

CuCl catalyst heterogenized on diamide immobilized SBA-15 for efficient oxidative carbonylation of methanol to dimethylcarbonate†

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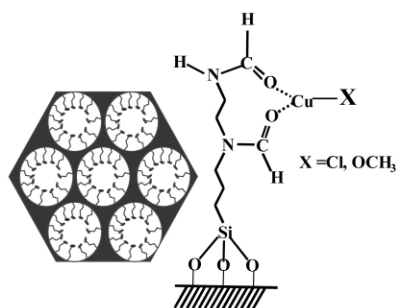
CuCl has been successfully immobilized on a novel diamide modified SBA-15, and proven to be an efficient heterogenized catalyst for the oxidative carbonylation of methanol to dimethylcarbonate.

Dimethylcarbonate (DMC) is an environmentally benign chemical compound and unique intermediate with versatile chemical reactivity which has attracted increasing interest from both practical and fundamental points of view in recent years.¹⁻⁴ Simple copper salts are widely used as catalysts in the liquid phase oxidation carbonylation of methanol to dimethylcarbonate. Recently, new efficient homogeneous complex catalyst systems for DMC synthesis have been developed by us and others.^{5,6} However, a homogeneous catalytic system often has disadvantages, such as difficult separation of the products and corrosive effect of the catalyst on the reactor materials. In developing large-scale processes, it is extremely important to heterogenize homogeneous catalyst systems, because heterogeneous catalytic systems have attractive advantages over homogeneous counterparts in liquid-phase reactions, including easy removal of catalysts from reaction mixtures and recycling/reuse of catalysts.^{7,8} Recently, Sato and co-workers have developed heterogenized homogeneous catalyst systems by using polymers as supports,⁹⁻¹¹ but the catalytic results in terms of methanol conversion and DMC selectivity are far from satisfactory. SBA-15 is a newly discovered mesoporous silica molecular sieve with tunable uniform hexagonal channels ranging from 5 to 30 nm and thick framework walls (3–6 nm), which is therefore thermally and hydro-thermally more robust than a polymer support.¹² Here we report a novel heterogeneous catalyst system based on CuCl immobilized on a diamide-modified mesoporous SBA-15 silica (Scheme 1), which is air-stable and reusable, and exhibits excellent catalytic performance for the oxidative carbonylation of methanol to DMC.

The mesoporous silica material SBA-15 was prepared according to the literature procedure¹² using Pluronic P123 triblock polymer (EO₂₀PO₇₀EO₂₀, M_{av} = 5800, Aldrich) as template under acidic conditions. Briefly, a solution of

EO₂₀PO₇₀EO₂₀:2 M HCl:TEOS:H₂O = 2:60:4.25:15 (mass ratio) was prepared, stirred for several hours at 40 °C, and then heated at 95 °C for 3 days.¹³ The solid products were filtered off and calcined at 500 °C for 5 h. The aminosilylation procedure was performed with *N*-(2-aminoethyl-3-aminopropyl)trimethoxysilane (aapts) according to the procedure given in ref. 14 with some minor modification. SBA-15 dehydrated at 200 °C was contacted with a refluxing of toluene solution containing 10 wt% aapts for 5 h. This mixture was stirred vigorously at room temperature for 1 h and refluxed for 6 h. The solid was isolated by filtration to obtain the amine-grafted SBA-15. The obtained diamine-grafted SBA-15 (SBA-15-aapts) was then treated with 50 ml of a refluxing toluene solution containing 5 wt% ethyl formate for 6 h to obtain diamide-functionalized solids. Finally the amide modified SBA-15 (SBA-15-diamide) was dispersed in 150 ml of toluene, and 2 g CuCl were added and refluxed for 12 h, the heterogenized CuCl catalyst (SBA-15-diamide-CuCl) was obtained by filtration, washed and dried. Elemental analysis of the SBA-15-amide-CuCl using ICP gave a 3.38 wt% loading of copper. Into a 150 ml autoclave fitted with a Teflon® liner and containing 10 ml of methanol, the powdered catalysts were charged (Cu(I)/CH₃OH molar ratio = 1/240). Then, O₂ (P_{O_2} = 0.24 MPa) and CO (P_{CO} = 2.76 MPa) were introduced. After carrying out the reaction at around 120 °C for 5 h with a stirring rate of 1000 rpm, the liquid products were analyzed by GC (Shanghai Analysis GC-122) equipped with an FID using a SGE capillary column (0.5 μm × 30 m). Gaseous products (O₂, CO₂ and CO) were analyzed with TCD using a TDX-01 packed column (3.0 mm × 6 m). Products were also identified by GC-MS.

A number of analytical studies have been carried out to gain information on the copper loading and distribution, the material structure and the surface species. The powder X-ray diffraction patterns (XRD) of the all SBA-15 materials show a very intense peak and two weak peaks characteristic of 2-d hexagonal (*P6mm*) structure with excellent textural uniformity. There were no significant changes upon diamide and CuCl immobilization except for the expected changes in XRD peak intensity. Optical and scanning electron microscopic studies on the material reveal a homogeneous mass with elemental analysis (EDAX) carried out at randomly selected spots showing a consistent Cu:Si ratio of *ca.* 3:11. This suggests an evenly distributed copper complex rather than a simple mixture of a copper complex with the SBA-15 silica. It was confirmed that the nitrogen adsorption isotherms are type IV in nature and exhibited a H1 hysteresis loop, which is typical of mesoporous solids. The adsorption isotherms show a sharp inflection at relative pressures of 0.65–0.85, which is a characteristic of capillary condensation within uniform mesopores. Pore sizes are 6.5 nm and 6.4 nm and BET surface areas are 548 m² g⁻¹ to 364 m² g⁻¹ for SBA-15-diamide and SBA-15-diamide-CuCl, respectively. All these results indicate that the immobilization of CuCl does not affect the pore structures of the SBA-15 material or cause the decrease of surface area that is consistent with copper loading. TG-DTA studies on SBA-15-diamide and SBA-15-diamide-CuCl reveal that the organic moieties begin to decompose at temperatures above 523 K, which means the catalyst are stable at reaction temperature. The XPS-Auger



SBA-15-amide-CuCl
Scheme 1

† Electronic supplementary information (ESI) available: XPS and Auger spectra of the SBA-diamide-CuCl sample. See <http://www.rsc.org/suppdata/cc/b3/b301375h/>

Table 1 Catalytic performance of the amide-immobilized CuCl catalysts in the DMC synthesis^a

Entry	Catalyst	Pore size/nm	Cu loading (wt%)	CH ₃ OH ^c Conv. (%)	DMC (mass%)	DMC ^d sel.(CH ₃ OH) (%)	DMC ^e yield (O ₂) (%)	DMC ^f sel.(O ₂) (%)
1	CuCl	—	—	9.7	12.8	97.0	41.6	97.5
2	SBA-diamide-CuCl	6.4	3.38	22.1	28.0	99.2	96.5	99.8
3	Removed from #2	6.4	3.22	19.6	25.5	98.4	85.8	99.7
4	Removed from #3	6.4	3.19	16.5	21.7	97.9	72.6	99.4
5	Removed from #4	6.4	3.15	14.5	19.3	97.5	65.1	99.2
6 ^b	SBA-15-CuCl	7.0	3.35	7.1	8.7	95.5	30.0	92.6
7	MCM-diamide-CuCl	1.9	3.05	11.2	15.0	97.5	48.3	98.3
8	SiO ₂ -diamide-CuCl	11.0	2.80	10.3	13.8	97.2	44.3	97.6

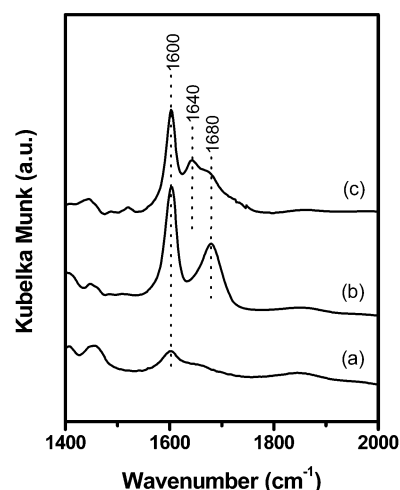
^a Reaction conditions: Cu(I)/methanol molar ratio = 1/240, 0.24 mol of methanol, 120 °C, 5 h. ^b Prepared by the conventional wet-impregnation method. ^c Methanol conv. % = reacted methanol/introduced methanol. ^d DMC sel.(CH₃OH) % = 2 produced DMC/reacted methanol. ^e Yield of DMC (O₂) % = produced DMC/2 introduced O₂. ^f Selectivity of DMC (O₂) % = produced DMC/(produced DMC + produced CO₂).

characterization confirms the presence of Cu(I) species over the surface of SBA-15-diamide-CuCl (ESI†).

The remarkable activity of the SBA-15-diamide-CuCl catalyst can be seen from Table 1. Entry 2 shows that SBA-15-diamide-CuCl is very active with a 22.1% conversion of methanol and a 96.5% yield of DMC based on O₂, which are more than twice those of the commercial CuCl catalyst (Aldrich, 99.9%, average size ~ 0.5–1 μm). Heterogeneous catalysts often suffer extensive leaching of active metal species during reactions and eventually lose their catalytic activity. To our surprise, SBA-15-diamide-CuCl maintained its high catalytic activity even after four recyclings and reuse of the catalyst (entries 3–5 in Table 1) although a Cu leaching of about ~ 7% occurred. SBA-15-diamide-CuCl maintained much higher catalytic activity than CuCl even after four runs. CuCl was also loaded onto SBA-15 using the conventional impregnation method. The catalytic activity of the impregnated catalyst was found to be inferior to that of CuCl. MCM-41 (surface area 940 m² g⁻¹) and amorphous silica gel (surface area 340 m² g⁻¹, mean pore size 11 nm) were also applied as supports. Clearly the catalytic performance of SBA-15-diamide-CuCl (mean pore size 6.4 nm) is superior to that of MCM-41-diamide-CuCl (mean pore size 1.9 nm) and amorphous silica-diamide-CuCl. The higher catalytic activity of SBA-15-diamide-CuCl might be due to the easy access and discharge of reactants in larger regular mesopores. It is also interesting to note that SiO₂-diamide-CuCl and MCM-41-diamide-CuCl exhibit comparable activities although the former has a much larger pore size; this could possibly be due to their similar low CuCl loadings.

The dramatic increase in the reaction efficiency of the CuCl catalyst upon immobilization in the present case can be understood by a strong ligand interaction between the copper species and the amide moieties in the SBA-15 material.⁵ The DRIFT spectrum of SBA-15-diamide material shows a C=O stretching absorption band at ca. 1680 cm⁻¹ and N-H bending band at ca. 1600 cm⁻¹ (Fig. 1). Compared to that of SBA-15-diamide, the amide carbonyl band was shifted to lower wavenumber at 1640 cm⁻¹ for SBA-15-diamide-CuCl, indicating the existence of strong ligand interactions between the amide carbonyl group and the copper species. Thus, the promotional effect of CuCl catalyst upon immobilization in the present reaction system is to facilitate the intrinsic Cu(II)/Cu(I) redox processes by a strong electronic modification of the copper species by the amide moieties in the SBA-15-diamide material,¹⁵ leading to dramatically enhanced methanol oxidative carbonylation activity in DMC synthesis.

In conclusion, we have successfully demonstrated for the first time that CuCl immobilized on diamide modified SBA-15 is an excellent heterogeneous candidate for oxidative carbonylation of methanol to DMC. The catalyst systems can be separated easily and are reusable, showing attractive potential for practical applications.

**Fig. 1** DRIFT spectra of (a) SBA-15-aapts, (b) SBA-15-diamide, (c) SBA-15-diamide-CuCl.

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