

Research Article

Porous Diatomite-Immobilized Cu–Ni Bimetallic Nanocatalysts for Direct Synthesis of Dimethyl Carbonate

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A series of diatomite-immobilized Cu–Ni bimetallic nanocatalysts was prepared under ultrasonication and evaluated for the direct synthesis of dimethyl carbonate under various conditions. Upon being fully characterized by TPR, TPD, BET, SEM, XRD, and XPS methodologies, it is found that the bimetallic composite is effectively alloyed and well immobilized inside or outside the pore of diatomite. Under the optimal conditions of 1.2 MPa and 120°C, the prepared catalyst with loading of 15% exhibited the highest methanol conversion of 6.50% with DMC selectivity of 91.2% as well as more than 10-hour lifetime. The possible reaction mechanism was proposed and discussed in detail. To our knowledge, this is the first report to use diatomite as a catalyst support for direct DMC synthesis from methanol and CO₂.

1. Introduction

Dimethyl carbonate (DMC), an environment-friendly chemical, has attracted much attention as methylating and carbonylating agents, fuel additives, as well as polar solvents [1–4]. Several commercial processes have been introduced for synthesis of DMC, including methanolysis of phosgene [5], ester exchange process [6, 7], methanolysis of urea [8], and gas-phase oxidative carbonylation of methanol [9]. However, all these processes use toxic, corrosive, flammable, and explosive gases such as phosgene, hydrogen chloride, and carbon monoxide. Therefore, direct synthesis of DMC from CH₃OH and CO₂ is highly desired since such an approach is environment friendly by nature [1].

Carbon dioxide, the main greenhouse gas, can be converted into synthetic gas, methanol, acetic acid, carbonate, and so forth, [10]. However, it is still a big challenge for synthetic chemists to utilize CO₂ effectively due to its in-built thermodynamic stability and kinetic inertness. Recently, a large number of catalysts have been reported for the

direct synthesis of DMC from CO₂ and CH₃OH including organometallic compounds [11], potassium methoxide [12], ZrO₂, Ce_{0.5}Zr_{0.5}O₂ and H₃PW₁₂O₄-Ce_xTi_{1-x}O₂, [13–15], H₃PO₄-V₂O₅ catalyst [16], and so forth. However, the highest DMC yield was still very low without addition of strong base and dehydrating agent due to the difficulties in activation of CO₂ and the deactivation of catalysts by in situ produced water. Copper and nickel composite, a type of novel bimetallic catalyst, was firstly proved highly active for direct synthesis of DMC by the Zhong Group [17]. In our group, Wu et al. further optimized the preparation condition and catalytic process of the catalysts [18]. For enhancing the efficiency of Cu–Ni catalysts, Wang et al. tested the similar Cu–(Ni,V,O)/SiO₂ catalyst with UV irradiation and pushed DMC yield close to 5% [19, 20]. Recently Bian et al. pioneered to support Cu–Ni composite on conductive carbon materials and firstly improved the methanol conversion to 10.13% with DMC selectivity of 90.2% [21, 22]. The catalysts above mentioned offer different advantages over others before them but also have considerable shortcomings

such as complicated preparation process, expensive support, and bleak prospect for industrialization. Therefore, new catalysts with low cost, high catalytic performance, and simple preparation process are urgently required.

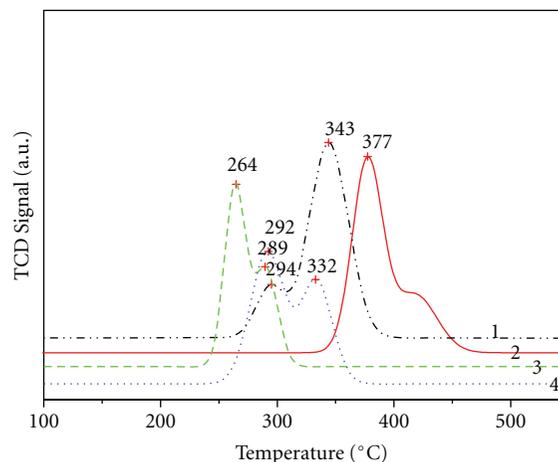
Diatomite, a type of widespread natural porous material, has been widely used as filler aid, adsorbent, and catalytic support in the reaction such as hydrogenation [23], oxidation [24], Fischer-Tropsch synthesis [25], CO₂ reduction [26] and so forth due to its unique high-adsorption capacity, high surface area, and cheap availability. In this connection, a series of Cu–Ni/diatomite bimetallic catalysts were prepared and evaluated under variable reaction conditions in this work.

2. Experimental

2.1. Catalyst Preparation. Natural diatomite was pretreated by calcining at 500°C for 3 h, soaking in 5% hydrochloric acid for 24 h, and washing and drying at 110°C overnight. Cu–Ni/diatomite nanocatalyst was prepared by the wetness impregnation method. Firstly Cu(NO₃)₂·3H₂O (0.517 g) and Ni(NO₃)₂·6H₂O (0.311 g) were dissolved in 25 mL of 25 wt% ammonia solution by stirring, then 5 g of diatomite was dispersed in metallic ammonia solution. The resulting mixture was stirred at room temperature for 24 h, ultrasonicated for another 3 h, followed by rotavaporation to remove the solvent. Thereafter, it was dried at 110°C overnight. The fully dried solid was calcined at 500°C for 5 h and further reduced by 5% H₂/N₂ mixture at 550°C for 6 h.

2.2. Catalyst Characterization. The surface area of the samples was detected in liquid N₂ by the Brunauer-Emmett-Teller (BET) approaches using a Micromeritics ASAP 2010 instrument. Thermogravimetric analyses (TGA) of samples were performed on a PerkinElmer Pyris Diamond SII thermal analyzer (high-purity N₂, 20°C/min). The morphologies of the samples were examined using a scanning electron microscopy (SEM) (JSM-5600LV system of JEOL) equipped with an energy dispersive X-ray spectrometer (EDX) to check the components of the catalysts. The phase structure of the samples were determined by X-ray diffraction (XRD) on a D/Max-III A power diffractometer using Cu (K α) (0.15406 nm) radiation source. X-ray photoelectron spectrum (XPS) of the catalysts was obtained by ESCALAB 250 (Thermo-VG Scientific) analyzer using the monochromatized Al (K α) radiation source. Temperature-programmed reduction (TPR)/temperature-programmed desorption of ammonia (NH₃-TPD) experiments of the samples were detected by Quantachrome ChemBET 3000 apparatus equipped with a thermal conductivity detector (TCD) [22].

The evaluation of the catalysts was performed in a continuous tubular fixed-bed microgaseous reactor with 2 g of the fresh catalyst and 2/1 molar ratio of CH₃OH/CO₂ (30 mL/min flux). It was carried out at different temperatures and different pressures. The product was analyzed by on-line GC (GC7890F) equipped with a flame ionization detector



- (1) 15% CuO/diatomite
- (2) 15% NiO/diatomite
- (3) 15% (2CuO-NiO)
- (4) 15% (2CuO-NiO)/diatomite

FIGURE 1: TPR test of the samples.

and GCMS-QP2010 Plus. The final results were calculated by the following equations:

$$\text{CH}_3\text{OH conversion (\%)} = \frac{[\text{CH}_3\text{OH reacted}]}{[\text{CH}_3\text{OH total}]} \times 100\%,$$

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

$$\text{DMC yield (\%)} = \text{CH}_3\text{OH conversion}$$

$$\times \text{DMC selectivity} \times 100\%.$$

(1)

3. Results and Discussion

3.1. Structural Investigation of the Catalysts. Natural diatomite was simply pretreated to further enlarge the surface area. Intensive stirring and more than 3 h strong ultrasonication were pretty favorable for impregnation of bimetallic solution. TPR of the samples was shown in Figure 1. The supported bimetallic catalyst shows two closely overlapped reduction peaks, one was the reduction of CuO (292°C) and the other was the reduction of NiO (332°C). Moreover, the reduction temperature of supported bimetallic catalyst shifted to lower temperature than monometallic catalyst, indicating the tremendous contribution of strong interaction of copper and nickel. In addition, the reduction temperature of supported bimetallic catalyst was higher than unsupported bimetallic composite (CuO 264°C, NiO 289°C), attributing to the strong interaction of bimetallic composite with support.

Morphology of the samples was observed by SEM as presented in Figure 2. Diatomite was porous disc with some blocked pore before pretreatment (a). After pretreatment, it was disintegrated into fragment with all over straightway

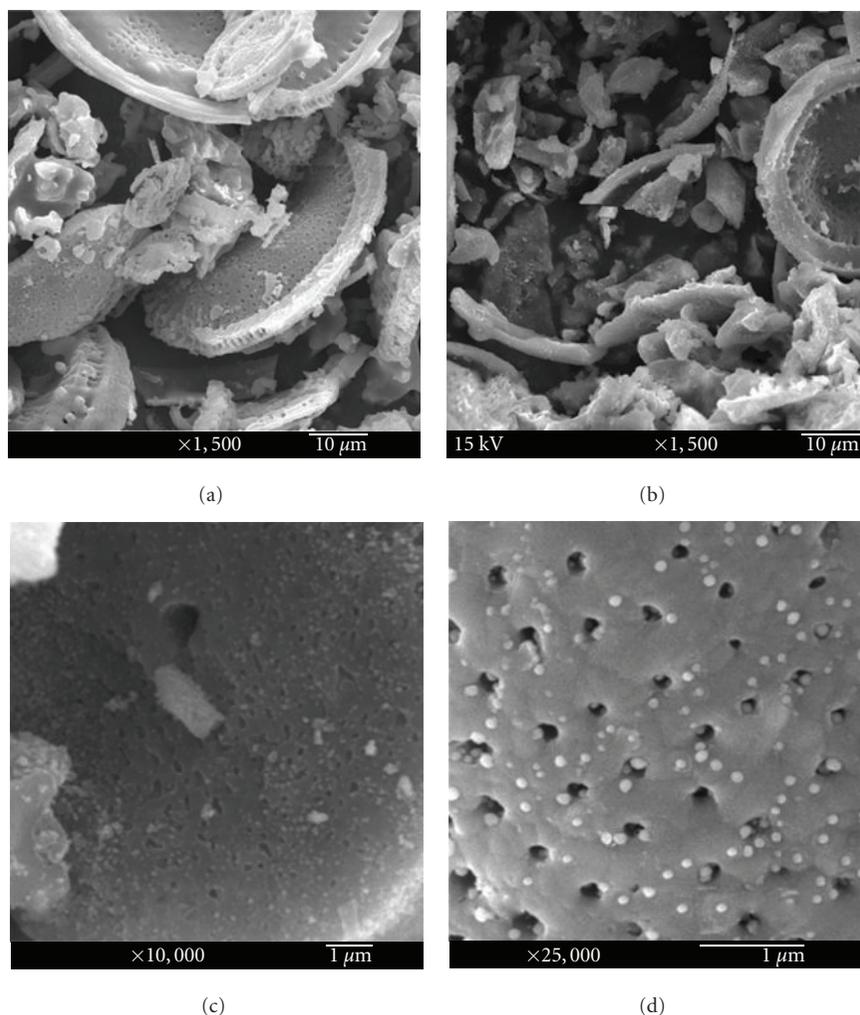


FIGURE 2: SEM of the samples. (a) Natural diatomite, (b) treated diatomite, (c) 15% (2Cu–Ni)/diatomite ($\times 10000$), and (d) 15% (2Cu–Ni)/diatomite ($\times 25000$).

pore (b), which was quite preferable for bimetallic dispersion and catalytic activity improvement. As shown in (c), diatomite was homogeneously covered by bimetallic nanoparticles not only immobilizing on the surface, but also a great deal of them inlaying, the inner wall of the pore (d) which is quite preferred for bimetallic dispersion and stabilization.

Quantitative element analysis of the catalyst was performed by EDS (Figure SM1 which is available online at doi:10.1155/2012/610410). The average results of area analysis were Cu 8.12%, Ni 3.86%, Si 38.73%, O 47.87% with a little amount of Fe, Al, Mn which further confirmed that the bimetallic components were effectively loaded. Oxidative state of the element was determined by XPS (Figure 3). The survey scan spectra indicated bimetallic components of Cu and Ni was dispersed throughout the surface of the support besides a little ferric, manganic and aluminous oxides were also included in this system coming from diatomite which may be good active additives (c). Cu 2p scan (a) and Ni 2p scan (b) displayed that binding energy of Cu and Ni was located at 932.73 (Cu 2p_{3/2}), 852.80 (Ni 2p_{3/2}),

951.70 (Cu 2p_{1/2}), 858.60 (Ni 2p_{1/2}), 918.70 (Cu LMM), and 846.20 (Ni LMM) respectively, which indicated that Cu–Ni composite was almost fully reduced. The XRD patterns of the samples were shown in Figure 4. Curve (a) was the typical patterns of diatomite with some weak diffractions of ferric oxide, alumina, and manganese dioxide. Compared with curve (a), curve (b) displayed new peaks of CuO and NiO accompanied by little diffraction of Cu₂O. Instead of diffraction of CuO and NiO, these newly emerged peaks in curve (c) ($2\theta = 43.62, 51.06, 74.94, \text{ and } 91.04$) were characteristic diffraction of Cu–Ni alloy. Interestingly it was not two close diffraction peaks of Cu and Ni as depicted in [27] but a single peak of Cu–Ni alloy, which may be due to the highly homogeneous distribution of Cu and Ni in Cu–Ni nanoparticles resulting from the contribution of ultrasonic dispersion and support effect.

3.2. Adsorption Behavior of the Support and Catalyst. The specific surface area of the support and catalyst was conducted by the BET method. Natural and treated diatomite

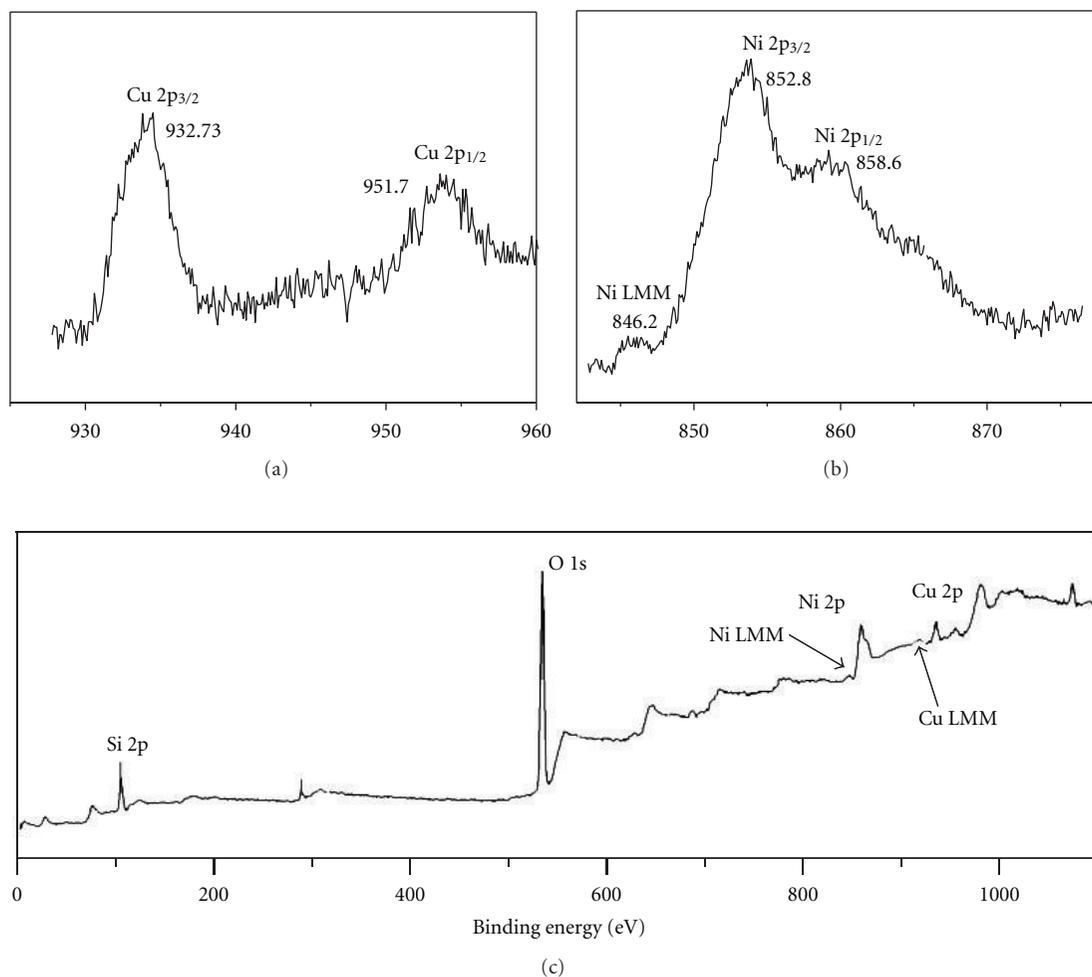


FIGURE 3: XPS of 15% (2Cu-Ni)/diatomite catalyst. (a) Cu 2p scan, (b) Ni 2p scan, and (c) survey scan.

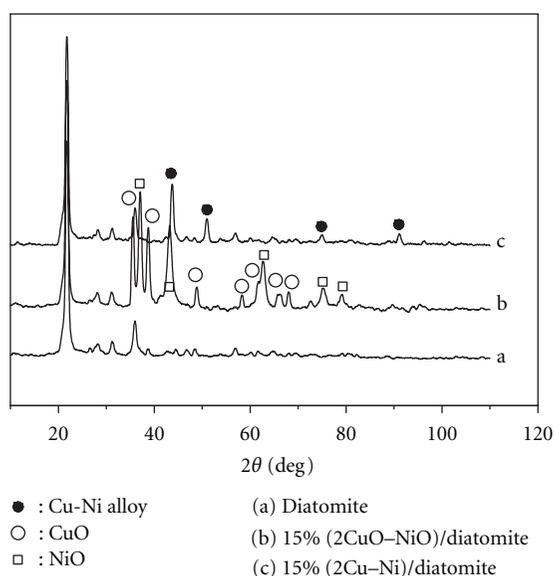
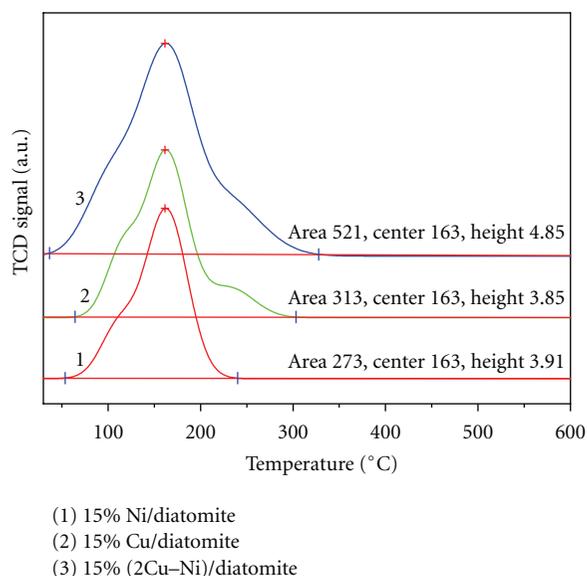


FIGURE 4: XRD patterns of the samples. (a) treated diatomite, (b) 15% (2CuO-NiO)/diatomite, and (c) 15% (2Cu-Ni)/diatomite.

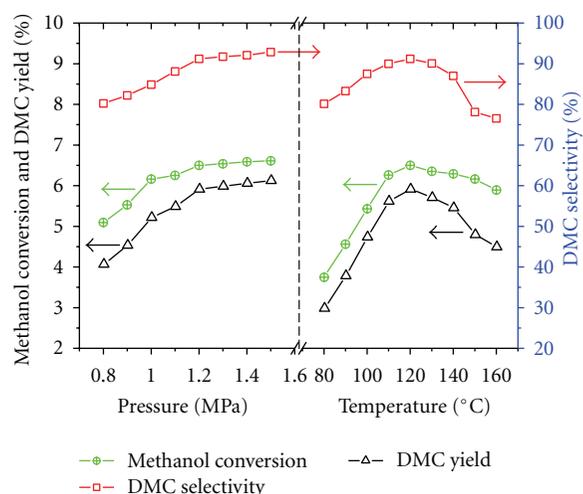
were 58.36 and 77.57 m²/g, respectively. NH₃-TPD profiles of the samples were presented in Figure 5, it can be found that the desorption peak area of bimetallic catalyst was larger than those of monometallic catalyst, and all desorption was divided into three stages that were physical desorption, hydrogen-bonding desorption, acid-centered desorption around 130°C, 180°C, and 270°C, respectively. Physical desorption mainly results from surface sorption of the catalyst in order to reduce its surface free energy. In addition, bimetallic catalyst showed a little stronger physical desorption than monometallic catalyst. Hydrogen-bonding desorption comes from the strong interaction between free Si-OH and NH₃. Strong acid-centered desorption arises from the nude M⁺ center (M = Si, Cu, Ni, Al, etc.), and the number of the acid center increases with increasing of their desorption peak area. Meanwhile, the higher the temperature of the peak is, the stronger the acid center represents. It was worth noting that the acid strength increased with the order of 15% (2Cu-Ni)/diatomite, 15% Cu/diatomite, and 15% Ni/diatomite, which was consistent with the order of their catalytic activity (see Table 1) and the acid-base catalysis mechanism [13, 28].

FIGURE 5: NH₃-TPD profiles of the catalysts.

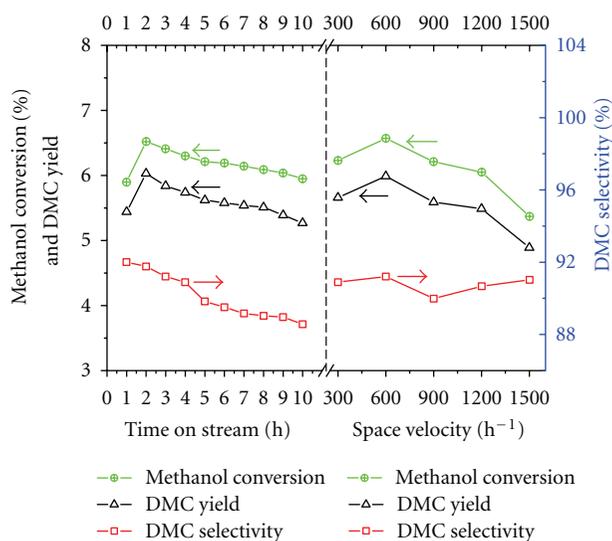
3.3. Study on Performance of the Catalyst. The effect of loading on DMC synthesis was listed in Table 1. The loading ranges from 3 wt% to 25 wt% with 2/1 of Cu/Ni [21], and the optimum loading was 15%. The bimetallic catalysts were superior to monometallic catalysts which further verified the synergetic effect of the Cu–Ni alloy [21].

The effect of pressure, temperature, and space velocity on highly active 15% (2Cu–Ni)/diatomite catalyst was evaluated as the most important factors (Figure 6). The CH₃OH conversion, DMC yield, and selectivity were enhanced noticeably with pressure increase (6a). Nevertheless, it leveled off when pressure climbed over 1.2 MPa, indicating much higher pressure would have less effect on the reaction. Under set conditions of 1.2 MPa and 600 h⁻¹, it gives the highest methanol conversion of 4.50% with DMC selectivity of 88.4% at 120°C (6b). Although increasing temperature was more favorable for activation of CH₃OH and CO₂, the catalytic performance decreased obviously over 120°C likely due to the CO₂ and methanol desorption and the change of catalytic transition state. When the reaction was fixed at 120°C and 1.2 MPa, methanol conversion increased a little with increasing space velocity from 300 to 600 h⁻¹ (6c), after that it collapsed gradually from 600 to 1500 h⁻¹ because the reaction time correspondingly decreased with the increase of space velocity.

Stability test of the catalyst was conducted at 120°C, 1.2 MPa and 600 h⁻¹ (6d). The variation of CH₃OH conversion and DMC selectivity with time was represented by stream on hour (5c). The CH₃OH conversion climbs to the highest value of 4.57% within 2 h likely due to the initiation of active species in the initial reaction stage, finally it decreased slowly to 2.95%. Simultaneously the DMC selectivity fluctuated from 92.0 to 88.6% probably resulting from the active center was poisoned by in situ produced water and surficial oxidation of the catalyst. The byproducts were CO, HCHO, and dimethyl ether (DME) detected by



(a) (b)



(d) (c)

FIGURE 6: (a) Dependence of 15% (2Cu–Ni)/diatomite performance on pressure (120°C, 600 h⁻¹ GHSV). (b) Dependence of 15% (2Cu–Ni)/diatomite performance on temperature (1.2 MPa, 600 h⁻¹ GHSV). (c) Dependence of 15% (2Cu–Ni)/diatomite performance on space velocity (1.2 MPa, 120°C). (d) Stability test of 15% (2Cu–Ni)/diatomite (120°C, 1.2 MPa, 600 h⁻¹ GHSV). 2 g catalyst and $n\text{CH}_3\text{OH}/n\text{CO}_2 = 2/1$ were used for all tests.

GC-MS in this reaction. CO presumably came from the cleavage of C–O bond of the activated CO₂, whilst HCHO and DME may result from the activated CH₃OH.

4. Proposed Reaction Mechanism

In view of the above experimental results, a different reaction mechanism from the literatures [21, 22] was proposed based on the results of GC-MS and in situ FTIR. As shown in

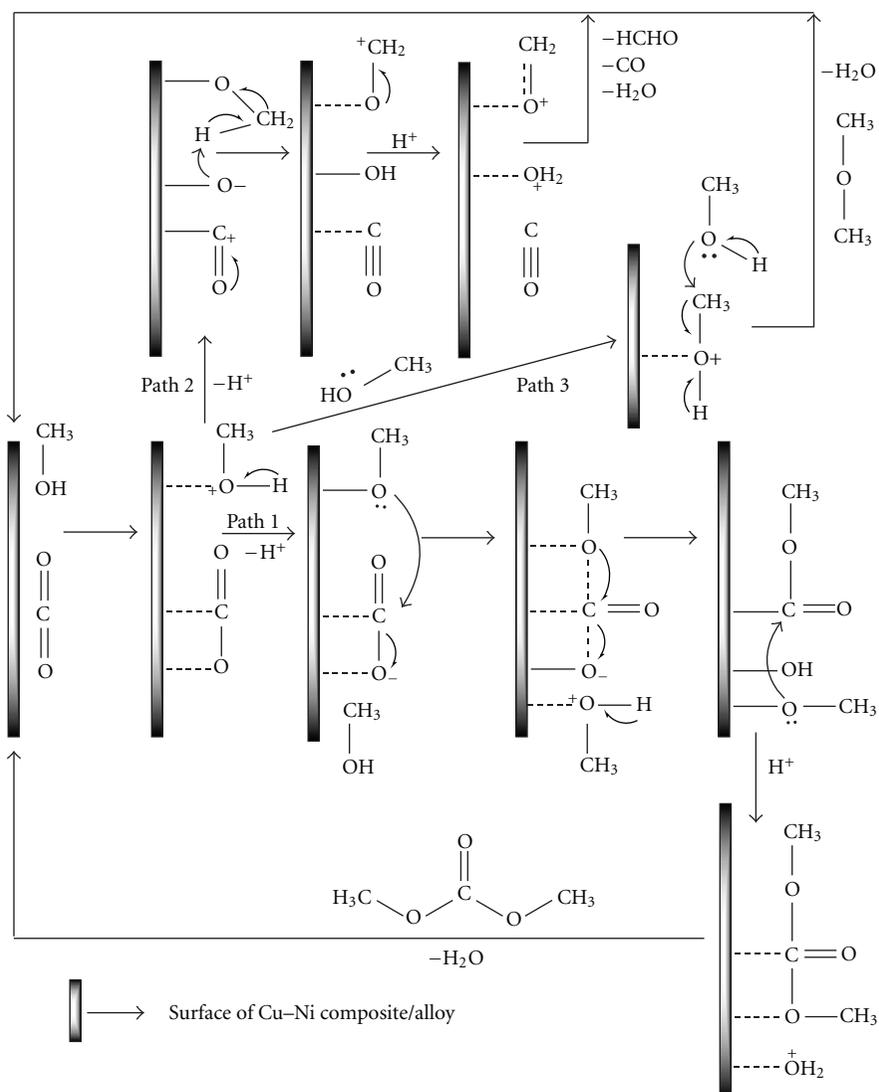


FIGURE 7: The proposed catalytic reaction mechanism for direct DMC synthesis from CH₃OH and CO₂ over Cu-Ni/diatomite.

TABLE 1: Influence of bimetallic loading on the direct synthesis of DMC.

Entry	Loading (wt%) ^a (2CuO + NiO)	Methanol conversion ^b (%)	DMC selectivity (%)	DMC yield (%)
1	3	2.32	89.4	1.86
2	5	2.73	90.2	2.17
3	10	3.96	90.9	2.42
4	15	4.50	91.2	3.93
5	20	4.05	88.7	3.36
6	25	3.67	86.1	2.88
7 ^c	15	2.31	92.0	2.13
8 ^d	15	0.58	91.5	0.53

^aMolar ratio of CuO/NiO is 2/1; ^breaction conditions: 120°C; 1.2 MPa; ^conly Cu was loaded; ^donly Ni was loaded.

Figure 7, a large number of basic (M⁻) and acid (M⁺) centers existed on the surface of Cu-Ni nanocomposite or the interface between Cu-Ni and support, which were the residual bonds resulted from the synergetic interaction of Cu with Ni or Cu-Ni with support. CH₃OH and CO₂

were firstly adsorbed on those M⁺ and M⁻, respectively, simultaneously accompanied by methanol dehydrogenation and CO₂ deoxygenation, which was the rate-determining step. DMC was formed by reaction path 1; CO and HCHO came out by path 2; DME was produced by dehydration

of two methanol molecules through path 3. M^+ and M^- centers were regenerated and recycled by desorption of those produced molecules under heating. Otherwise those active centers were deactivated by O or $-OH$ groups which were responsible for the loss of catalysis activity and the oxidization of Cu–Ni, so the existence of H_2O may be lethal for this reaction. Although the real reaction path was not well understood and verified, this proposed reaction mechanism compared to the literatures [21, 22] will help us to better understand and explain the reaction results, and it offers us a direction to improve the catalytic efficiency of this reaction.

5. Conclusions

In this work, low-cost and porous natural diatomite can be effectively introduced as a catalyst support by simple pretreatment for direct synthesis of DMC from carbon dioxide and methanol. The 2Cu–Ni/diatomite catalysts prove highly active for direct synthesis of DMC, and 15% (2Cu–Ni)/diatomite gives the highest methanol conversion of 4.50 with DMC selectivity of 91.2% together with more than 6-hour lifetime ($120^\circ C$, 1.2 MPa). From the results of experiments, the bimetallic nanoparticles are well dispersed and presumably alloyed under the preparation conditions. The existence of electron-rich and electron-deficient centers resulted from the strong interaction of diatomite with Cu–Ni, and the synergy of Cu–Ni alloy may be responsible for the high activity of this catalyst. This work can facilitate us to better understand the mechanism of this reaction and speed the scientific progress of peers in direct synthesis of DMC.

Acknowledgments

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