Direct synthesis of dimethyl carbonate from carbon dioxide and methanol using supported copper (Ni, V, O) catalyst with photo-assistance

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Abstract

The photo-catalytic effect of a copper modified (Ni, V, O) semiconductor complex catalyst on the direct synthesis of dimethyl carbonate (DMC) from CO_2 and CH_3OH was investigated. The synthesized catalysts were fully characterized by temperature programmed reduction (TPR), X-ray diffraction (XRD), Ultraviolet visible drift reflection spectra (UV–vis DRS) and transmission electron microscopy (TEM). The nano-scale catalyst particles were observed with TEM and light absorbance was then predicted by UV–vis DRS spectra. The pressure and temperature dependencies of the photo-catalytic activity were studied. The results demonstrated that the catalytic activity was enhanced with the assistance of ultraviolet (UV) irradiation compared with the pure thermal and surface catalytic reaction under the same reaction conditions.
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1. Introduction

Dimethyl carbonate (DMC) has received much attention as an environment friendly intermediate and a non-toxic substitute for poisonous and corrosive phosgene and dimethyl sulfate in the reaction of carbonylation and methylation [1,2]. Further, DMC can also be used as a good solvent, an alkylation agent and a fuel additive in place of MTBE to reduce the tail gas pollution [3,4].

The traditional DMC synthesis route takes use of phosgene, an intense toxic substance and co-produces hydrochloric acid, which will erode the equipment seriously [3,4]. The oxidative carbonylation of methanol with carbon monoxide and oxygen is another route for the synthesis of DMC, which is dangerous and potentially explosive, however, to use carbon monoxide and oxygen mixture as starting materials [5]. The transesterification

route reports high DMC yield, but it has the disadvantages of high cost of the starting materials and difficulty in the product separation [6].

Recently, one step synthesis of DMC from CO_2 and CH_3OH has become attractive due to the low cost of the starting materials and its alleviating the global climate change caused in part by the increasing CO_2 emissions [7–9]. However, DMC yield in this route is relatively low due to the fact that CO_2 is highly thermodynamically stable and kinetically inert and due to the deactivation of catalysts induced by water formation in the reaction process [8,9]. Therefore, the removal of water from the reaction system and the activation of CO_2 are two major obstacles in the direct synthesis of DMC from methanol and CO_2. The dehydrates and additives has been applied to the system, such as $CaCl_2$ [10], 2,2-dimethoxy propane (DMP) [11] acetals [7,12] and molecular sieves [13] to minimize the water concentration in the reaction system.

CO_2 activation has long been a challenge for synthetic chemists to convert CO_2 into the industrially useful compounds. Various catalysts have been used to activate CO_2 for the direct synthesis of DMC from CO_2 and methanol, such as

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Cu-Ni/VSO [8], V_2O_5/H_3PO_4 [9], ZrO_2-CeO_2 [11], BuSn (OMe)$_2$ [14,15], metal(IV)tetra-alkoxide [16], magnesium dialkoxide [17], potassium carbonate [18], ZrO_2 [19], etc. In recent decades semiconductor catalysts have drawn much attention due to their photo-catalytic activity of initiating redox reactions [20–23]. Both photo-catalytic ($\Delta G < 0$) and photo-synthetic ($\Delta G > 0$) processes have widely introduced the light-driven redox reactions with semiconductor catalysts [24,25]. The photo-reduction of CO_2 has long been investigated in the past to produce formaldehyde, formic acid, methanol, methane and oxalate, etc. with $SrTiO_3$, TiO_2 (pure or doped), SiC, CdS, ZnO, WO_3 and $BaTiO_3$ semiconductor photocatalysts [20,23,24]. UV and visible light photoenergies have been used to break the thermodynamic limitations of some thermodynamically unfavorable reactions that have been proved to be effective, like water splitting [20,23,24,26]. In this paper, we introduce a copper doped (Ni, V, O) semiconductor complex as the catalyst into photosynthesis of DMC from CO_2 and methanol directly in the continuous flow fixed-bed reactor to enhance the CO_2 activation and DMC yield. Moreover, the continuous flow fixed-bed reactor can remove the produced water and build a water-free reaction system to favor the DMC formation.

2. Experimental

2.1. Materials

Vanadium pentoxide, hydrochloric acid, ammonia solution, nickel nitrate, cupric nitrate and dried methanol with analytical pure were purchased from commercial sources. Carbon dioxide was supplied by Shanghai SGIG Co., China with purity higher than 99.99%. Silica gel, commercially available from Qingdao Ocean Chemical Factory, China, was in 100–200 mesh with a specific surface area of $360 \, m^2/g$.

2.2. Catalyst preparation

2.2.1. Catalyst precursor of (Ni, V, O) semiconductor complex

V_2O_5 was added into HCl (38 wt%) at 363 K for 1 h to form dark blue $VOCl_3$ solution. Silica gel was pre-treated at 363 K for 2 h and the required liquid volume for stoichiometric impregnation was measured. Silica gel was impregnated stoichiometrically into $VOCl_3$ solution, aged at room temperature for 24 h and carried out the surface reaction at 363 K for another 24 h. Ammonia solution was added into the reaction system to neutralize excessive acid at room temperature. The diluted ammonia solution (1:10 vol.%) and distilled water was used to wash several times and get completely rid of the Cl^- ion retained in the system, which was verified by 0.1 mol/L $AgNO_3$ solution. The mixture was filtered, dried at 383 K for 6 h and calcined at 723 K in air for 5 h to produce the complex of V_2O_5 dispersed on SiO_2 (V_2O_5 8.88 wt%). The complex was impregnated stoichiometrically into the solution of nickel ammonia, aged in room temperature for 24 h, and finally carried out the surface reaction at 363 K for 24 h. The produced product was dried at 383 K for 6 h and calcined at 723 K in air for 5 h to yield the catalyst pre-

cursor of (Ni, V, O) semiconductor complex supported on SiO_2 (Ni 2 wt%).

2.2.2. Copper modified catalyst

The above catalyst precursor was treated in its turn as follows: impregnated stoichiometrically into the solution of cupric ammonia, aged in room temperature for 24 h, carried out the surface reaction at 363 K for 24 h, dried at 383 K for 6 h and calcined at 723 K in air for 5 h. Prior to use the product was reduced under the atmosphere of by $5\% H_2/N_2$ mixture at 623 K for 2 h to form the copper modified semiconductor complex catalyst (Cu 1 wt%).

2.3. Catalyst characterization

2.3.1. Temperature programmed reduction (TPR)

The semiconductor complex catalysts copper (Ni, V, O) were reduced in the temperature programmed reduction mode of Quantachrom ChemBET 3000 apparatus using a quartz U-shaped reactor at temperature range from room temperature to 1073 K at a heating rate of 8 K/min, in $10\% H_2/Ar$ atmosphere. The sample weight was 50 mg.

2.3.2. X-ray diffraction (XRD)

X-ray analysis was carried out on a D/Max-IIIA powder diffractometer in a step mode between $3°$ and $60°$ 2θ using Cu $K\alpha_1$ radiation.

2.3.3. Transmission electron microscopy (TEM)

The catalyst sample was examined by using transmission electron microscopy (JEM-2010HR operated at 200 kV).

2.3.4. UV–vis spectra

UV–vis diffuse reflectance spectra were recorded by a spectrophotometer (UV-2501PC range from 190 to 900 nm) using barium sulphate as reference sample.

2.4. Direct synthesis of DMC with photo-assistance from CH_3OH and CO_2

The title synthesis of DMC was carried out in the photo-reactor as illustrated in Fig. 1. The setup comprised a photo-reactor, a CO_2 mass flow controller, a HLPC syringe pump, a six-way valve, a back-pressure regulator and a gas chromatography (GC). The six-way valve was placed into an oven. The oven, heater and reactor were each equipped with a thermometer, measured by thermocouples with an accuracy of $\pm 1 °C$. The system pressure was determined by pressure sensor and controlled by the back-pressure regulator with an accuracy of ± 0.01 MPa.

During the experiment, the catalyst was first loaded into the reactor and the reactor was sealed and purged using CO_2 gas flow for 10 min to exhaust the air inside. Prior heating up CO_2 was charged into the reactor to a certain pressure and the flow rate was measured and controlled by the mass flow controller. When the heater, reactor and oven were heated to the desired temperature, the methanol was pumped into the system by the HPLC syringe
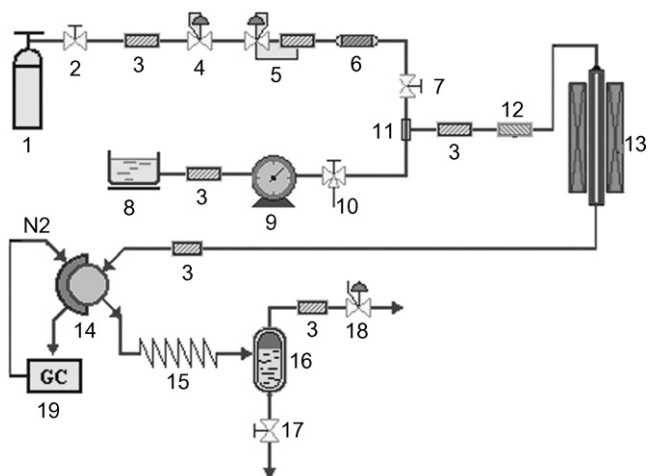
Fig. 1. Schematic diagram of apparatus for photo-assistant synthesis of DMC. (1) CO_2 cylinder; (2) pressure reducer valve; (3) filter; (4) pressure regulator; (5) mass flow controller; (6) buffer; (7) one-way valve; (8) methanol carrier; (9) HLPC syringe pump; (10) three-way inlet wave; (11) blender; (12) heater; (13) photo-reactor; (14) six-way valve; (15) cooler; (16) cooling separator; (17) cut-off valve; (18) back-pressure regulator; (19) gas chromatography.

pump and simultaneously the ultrahigh pressure mercury lamp (365 nm wavelength) was turned on with a power of 125 W. An electric fan was used to remove the excessive heat accumulated by the UV irradiation. The resulting mixture was introduced into the on-line gas chromatograph (GC7890F) to analyze the reaction composition with a flame ionization detector (FID). The condensed liquid from the cut-off valve was collected and analyzed by the gas chromatograph mass spectrometer (GCMS-QP2010 plus) to confirm the formation of DMC.

3. Results and discussion

3.1. Investigation of catalyst structure

Fig. 2 presents the TPR profiles for different samples. Curves 1, 2, 3 shows the reduction peaks for the pure V_2O_5, NiO and CuO dispersed on SiO_2 at 559, 443 and 280 °C, respectively. It should be noted that curve 3 has a peak shoulder at 263 °C, which is due to the reduction of the well-dispersed CuO particles compared with the peak shoulder at 280 °C for the bigger CuO particles. From curve 4 we can see that the NiO reduction peak
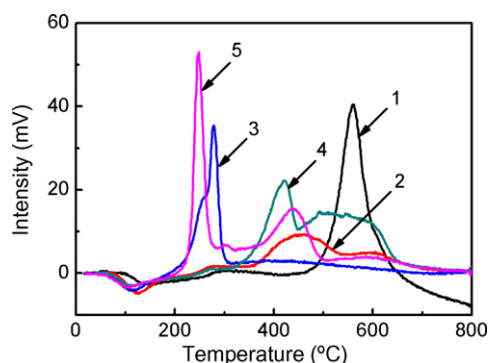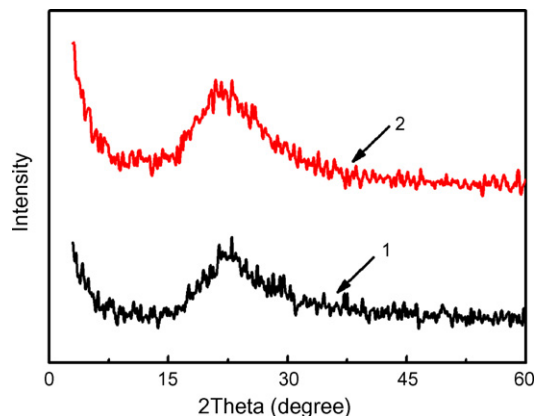

Fig. 2. TPR profiles of different samples.

Fig. 3. XRD patterns of SiO_2 and the copper modified (Ni, V, O) complex catalyst.

is shifted to lower temperature of 400 °C, indicating that NiO particles were well dispersed on SiO_2. The broad peak appeared between 450 and 540 °C indicates that NiO reacted with V_2O_5 and produced the catalyst precursor of semiconductor complex (Ni, V, O). The reduction peak of CuO particles was reduced to 249 °C and a new peak appeared at 438 °C (curve 5), demonstrating that CuO particles were also well dispersed within the semiconductor complex (Ni, V, O) under the experimental conditions.

Fig. 3 shows that the amorphous XRD patterns of the copper modified (Ni, V, O) semiconductor complex catalysts, which is similar to the pattern of SiO_2. This indicates that the catalyst was well dispersed on the surface of SiO_2 particles.

As further disclosed in TEM of Fig. 4 for the copper modified (Ni, V, O) semiconductor complex catalyst, the brighter grayish portions correspond to SiO_2 support, whereas the darker dots are the catalyst particles with nano-scale of 4–8 nm. These facts are also consistent with the findings in both TPR profiles and XRD patterns. The energy diffraction spectrometer (EDS) suggests that these darker dots include Cu, Ni and V elements. In a nano-crystal, the wave function of the charge carrier spreads over the whole semiconductor particle and the charge carriers can accomplish reactions with species present at the surface without diffusion, therefore, the semiconductor catalyst exhibits highly catalytic activity [24].

Fig. 5 shows the UV–vis drift reflection spectra (DRS) for the V_2O_5 supported on SiO_2, the catalyst precursor (Ni, V, O) semiconductor complex and the copper modified (Ni, V, O) semiconductor complex catalyst, respectively. There exists a cross-point at 510 nm between curves 1 and 2. It can be seen that for the wavelength less than 510 nm the light reflectivity of catalyst precursor (Ni, V, O) semiconductor complex has decreased due to the formation of solid solution of catalyst precursor (Ni, V, O) semiconductor complex which increases the absorbance of UV–vis light. By comparing curve 2 with 3, one can also see that the reflectivity increases slightly from about 7 to 12% for the wavelength less than cross-point 446 nm, while the reflectivity decreases greatly from about 45% to below 15% for the wavelength over 446 nm, suggesting that the introduction of copper can increase the absorbance of catalyst in visible
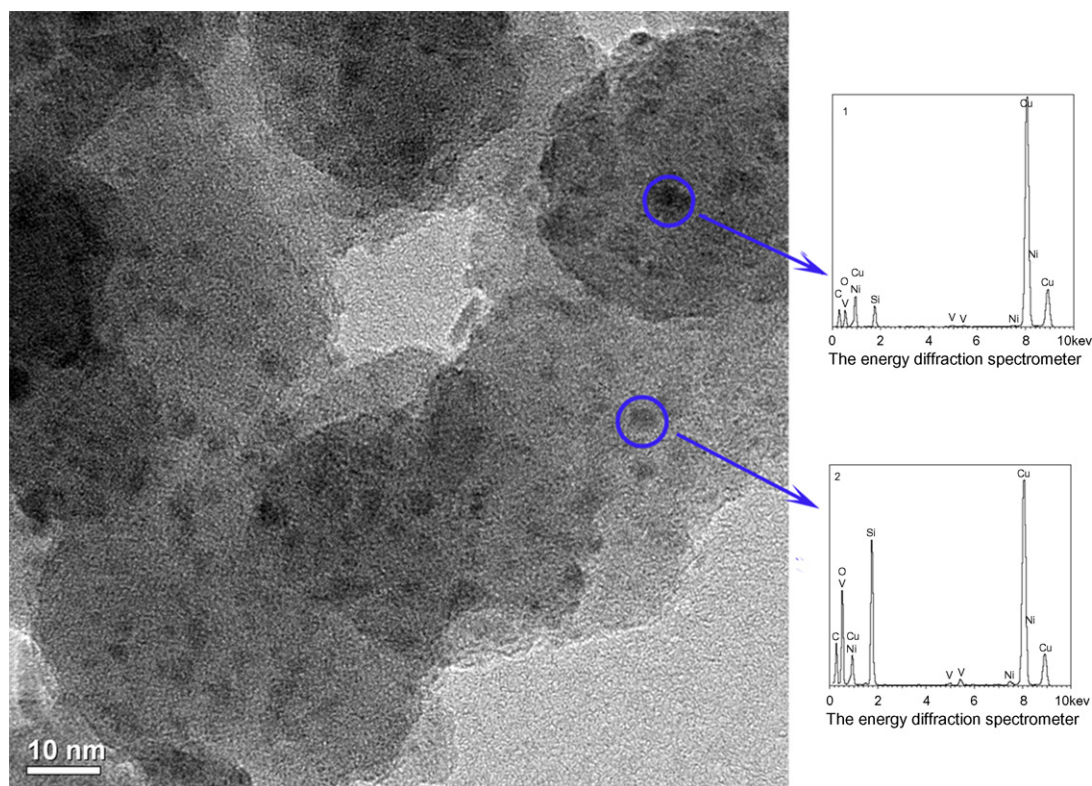
Fig. 4. TEM image of copper modified (Ni, V, O) complex catalyst.

light range. Coupled semiconductor photo-catalyst with copper doping provides a potential way to increase the efficiency of a photo-catalytic process by increasing the charge separation and extending the energy range of photo-excitation for the system and by the improved trapping of electron to inhibit electron–hole recombination during illumination [20].

3.2. Photo-catalytic synthesis of DMC from CO_2 and CH_3OH

Fig. 6 shows the pressure dependence of DMC synthesis on different catalytic system, with (curves 2 and 3) or without (curves 1 and 4) UV irradiation, at the constant temperature of 120 °C. Under the same pressure, the DMC selectivity with

UV irradiation appears a little lower than that without UV irradiation, while the DMC yield with UV irradiation exhibits 33–56% higher than that without UV irradiation. Both yield and selectivity of DMC with or without UV irradiation increased with increasing pressure. DMC yield and selectivity without UV irradiation seems more sensitive to the pressure change in case the system pressure goes up over 6 atm. Presumably, this is resulted from different reaction mechanisms. However, the yield and selectivity of DMC with UV irradiation shows little dependence on the pressure, increasing only 16% when system pressure increases from 1 to 12 atm. Considering the relationship among the DMC yield, selectivity and the operation pressure, it is preferred to perform the DMC synthesis under the pressure of 1 atm.
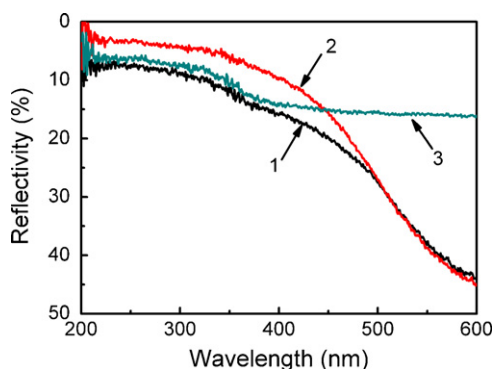

Fig. 5. UV–vis DRS spectra of (1) V_2O_5 supported on SiO_2, (2) catalyst precursor (Ni, V, O) complex and (3) copper modified (Ni, V, O) complex catalyst.
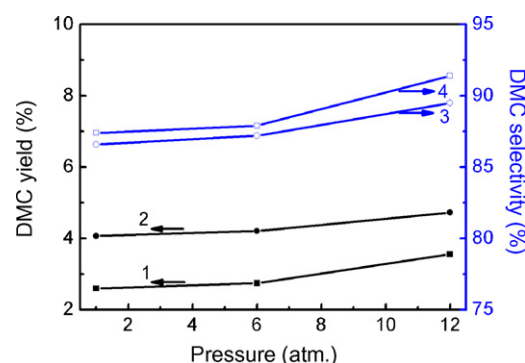

Fig. 6. The dependence of DMC yield and selectivity on pressure with (curves 2 and 3) or without (curves 1 and 4) UV irradiation.
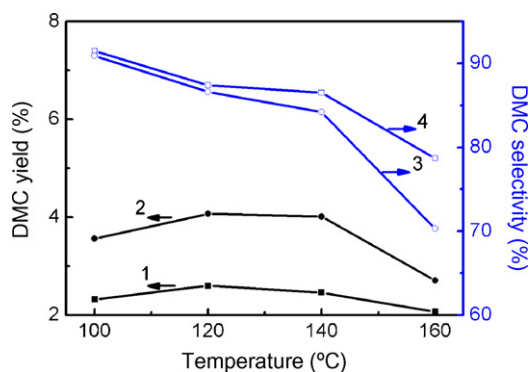
Fig. 7. The dependence of DMC yield and selectivity on temperature with (curves 2 and 3) or without (curves 1 and 4) UV irradiation.

Fig. 7 presents the temperature dependence of DMC synthesis on different catalytic systems, with (curves 2 and 3) or without (curves 1 and 4) UV irradiation, under the constant pressure of 1 atm. At the same temperature, the DMC selectivity with UV irradiation shows a little lower than that without UV irradiation, while the DMC yield with UV irradiation exhibits 53–63% higher than that without UV irradiation. This demonstrated the effectiveness of UV irradiation or photocatalysis for the reaction. Both yield and selectivity of DMC with or without UV irradiation increased with increasing temperature from 100 to 120 °C, followed by leveling off from 120 to 140 °C and finally decreased sharply from 140 to 160 °C. It is apparent that the optimized operation temperature appears to be 130 °C. At low temperature, the increasing of temperature favors the synthesis of DMC, however, too high temperature (>140 °C) leads to DMC decomposition. The increased temperature accelerates the recombination of photoelectrons and holes generated by UV irradiation which could be another reason for the lower activity. Overall, under the optimized operation conditions of normal pressure, 130 °C and 125 W UV irradiation, the conversion of CH_3OH was up to 4.04% with the DMC selectivity of 85.4% over copper (Ni, V, O) catalyst. The major by-products are methoxyl methalic acid and carbon monoxide in this reaction [27]. Presumably, methoxyl methalic acid is resulted from the un-completely reaction between carbon dioxide and methanol, while carbon monoxide is produced from the cleavage of the C—O bond of the $^\bullet CO_2{}^-$ anion radical.

4. Conclusions

Copper modified (Ni, V, O) semiconductor complex catalysts can be characterized by TPR technology. The direct synthesis of DMC from methanol and CO_2 was successfully carried out with and without the UV radiation. The experimental results showed that the nano-scale catalyst particles had a size of 4–8 nm. The UV–vis DRS spectra of the catalyst showed its feature of good light absorbance. UV irradiation reduced the reaction pressure to 1 atm and the DMC yield increased 57% compared with pure thermal surface catalytic reaction. The optimized operation condition profile for the direct DMC synthesis was at 120–140 °C and under 1 atm with the assistance of UV light irradiation.

Acknowledgements

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