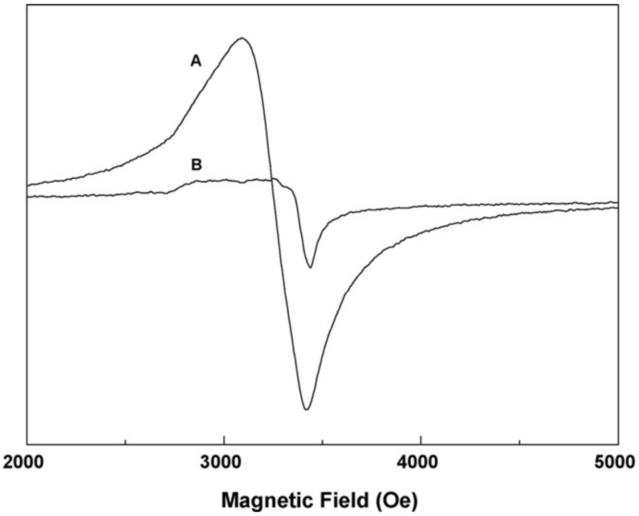


Fig. 6. ESR spectra of $CuCl_2$-$PdCl_2$-TEAB/HMS samples (A: before reaction; B: after reaction).

ESR spectra of the $CuCl_2$-$PdCl_2$-TEAB/HMS catalysts were observed to make significant changes in Fig. 6. A strong sharp signal at $g \sim 2$ with a peak-to-peak width $\Delta H = 320$ Oe due to the Cu^{2+} species could be shown in the ESR spectra of the $CuCl_2$-$PdCl_2$-TEAB/HMS catalyst before reaction. In the ESR studies on alumina-supported $CuCl_2$ catalysts [24] and activated carbon-supported $CuCl_2$-$PdCl_2$ catalysts [25], a similar signal at $g \sim 2$ has been observed. The signal could be attributed to Cu^{2+} located in the octahedral vacancies on the support surface. From Fig. 6, this signal gradually broadened and weakens after reaction. The intensity of this signal determined from accurately weighed samples was found to reduce gradually after reaction. This indicated that the copper chloride species might be interacting with the nonpolar groups on the HMS surface from the QAS and formed some interaction in this process. After reaction, the interaction between copper species and nonpolar groups on HMS surface weaken with the losing of the chloride anion during reaction. From the modification mechanism of promoters in Scheme 1, the losing of halogen anion in reaction may result in the breakage of the film composed of hydrophobic nonpolar groups. Consequently, the signal attributed to the interaction between copper species and nonpolar groups weaken.

4. Conclusion

In this work, the effects of the various QAS promoters and the promoter loading level for the synthesis of diethyl carbonate by oxidative carbonylation of ethanol were evaluated in terms of ethanol conversion and STY of DEC. The possible modification mechanism of promoters for the surface structure of catalysts was proposed to easily understand that the promoters modified $PdCl_2$-$CuCl_2$/HMS catalysts have shown better catalytic performance. XRD, IR, XPS and ESR were employed to characterize the catalyst. Compared with other promoters, the essential role of TEAB promoter facilitated the formation of Cu^+ species and a high dispersal of active species, which indicates that a strong dependence of catalytic activities on mesoporous HMS supported $PdCl_2$-$CuCl_2$ catalyst was the presence of surface-stabilized copper species.

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