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A novel synthetic approach for preparing dimethyl carbonate from dimethoxymethane and O₂ over Cu-MCM-48

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ABSTRACT

A new convenient method for the synthesis of dimethyl carbonate from dimethoxymethane and O_2 in the presence of catalytic amounts of Cu-MCM-48 was described. The XRD results indicate that the structure of Cu-MCM-48 is gradually distorted with the increase in the copper content, whereas the framework structure of Cu-MCM-48 is basically retained until the incorporated copper content reaches to 0.62 wt%. The SEM, TEM and N_2 adsorption studies show that copper content of 9.51 wt% completely changes the morphology and structure of Cu-MCM-48. Effects of the amount of the incorporated copper in catalyst, catalyst amount used and other reaction conditions on the catalytic activity are investigated in details to obtain the optimized reaction conditions. Short reaction time, easy recycling of the catalyst and excellent yields are the main advantages of this process.

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1. Introduction

Many of the traditional industrial processes for preparing fine and bulk chemicals are known to have negative impact on human health and the environment due to the various disadvantages such as pollution, high costs, poor chemical selectivity, long reaction times, high reaction temperatures, to name just a few. Consequently, the search for clean, energy efficient, selective, and environmentally sustainable processes for such chemicals is attracting considerable research attention. Dimethyl carbonate (DMC) is a versatile compound that represents an attractive eco-friendly alternative to methylhalides or dimethylsulfate in methylation reactions and to poisonous phosgene (COCl₂) in polycarbonate and isocyanate syntheses [1]. It is also considered as an ideal additive for transportation fuels due to its higher oxygen content (53.3%) and good blending properties with octane [2]. Additionally, DMC is also considered as a promising alternative to the use of ketones and ester acetates in the field of paints and adhesives due to a strong solvation power. The latter, combined with its low

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viscosity also renders it useful in lithium ion battery applications [3].

There are several routes for DMC synthesis, such as phosgenation of methanol, oxidative carbonylation of methanol, transesterification and direct synthesis from carbon dioxide and methanol [4–13]. However, the first two processes use toxic, corrosive, flammable and explosive gases such as phosgene, hydrogen chloride and carbon monoxide [14]. The transesterification route has the disadvantages of high cost of the starting materials and difficulty in the product separation [15]. DMC yield in carbon dioxide and methanol route is relatively low due to the fact that CO₂ is highly thermodynamically stable and kinetically inert and due to the deactivation of catalysts induced by water formation in the reaction process [16,17].

DMC could be obtained from selective oxidation of dimethoxymethane (DMM), as the following reaction equation:

$$CH_2(OCH_3)_2 + O_2 \rightarrow C_3H_6O_3 + H_2O_3 + H_2$$

In the reaction, the by-product is water; furthermore, DMM has extremely low toxicity and can be produced on a large scale [18]. Compared to the conventional synthesis methods of DMC, the synthesis process of DMC from selective oxidation of DMM is simple, eco-friendly and high atom-economic. To the best of our knowledge, although there have been a limited number of studies on the synthesis of DMC by this route reported in the literature [19], they suffer many disadvantages such as the tedious preparation process





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Table 1

The adding amount of TEOS and $Cu(NO_3)_2$ ·3H₂O in the preparation procedure and the Cu content in Cu-MCM-48-X products.

Samples	$Cu(NO_3)_2 \cdot 3H_2O(g)$	TEOS (g)	Cu content in products (wt%)
Cu-MCM-48-1	0.02	8.6	0.27 (0.21 ^b)
Cu-MCM-48-2	0.05	8.6	0.62 (0.53 ^b)
Cu-MCM-48-3	0.10	8.6	1.16 (1.05 ^b)
Cu-MCM-48-4	0.25	8.6	2.75 (2.58 ^b)
Cu-MCM-48-5	0.50	8.6	5.16 (5.00 ^b)
Cu-MCM-48-6	1.00	8.6	9.51 (9.41 ^b)
CuO/SiO ₂	0.16	3.5 ^a	4.1 (4.0 ^b)

^a The calculated value in term of the conversion of 1.0 g SiO₂ into TEOS.

^b The calculated Cu content in final product(CuO/SiO₂ materials) according to the adding amount of TEOS and Cu(NO₃)₂· $3H_2O$.

of catalysts, the low selectivity on of DMC and the conversion of DMM ($Y_{\text{DMC/max}}$ = 35.4%).

In this paper, we introduce a new synthesis method of DMC from DMM and O_2 over copper modified mesoporous molecular sieve Cu-MCM-48 in a batch reactor. The optimal reaction conditions for DMC synthesis and a plausible mechanism for the selective oxidation of DMM and O_2 over Cu-MCM-48 catalyst was proposed.

2. Experimental

2.1. Catalyst preparation

The samples were prepared with tetraethyl orthosilicate (TEOS) as silica source, and cetyltrimethylammonium bromide (CTAB) as a template [20]. In a typical synthesis, 0.79 g NaOH and 6.20 g CTAB were dissolved in deionized water and the resulting solution was stirred at 35 °C for about 40 min, and then 0.02 g Cu(NO₃)₂·3H₂O was added into the solution, followed by slow addition of 8.6 g TEOS (Cu/Si = 0.002, mole ratio). The mixture was stirred for 1 h before it was loaded into a Teflon-lined stainless steel vessel, and kept at 110°C for 3 days. The solid product was filtered, washed with deionized water, dried in air at 110 °C for 1 day and calcined at 550 °C for 6 h to obtain the solid catalysts. This synthesized sample was designated as Cu-MCM-48-1 (1 is the sample number). A similar procedure was followed for the synthesis of the Cu-MCM-48-X (X=2-6; the sample number) through adding different amount of Cu(NO₃)₂·3H₂O (Table 1) in the synthesis mixtures.

For comparison, a SiO₂ supported CuO catalyst (CuO/SiO₂) with 4.0 wt% copper content was prepared by the traditional impregnation method. 1.0 g SiO₂ powders (surface area, 270 m²/g) were added into 11 ml of aqueous solution containing Cu(NO₃)₂·3H₂O(0.06 M). After being aged at room temperature for 2 h, the samples were vaporized at 45 °C in the water bath. Finally, the prepared sample was dried at 110 °C for 1 day, followed by calcination at 550 °C for 6 h to obtain the SiO₂-supported catalysts.

2.2. Catalyst characterization

Powder X-ray diffraction patterns (XRD) were recorded on a Rigaku D/Max-2500 diffractometer (40 kV, 40 mA) with CuK α radiation. TEM images were obtained on a JEM-2010 transmission electron microscope at an acceleration voltage of 200 kV. N₂ adsorption/desorption measurements were carried out at 77 K on a Micromeritics Tristar 3000 analyzer. FTIR spectra were collected on a Thermo-Nicolet Nexus 670 FTIR spectrometer by using conventional KBr pellet method. The Cu content of catalyst was determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (IRIS intrepid II XSP, Thermo). The X-ray photoelectron spectra measurements were performed on the instrument of Thermo ESCALAB 250 using Al K α radiation (1486.6 eV), and C 1s (284.6 eV) was utilized as a reference to correct the binding energy. Temperature programmed reduction (TPR) with H₂ were performed using a Belcat instrument. Typically, the U-tube quartz microreactor was loaded with 50 mg catalyst along with quartz wool and heated at a temperature ramp from 25 to 800 °C at 10 °C/min with a gas consisting of 5% H₂ in Ar. The gas flow rate was 30 ml/min. The H₂ consumption (TCD signal) was recorded automatically by TCD detection.

2.3. Catalytic reaction

The oxidative reaction of DMM with molecular oxygen was conducted in a 100 ml stainless steel batch reactor. A typical reaction process was as follows: 20 mmol DMM were dissolved into the acetonitrile solvent (20 ml) in the reactor, and then 1 mmol Nhydroxyphthalimide (NHPI) used as inducing agent and 1 mmol chlorobenzene as the internal standard agent for quantitative analysis were added into the solution. After that, 0.5 g Cu-MCM-48 powders were added into the mixed solution above. Subsequently, the reactor was sealed after adding the reaction mixtures and purged with O_2 for 5 min. Finally, the reactor with 2.0 MPa O_2 was heated to the setting temperature for the desired time under the magnetic stirring. At the end of the reaction, the products were analyzed with a GC9890A Gas Chromatographer (GC) equipped with a DB-WAX column and a flame ionization detector (FID).

3. Results and discussion

3.1. Characterization of Cu-MCM-48

The ICP analyses reveal that the copper amount in the prepared samples can be tuned in the range from 0.27 to 9.51 wt% (Table 1) by changing the content of $Cu(NO_3)_2 \cdot 3H_2O$ in the reaction mixtures using the method described in the Section 2. The measured amount of copper in these samples shows a slight higher value than that in the synthesis mixtures, probably owing to the loss of silicon-containing materials in the process of synthesis, which indicates that all of $Cu(NO_3)_2 \cdot 3H_2O$ in the synthesis mixture is almost introduced into the prepared catalyst. Disappearance of the bands at 2925 and 2854 cm⁻¹ in the FI-IR spectra of Cu-MCM-48-*Xsamples* calcined at 550 °C for 6 h showed that the template in the samples had been effectively removed (see Supporting information, Fig. S1).

Fig. 1 shows the SEM and TEM images of Cu-MCM48-2 (a and c) and Cu-MCM-48-6 (b and d), respectively. The Cu-MCM-48-2 containing 0.62 wt% copper retains the similar morphology and structural integrity to that of MCM-48 [20] (Fig. 1a and c), whereas the ordered channels in the structure of MCM-48 were not observed in Cu-MCM-48-6 which contains a copper content of 9.51 wt%. On the other hand, the TEM studies revealed that no obvious extra phases of the copper species were presented in those samples containing less copper, indicating that the copper species is well dispersed in these samples. These results were also confirmed by the XRD patterns of the samples (see Fig. 2B). No diffraction peaks at 2θ = 36.18° and 38.78° corresponding to the crystalline CuO particles were presented in the high-angle XRD patterns for the prepared Cu-MCM-48-X (X = 1-5) samples. However, two very weak diffraction peaks of CuO were observed for Cu-MCM-48-6 with higher copper content corresponding to a thimbleful of the tiny crystalline CuO. It can be seen from Fig. 2A that the stronger diffraction peaks at 2θ = 2.7° and 2θ = 3.2° corresponding to an ordered MCM-48 structure were observed for Cu-MCM-48-1 and 2, while these peaks disappeared for Cu-MCM-48-4 and 6. These experimental results illustrate that the content of copper precursors in the synthesis mixtures has a remarkable effect on the morphology and structure of the synthesized Cu-MCM-48-X.



Fig. 1. SEM and TEM images of Cu-MCM48-2 (a and c) and Cu-MCM48-6 (b and d).

The N₂ adsorption-desorption isotherms of the Cu-MCM-48-2, -4 and -6 belong to Type IV with H4 type of hysteresis loops (see Fig. 3). The investigation results in Table 2 indicate that their BET surface area, average pore size and pore volume decreased with increasing copper content in the prepared samples. Cu-MCM-48-2 (0.62 wt% copper) possesses a $343.0 \text{ m}^2/\text{g}$ surface area with a pore size distribution centered at 2.7 nm. When the copper content of the sample (Cu-MCM-48-4) reaches to 2.75 wt%, its BET surface area and average pore size decrease to 207.1 m²/g and 2.3 nm, respectively. These facts clearly indicate the copper modified mesoporous molecular sieve (Cu-MCM-48-2) containing the incorporated copper content of 0.62 wt% still retains the ordered structure of MCM-48 and the uniform dispersion of copper, and the higher incorporated copper content can result not only in the structure breakage of MCM-48 but also in the formation of CuO in the Cu-MCM-48-X. Based on the investigation of XRD, TEM and N₂ adsorption-desorption isotherms, we conclude that the typical mesoporous structure of MCM-48 is gradually destroyed with the increase of the incorporated copper content in the prepared samples.

In ordered to explore the chemical environment of Cu elements in the surface of the Cu-MCM-48-X catalysts, their X-ray photoelectron spectroscopy (XPS) were measured. Fig. 4 depicts the Cu 2p spectra of the different samples. All Cu 2p spectra show the typical

Table 2	
Textual properties of the prepared catalysts G	Cu-MCM-48-X

Samples	BET surface area (m²/g)	Average pore size (nm)	Pore volume (cm ³ g ⁻¹)
Cu-MCM-48-2	343.0	2.7	0.58
Cu-MCM-48-4	207.1	2.3	0.21
Cu-MCM-48-6	53.5	-	0.24

structure for copper oxides with broad main peaks (Cu 2p3/2 and Cu 2p1/2) and typical shake-up satellites except that of Cu-MCM-48-1. Electron binding energies of the Cu 2p3/2 peaks between 933.8 and 934.4 eV and typical shake-up satellites are observed for the sample of Cu-MCM-48-X, which corresponds to divalent Cu [21,22]. Their Cu 2p3/2 spectra can be deconvoluted into two individual peaks as shown in Fig. 4. The binding energies at 934.4 (Cu-MCM-48-2), 934.1 (Cu-MCM-48-4) and 933.8 eV (Cu-MCM-48-6) are apparent along with CuO on the surface of MCM-48, which is higher than that of bulk CuO (933.7 eV). Such a shift of Cu 2p3/2 peak toward high energy was believed from the better dispersion of CuO on mesoporous silica. The other deconvolution peak for Cu-MCM-48-X (X = 2, 4, 6) observed at around 936.1 eV indicates the existence of Cu-O-Si-O species [23,24]. It is interesting that only a weak peak at 936.1 eV corresponding to Cu-O-Si-O were found in the Cu 2p3/2 spectrum of Cu-MCM-48-1with very low copper content (0.27 wt%). These results testified that a part of copper species were incorporated into the silica framework in the form of Cu–O–Si–O in the Cu-MCM-48-X with the higher copper content, whereas all the copper species were incorporated into the MCM-48 framework in the Cu-MCM-48-X with very low copper content.

The reducibility of copper species in Cu-MCM-48 catalysts was investigated by H₂-TPR experiments. Fig. 5 shows TPR profile of Cu-MCM-48-2 sample by H₂. There are four reduction peaks for Cu-MCM-48-2 sample observed in the range of 150–800 °C. The peaks centered at around 265 and 482 °C are associated with the reduction of Cu²⁺ to Cu⁺ and Cu⁺ to Cu⁰ as highly dispersed CuO, respectively. This phenomenon is similar to the reduction of CuO supported on the mesoporous MCM-41, MCM-48 and SBA-15 silica [21,25]. Nonetheless, peaks corresponding to around 638 and 720 °C may be ascribed to the reduction of Cu²⁺ to Cu⁺ and Cu⁺ to Cu⁰ in the Cu–O–Si–O form incorporated into the MCM-48 framework. The reduction feature of Cu²⁺ species at the high temperature



Fig. 2. The low-angle (A) and high-angle (B) XRD patterns of the MCM-48 and Cu-MCM-48-X (X = 1, 2, 4, 6).

can be attributed to the formation of Cu-containing stable materials which are more difficult to be reduced than free CuO species [26]. It is consistent with the fact of formation of Cu–O–Si–O in the prepared catalyst identified by XPS investigation.

3.2. Catalytic oxidation reaction of DMM with O_2

The systematic studies on the preparation of DMC from DMM and O_2 over Cu-MCM-48-X catalysts indicated that the reaction conditions for the preparation of DMC and the use of different catalysts apparently affect the yield of DMC.

The change in the amount of the incorporated copper in catalysts did not profoundly influence the selectivity of DMC (Fig. 6). However, The DMM conversion increased with the increase of the amount of incorporated copper, reaching the maximum value of 85.4% over Cu-MCM-48-2 catalyst with 0.62 wt% copper content, and then decreased to 67.8% over Cu-MCM-48-6 containing 9.51 wt% copper. But for all that, yield of DMC obtained over various Cu-MCM-48-X is much higher than that obtained over the SiO₂ supported CuO (CuO/SiO₂) catalyst (see Fig. 6), on which noncrystalline CuO was highly dispersed on SiO₂ (see Fig. S2, XRD diffraction pattern and XPS spectrum of CuO/SiO₂). Based on these experimental facts and the characterization results for Cu-MCM-48-X mentioned above, it can be deduced that the Cu–O–Si–O linkage is the active center for the catalytic oxidation reaction of DMM with O₂. The number of Cu–O–Si–O active sites for DMM



Fig. 3. N_2 adsorption-desorption isotherms and pore size distribution curves of samples.

conversion increases with increasing copper content among different samples with lower copper content. When the excessive copper was included in the catalysts (i.e.Cu-MCM-48-6), the effective Cu-O-Si-O active sites were covered partially by the dispersed CuO, which have a lower catalytic activity (see Fig. 6, CuO/SiO₂), thus leading to a poor performance. In addition, this experimental result also indicates that the number of exclusive functional active



Fig. 4. Cu 2p XPS spectra of Cu-MCM-48-X (X = 1, 2, 4, 6). (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)



Fig. 5. H₂-TPR profile of Cu-MCM-48-2.

sites in the prepared catalysts does change by the excessive copper. For the Cu-MCM-48 catalysts, the optimal amount of incorporated copper is 0.62 wt%.

It was found that the yield and selectivity of DMC were about 1.6% and 23.5% without the use of Cu-MCM-48 catalyst, respectively. When 0.1 g Cu-MCM-48-2 catalyst was used, the yield and selectivity of DMC reached 55.3% and 81.6%, respectively (see Fig. 7A). However, a further increase in the amount of catalyst used did not obviously improve the yield and selectivity of DMC. These phenomena provide a proof that Cu-MCM-48 plays a catalytic role in selective oxidation of DMM with O₂ as oxidant and indicate that the rate of chemical reaction in which the catalysts were initially involved is very fast.

The change of O_2 pressure did not markedly change the selectivity of DMC, but the effect of O_2 pressure on the conversion of DMM was obvious with the O_2 pressure increasing from 1.0 to 3.0 MPa (Fig. 7B). When the O_2 pressure was 2.0 MPa, the DMM conversion reached the maximum value. If O_2 pressure was further increased, the DMM conversion decreased slowly. It is concluded that the competitive adsorption between reactants DMM, O_2 and free radical initiator NHPI on the catalyst leads to the decrease of DMM conversion under the exorbitant O_2 pressure. Therefore, the optimal O_2 pressure is 2.0 MPa.

The conversion of DMM and the selectivity of DMC were greatly improved with the increase in reaction temperatures ranging from 140 to 180 °C (Fig. 7C). Further increase in the temperature did not cause obvious change of DMM conversion and DMC selectivity. The



Fig. 6. The effect of the amount of incorporated copper on selective oxidation of DMM. Reaction conditions: O₂ pressure 2.0 MPa, temperature 140 °C, reaction time 2 h, catalyst 0.5 g, NHPI 1 mmol.



Scheme 1. Mechanism for the oxidation reaction of DMM with O_2 catalyzed by Cu-MCM-48 catalyst in the presence of NHPI.

highest conversion of DMM and highest selectivity of DMC were obtained at 180 °C. Furthermore, the results in Fig. 7D indicate that the conversion of DMM and the selectivity of DMC are improved dramatically with the increase of the reactive time in the initial period of the reaction, and then kept unchanged beyond 2 h because the thermodynamic equilibrium of this reaction had been reached for 2 h at 180 °C.

In the absence of NHPI, the conversion of DMM and the selectivity of DMC was very low (Fig. 7E). Only a small amount of NHPI might extremely improve the yield and selectivity of DMC. The effect of further increasing the NHPI amount on the selective oxidation of DMM is negligible. From these phenomena it is inferred that NHPI acts only as an initiator for the reaction and that the synergistic effect between NHPI and Cu-MCM-48 catalyst accelerates the selective oxidation of DMM with O₂.

Based on the above results, the reactive conditions for synthesis of DMC from DMM with O_2 were optimized. The highest the DMM conversion (92.0%) and the DMC selectivity (88.9%) were obtained over the 0.3 g Cu-MCM-48-2 catalysts containing 0.62 wt% copper under 2.0 MPa O_2 pressure at 180 °C for 2 h in presence of the initiator NHPI (1 mmol). These values are greatly superior to those previously reported in the literature [19].

The results in Fig. 7-F suggested the possibility of recycling Cu-MCM48-2 under the optimal reactive conditions. In the five-time recycling operations, no deactivation was observed, indicating that the catalyst of Cu-MCM-48-2 is stable in the reaction system and has a favorable potential for the large-scale production of DMC from DMM and O_2 in chemical industry.

3.3. Suggested mechanism for the oxidation reaction of DMM

On the basis of the results of our studies and available published literature data [27,28], a plausible mechanism for the selective oxidation reaction of DMM with O_2 in the presence of NHPI over Cu-MCM-48 catalyst was proposed (Scheme 1).

The Scheme 1 shows the oxidation of DMM to DMC through radical pathways. The initial stage of the reactive procedure includes the reaction of NHPI with O_2 to create the PINO[•] radical over Cu-MCM-48 [29], and then PINO[•] radical can abstract the hydrogen atom from the DMM to produce the dimethoxymethyl radical (DMM[•]) and regenerate the NHPI. The resulting carbon-centered radical (DMM[•]) reacts with O_2 to form a peroxyl



Fig. 7. The effect of reactive conditions on the selective oxidation of DMM. Reaction conditions: (A) O₂ pressure 2.0 MPa, temperature 140 °C, reaction time 2 h, NHPI 1 mmol; (B) temperature 140 °C, reaction time 2 h, catalyst 0.3 g, NHPI 1 mmol; (C) O₂ pressure 2.0 MPa, reaction time 2 h, catalyst 0.3 g, NHPI 1 mmol; (D) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g, NHPI 1 mmol; (E) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g, NHPI 1 mmol; (E) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reaction time 2 h, catalyst 0.3 g; (F) O₂ pressure 2.0 MPa, temperature 180 °C, reactio

radical (DMMOO[•]), which is further converted to DMC and a hydroxyl radical (HO[•]) [30]. HO[•] radical can abstract hydrogen from either NHPI or a molecule of DMM to form H_2O and PINO[•] or DMM[•], respectively. Through the above-mentioned radical pathways, DMC is obtained by oxidizing the DMM with O_2 over Cu-MCM48.

4. Conclusion

The Cu-MCM-48 catalyst exhibits a very high catalytic activity for the synthesis of DMC by selective oxidation of DMM with O_2 . DMM conversion of 92.0% and DMC selectivity of 88.9% are achieved over the catalysts Cu-MCM-48-2, which are much higher than those previously reported results. At the same time, this new method for the preparation of DMC possesses the advantages of short reaction time, easy recycling of the catalyst and excellent yields. In addition, the oxidation reaction of DMM with O_2 over catalyst Cu-MCM-48 may proceed by a radical pathway.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata. 2013.01.014.

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