

2. Experimental

2.1. Catalyst Preparation

Cu-HMS were synthesized following the procedures similar to those proposed by Tanev et al. via a neutral templating pathway using dodecylamine (DDA) as a surfactant.¹ In a typical synthesis, 3.85 g of DDA was dissolved in 130 ml of water, then 32.5 ml of ethanol was then added to generate a 40:10 H₂O/EtOH solution of the surfactant. The surfactant solution was stirred for 15 min. At the same time, 0.35 g of 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 room temperature (25 °C) to obtain crystalline products. 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 experiments.

A Pd-containing solution was prepared by heat-dissolving palladium chloride (PdCl₂) in methanol solution at a temperature of 65 °C. Fully dried Cu-HMS supports were mixed with the solution and was then 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 one hour to get a solid catalyst. The total contents of the metal compound in terms of metallic palladium was 0.25 % by weight based on the weight of carrier.

2.2. Production and Analysis of Diethyl Carbonate (DEC)

Catalytic activity was measured by a computer-controlled continuous micro reactor system

(WFS-3015) with a quartz tubular reactor of 4 mm inner diameter. The reaction products collected by a cooling trap were taken out and sampled each hour, and 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-01 and Propak-Q packed column. The reaction conditions were steadily kept at a reaction temperature of 140 °C and a reaction pressure of 0.64 MPa.

2.3. Thermodynamic data

The Thermodynamic data of DEC was not found in the thermodynamics notebook. So it could be estimated by group contribution method.² And the Gas standard thermodynamic data of other molecules was got from the thermodynamics notebook.²

- 1 (a) P.T. Tanev, T.J. Pinnavaia, *Science*, 1995, 267, 865 ; (b) T.R.Pauly, T.J. Pinnavaia, *Chem. Mater.*, 2001, 13, 987.
- 2 (a) I. Prigogine, R. Defay, *Chemical Thermodynamics*, London: Longmans Green, 1954, pp. 38–42; (b).P.S. Ma, *Chemical data*, Beijing: China petrochemical press, 2003; (c) S. Wang, *The handbook of Petrochemical design (The first volume)*, Beijing: Chemical industry press, 2002, pp. 452–459.