Effect of Hydrophobic Modification on the Catalytic Performance of PdCl₂/Cu-HMS with Different Silylation Temperatures

**Pingbo Zhang · Yan Zhou · Mingming Fan ·
Pingping Jiang · Xianglan Huang · Jiang Lou**

Abstract A new class of organic–inorganic hybrid materials were prepared by combining Cu-HMS with a silylation agent, trimethylchlorosilane (TMCS) via a simple silylation process at different silylation temperatures. They were characterized by a series of techniques including FT-IR, powder XRD, Nitrogen adsorption–desorption, TG analysis and water adsorption capacity test. It was demonstrated that silylation of PdCl₂/Cu-HMS catalysts with TMCS enhanced their hydrophobicity, improved their activity and stability and importantly kept the excellent selectivity to diethyl carbonate (DEC) by oxidative carbonylation of ethanol in the gas-phase reaction. Moreover, the silylated samples obtained at 60 °C showed a better conversion of EtOH of 6.1 % and STY of DEC of 140.8 mg g^{-1} h^{-1}.

Keywords Organic–inorganic hybrid materials ·
Trimethylchlorosilane (TMCS) · Hydrophobicity ·
Silylation temperature · Diethyl carbonate (DEC)

1 Introduction

Diethyl carbonate (DEC) is recognized as an environmentally benign chemical because of its negligible ecotoxicity and low bioaccumulation and persistence. 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, 2]. In addition, as a chemical intermediate, DEC is also drawing attention as a safe solvent and an additive in lithium cell electrolyte [3, 4]. Currently, oxidative carbonylation of ethanol in the gas-phase has been deemed as one of the most promising routes for DEC synthesis based on the "green chemistry" principles [5].

Various catalysts have been investigated for oxidative carbonylation which were prepared by impregnating the active carbon [2, 6, 7], oxides [8, 9] or other zeolites in methanol solution of CuCl₂ [5, 10–13]. In the previous research [14, 15], PdCl₂/Cu-HMS has been demonstrated an excellent selectivity to DEC by oxidative carbonylation of ethanol in the gas-phase reaction. Moreover, it was also found that H₂O in the feed decreased the conversion of methanol and the selectivity of carbon monoxide to dimethyl carbonate [16, 17]. So removal of water from the catalyst surface would reduce the hydrolysis of DEC and, therefore, would benefit activity and stability of the reaction.

Catalytic activities can be improved by taking different approaches to control of the surface hydrophobicity. Recently, modification of MCM-41 by surface silylation with various silylation agents has been extensively reported and many researchers have studied their adsorption and application [18–22]. The experimental results have shown that surface silylation indeed improved the hydrophobicity and thus benefited removal of water from the catalyst surface in other systems. However, little has been written about surface silylation of HMS and its application [23].

In this article, we described the synthesis of TMCS-modified Cu-HMS and investigated the effect of different temperatures. These materials were used to catalyze the synthesis of DEC by oxidative carbonylation of ethanol

P. Zhang · Y. Zhou · M. Fan (✉) · P. Jiang · X. Huang · J. Lou
The Key Laboratory of Food Colloids and Biotechnology,
Ministry of Education, School of Chemical and Material
Engineering, Jiangnan University, Wuxi 214122,
People's Republic of China
e-mail: fanmm2000@126.com

aimed to improving the activity of catalysts while maintaining the selectivity similar to unsilylated catalysts.

2 Experimental

2.1 Materials and Methods

All chemicals were of analytical grade and used as received. FT-IR spectra was carried out with an ABB Bomem FTLA2000-104 spectrometer using KBr pellets in the 4,000–500 cm^{-1} region. The composition and phase of the product were identified by powder X-ray diffraction (XRD) on an D8 X-ray diffractometer (Bruker AXS, German) using Cu Kα radiation (λ = 1.5406 Å) with a scanning rate of 2°/min from 2θ = 1° to 10°. The specific surface area of the catalysts was measured according to the Brunauer–Emmet–Teller (BET) method with nitrogen adsorption–desorption on a ASAP 2020 instrument (Micromeritics, USA) and the degas condition was 200 °C for 2 h. TG of the samples was recorded using a Mettler TGA/SDTA 851 E analyzer in the temperature range 25–600 °C at a heating rate of 10 °C/min. Water adsorption capacity test was seen in GB 6287-86.

2.2 Catalyst Preparation

2.2.1 Synthesis of Cu-doped Hexagonal Mesoporous Silica (Cu-HMS)

The Cu-HMS was synthesized following the procedures similar to those proposed by Tanev et al. [24, 25] via a neutral templating pathway using dodecylamine (DDA) as a surfactant. The method for synthesis of Cu-HMS in detail was shown in paper [14, 15].

2.2.2 Surface Modification with Trimethylchlorosilane (TMCS)

Cu-HMS (2 g) was impregnated into a trimethylchlorosilane (TMCS) solution dissolved in benzene with a concentration of 5 % (volume fraction) and total liquid volume was 100 mL under stirring for 8 h at a desired temperature (25, 50, 60, 70 and 75 °C) [19]. The mixture was then extensively washed with acetone to rinse away any residual chemicals. Finally, the suspension was dried at 80 °C for 2 h.

2.2.3 Loading Palladium Chloride

The catalysts were prepared by impregnating the silylated Cu-HMS supports with methanol solution of palladium chloride (PdCl$_2$). The total contents of the metal compound in terms of metallic palladium was 0.25 % by weight based on the weight of carrier [26]. The prepared samples were denoted as PdCl$_2$/Si-Cu-HMS-x, where x described the silylation temperatures (25, 50, 60, 70 and 75 °C, respectively).

2.3 Catalytic Performance

Catalytic activity was measured by a computer-controlled continuous micro reactor system with a stainless steel tubular reactor of 8 mm inner diameter. The reaction conditions were as follows: 3 mL catalyst, 0.1 mL min^{-1} ethanol (as liquid), 10 sccm O$_2$, 80 sccm CO, 50 sccm N$_2$, reaction temperature 423 K and reaction pressure 0.64 MPa. Analytical method for production in detail was seen in the paper [14, 15].

3 Results and Discussion

3.1 Catalytic Performance of Different Catalysts

PdCl$_2$/Cu-HMS and PdCl$_2$/Si-Cu-HMS-x were used as catalysts and compared in the synthesis of DEC by oxidative carbonylation of ethanol (Table 1). Compared with PdCl$_2$/Cu-HMS, the silylated PdCl$_2$/Si-Cu-HMS-x catalysts maintained the advantage in the remarkable selectivity of 100 % to DEC based on ethanol, what's more, the conversion of EtOH and STY of DEC were all improved in some degree. Based on these results, a conclusion could be drawn that silylation had enhanced surface hydrophobicity of Cu-HMS. On one hand, surface modification reduced the contact between DEC and water, avoiding the hydrolysis of DEC. On the other hand, the removal of water significantly increased the reaction rates over the copper zeolite catalysts, both by the effect of water on the equilibrium of ethoxide formation also by water adsorption onto the active sites [26], resulting in the increase of catalytic performance. In addition, as the efficiency of the silylation increases with silylation temperature until the boiling point of TMCS was obtained and at this point decreased. When silylation temperature was 60 °C, TMCS partly became vapor, in other words, silylation was considered as vapor–liquid–solid reaction, while silylation could be thought of as liquid–solid reaction below 60 °C. Compared with liquid–solid reaction, vapor–liquid–solid reaction had advantages of weak molecular force, small influence of liquid viscosity and severe molecular motion, which contributed to TMCS contacting hydroxy group on the surface of Cu-HMS. However, when silylation temperature was above 60 °C, catalytic performance began to decline, because too severe molecular motion of TMCS and even partly volatilizing resulted in the unsufficient contact between TMCS and surface hydroxyl of Cu-HMS. In

Table 1 Catalytic performance[a] over PdCl$_2$/Cu-HMS and PdCl$_2$/Si-Cu-HMS-x

Samples	Conversion of EtOH (%)	STY of DEC (mg g^{-1} h^{-1})	S$_{DEC}$/EtOH (%)
A (PdCl$_2$/Cu-HMS)	4.6	97.2	100
B (PdCl$_2$/Si-Cu-HMS-25)	4.9	115.8	100
C (PdCl$_2$/Si-Cu-HMS-50)	5.4	125.6	100
D (PdCl$_2$/Si-Cu-HMS-60)	6.1	140.8	100
E (PdCl$_2$/Si-Cu-HMS-70)	5.9	136.5	100
F (PdCl$_2$/Si-Cu-HMS-75)	5.6	130.2	100

[a] Reaction condition: T = 423 K, P = 0.64 MPa, O$_2$ = 10 sccm, CO = 80 sccm, N$_2$ = 50 sccm
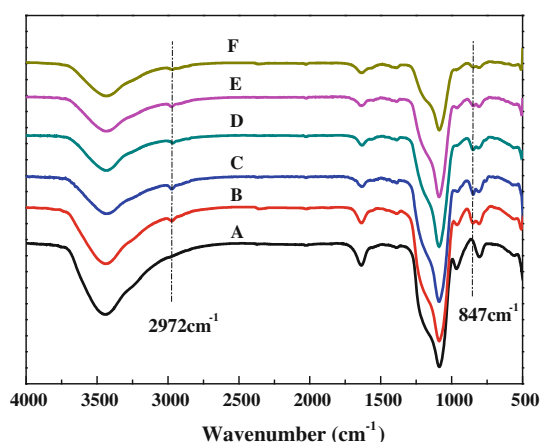
Fig. 1 The FT-IR spectra for PdCl$_2$/Cu-HMS and PdCl$_2$/Si-Cu-HMS-x *A* PdCl$_2$/Cu-HMS, *B* PdCl$_2$/Si-Cu-HMS-25, *C* PdCl$_2$/Si-Cu-HMS-50, *D* PdCl$_2$/Si-Cu-HMS-60, *E* PdCl$_2$/Si-Cu-HMS-70, *F* PdCl$_2$/Si-Cu-HMS-75

conclusion, 60 °C was regarded as the best silylation temperature.

3.2 Characterization

3.2.1 FT-IR

The FT-IR spectra obtained for PdCl$_2$/Cu-HMS and PdCl$_2$/Si-Cu-HMS-x was shown in Fig. 1. The bands at 1,087 and 804 cm^{-1} were for stretching vibration of Si–O–Si. In contrast with curve A, it can be seen that two new absorption bands at 2,972 and 847 cm^{-1} respectively in other curves, attributed to the attached CH$_3$ groups, which indicated that –Si(CH$_3$)$_3$ group had been successfully grafted on the Cu-HMS surface. The intensities of the absorption band at 3,440 and 1,636 cm^{-1} which were ascribed to the free SiOH groups and adsorbed water molecules, were obviously decreased after silylation, which indicated that the SiOH groups of Cu-HMS surface decreased and hydrophobicity
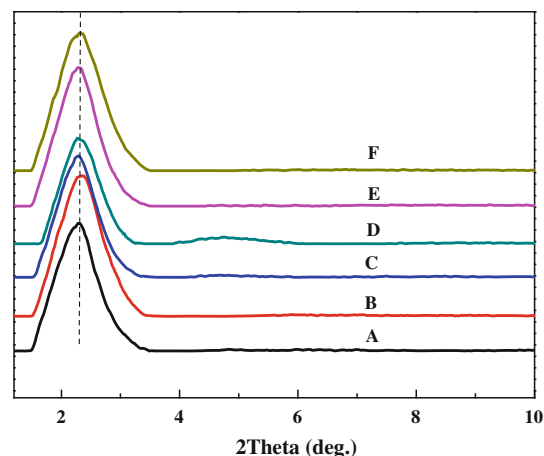
Fig. 2 XRD patterns of PdCl$_2$/Cu-HMS and PdCl$_2$/Si-Cu-HMS-x *A* PdCl$_2$/Cu-HMS, *B* PdCl$_2$/Si-Cu-HMS-25, *C* PdCl$_2$/Si-Cu-HMS-50, *D* PdCl$_2$/Si-Cu-HMS-60, *E* PdCl$_2$/Si-Cu-HMS-70, *F* PdCl$_2$/Si-Cu-HMS-75

enhanced. It was the surface hydrophobic groups that efficiently reduced activity sites adsorbed by water, which was beneficial to the improvement of catalytic performance of catalysts.

3.2.2 XRD Analysis

The XRD pattern (Fig. 2.) for parent PdCl$_2$/Cu-HMS and modified PdCl$_2$/Si-Cu-HMS-x displayed the featured diffraction peaks. It could be seen that the patterns of PdCl$_2$/Si-Cu-HMS-x were similar to that of the parent PdCl$_2$/Cu-HMS except the observed slight differences both in terms of the width and intensities of the (100) peak, showing that the pore structure integrity was kept after silylation. The observed increase in the (100) peak width and decrease in the peak intensity of PdCl$_2$/Si-Cu-HMS-60 were probably due to slight structure collapses during modification, reflecting a worse crystallinity degree and order of pore structure, which demonstrated that silylation was more complete at 60 °C in consistent with Table 1.

3.2.3 N$_2$ Adsorption–Desorption and Water Adsorption Capacity Test

In order to further explore silalytion effect on pore structure of Cu-HMS, N$_2$ adsorption–desorption was performed, shown in Fig. 3. All samples exhibited complementary textural framework-confined mesoporosity, as evidenced by the presence of type IV isotherms and H$_1$ hysteresis loops, implying that silylation did not damage the framework of Cu-HMS [27]. The rapid rise in the adsorption branches for all the samples at a relative pressure (P/P$_0$) of 0.2–0.3 stemmed from capillary condensation in the mesopores. Moreover, the knees for the
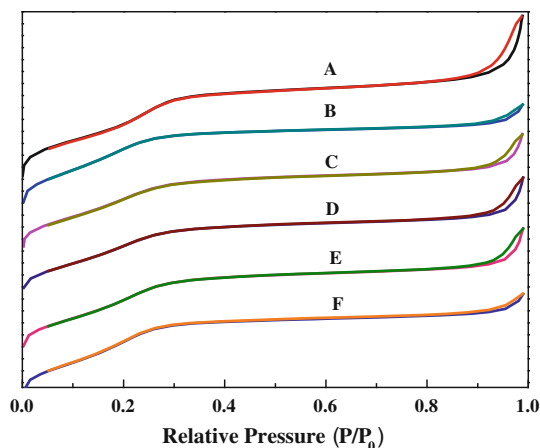
Fig. 3 N$_2$ adsorption–desorption isotherms of PdCl$_2$/Cu-HMS and PdCl$_2$/Si-Cu-HMS-x *A* PdCl$_2$/Cu-HMS, *B* PdCl$_2$/Si-Cu-HMS-25, *C* PdCl$_2$/Si-Cu-HMS-50, *D* PdCl$_2$/Si-Cu-HMS-60, *E* PdCl$_2$/Si-Cu-HMS-70, *F* PdCl$_2$/Si-Cu-HMS-75

Table 2 The textural properties and water adsorption capacity of PdCl$_2$/Cu-HMS and PdCl$_2$/Si-Cu-HMS-x

Samples	S$_{BET}$ (m^2 g^{-1})	Pore size (nm)	V$_{pore}$ (cm^3 g^{-1})	Water adsorption capacity (%)
A (PdCl$_2$/Cu-HMS)	1,068.21	4.14	1.11	44.76
B (PdCl$_2$/Si-Cu-HMS-25)	1,053.10	2.70	0.71	7.10
C (PdCl$_2$/Si-Cu-HMS-50)	876.17	3.56	0.78	6.58
D (PdCl$_2$/Si-Cu-HMS-60)	880.01	3.58	0.80	7.90
E (PdCl$_2$/Si-Cu-HMS-70)	963.63	3.48	0.84	8.73
F (PdCl$_2$/Si-Cu-HMS-75)	1,035.58	2.77	0.72	5.35

modified samples were not as steep as that before modification, suggesting a slightly decline hexagonal order after silylation.

Table 2 showed the textural properties and water adsorption capacity on various samples, reflecting the success of the modification. It could be seen that the subsequent modifications performed on the Cu-HMS material led to a concomitant decrease of the specific surface areas (S$_{BET}$) and mesoporous volumes (V$_{pore}$), which was ascribed to decrease of efficient pore channels by large trimethylsilyl groups grafted. Pore diameter reached the largest among silylated samples at 60 °C, which might be another reason for the best catalytic performance besides hydrophobicity (table 1), because large pore was more favorable to the contact between reactants and active sites in pore channel of catalyst. As expected, the TMCS-modified Cu-HMS samples contained a much stronger hydrophobicity compared to the parent sample because of hydrophobic groups grafted on the surface of Cu-HMS. The small amount of adsorbed water possibly occurred at the residual SiOH sites through hydrogen bonding and/or the strained siloxane bridges by rehydroxylation [19]. However, there was a little difference in water adsorption capacity of the silylated samples under different silylation temperatures, which was attributed to the difference of pore volume [28]. Surprisedly, for PdCl$_2$/Si-Cu-HMS-25 catalyst, there did not exist such a relevance between water adsorption capacity and pore volume. It was surmised that there was more residual –OH on PdCl$_2$/Si-Cu-HMS-25 catalyst due to low degree of silylation, which increased its water adsorption capacity.

Figure 4 showed the weight loss of PdCl$_2$/Cu-HMS and PdCl$_2$/Si-Cu-HMS-x through thermogravimetric analysis. The first weight loss below 150 °C was due to the loss of

physisorbed water in the voids of mesoporous structure. The second weight loss between 250 and 350 °C was attributed to the template. Finally, the third weight loss in the temperature range of 400–550 °C was assigned to the water loss from the condensation of adjacent silanol groups to form siloxane bond [29, 30]. Moreover, all the weight loss of silylated samples decreased, indicating that they had a better hydrophobicity and a fewer existence of –OH on the catalyst surface than PdCl$_2$/Cu-HMS. So silylated catalysts exhibited a better activity because decline of -OH might benefit the removal of water, thus reducing activity sites adsorbed by water and hydrolysis of DEC, which improved catalytic performance of catalysts in a certain degree.
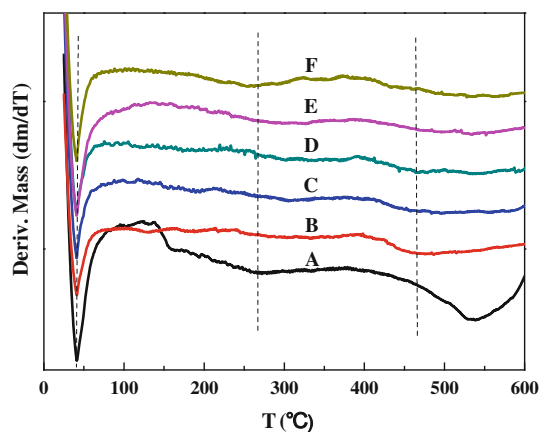

Fig. 4 TG patterns of PdCl$_2$/Cu-HMS and PdCl$_2$/Si-Cu-HMS-x *A* PdCl$_2$/Cu-HMS, *B* PdCl$_2$/Si-Cu-HMS-25, *C* PdCl$_2$/Si-Cu-HMS-50, *D* PdCl$_2$/Si-Cu-HMS-60, *E* PdCl$_2$/Si-Cu-HMS-70, *F* PdCl$_2$/Si-Cu-HMS-75

4 Conclusion

This work synthesized a family of organic–inorganic hybrid materials by combining TMCS with Cu-HMS, and investigated the influence of temperature to silylation. The obtained $PdCl_2$/Si-Cu-HMS-x exhibited a higher conversion and activity in comparison with $PdCl_2$/Cu-HMS, coupled with an excellent selectivity for the synthesis of DEC by oxidative carbonylation of ethanol. It was obviously demonstrated that silylation had modified the Cu-HMS surface and improved hydrophobicity, which benefited the removal of water and thus reduced activity sites adsorbed by water and hydrolysis of DEC. It was noteworthy that there existed a higher catalytic activity at 60 °C, which was due to that 60 °C was just above boiling point of TMCS, where silylation was considered as vapor–liquid–solid reaction, benefiting fully silylating. This simple but effective strategy for designing organic–inorganic hybrid materials may draw an outline for applying in the removal of water.

References

1. Pacheco MA, Marshall CL (1997) Energy Fuel 11:2
2. Briggs DN, Lawrence KH, Bell AT (2009) Appl Catal A 366:71
3. Moumouzias G, Ritzoulis G, Siapkas D, Terzidis D (2003) J Power Sources 122:57
4. Herstedt M, Stjerndahl M, Gustafsson T, Edstrom K (2003) Electrochem Commun 5:467
5. Dunn BC, Guenneau C, Hilton SA, Pahnke J, Edward M (2002) Energy Fuel 16:177
6. Briggs DN, Bong G, Leong E, Oei K, Lestari G, Bell AT (2010) J Catal 276:215
7. Li Z, Niu YY, Zhu QF, Fu TJ, Zhu QF, Yin LY (2011) Chin J Inorg Chem 27:1277
8. Zheng HY, Ren J, Zhou Y, Niu YY, Li Z (2011) J Fuel Chem Technol 39:282
9. Eta V, Maki-Arvela P, Salminen E, Salmi T, Murzin DYu, Mikkola J-P (2011) Catal Lett 141:1254
10. Rebmann G, Keller V, Ledoux MJ, Keller N (2008) Green Chem 10:207
11. Richter M, Fait MJG, Eckelt R, Schreier E, Schneider M, Pohl M-M, Fricke R (2007) Appl Catal B 73:269
12. Zhang PB, Huang SY, Wang SP, Ma XB (2011) Chem Eng J 172:526
13. Huang SY, Wang Y, Wang ZZ, Yan B, Wang SP, Gong JL, Ma XB (2012) Appl Catal A 417–418:236
14. Zhang PB, Ma XB (2010) Chem Eng J 163:93
15. Zhang PB, Zhang Z, Wang SP, Ma XB (2007) Catal Commun 8:21
16. Zhang PB, Fan MM, Jiang PP (2012) RSC Adv 2:4593
17. Itoh H, Watanabe Y, Mori K, Umino H (2003) Green Chem 5:558
18. de Juan F, Hitzky ER (2000) Adv Mater 12:430
19. Zhao XS, Lu GQ (1998) J Phys Chem B 102:1556
20. Antochshuk V, Jaroniec M (2000) Chem Mater 12:2496
21. Igarashi N, Hashimoto K, Tatsumi T (2007) Micro Meso Mater 104:269
22. Lin KF, Pescarmona PP, Houthoofd K, Liang DD, Tendeloo GV, Jacobs PA (2009) J Catal 263:75
23. Li XF, Gao HX, Jin GJ, Chen L, Yang HY, He X, Chen QL (2007) Chin J Catal 28:551
24. Tanev PT, Pinnavaia TJ (1995) Science 267:865
25. Pauly TR, Pinnavaia TJ (2001) Chem Mater 13:987
26. Anderson SA, Root TW (2004) J Mol Catal A 220:247
27. Wang L, Han XL, Li JD, Qin L, Zheng DJ (2012) Powder Technol 231:63
28. Park DH, Nishiyama N, Egashira Y, Ueyama K (2001) Ind Eng Chem Res 40:6105
29. Ye X, Jiang PP, Zhang PB, Dong YM, Jia CS, Zhang XM, Xu HZ (2010) Catal Lett 137:88
30. Occellia ML, Biz S, Auroux A, Ray GL (1998) Micro Meso Mater 26:193