

K-doped CuO/ZnO with Dual Active Centers of Synergism for Highly Efficient Dimethyl Carbonate Synthesis

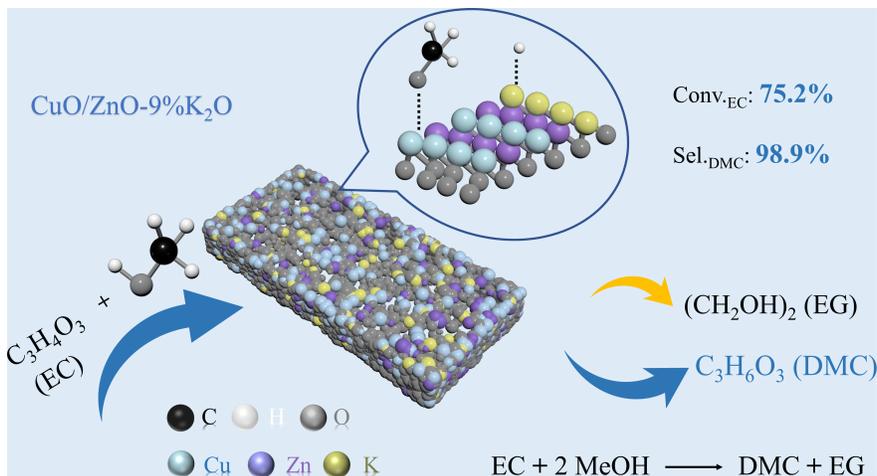
Han Han¹, Xue Ye¹, Jie Yao¹, Xinhua Gao¹, Jinghao Yu¹, Lisheng Guo¹, and jie Li¹

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Abstract

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Abstract

The application of heterogeneous catalysts in dimethyl carbonate (DMC) synthesis from methanol is hindered by low activation efficiency of methanol to methoxy intermediates (CH_3O^*), which is the key intermediate for DMC generation. Herein, a catalyst of alkali metal K anchored on the CuO/ZnO oxide is rationally designed for offering Lewis acid-base pairs as dual active centers to improve the activation efficiency of methanol. Characterizations of CO_2 -TPD, NH_3 -TPD, XPS, and DRIFTS revealed that the addition of Lewis base K observably boosted the dissociation of methanol and combined with Lewis acid CuO/ZnO oxide to adsorb the formed CH_3O^* stably, thus synergistically promoted the transesterification. Finally, the CuO/ZnO-9% K_2O catalyst exhibited the optimal catalytic activity, achieving a high yield of 74.4% with an excellent selectivity of 98.9% for DMC at a low temperature of 90 °C. The strategy of constructing Lewis acid-base pairs provides a reference for the design of heterogeneous catalysts.

KEYWORDS

Dimethyl carbonate, Transesterification, Copper-zinc-potassium mixed oxides, Activation and catalysis of methanol.

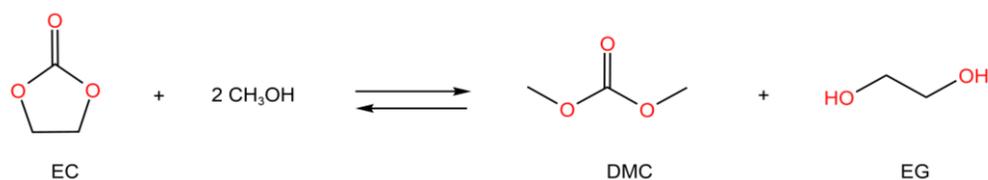
1. INTRODUCTION

Due to its low toxicity, easy transportation and environmental protection^{1,2}, dimethyl carbonate (DMC) has recently been industrially applied in various chemical syntheses, including organic intermediates and efficient solvents. In addition to replacing phosgene via green carbonyl synthesis, the demand for DMC in emerging fields represented by electrolytes and polycarbonates is fast growing. Thus, the improvement of the DMC production process has drawn much attention. Currently, several main DMC synthesis routes have been developed, including phosgenation³, oxidative carbonylation⁴⁻⁶, alcoholysis of urea^{7,8}, transesterification⁹⁻¹², direct methanol syntheses from CO₂^{13,14}, and so on. Among the routes, transesterification represents one of the main carbonate synthesis processes owing to its high atomic utilization, high yield of DMC, and mild reaction conditions (Scheme 1).

The leading homogeneous catalyst currently used in the transesterification to synthesize DMC from ethylene carbonate (EC) and methanol is sodium methoxide^{15,16}. Although the catalyst has good catalytic activity, it is sensitive to water and liable to produce strong alkaline solid waste, which causes extraordinary difficulties in product purification and catalyst recovery. In contrast, heterogeneous catalysts are easier to separate and possess higher stability, while the performance of the catalysts displays low activity due to poor mass transfer efficiency and weak methanol activation ability. Today, more literature¹⁷⁻²¹ has reported on heterogeneous catalysts for transesterification, which generally hold high reaction temperatures and low DMC selectivity (Table S1). Consequently, developing an efficient heterogeneous catalyst for

the transesterification synthesis of DMC under mild conditions is of great practical significance.

Wang²² et al. found that the CH_3O^* species formed by the activation of methanol with basic catalysts is the key to the synthesis of DMC. Valentina²³ et al. reported that it was paramount for a catalyst to have a desirable dissociation and adsorption capacity of methanol. Moreover, the ability of the catalyst to stabilize the reaction intermediates also emphatically affects the performance of the catalyst. Herein, the surface of the CuO/ZnO catalyst was modified by the alkali metal K. Thereafter, utilizing the Lewis base property of K to facilitate the activation of methanol to form CH_3O^* species, which were adsorbed and stabilized by Lewis acid CuO/ZnO. The Lewis acid-base pairs with double active centers in the catalyst can form the synergistic interaction that promotes methanol dissociation and adsorption alongside stabilizing the essential CH_3O^* species. Furthermore, the experimental results suggested that changing the loading of alkali metal could effectively regulate the synergy of the double active centers to acquire the excellent-performance heterogeneous catalyst for transesterification.



Scheme 1. Chemical equation for the synthesis of dimethyl carbonate from methanol and ethylene carbonate.

2. EXPERIMENTAL

2.1. Materials

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.0%) and ethylene carbonate were obtained from the Shanghai Aladdin Biochemical Technology Co., Ltd., China. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.0%) and KNO_3 were obtained from the Sinopharm Chemical Reagent Co., Ltd. Anhydrous glucose, anhydrous ethanol and anhydrous methanol were obtained from the Shanghai Lingfeng Chemical Technology Co., Ltd. n-Butanol was obtained from the Shanghai Macklin Biochemical Co., Ltd. All the reagents and solvents were used directly without further purification.

2.2. Catalyst preparation

Firstly, carbonaceous microspheres were synthesized via the hydrothermal reaction of glucose as described elsewhere²⁴, and then $\text{CuO}/\text{ZnO}/\text{K}_2\text{O}$ catalysts were prepared by the carbon microspheres-assisted template method. In a typical experiment, the copper nitrate trihydrate and zinc nitrate hexahydrate, were made into a solution with a molar ratio of 2.5. Potassium nitrate with different proportions (molar proportions in total) was then added to the above solution. Then the solution was immersed in carbon microsphere precursor under ultrasound and aged for 2 h, then dried at 80 °C for 12 h. Finally, the obtained solid was calcined in an air atmosphere at 500 °C for 2 h. The prepared metal oxide product was labeled as $\text{CuO}/\text{ZnO}-x\text{K}_2\text{O}$, where x represented the molar percentage of potassium nitrate in the total catalyst. For comparison, $\text{CuO}/\text{ZnO}/\text{K}_2\text{O}$ catalysts with the same composition were also prepared by coprecipitation and physical mixing and labeled as $\text{CuO}/\text{ZnO}-9\%\text{K}_2\text{O}$ (C) and

CuO/ZnO-9%K₂O (PM), respectively (SI displayed the detailed steps of hydrothermal synthesis of carbon microspheres and the coprecipitation method of CuO/ZnO-9%K₂O (C)).

2.3. Catalyst characterization

The morphology and particle size of the catalyst were studied by the field emission scanning electron microscope (SEM, s-4800, Japan), which connected with an X-ray energy dispersion spectrometer (EDS) to detect the content of various components. High-resolution transmission electron microscopy (HRTEM) was performed on the Tecnai G2 F30 S-TWIN electron microscope. The powder samples were dispersed in ethanol by ultrasound, and then transferred to a copper grid by impregnation. The X-ray diffraction (XRD) spectrum of the catalyst was analyzed by the Bruker D8 advanced diffractometer. Under the working voltage of 40 kV and 20 mA, using monochromatic Cu K α radiation, the angle range was 5-80 ° at room temperature, and the scanning speed was 2 °/min. Nitrogen adsorption and desorption isotherms were measured at -196 °C using the Quadrasorb EVO analyzer. The specific surface area of the catalyst was calculated by the Brunauer-Emmet-Teller (BET) method. The pore size distribution was estimated by the Barret-Joyner-Halenda (BJH) method. The basic amount and basic strength of the sample were determined by temperature-programmed desorption of CO₂ (CO₂-TPD) on the BUILDER PCA-1200 analyzer, and the acidity of the sample was determined by NH₃-TPD on the AutoChem2920 analyzer. X-ray photoelectron spectroscopy (XPS) was performed with the ESCALAB 250Xi spectrometer. Indeterminate carbon (C1s peak 284.8 eV) was used as the reference stand of binding

energy. In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (In situ DRIFTS) was analyzed with the Bruker Equinox 55 infrared spectrometer. Put the powder sample into the in-situ pool and pretreat it for 1 h under the Ar atmosphere and target temperature. Ar bubbling was used to bring methanol, and the infrared signal was collected simultaneously to obtain the infrared spectrum of the methanol adsorbed intermediate.

2.4. Catalytic test

The transesterification reaction of EC and methanol was carried out in a stainless-steel autoclave equipped with magnetic stirring. At first, EC, methanol and catalyst were loaded into the reactor (the molar ratio of methanol to EC was 8 and catalyst mass accounted for 4% of the EC mass). Then the reactor was purged with nitrogen three times, pressurized to 0.7 MPa, heated to 90 °C and stirred continuously for 5 h. After the reaction, the reactor was cooled in an ice water bath. Then, the catalyst was separated from the reaction mixture. The product mixture was quantified with GC(HF-900), equipped with the FID detector and FFAP capillary columns (60 m × 0.25 mm). The content of the product was measured by the internal standard method (n-Butanol as the internal standard). The main products were dimethyl carbonate (DMC) and ethylene glycol (EG), as well as trace products such as hydroxyethyl methyl carbonate (HEMC). EC conversion and DMC selectivity were calculated according to the following formulae:

$$\text{Conv.} = \frac{n_{\text{EC, feed}} - n_{\text{EC, detected}}}{n_{\text{EC, feed}}}$$

$$\text{Sel.} = \frac{n_{\text{DMC, detected}}}{n_{\text{EC, feed}} - n_{\text{EC, detected}}}$$

3. RESULTS AND DISCUSSION

3.1. Catalytic activity

The performance tests of CuO/ZnO-*x*K₂O catalysts and comparative catalysts were evaluated (Figure 1). In Figure 1a, the performance of the CuO/ZnO catalyst was substantially improved after adding alkali metal K. The CuO/ZnO-9%K₂O catalyst displayed the highest catalytic activity, and the EC conversion and DMC yield were up to 87.3% and 69.9%, respectively. In contrast, the CuO/ZnO catalyst exhibited relatively low EC conversion and DMC yield (36.1% and 19.2%, respectively). Accompanied by the change in the amount of alkali metal, the conversion of EC showed a normal distribution that first increased and then slightly decreased, thus indicating that the appropriate amount of alkali metal possessed the optimal ratio. Additionally, based on the composition of the CuO/ZnO-9%K₂O catalyst, the diversity of the catalyst obtained by different preparation methods was compared, as shown in Figure 1b, to which the catalyst prepared by the carbon microsphere-assisted template method outperformed the coprecipitation method and the physical mixing method. As for the different CuO/ZnO molar ratios (Figure 1c), their catalytic activity remained constant. Combined with Figure 1a, the synergistic interaction between the alkali metal and metal oxides is known to be affected by the preparation method, and an optimal proportion of the alkali metal exists.

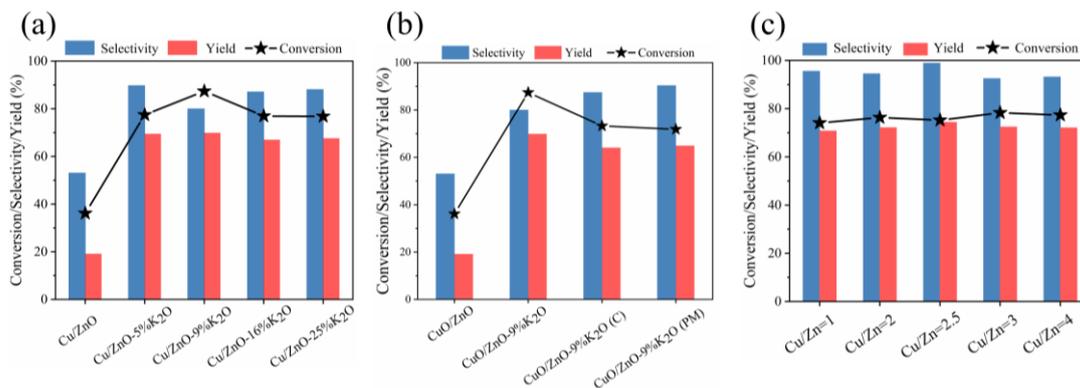


Figure 1. DMC yield/selectivity and EC conversion of (a) different loadings of alkali metal, (b) CuO/ZnO, CuO/ZnO-9%K₂O, CuO/ZnO-9%K₂O (C), CuO/ZnO-9%K₂O (PM), (c) different molar ratios of CuO and ZnO at 9% K₂O. Reaction conditions ((a,b) $n_{\text{methanol}}/n_{\text{EC}} = 8$, $m_{\text{catalyst dose}} = 3$ wt% of EC, $T = 150$ °C, $t_r = 5$ h. (c) $n_{\text{methanol}}/n_{\text{EC}} = 8$, $T = 90$ °C, $t_r = 5$ h, $m_{\text{catalyst dose}} = 4$ wt% of EC.)

Subsequently, the reaction parameters were further investigated, including different reaction temperatures, times, and catalyst doses (Figure S1). In Figure S1a, with the decrease in reaction temperature, the selectivity of DMC was awfully improved, indicating that a lower temperature is more favorable for converting HEMC to DMC. At 90 °C, the optimal yield of DMC achieved 73.9%. Similarly, as the reaction time increased from 2 to 5 h, the DMC yield increased monotonically from 62.8% to 73.9%, respectively (Figure S1b). However, the yield of DMC gradually declined with time on stream, marking that the reaction had entered an equilibrium stage. The effect of the catalyst dose kept pace with the above analysis of reaction parameters. The DMC selectivity and yield of the catalyst at 4 wt% were as high as 98.9% and 74.4%, respectively (Figure S1c). Compared with other heterogeneous catalysts (Table S1), we found that there were more or fewer problems such as high reaction temperature (>

130 °C) and low DMC selectivity (< 90%). This catalyst effectively improved the above problems and achieved an EC conversion of 75.2% and DMC selectivity of 98.9% at 90 °C for 5 h. Then we evaluated the stability of the catalyst through reaction cycles, as shown in Figure S2. It is obvious that the first use can achieve 76.9% EC conversion. Unfortunately, with the increase in the number of cycles, the EC conversion had declined within a certain range, but DMC selectivity decreased slightly (< 5%). Then we speculate that the K in the catalyst leached into the reaction solution, thus affecting the stability of the catalyst.

We also studied the kinetics related to the reaction. In this work, in consequence of the ratio of methanol to EC being 8, it was obvious that methanol and EC were used as an excess and a limit reactant, respectively. The kinetic analysis of this reaction can be carried out using the kinetic equation proposed by Kumar et al²⁵. According to the kinetic equation curve drawn in Figure 2, $\ln [(C_{EC, 0} - C_{EC, e}) / (C_{EC, t} - C_{EC, e})]$ has a good linear relationship ($R^2 = 0.9868$) with the reaction time t , and the reaction rate constant k is ≈ 0.541 mol/(L·h). Through analysis, the transesterification reaction is considered a pseudo-first-order reaction.

$$\ln \left(\frac{C_{EC, 0} - C_{EC, e}}{C_{EC, t} - C_{EC, e}} \right) = kt$$

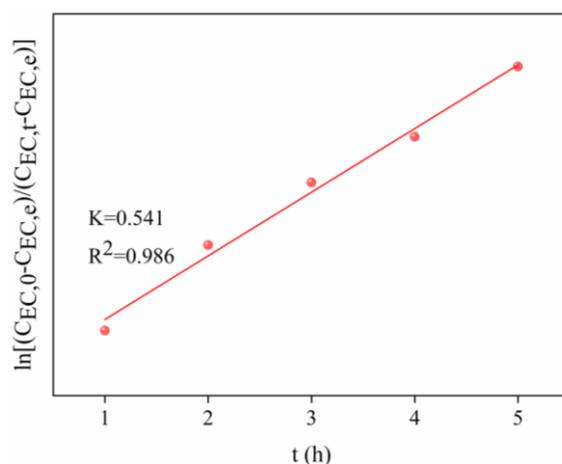


Figure 2. Kinetic curve of the transesterification of EC with methanol for DMC synthesis.

(Reaction conditions: $n_{\text{methanol}}/n_{\text{EC}} = 8$, $m_{\text{catalyst dose}} = 4 \text{ wt\%}$ of EC, $T = 90 \text{ }^\circ\text{C}$.)

3.2. Characterization of catalyst structure

As shown in Figure 3a, the CuO/ZnO-9%K₂O catalyst exhibited a nanoparticle-like distribution. According to the HRTEM image in Figure 3b, the mean size of the CuO/ZnO-9%K₂O catalyst was about $33.75 \pm 2.5 \text{ nm}$. As was evident in Figure 3c, the lattice spacing of 0.232 nm and 0.252 nm corresponded to the (111) and (-111) crystal planes of CuO, respectively, while the lattice distance of 0.247 nm corresponded to the (101) crystal plane of ZnO. Meanwhile, the obvious particle boundary between CuO and ZnO was not found, but they contacted in the form of grain boundaries through stronger interaction, forming more discontinuous active interfaces. Although K particles were not observed, EDS elemental analysis manifested that the main metal elements, including K, were uniformly distributed on the catalyst. Figure 3d and Figure 3e were the HRTEM images of CuO/ZnO-9%K₂O(C) and CuO/ZnO-9%K₂O(PM), respectively. The lattice spacings of 0.254 nm and 0.248 nm in Figure 3d corresponded to the CuO (-111) and ZnO (101) crystal planes, respectively. A direct comparison of

Figure 3c-3e detected that the crystal particles of CuO/ZnO-9%K₂O(C) were larger than CuO/ZnO-9%K₂O. The interface between different crystals was clearer and more continuous, whereas clear particle boundaries were observed in CuO/ZnO-9%K₂O(PM), and no interaction interface was generated between CuO and ZnO. Combined with Figure 1b, the activity of the catalyst has a positive correlation with the interface of the CuO/ZnO oxide, and the catalytic performance in CuO/ZnO-9%K₂O with strong interaction and an abundant interface distinctly outstripped that of CuO/ZnO-9%K₂O (C) and CuO/ZnO-9%K₂O (PM).

As the above results reveal, the catalyst structure has a prominent impact on the catalytic performance. XRD further characterized the catalysts with different K contents, suggesting that they all displayed intact CuO and ZnO crystal phases (Figure S4). The characteristic diffraction peaks appeared at 35.5 °, 38.7 °, and 36.2 °, mainly contributing to the CuO (-111), (111) (PDF 80-1916), and ZnO (101) crystal planes (PDF 79-2205). Simultaneously, the intensity of the CuO characteristic diffraction peaks in the CuO/ZnO-xK₂O catalysts increased with the addition of K₂O, demonstrating that the addition of K₂O is more favorable for improving the crystallinity of CuO. Nevertheless, the characteristic diffraction peaks of K₂O were not found in the XRD spectrum, illustrating that K₂O may be in a highly dispersed state.

The decrease in the specific surface area, pore volume, and pore size of the CuO/ZnO-xK₂O with an increase in K₂O contents was displayed in Table S2, regarding the physical structure of the catalyst. Figure S5 displays the N₂ adsorption-desorption isotherms and pore size distributions of the CuO/ZnO-xK₂O catalysts. In Figure S5a,

all samples showed type IV isotherms and H4 hysteresis loops, which testified that the internal structure of these catalysts was mainly mesoporous. Combined with Figure S5b, the pore size distribution of CuO/ZnO- x K₂O was more complicated, revealing that the mesopores were probably generated by the accumulation of catalyst nanoparticles. The XRD characterization results also demonstrated that the addition of K increased the crystallinity and crystal size of the catalyst, which in turn affected its specific surface area and pore structure.

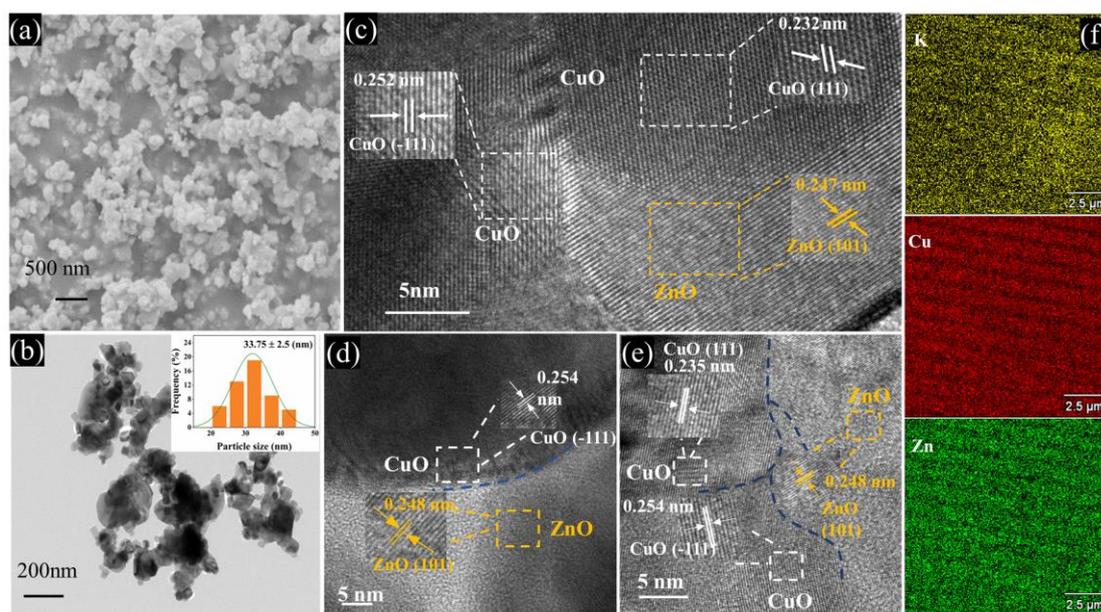


Figure 3. (a) SEM image of the CuO/ZnO-9%K₂O, (b-c) HRTEM images of the CuO/ZnO-9%K₂O, (d) HRTEM image of the CuO/ZnO-9%K₂O (C), (e) HRTEM image of the CuO/ZnO-9%K₂O (PM), (f) EDX element distribution of CuO/ZnO-9%K₂O.

Figure 1 illustrated that the addition amount of alkali metal had a significant impact on the catalyst's performance. However, there was no conspicuous difference in the structure of the catalyst accessible to the XRD and BET characterization. Therefore,

CO₂-TPD technology was utilized to quantitatively analyze the basic site strength and its corresponding amounts of the CuO/ZnO-*x*K₂O catalysts. As shown in Figure 4a, an extremely weak CO₂ desorption peak was observed in the CuO/ZnO catalyst in the low-temperature range. Nevertheless, after adding K₂O, several CO₂ desorption peaks corresponded to different basic site strengths. While desorption temperatures of < 200 °C, 200-450 °C, and > 450 °C correspond to weak, medium, and strong basic sites strength, respectively²⁵. As the content of K₂O increased, the total basic site amounts of the catalyst also gradually increased. The total basic site amount was the highest when the content of K₂O was 16%. However, since the content of K₂O increased to 25%, the total basic site amounts decreased instead (Figure 4b). The higher addition of alkali metal is noted to cause a decrease in alkali metal dispersion, resulting in the partial accumulation of potassium, to which this phenomenon can be attributed. In addition, the small specific surface area of CuO/ZnO-25%K₂O also decreases in the exposure of partial basic sites. However, combined with Figure 1a, the DMC yield distribution cannot be positively correlate with the total basic site amount. Subsequently, the explicit analysis of the basic site amounts of different strengths for the series of catalysts was carried out. By comparison, the DMC yield distribution was directly proportional to the variable number of medium basic sites, with the most medium basic sites (38.0 μmol/g) in CuO/ZnO-9%K₂O, expressing that the number of medium basic sites in the catalyst plays a vital role in the catalytic performance. Furthermore, the number of strong basic sites in CuO/ZnO-25%K₂O outclassed that of CuO/ZnO-9%K₂O, while the EC conversion was far lower than in CuO/ZnO-9%K₂O. The

CuO/ZnO-16%K₂O catalyst with the strongest basic sites exhibited the lowest catalytic activity in the transesterification except for CuO/ZnO, manifesting that not all basic active site strengths have a positive effect on the catalyst.

Then we investigated the acidic characteristics of the catalyst. From Figure 5a, the desorption peaks at 150-250 °C, 250-400 °C, and > 400 °C correspond to weak, medium, and strong acid sites, respectively. It can be observed that CuO/ZnO belonged to the weak acid sites. With the addition of K, the desorption peak of NH₃ gradually shifted to the higher temperature, which indicated that the acid strength gradually became stronger. When added to 9%K, there were relatively obvious NH₃ desorption peaks in the weak and the medium acid sites. When further adding K content, the peak of the weak acid sites gradually decreased, reaching 25%K content, which was completely gone. Meanwhile, the medium acid sites also gradually became smaller, which indicated that CuO/ZnO-9%K₂O with the best catalytic activity had the most total acidity, and the numbers of both weak and medium acid sites were also the largest. The relative content was shown in Figure 5b.

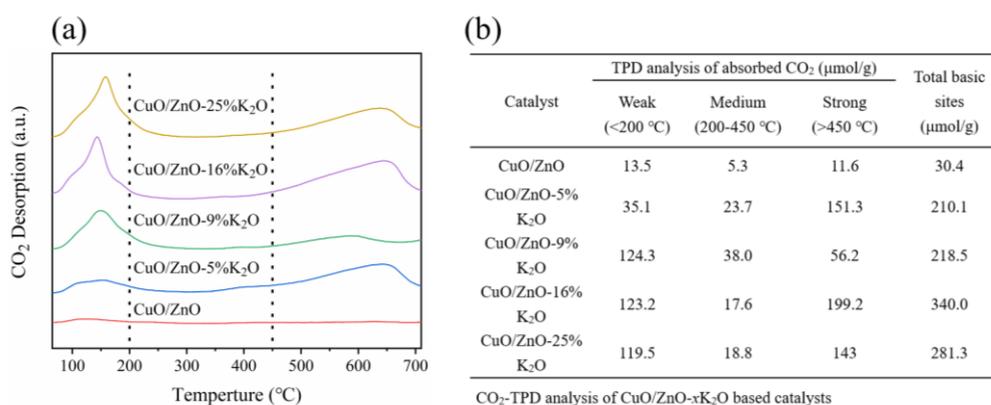


Figure 4. (a) CO₂-TPD image of the CuO/ZnO-xK₂O catalysts, (b) CO₂-TPD analysis of the CuO/ZnO-xK₂O catalysts.

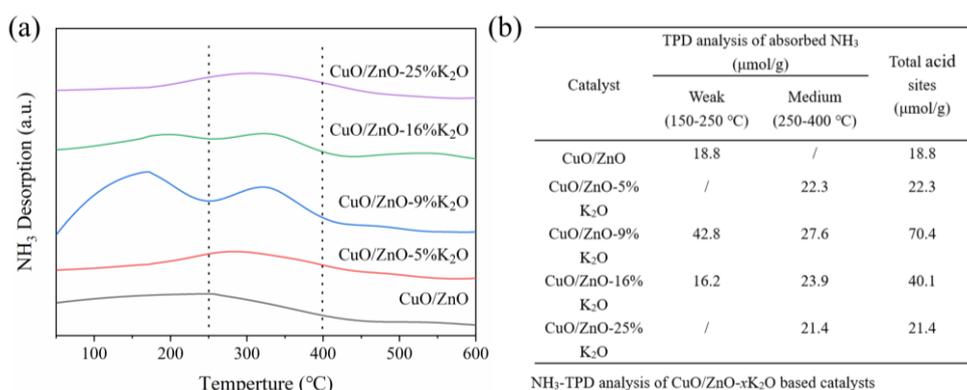


Figure 5. (a) NH₃-TPD image of the CuO/ZnO-xK₂O catalysts, (b) NH₃-TPD analysis of the CuO/ZnO-xK₂O catalysts.

To further clarify the reasons for the effect of alkali metal addition on catalyst performance, XPS characterization provides additional insights into the electronic structure of the series of catalysts (Figure 6). In Figure 6a, the binding energies of 933.3-931.8 eV and 952.6-951.8 eV corresponded to Cu 2p_{3/2} and Cu 2p_{1/2} peaks. In addition, Cu 2p_{3/2} peaks at 933.1 eV belonged to Cu²⁺ species²⁶. The significant jitter satellite peaks that occurred at 940.8 eV, 943.3 eV, and 961.6 eV were caused by charge transfer between the 3d orbit of transition metal and the 2p orbit of oxygen. In Figure 6b, the peaks of binding energies at 292.4-292.6 eV and 295.2-295.3 eV belonged to K 2p_{3/2} and K 2p_{1/2}, respectively, which corresponded to the K⁺ species. In Figure 6c, the binding energies of 1020.7-1021.5 eV and 1043.8-1044.6 eV were ascribed to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively, where the distance between the two peaks (23 eV) was due to spin-orbit splitting²⁷. Compared with CuO/ZnO and CuO/ZnO-9%K₂O, an incomplete reduction of Cu species took place in CuO/ZnO-9%K₂O, as evidenced by the transition from Cu²⁺ to Cu⁺ and the shift of the Cu 2p bands to lower binding energies. The phenomenon of the Zn species was similar to that of the Cu species, while

the K species showed a rise in binding energy (manual K^+ 295.0 eV).

Based on the above results, we speculate that alkali metal K interacts with the CuO/ZnO oxide and the transfer of electrons results in the formation of the Lewis acid-base pair between them. Among them, alkali metal K can provide electrons to form the Lewis base, whereas the CuO/ZnO oxide can obtain electrons to form the Lewis acid. Through peak fitting, the change of the Cu 2p binding energy of CuO/ZnO-25%K₂O with higher alkali metal content was more significant, which found that a large amount of Cu²⁺ was converted into Cu⁺, and the binding energy of K species also continued to shift in a higher direction. Combined with the catalytic performance, CO₂-TPD, and NH₃-TPD characterization, we suggest that the activity of the catalyst is due to the synergy between the alkali metal and metal oxides, while the strong basic sites caused by adding more alkali metal led to a change in the electronic structure of the CuO/ZnO, the weakening of acidity, and in turn, destroyed the synergy.

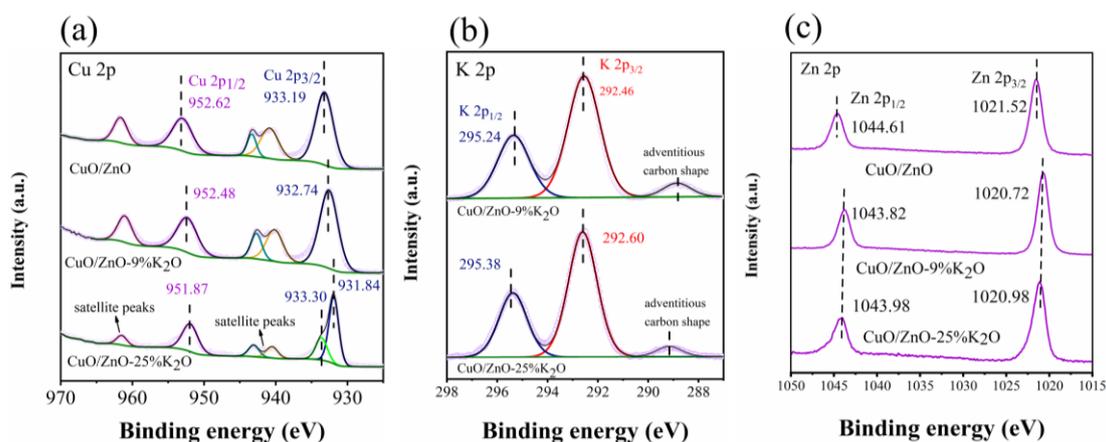


Figure 6. XPS spectra for (a) Cu 2p of the CuO/ZnO, CuO/ZnO-9%K₂O and CuO/ZnO-25%K₂O, (b) K 2p of the CuO/ZnO-9%K₂O and CuO/ZnO-25%K₂O, (c) Zn 2p of the CuO/ZnO, CuO/ZnO-9%K₂O and CuO/ZnO-25%K₂O.

Meanwhile, we designed a series of experiments to illustrate the specificity of this catalyst in transesterification. We have investigated CuO/ZnO loaded with the alkali metal Na and the alkaline earth metals Mg and Ca with the same content (Figure 7a). The research showed that the catalytic performance of the supported alkali metal was much greater than that of the alkaline earth metal for this reaction, which could be due to the stronger alkalinity and metallicity of alkali metals. Subsequently, we analyzed the effect of loaded Na and K in this reaction (Figure S6). The results showed that for Na, although Cu 2p_{3/2} shifted to low binding energy, the shift was still small for Cu²⁺, but for K, the transition from Cu²⁺ to Cu⁺ had been achieved, which indicated that the interaction between Na and CuO/ZnO was weaker than that between K and CuO/ZnO. Because we take advantage of methanol catalysts to stabilize intermediates (CH₃O*) in reverse, we also tested catalytic activity on other methanol catalysts (Figure 7b). Obviously, although the same amount of K was added to common methanol catalysts, we found that the conversion of In₂O₃ and InZrO_x based catalysts was at a low level. It is possible that the reaction will remain in the methanol activation step, which is not conducive to the formation of CH₃O*, reducing the yield of DMC. Through the above results and analysis, we can conclude that K is more suitable for CuO/ZnO under the same alkali metal loading. Meanwhile, under the different methanol catalyst supports, other oxide supports are likely to destroy the synergy with alkali metal K, resulting in a decrease in synergy. Therefore, CuO/ZnO and alkali metal K show the best matching degree. Finally, for the transesterification reaction, CuO/ZnO and the alkali metal K with the best synergy ability are the best choices for each other.

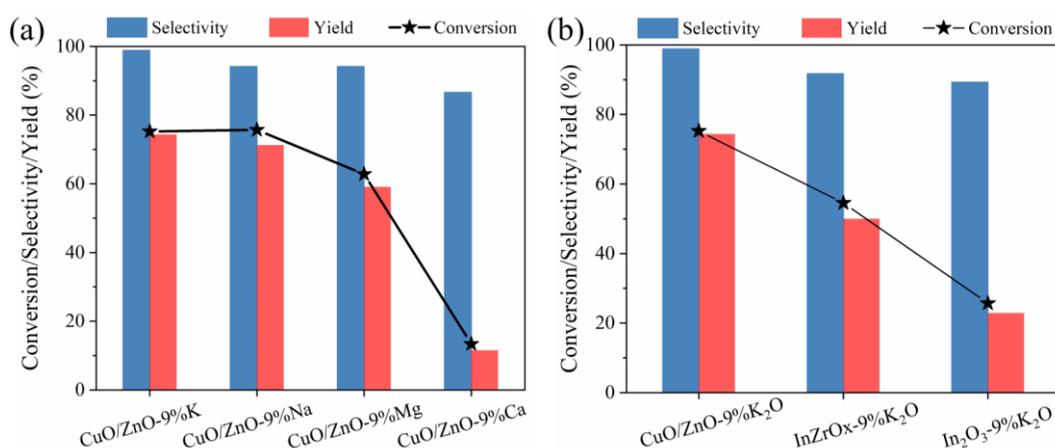


Figure 7. DMC yield/selectivity and EC conversion of (a) effect of supported alkali or alkaline earth metal, (b) effect of other methanol catalysts. (Reaction conditions: $n_{\text{methanol}}/n_{\text{EC}} = 8$, $m_{\text{catalyst}} \text{ dose} = 4 \text{ wt\% of EC}$, $T = 90 \text{ }^\circ\text{C}$, $t = 5 \text{ h.}$)

In order to verify the synergistic effect of Lewis acid-base pairs formed between alkali metal and metal oxides and to clarify the structure-activity relationship in the catalyst, in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was utilized to characterize the degree of methanol adsorption and activation of the catalysts with different alkali metal contents (Figure 8). As shown in Figure 8a, the infrared (IR) peak at $3600\text{-}3800 \text{ cm}^{-1}$ was assigned to the -OH stretching mode of methanol, and the IR peak at 2969 cm^{-1} was attributed to the vibration absorption peak of the methanol C-H bond²⁸. Meanwhile, the IR peaks at 1460 cm^{-1} and 1450 cm^{-1} were of the bending vibration of the -CH₃ unit. The typical IR peaks attributed to CH₃O* species^{29,30} ($2926, 2846, 1462, 1080 \text{ cm}^{-1}$) were notably higher with the adsorption time passing, implying that the catalyst can adsorb and activate methanol and then generate CH₃O* active species, which is thought to be the key intermediate in transesterification. While the wide signal at $\sim 1400 \text{ cm}^{-1}$ could be ascribed to the -OH bending vibration

mode of methanol, indicating that methanol molecules are also adsorbed on the catalyst surface. Similar to Figure 8a, Figure 8b-c also show similar spectra, and the height and area of adsorption peaks were remarkably increased after the addition of alkali metal. CuO/ZnO-9%K₂O existing the strongest adsorption peaks illustrate that it possesses excellent adsorption and activation ability for methanol and thus forms more CH₃O* species. As a result, although CuO/ZnO can also activate methanol to form the key intermediate CH₃O*, the adsorption and dissociation ability of the catalyst for methanol were substantially boosted after adding alkali metal K, accompanied by the intensified ability to form active intermediates (CH₃O*). Then, the sample adsorbed methanol vapor was purged with the inert atmosphere, and the desorption results were shown in Figure 8d-f. By comparing, it was detected that the peak intensity of CuO/ZnO-25%K₂O belonging to the CH₃O* species was lower than that of CuO/ZnO-9%K₂O. Combining with CO₂-TPD, NH₃-TPD, and XPS characterization, we propose that the catalyst with too strong basicity not only affects the electronic structure of CuO/ZnO but also reduces the acidity of the catalyst, which weakens the adsorption of the intermediate CH₃O*. Based on the above analysis, it can be concluded that the activity of the catalyst comes from the alkali metal and metal oxides with an advanced synergistic dissociation-adsorption effect. The alkali metal K serves as the Lewis base active center, which affects the dissociation of methanol, while the metal oxides behave as the Lewis acids and play a key role in the stability of the active intermediate CH₃O*. Both realize the adsorption and dissociation of methanol and the further stable adsorption of the active intermediate CH₃O* through the formed Lewis acid-base pairs,

which synergistically promote the transesterification. Afterwards, the adsorption rates of a series of catalysts were further compared (Figure S7). In the beginning, the dissociation adsorption rate of the CuO/ZnO catalyst for methanol was the fastest. However, with time on stream, the different catalysts had similar adsorption rates, but the attenuation of adsorption rate is the least in CuO/ZnO-9%K₂O with the best performance. On the contrary, the adsorption rates of the other catalysts declined observably and formed an adsorption platform, which confirms that the appropriate addition of alkali metal has the optimal activity for methanol adsorption activation and affects the synergistic interaction between Lewis acid-base pairs.

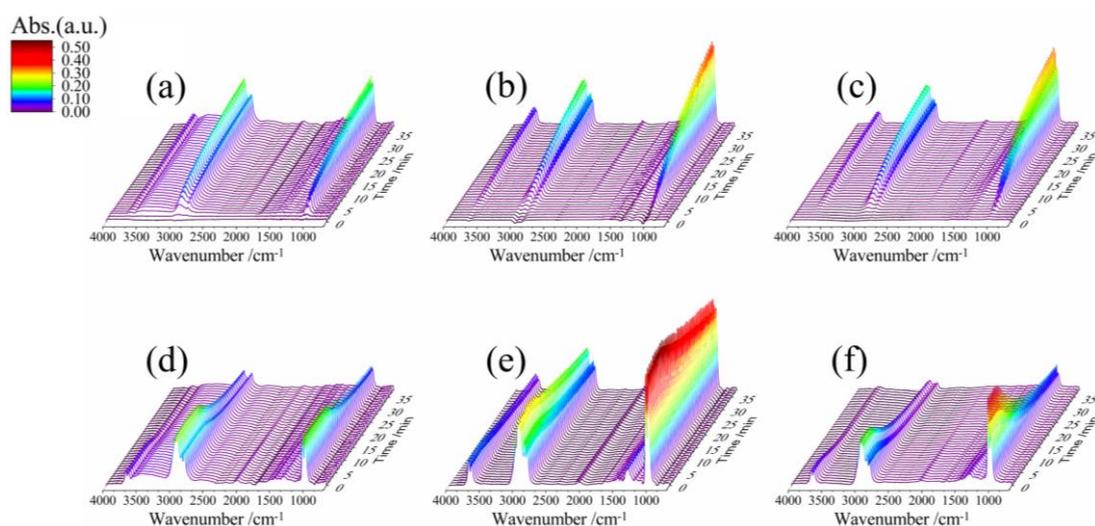
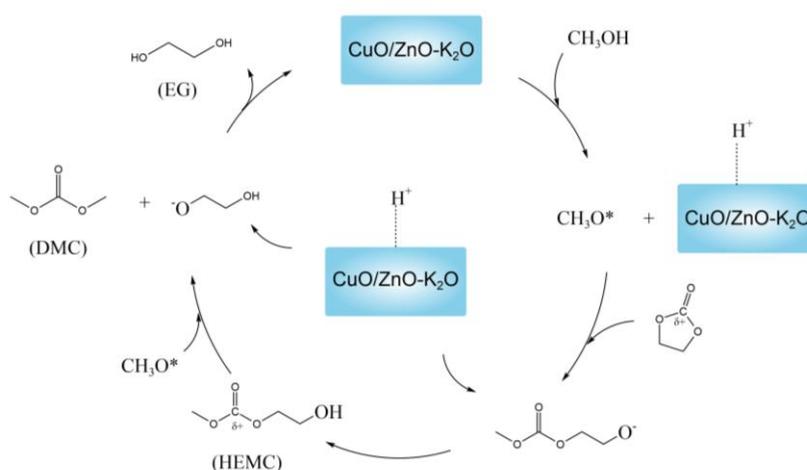


Figure 8. In situ FTIR spectra of methanol adsorption reaction: (a) CuO/ZnO, (b) CuO/ZnO-9%K₂O, (c) CuO/ZnO-25%K₂O and methanol desorption reaction: (d) CuO/ZnO, (e) CuO/ZnO-9%K₂O, (f) CuO/ZnO-25%K₂O.

Based on the above results and analysis of this work, we propose a possible transesterification mechanism, as shown in Scheme 2. The Lewis base was formed on

the surface of the catalyst by doping with the alkali metal K and then adsorbed the proton H^+ to boost the dissociation of methanol and generate CH_3O^* . At the same time, the CuO/ZnO served as the Lewis acid adsorbed and stabilized CH_3O^* . Then, CH_3O^* attacked the carbonyl carbon ($C^{\delta+}$) of EC to decompose EC from cyclic ester into chain ester. Subsequently, the proton H^+ on the catalyst surface adsorbed the charged chain carbonate 1, and performed the corresponding molecular rearrangement to generate the intermediate $CH_3OCOC_2H_4OH$ (HEMC). After that, CH_3O^* attacked the carbonyl carbon of HEMC again. The intermediate 2 also combined with the proton H^+ adsorbed on the catalyst surface, and finally formed dimethyl carbonate (DMC) and ethylene glycol (EG). Wang et al. proved that the second attack on the carbonyl carbon is much more arduous than the first attack. Hence, a catalyst with the strong ability to activate methanol and stabilize active intermediates (CH_3O^*) is pivotal for high catalytic activity.



Scheme 2. Proposed mechanism for DMC synthesis over CuO/ZnO-9%K₂O catalyst.

4. CONCLUSIONS

We report on the doping of CuO/ZnO catalysts with alkali metal K for the synthesis of DMC via EC and methanol. The synergistic effect of the Lewis acid-base pair with double active centers composed of alkali metal K and CuO/ZnO oxide is helpful for the dissociation of methanol and the stable adsorption of the key intermediate CH_3O^* , which is affected by the basicity and acidity of the catalyst. Meanwhile, adjusting the amounts of alkali metal could determine the appropriate basicity and acidity. The low alkali metal content has weaker basicity and acidity and poorer synergy, making it impossible to decompose methanol effectively. On the contrary, the higher alkali metal content causes too strong basicity, which reduces the acidity, destroys the electronic structure of CuO/ZnO, weakens the stability of the catalyst on the adsorption of the key active intermediate CH_3O^* , and further ruins the synergy of the catalyst. The CuO/ZnO-9%K₂O catalyst exhibited the best basicity, acidity, and intermediate stabilization ability, as well as the best DMC selectivity (98.9%) and DMC yield (74.4%). Our work provides new insights and references for the design and synthesis of heterogeneous catalysis to complete the synthesis of DMC and highlights the potential for industrial application with reasonable design ideas and high catalytic performance.

CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

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