Effect of In-Situ Dehydration on Activity and Stability of Cu–Ni–K$_2$O/Diatomite as Catalyst for Direct Synthesis of Dimethyl Carbonate

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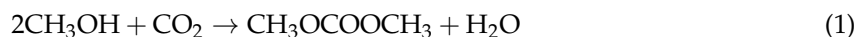
Abstract: An in-situ dehydrating system built in a continuous flow fixed-bed bubbling reactor for direct synthesis of dimethyl carbonate (DMC) was designed. 3A molecular sieve (MS) was selected as the ideal dehydrating agent and the water trapping efficiency was studied. The effect of dehydrating agent/catalyst ratio, the dehydrating temperature and pressure, as well as the space velocity on the direct DMC synthesis catalyzed by K$_2$O-promoted Cu–Ni was further investigated. These results demonstrated that 3A MS could effectively dehydrate the reaction system at the optimal conditions of 120 °C and 1.0 MPa with gas space velocity (GHSV) of 600 h^{-1}, thereby greatly shifting the reaction equilibrium toward high DMC yield. Higher DMC yield of 13% was achieved compared with undehydrated reaction. Moreover, the catalyst can be highly stabilized by 3A MS dehydration with stable performs over 22 h.

1. Introduction

The environment-friendly dimethyl carbonate has aroused great interest in fuel additives, polar solvents, and methylating and carbonylating agents [1–3]. It has been produced worldwide by several commercial methods such as ester exchange process [4,5], methanolysis of phosgene [6], and gas-phase oxidative carbonylation of methanol [7]. Recently, some green and economic dimethyl carbonate (DMC) synthesis routes have been studied all over the world. In these routes, DMC was directly synthesized from CH$_3$OH and CO$_2$ instead of using toxic, corrosive, flammable, and explosive gases such as phosgene, hydrogen chloride, and carbon monoxide as feedstock [8,9].

Over the last decades, improving the yield of DMC from the direct synthetic route has been mainly focused on catalyst development and optimization of reaction conditions. A large number of examples have been devoted to the direct synthesis of DMC from CO$_2$ and CH$_3$OH using organometallic compounds [10], CeO$_2$ [11], CeO$_2$-ZrO$_2$, Ce$_{0.5}$Zr$_{0.5}$O$_2$, Co$_{1.5}$PW$_{12}$O$_{40}$ [12–14], or H$_3$PO$_4$–V$_2$O$_5$ catalyst [15], modified Cu–Ni bimetallic catalyst [8,16–19], ionic liquid [20], etc. The direct synthetic route of DMC was represented as follows:

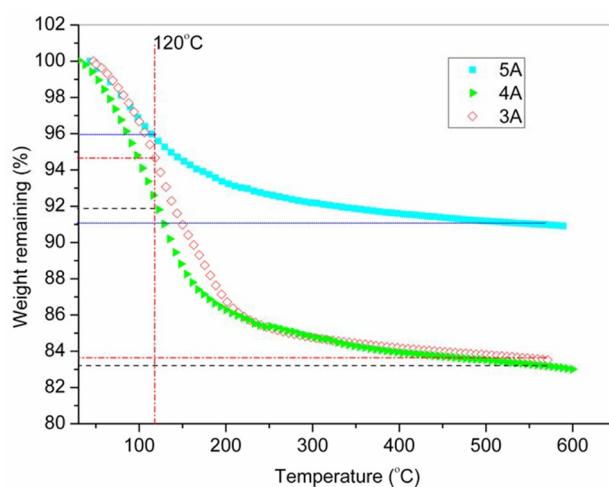$$2CH_3OH + CO_2 \rightarrow CH_3OCOOCH_3 + H_2O \tag{1}$$

The drawback of this strategy is the low methanol conversion, which is ascribed to the thermodynamic limitations and/or catalyst deactivation by the water byproduct that hydrolyze the formed DMC, the high bond energy of CO_2, the reversible nature of the reaction, and the inability to utilize physical absorption agents of water such as zeolites, $CaCl_2$, and molecular sieves due to high operating temperatures and pressures, but no report had addressed these problems. Since the reaction is nonspontaneous (Equation (1)) and the reaction equilibrium is quickly established, the dehydrating agent can enhance the yield of DMC by shifting the equilibrium toward higher DMC yields.

For batch reaction, the dehydrating additives such as trimethyl orthoacetate [21], 2,2-dimethoxypropane [22], acetonitrile [23], butylene oxide [24], and a recyclable dehydrating tube packed with molecular sieves 3A [25] can improve the yield of DMC by shifting the equilibrium. However, the economy of this process, the activity of the catalyst, the separation of product and by-product become the new subjects for further research. For continuous flow reaction, these obstacles were evidently cleared away. Herein, a concept of in-situ water removal via the addition of an inorganic dehydrating agent during the direct DMC synthesis from methanol and CO_2 catalyzed by K_2O-promoted Cu–Ni is presented. The 3A MS is selected as the optimal dehydrating agent effects of the mass ratio of dehydrating agent and catalyst, the dehydrating temperature and pressure, together with the space velocity on the catalytic performance for direct synthesis of DMC were investigated and discussed.

2. Results and Discussion

2.1. Selection of the Dehydrating Agent

There have been many previous attempts to remove the water from the reaction of direct synthesis of DMC using $MgSO_4$, Na_2SO_4, $CaCl_2$, etc. as inorganic dehydrating agents, however, no successful result was obtained because of high reaction temperatures and pressures. In this paper, low-cost and readily available molecular sieve of 3A, 4A, and 5A are chosen as the dehydrating agents. Prior to use, the three molecular sieves were treated at 500 °C for 6 h, and then allowed to fully hydrate under saturation pressure of water vapor (25 °C), followed by dehydration from 50 to 600 °C. The weight loss of the samples was recorded by Thermogravimetric analyses (TGA). As shown in Figure 1, 3A molecular sieve shows 11 wt. % of water escaped out at the reaction temperature of 120 °C, indicating that the 3A molecular sieve is the best candidate in this issue.

Figure 1. Thermogravimetric analyses (TGA) traces of molecular sieves (3A, 4A, and 5A) saturated by water vapor (1 atm, 25 °C).

2.2. Characterization of the Catalyst

In our previous work [26], it is investigated that the incorporation of alkali is conducive to the preparation of the catalysts precursor by decreasing the decomposition and reduction temperatures, which is favorable for the formation of a Nano-scale dispersion of bimetallic particles on the surface of supports. The well-dispersed characteristic in turn endows the catalyst with more lattice drawbacks and a polarized Cu-Ni lattice. It is proved that alkali doping can significantly improve the catalytic efficiency of Cu-Ni composites. Based on this, Cu-Ni-K_2O/diatomite catalysts are employed in this work. Temperature-programmed reduction and desorption (TPR, NH_3–TPD, CO_2–TPD) of the sample are all included in Figure 2. It can be seen that the catalyst precursor can be fully reduced below 450 °C with two closely combined peaks attributed to the reduction of CuO–NiO–K_2O solid composite. The NH_3–TPD and CO_2–TPD of the catalyst both exhibit one desorption peak around 200 °C, indicating that the catalyst has only one type of medium acid center and basic center, which are essential for direct catalytic synthesis of DMC. Figure 3 presented the powder X-ray diffraction of the samples. The reduced catalyst clearly shows four typical diffraction peaks of Cu, Ni or Cu–Ni alloy (2θ = 43.62 (111), 51.06 (200), 74.94 (220), and 91.04 (311)). Compared with 15%(2Cu–Ni)/diatomite (i.e., 15 CN/diatomite), the characteristic diffraction peaks of 15CN2K/diatomite became obviously broader than the undoped catalyst, which implies that the K-doped catalyst has better dispersion and smaller particle size than 15%(2Cu–Ni)/diatomite catalyst. According to Scherrer equation (D = Kλ/βcosθ, λ= 0.15406, and K = 0.89), the partical size of 15%(2Cu-Ni)/diatomite is about 22 nm and which of 15CN2K/diatomite is about 30 nm. Figure 4 displayed the SEM (a) and TEM (b) observation results of 15CN2K/diatomite. It shows that the Cu–Ni–K_2O composite homogenously covered the support and the single particle size of the catalyst is less than 50 nm.
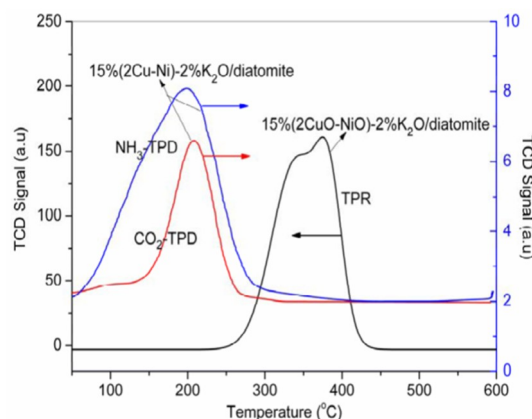

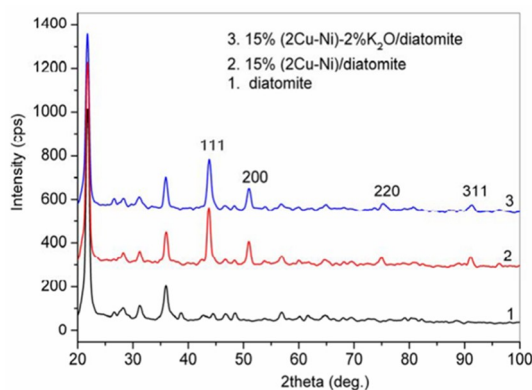**Figure 2.** TPR, CO_2–TPD and NH_3–TPD of 15CN2K/diatomite.

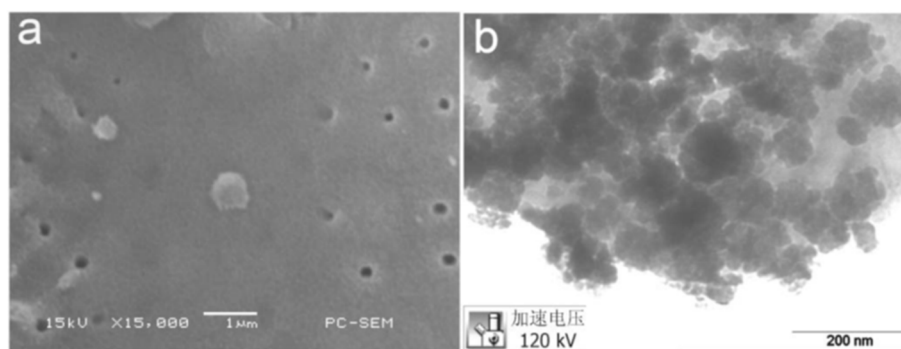**Figure 3.** Powder X-ray diffraction patterns of the samples.

Figure 4. SEM (**a**) and TEM (**b**) of 15CN2K/diatomite catalyst.

2.3. Effect of Dehydration on Properties of the Catalyst

2.3.1. Effect of Mass Ratio of 3A MS and 15CN2K/Diatomite on the Activity of the Catalyst

As shown in Figure 5, the mass ratio of 3A MS and 15CN2K/diatomite ranges from 0 to 5. The average value of 4-h methanol conversion climbs from 7.55 to 8.41% and the corresponding DMC selectivity fluctuates from 90.3 to 89.9%. The optimal methanol conversion of 8.27% with highest DMC selectivity of 91.2% has been achieved with 3/1 of 3A MS and the catalyst. The results indicated that 3A MS can effectively dehydrate the reaction system and shift the reaction equilibrium toward high DMC yield. The mass ratio of 3/1 is most preferable for this reaction from the economic point of view.
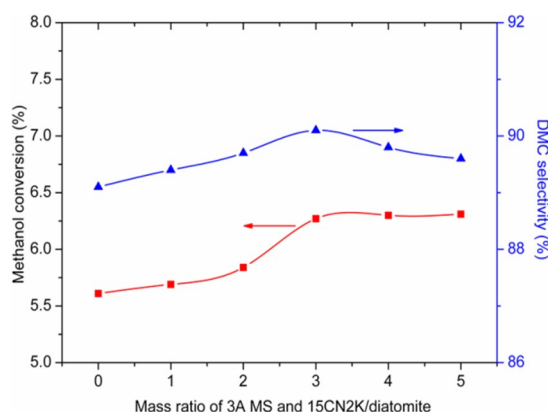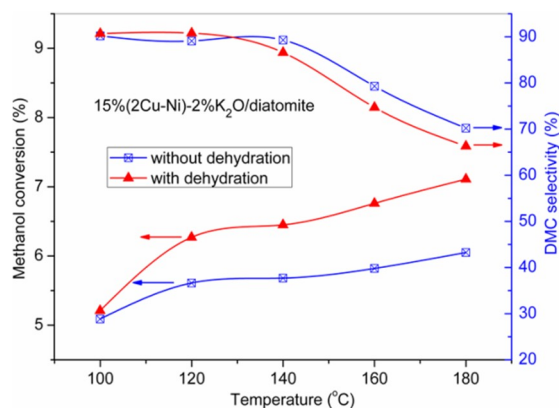

Figure 5. The effect of mass ratio of 3A MS and 15CN2K/diatomite on performance of 15CN2K/diatomite.
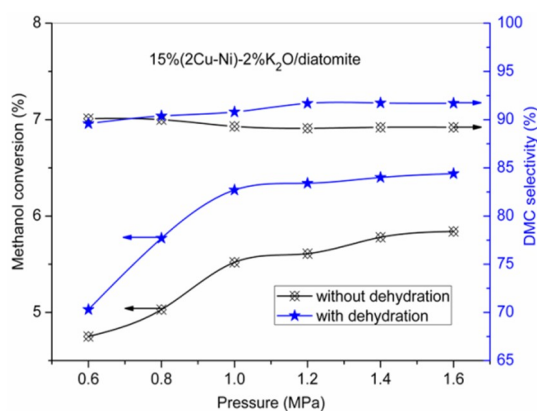
2.3.2. Effect of Dehydrating Temperature and Pressure on Properties of the Catalyst

The effect of dehydrating temperature on DMC synthesis was exhibited in Figure 6, the methanol conversion of this reaction is enhanced with the increase of temperature under the set pressure and space velocity. Moreover, the in-situ dehydrated catalyst performs superiorly to the catalyst without dehydration in methanol conversion. Nevertheless, DMC selectivity dropped dramatically over 140 °C due to the intensified side reaction of dimethyl ether (DME) and formic acid formation. Furthermore, the DMC selectivity of dehydrated catalyst collapsed more quickly at high temperature because 3A MS gradually fails to dehydrate the catalyst at high temperature, and 3A MS may serve as the catalyst for DME production. So 120 °C is chose in the reaction.

Figure 6. The effect of temperature on performance of catalyst with or without dehydration.
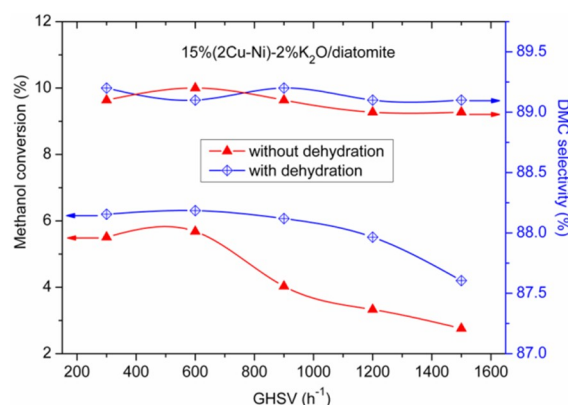
The effect of dehydrating pressure on DMC synthesis is presented in Figure 7. The methanol conversion is obviously improved with the increase of reaction pressure at fixed temperature and space velocity, and it levels off over 1.0 MPa. Compared with the undehydrated catalyst, the in-situ dehydrated catalyst shows higher activity, suggesting that the increased pressure is more favorable for dehydrating this reaction. The DMC selectivity keeps closely around 90% for undehydrated catalyst. For the dehydrated catalyst, it shows a little increase under 0.8 MPa and leveling off under 1.0 MPa, which implies that in-situ dehydration can produce more active sites for DMC catalytic synthesis. In general, the optimum conditions for effective dehydrating this reaction system are 120–140 °C and 1.0 MPa from the economic angle. Herein, 1.0 MPa is used in the following reaction.

Figure 7. The effect of pressure on performance of catalyst with or without dehydration.

2.3.3. Effect of Space Velocity on Dehydrating the Catalyst

At fixed 120 °C and under 1.0 MPa, the methanol conversion of undehydrated catalyst is evidently lower than dehydrated catalyst. The methanol conversion of dehydrated catalyst decreases from 6.25 to 4.51% with increasing gas space velocity (GHSV) from 300 to 1500 h^{-1} (Figure 8). However, the methanol conversion of dehydrated catalyst goes up a little at first with increasing GHSV from 300 to 600 h^{-1}, and then it decreases gradually from 8.35 to 6.19% with increasing GHSV from 600 to 1500 h^{-1}. As for the two catalytic reaction processes, space velocity seems no effect on DMC selectivity which keeps around 90%. So 600 h^{-1} is chose in the reaction.

Figure 8. The effect of gas space velocity (GHSV) on performance of catalyst with or without dehydration.

To summarize, the optimal condition is that the mass ratio of 3/1 (3A MS and 15CN2K/diatomite), temperature of 120 °C, dehydrating pressure of 1.0 MPa with GHSV of 600 h^{-1}. In this condition, the DMC selectivity is 89.2%, and methanol conversion of 6.49%. Regarding the pathway of the catalysis, which is similar to our previous work [17,19]. In general, there are three types of active centers: Cu-Ni metal sites, Lewis acid sites and Lewis base sites. Firstly, Horizontal adsorption state of CO_2 can be formed under the synergistic action of Lewis acid sites and metal sites and this adsorption state is reactive. The addition of K_2O additive is more conducive to the adsorption of CO_2 on the catalyst surface [26]. Secondly, dissociated adsorption states of CH_3OH could be formed in the association of Lewis acid sites and Lewis base sites. After that, adsorption state of CO_2 reacts with dissociated adsorption states of CH_3OH to form DMC. The main product of CO_2 and CH_3OH on the surface of catalyst is DMC.

2.3.4. Effect of In-Situ Dehydration on Stability of the Catalyst

The effect of in-situ dehydration on stability of the catalyst is evaluated within 22 h at 120 °C and under 1.0 MPa with GHSV of 600 h^{-1} (Figure 9). The methanol conversion of the reaction without dehydration increases to 7.55% at the beginning, and then gradually decreases to 6.18% within 8 h, after that it sharply collapses and deactivates at the end of the evaluation. The methanol conversion of reaction with dehydrating process keeps around 8% within 10 h, followed by decreasing to 1.84% at the end. The DMC selectivity of the reaction without dehydration decreases slowly from 88% to 83%, thereafter rapidly falls down to about 71%. However, the DMC selectivity with dehydration maintains over 88% within 13 h; and finally decreases to 78% at the end of the evaluation. By comparison, it is apparent that the catalyst dehydrated by 3A MS exhibited much higher activity and longer stability than the catalyst without dehydration, which indicated 3A MS can effectively dehydrate this catalytic reaction system at lower temperature and pressure. The main reason for the deactivation of the catalyst is that the chemical environment of the active species on the surface of the catalyst changes after a period of catalytic reaction, which means that the active site of the catalyst is gradually deactivated during the reaction, resulting in a decrease in the yield of DMC. The reasons for the deactivation of catalysts are believed to result from the reaction between the catalyst with formed water, followed by the oxidation of catalyst.
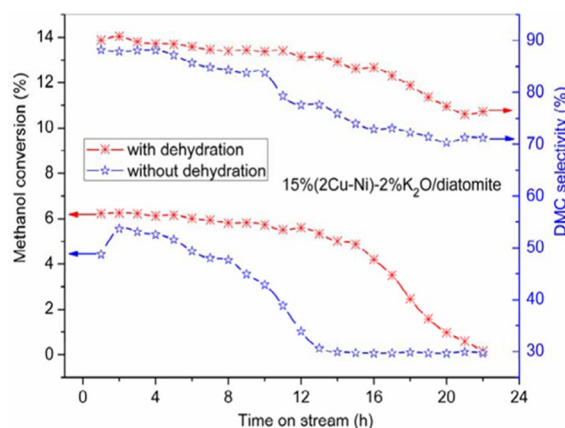
Figure 9. Stability study of the catalyst evaluated with or without dehydration.

3. Experimental

3.1. Catalyst Preparation

Natural diatomite was pretreated by calcining at 500 °C for 3 h, soaking in 5% hydrochloric acid for 24 h, washing by deionized water and drying overnight at 110 °C. Cu–Ni–K/diatomite nano-catalysts were prepared by wetness impregnation method. Firstly, $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and KNO_3 were dissolved in ammonia solution with stirring, then the diatomite was dispersed in metallic ammonia solution. The resulting mixture was stirred at room temperature for 24 h, ultra-sonicated for another 3 h, followed by rotary evaporation to remove the solvent. Thereafter, it was dried at 110 °C overnight. The fully dried solid was calcined at 550 °C for 5 h and further reduced by mixed gas of H_2 (10%)/N_2 at 550 °C for 6 h. 3A MS was pretreated by calcining at 500 °C for 6 h, and then cooled down to room temperature, placed in a vacuum-desiccator for further use.

3.2. Catalyst Characterization

The surface area of the samples was detected in liquid N_2 by Brunauer-Emmett-Teller (BET) approaches using a Micromeritics ASAP 2010 (Micromeritics, Norcross, GA, USA) instrument. Thermogravimetric analyses (TGA) of samples were performed on a PerkinElmer Pyris Diamond SII thermal analyzer (high-purity N_2, 20 °C/min, PerkinElmer, Waltham, MA, USA). The morphologies of the samples were examined using a scanning electron microscopy (SEM) (JSM-5600LV system of JEOL (JEOL, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (EDX) (JEOL, Tokyo, Japan) to check the components of the catalysts. The phase structure of the samples were determined by X-ray diffraction (XRD) (Rigaku Corporation, Tokyo, Japan) on a D/Max-IIIA power diffractometer using Cu (Kα) (0.15406 nm) radiation source. X-ray photoelectron spectrum (XPS) of the catalysts was obtained by ESCALAB 250 (ThermoFisher Scientific, Waltham, MA, USA) analyzer using the monochromatized Al (Kα) radiation source. Temperature programmed reduction (TPR)/Temperature programmed desorption (CO_2/NH_3-TPD) experiments of the samples were detected by Quantachrom ChemBET 3000 apparatus (Quantachrom Instruments, Boynton Beach, FL, USA) equipped with a thermal conductivity detector (TCD) [23].
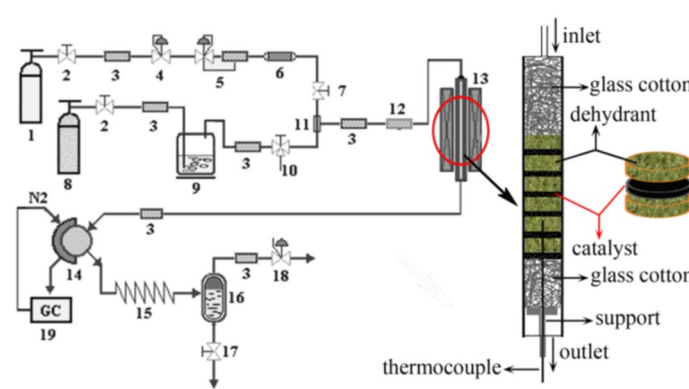
3.3. Catalyst Evaluation

The evaluation of the catalysts was performed in a continuous tubular fixed-bed micro-gaseous reactor with 5 g of the fresh 15%(2Cu–Ni)-2%K_2O /diatomite (marked as 15CN2K/diatomite) catalyst and set mass ratio of the selected 3A MS as dehydrating agent. (3A/catalyst = 0/5, 5/5, 10/5, 15/5, 20/5, 25/5). The filling of the catalyst and 3A MS was stacked layer by layer alternatively and the top layer was the dehydrating agent, that is, each layer of the catalyst was sandwiched by two layers of

dehydrating agent to ensure highly dehydrated. The methanol was bubbled into the reactor by N_2 and the molar ratio of CH_3OH and CO_2 was controlled by N_2 flux and the bubbling temperature (Scheme 1). The reaction was carried out at different temperatures, pressures and space velocity. The product was analyzed by GCMS-QP2010 Plus (SHIMADZU CORPORATION, Tokyo, Japan) and on-line GC (GC7890F) (TECHCOMP CORPORATE, Shang Hai, China) equipped with a flame ionization detector and thermal conductivity conductor. The final results were calculated by the following equations:

$$CH_3OH \text{ conversion } (\%) = \frac{[CH_3OH \text{ reacted}]}{[CH_3OH \text{ total}]} \times 100\% \tag{2}$$

$$DMC \text{ selectivity}(\%) = \frac{[DMC]}{[DMC + Byproduct]} \times 100\% \tag{3}$$

$$DMC \text{ yield}(\%) = CH_3OH \text{ conversion} \times DMC \text{ selectivity} \times 100\% \tag{4}$$

Scheme 1. Schematic diagram of the bubbling apparatus for direct synthesis of dimethyl carbonate (DMC).

4. Conclusions

An in-situ dehydrating process for the direct synthesis of DMC from methanol and CO_2 in a continuous flow fixed-bed bubbling micro-gaseous reactor was introduced, in which a sandwich structure of catalyst and 3A MS layer by layer was filled up. The effect of the mass ratio of 3A MS to catalyst, the dehydrating temperature and pressure, as well as the space velocity on the performance of the catalyst was investigated. The experimental results demonstrate that 3A MS can effectively dehydrate the catalytic reaction system at the optimal conditions of 120 °C, 1.2 MPa, with a GHSV of 600 h^{-1}. The in-situ dehydrating methodology enhances the methanol conversion and selectivity when compared with the dehydrating reaction system. Compared with the chemical dehydrating agents such as 2,2-dimethoxypropane [22], butylene oxide [24], etc., 3A MS is easily recyclable and they do not produce byproducts. Compared with the catalytic reaction system using a tin catalyst, a batch reactor separated from the recyclable dehydrating tube packed with 3A MS [25], this dehydrating reaction system using highly active K_2O-promoted Cu–Ni catalyst sandwiched by 3A MS was more preferable from the practical viewpoint. This report opens up a new way to circumventing the thermodynamic limitations of direct DMC synthesis, and would greatly prompt the researchers to design new dehydrating system for improving the efficiency of DMC synthesis directly from methanol and CO_2.

Author Contributions: D.H., Y.C., Y.M., S.W. and M.X. conceived and designed the experiments; D.H. and Y.C. performed the experiments and analyzed the data; Y.L. and S.W. contributed analysis tools. D.H. wrote this paper.

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