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A new type of catalyst $PdCl_2$/Cu-HMS for synthesis of diethyl carbonate by oxidative carbonylation of ethanol

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Abstract

A new type of catalyst, $PdCl_2$/Cu-HMS, for diethyl carbonate (DEC) synthesis by oxidative carbonylation of ethanol in the gas-phase reaction was investigated. The modified support Cu-HMS which was synthesized using the neutral templating pathway at the room temperature kept its mesoporous structure even after it was calcined repeatedly at 550 °C for 3 h to remove the template. From XRD, XPS and ICP analysis, it can be concluded that copper incorporated into HMS frame and was highly dispersed in the frame of silica. Notably, the degree of order of mesoporous molecular sieves was improved in a certain extent after $PdCl_2$ was loaded on Cu-HMS samples. The $PdCl_2$/Cu-HMS catalyst exhibited excellent selectivity for DEC. The catalytic reaction mechanism was illuminated by the interaction between Pd^{2+} loaded on the surface and Cu^{2+} in Cu-HMS frame.

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1. Introduction

Diethyl carbonate (DEC) has recently attracted increased attention as an important chemical materials 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 routes for DEC production: (i) the phosgene–ethanol process [3]; (ii) the oxidative carbonylation of ethanol over a slurry of CuCl [4]; (iii) the gas-phase oxidative carbonylation of ethanol using a heterogeneous supported $CuCl_2$/$PdCl_2$ catalyst [5–7]; (iv) transesterification reactions of DMC and ethanol [8]; (v) activation of carbon dioxide [9]; (vi) reaction of ethanol with urea over organotin catalysts [10]. Among them, oxidative carbonylation of ethanol in the gas-phase has been deemed as one of the most promising routes in the process of DEC synthesis. It is well known that support plays an important role in the structure and activity of supported catalysts. Since 1980s, investigations have been made in the development of supported copper-based catalysts for synthesis DMC. All kinds of catalysts were prepared by impregnating the active carbon, oxides (MnO, ZnO, TiO_2, SiO_2, and Al_2O_3) or HMS silica in methanol solution of $CuCl_2$ [6,11]. Previous results have shown that all of the tested catalysts deactivated quickly because of losing the chlorine anion and the remodel of active copper species on the surface. Recently, HY zeolite and mesoporous MCM-41silica have been reported as the promising supports for the oxidative carbonylation reaction [12–14], although CuY catalyst and CuCl/MCM-41 catalyst were prepared by the high

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temperature solid state ion-exchange method. However, in the case of synthesis of DEC by oxidative carbonylation, only active carbon is widely used as the support. Hence, efforts have been dedicated to develop more suitable supports other than active carbon for more efficient gas phase oxidative carbonylation of ethanol to DEC. And it would be highly interesting to further explore the possible application of the catalytically attractive materials in synthesis of DEC.

In the present work, modified Cu-HMS support was synthesized effectively and found that a reasonable amount of $PdCl_2$ loading were active for DEC synthesis. In addition, the synergic effect of Cu^{2+} in the frame and Pd^{2+} adhered on the surface for the DEC production has been investigated.

2. Experimental

2.1. Catalyst preparation

The HMS, Cu-HMS were synthesized following the procedures similar to those proposed by Tanev et al. via neutral templating pathway using dodecylamine (DDA) as the surfactant [15,16]. 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 following 0.35 g copper chloride 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 the 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, Cu-HMS was obtained for further experiment.

A Pd-containing solution was prepared by heat-dissolving palladium chloride ($PdCl_2$) in methanol solution at a temperature of 65 °C. With this solution, a fully dried Cu-HMS was mixed and the resultant mixture was stirred for about 3 h to impregnate the Cu-HMS with Pd-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 1 h 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 catalyst was 1/20.

2.2. Production and analysis of DEC

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 a FID detector. The uncondensed gas products were introduced to the a gas chromatograph (GC-8A, Shimadzu) through an on-line six-way valve and analyzed by a TCD detector with a TDX-01and Propak-Q packed column. Similar to the previous work [7], 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 $8^\circ\ \text{min}^{-1}$ from $2\theta = 1^\circ$ to $2\theta = 10^\circ$. The XPS analysis of the catalysts was carried out on a Perkin–Elmer 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). Further elemental analysis was performed by inductively coupled plasma-atomic emission spectroscopy (VISTA-MPX) operated at high frequency emission power of 1.5 kW and plasma airflow of 15.0 L/min. Sample was dissolved in the mixture of HNO_3, HF and HBO_3, and then diluted with water.

3. Results and discussion

3.1. Catalytic activity of $PdCl_2$/Cu-HMS

The binary catalyst systems $PdCl_2$–$CuCl_2$–TBAB employing mesoporous HMS silica as a support for gas phase oxidative carbonylation of methanol at atmospheric pressure have exhibited excellent catalytic performance in the reaction of dimethyl carbonate (DMC) synthesis [11]. HMS was reported to demonstrate more advantages than other supports, such as larger pores and being more stable. However, the loss of the chlorine and the remodel of active copper species on the surface for this Wacker-type catalyst limited its development of the bimetallic HMS catalyst.

For this reason, it may be interesting to introduce transition metals into the framework of molecular sieve when preparing oxidative carbonylation catalyst. Up to now, there had been no references about the use of Cu-substituted HMS as catalysts for DEC synthesis.

The catalytic results of $PdCl_2$/Cu-HMS catalysts on oxidative carbonylation of ethanol with CO and O_2 are shown in Table 1. The pure Cu-HMS did not show any catalytic activities, which is similar to $PdCl_2$/HMS catalyst at the

Table 1
Comparison of various catalyst systems on catalytic performance[a]

Catalyst[b]	Conversion of EtOH (%)	STY of DEC (mg/g h)	$S_{DEC/EtOH}$ (%)
Cu-HMS	No reaction		
$PdCl_2$/HMS	No reaction		
$PdCl_2$–$CuCl_2$/HMS	5.1	600.1	87.6
$PdCl_2$/Cu-HMS	4.8	587.9	100

[a] Reaction condition: $T = 423$ K, $P = 0.64$ MPa, $O_2 = 10$ sccm, CO = 80 sccm, $N_2 = 50$ sccm.

[b] Si/Cu (mole ratio) = 50:1, Pd-loading = 0.25 wt%, Pd/Cu (mole ratio) = 1:20.

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