

Direct synthesis of dimethyl carbonate (DMC) using Cu-Ni/VSO as catalyst

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Abstract

The catalytic effects of Cu-Ni/VSO catalysts on the synthesis of dimethyl carbonate (DMC) from CO₂ and CH₃OH were investigated. The Cu-Ni/VSO catalysts were fully characterized by infra-red spectra (FTIR), X-ray diffraction (XRD), and diffuse reflectance FTIR (DRIFT) spectra. The crystallinity of the catalysts was influenced by process of reduction, and the crystal type of V₂O₅ on the surface of VSO changed when the catalysts were reduced. DRIFT spectra of catalyst showed that CO₂ and CH₃OH were activated effectively by the catalysts.

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1. Introduction

Dimethyl carbonate (DMC) is an environmentally benign chemical product with a wide range of applications. DMC can serve as a non-toxic substitute for dimethyl sulfate and phosgene, which are highly toxic and corrosive methylation and carbonylating agents [1–3]. In addition, DMC is also a good solvent, a useful fuel additive and a monomer for the synthesis of polycarbonate resins [4,5]. One synthesis method of DMC requires phosgene as a reagent. This is highly undesired due to the extreme toxic nature of phosgene. Another route to the preparation of DMC is the oxidative carbonylation of CH₃OH with CO and oxygen [6,7]. However, both copper and palladium catalysts are required for this synthesis. The use of expensive metal catalysts makes such process unfavorable especially when the industrial scale preparation is concerned. In recent years, direct synthesis of DMC from CO₂ and CH₃OH became an attractive approach [8]. The low-cost of CO₂ is an apparent advantage.

Moreover, the process of converting “waste” CO₂ into a versatile chemical product is regarded as a highly “green” chemical process [9].

Organometallic compounds such as BuSn(OMe)₂ [10,11], metal (□) tetra-alkoxide [12], magnesium dialkoxide [13], potassium carbonate [14], zirconia [15], CeO₂–ZrO₂ [16] and Ni(CH₃COO)₂ [9] have been employed as catalysts for the synthesis of DMC from CO₂ and methanol. However, due to the limit of reaction thermodynamics, the activities of these catalytic systems were quite low even in the presence of dehydrating agents and additives. Recently, it was reported that a direct synthesis of DMC from CO₂ and CH₃OH could be carried out at the supercritical conditions [17,18]. Dehydrate agents, such as CaCl₂ [19], 2,2-dimethoxy propane (DMP) [16] acetals [9,20] and molecular sieves [21] were added to reaction system to remove water to facilitate the conversion of CO₂ and CH₃OH. However, the reaction conditions were difficult to control.

Now gaseous reaction can be adopted for the direct synthesis of DMC from CO₂ and methanol. The reaction can be carried out in a fixed bed reactor, and there is no water in the reaction system during reaction that favors the progress of the formation of DMC. Therefore, we report an efficient direct synthesis of DMC from gaseous methanol and CO₂, using a supported

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Cu-Ni/VSO heterogeneous catalyst due to their economy nature of both Cu and Ni. The Cu-Ni/VSO has been reported for the synthesis of DMC from methanol and CO₂; however, the authors had not discussed the preparation of the catalyst in details [22,23]. Therefore, the catalysts are characterized in new ways to disclose the reaction process of CH₃OH and CO₂ on it and the effect of reduction conditions of catalysts for the synthesis of DMC from CH₃OH and CO₂ have been researched.

2. Experimental methods

2.1. Catalyst preparation

Preparation of VSO (V₂O₅-SiO₂): V₂O₅ was reacted with HCl (38% wt.%) at 363 K to produce VOCl₃; SiO₂ was introduced into VOCl₃ solution to form a mixture which was aged for 24 h, and then surface reaction was proceeded on SiO₂ at 363 K for 24 h. NH₄OH was introduced into the reaction system to neutralize excessive acid at room temperature. Finally, VSO was filtered, dried at 393 K for 12 h and calcined at 723 K in the air for 5 h.

Preparation of Cu-Ni/VSO: VSO was soaked in a solution of copper and nickel ammonia for 48 h, and then dried at 393 K in the air for 12 h and calcined at 723 K in the air for 5 h.

2.2. Catalyst characterization

FTIR and DRIFT spectra were recorded on an EQUINOX 55 (Bruker Co. Fourier transformation infra-red spectrometer coupled with infra-red microscope). XRD patterns were measured with D/Max-III A (Powder X-ray Diffract meter). Pre-reduction for DRIFT spectra was performed by reducing the sample in a pure H₂ flow (5 K/min) at 0.2 MPa from 298 to 473 K, and held at this temperature for 30 min, then a mixture of CH₃OH/CO₂ was introduced at 473 K and kept for 30 min, pressure was maintained at 0.2 MPa. When temperature decreased to room temperature, DRIFT spectra were collected as soon as possible.

2.3. Synthesis of DMC from CO₂ and CH₃OH

A continuous tubular fixed-bed micro-gaseous reactor (15 mm i.d.) was used for the assessment of synthesized catalysts. A representative procedure is as follows: 0.5 g of catalyst was placed on the fiberglass stuffed in the reactor; CO₂ and CH₃OH were purged into the reactor at the same time. CH₃OH was introduced into the reactor using CO₂ flow. A 2:1 ratio of CH₃OH and CO₂ was kept during the reaction, which was controlled via vaporization temperature of CH₃OH and the flux of CO₂. Amounts of CH₃OH and CO₂ were controlled by gas-flow meter. CH₃OH/CO₂ = 500/250 mmol was kept for each test. The reaction was carried out at different temperatures (373–453 K) and different pressures (0.2–0.9 MPa). Products were absorbed in deionized water and analyzed by gas chromatograph (GC) equipped with a flame ionization detector (FID).

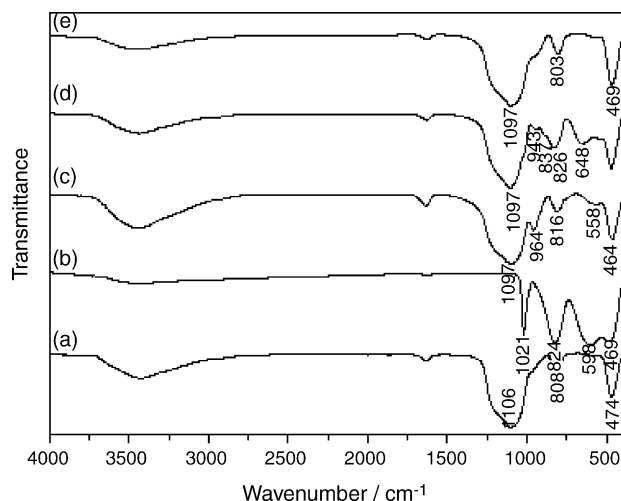


Fig. 1. FTIR spectra of (a) SiO₂, (b) V₂O₅, (c) VSO, (d) CuO-NiO/VSO and (e) Cu-Ni/VSO.

3. Result and discussion

3.1. Catalyst characterization

FTIR spectra of SiO₂ (a), V₂O₅ (b), VSO (c), CuO-NiO/VSO (d) and Cu-Ni/VSO (e) are shown in Fig. 1. Compared with FTIR spectra of SiO₂ and V₂O₅, FTIR spectra of VSO (c) has a new band at 964 cm⁻¹. This band can be assigned to the stretching of V–O–Si bond. Spectrum (b) has a band at 1021 cm⁻¹ and stretching of V–O bond at 824 cm⁻¹, the former disappears and V–O stretching band shifts to 816 cm⁻¹ in spectrum (c). Moreover, the bands of 598 and 469 cm⁻¹ in spectrum (b) shifts to 558 and 464 cm⁻¹, which are related to the vibration of V–O bond. These spectra data clearly show that there is no dissociated V₂O₅ on the surface of VSO. The FTIR spectrum of CuO-NiO/VSO (d) showing the band of 964 cm⁻¹, corresponding to the stretching of V–O–Si in spectrum (c), shifts to 943 cm⁻¹, indicating the change of chemical environment around V–O–Si. In addition, three new bands at 826, 887 and 648 cm⁻¹ are observed, corresponding to the presence of CuO and NiO on the surface of VSO. FTIR spectra of Cu-Ni/VSO seem similar to that of SiO₂ due to the disappearance of bands at 826, 887 and 648 cm⁻¹ and the band at 943 cm⁻¹ that was overlapped by the broad band at 1097 cm⁻¹.

Fig. 2 shows the XRD patterns of SiO₂ (a), V₂O₅ (b), VSO (c) and Cu-Ni/VSO (d). XRD of (a) shows that SiO₂ is amorphous. Based on the XRD of V₂O₅, it is mainly rhombic crystal. The crystal of V₂O₅ was on the surface of VSO, and it exists as micro-crystal structure. On the XRD of Cu-Ni/VSO (d) in Fig. 2, two new diffraction peaks at 2θ = 43 and 50° appeared. This is assigned to the diffraction of Cu–Ni alloy with 20% Ni and 80% Cu. The peaks of 0 0 1, 1 0 1, 1 1 0, 2 1 1 and 0 1 2 disappeared, while the peak of 1 1 1 became a main peak. Three new peaks at 2θ = 24, 36 and 41° appeared on the XRD of Cu-Ni/VSO. Presumably, the crystal structure of V₂O₅ has changed greatly after the sample was reduced. This change can be observed on the FTIR spectra of (c) and (e). A new strong peak at 2θ = 53°

Table 1
Reduction conditions for different CuO–NiO/VSO samples

No.	Amount of gas	Interval of temperature (K)	Rate of temperature	Note
(b)	N ₂ : 60 ml/min H ₂ : 6 ml/min	373–793	4 K/min	H ₂ : 10 ml/min during 573–673 K
(c)	N ₂ : 60 ml/min H ₂ : 6 ml/min	373–793	8 K/min	H ₂ : 10 ml/min during 573–673 K
(d)	N ₂ : 60 ml/min H ₂ : 6 ml/min	373–793	8 K/min and stay 20 min at 626 K	H ₂ : 10 ml/min at <i>T</i> =626 K

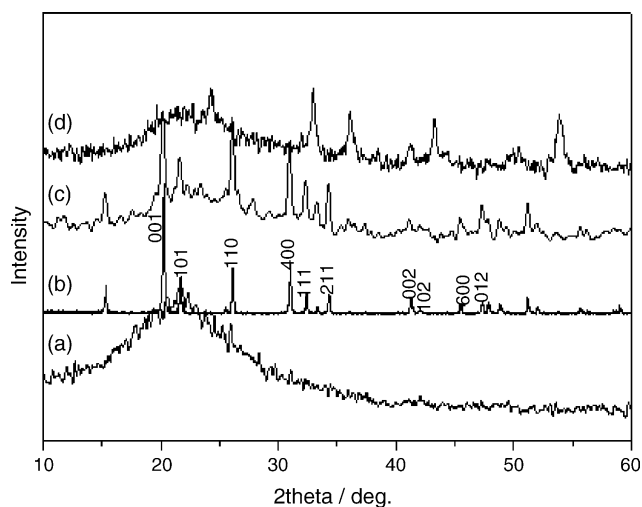


Fig. 2. XRD traces of (a) SiO₂, (b) V₂O₅, (c) VSO and (d) Cu–Ni/VSO.

appeared on the XRD of Cu–Ni/VSO, which may result from the reaction of V₂O₅ and Cu–Ni alloy.

The reducing conditions of CuO–NiO/VSO into Cu–Ni/VSO are summarized in Table 1, and the XRD patterns of the reduced products are shown in Fig. 3. Sample (b) was reduced in a mixture of 1:10 H₂/N₂, at a temperature profile from 373 to 793 K with a gradient of 4 K/min, and the ratio of H₂/N₂ was changed to 1:6 at temperature between 573 and 673 K. For sample (c), the reduction of CuO–NiO/VSO was carried out under otherwise

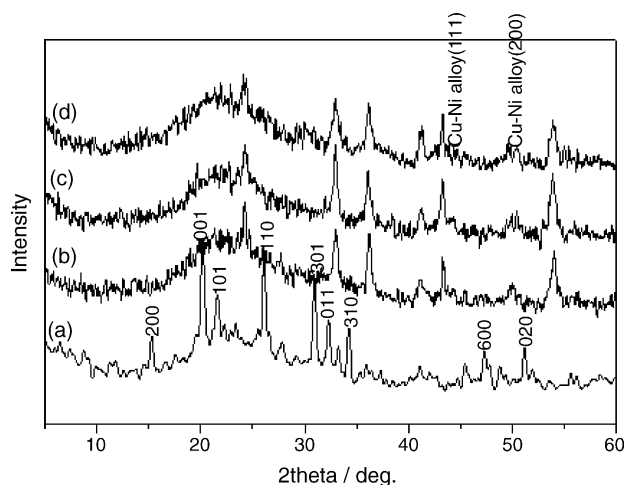


Fig. 3. XRD traces of (a) CuO–NiO/VSO and (b), (c), (d) Cu–Ni/VSO as described in Table 1.

identical conditions as those of sample (b) except the temperature gradient was set at 8 K/min. The reduction conditions of sample (d) were similar to those of sample (c), except that the temperature was held at 626 K within 20 min. XRD patterns indicate that the different reduction processes gave the same V₂O₅ crystals on the reduced catalysts, although they were different from V₂O₅ on surface of VSO (a). The crystallinity decreased in an order of sample (c) > (d) > (b) based on the examination of the ratios of intensity/FWHM of the above samples. The same is true for the crystallinity of Cu–Ni alloy.

DRIFT spectra for the adsorption of CO₂ and CH₃OH on Cu–Ni/VSO are shown in Fig. 4. As shown in Fig. 4(a), the absorption of CO₂ and CH₃OH on the catalyst led to the appearance of new bands at 937, 670, 593 and 571 cm^{−1}. These can be assigned to the stretching of horizontal adsorption CO₂ on the surface of Cu–Ni/VSO catalyst. In the region of 2000–1300 cm^{−1} in Fig. 4 (b), new bands at 1300, 1573 and 1554 cm^{−1} associated with the vibration of bidentate carbonate on V=O bond was observed. Two characteristic bands, located at 1983 and 1946 cm^{−1}, can be assigned to the linear type adsorption of CO₂ on Ni and Cu, respectively. Peaks at 1588 and 1341 cm^{−1} are characteristic bands of horizontal adsorption of CO₂ on the surface of Cu–Ni alloy. The bands at 1603, 1537, 1472 and 1365 cm^{−1} arisen after the adsorption of CO₂ and CH₃OH. These can be assigned to the formation of methyl carbonate-type species. The band at 1700 cm^{−1} is related to bond of C=O. The bands at 2817, 2895 and 3015 cm^{−1} associated with C–H stretching vibrations of monodentate and bidentate of methoxide groups were observed as shown in Fig. 4(c). Bands at 2352 cm^{−1} corresponding to the molecular type adsorption CO₂ were also observed in the same figure. In the region of 4000–3500 cm^{−1} in Fig. 4(d), molecular adsorption of the methanol hydroxyl group at 3640 cm^{−1} can be observed. Moreover, bands at 3680, 3689 and 3668 cm^{−1} were also observed, due to the vibration of V–OH bond resulted from the interaction of V=O and H of CH₃OH. Multi-peak bands in the same region showed the presence of several types of hydroxyl groups on the surface of Cu–Ni/VSO. The bands at 3768 and 3737 cm^{−1} are owing to the presence of terminal, bi-bridged and tri-bridged hydroxyl groups, respectively. Such spectra clearly suggest that CO₂ and CH₃OH have been activated on the supported catalyst system.

3.2. Synthesis of DMC from CO₂ and CH₃OH

Fig. 5 shows the temperature dependence of DMC synthesis on different catalytic systems. The yields of DMC increased

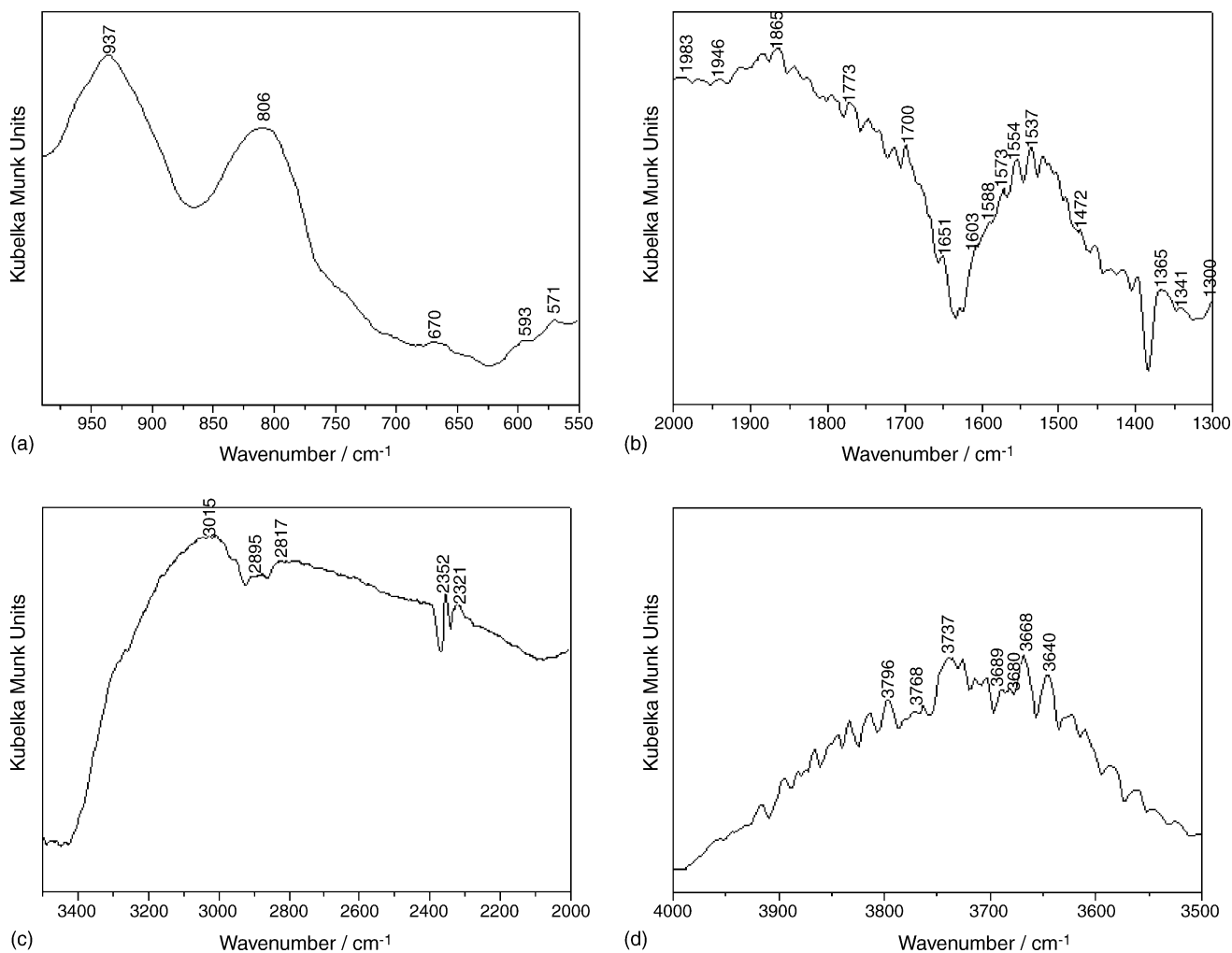


Fig. 4. DRIFT spectra of CO_2 and CH_3OH absorbed onto Cu-Ni/VSO.

with increasing temperature, while the increase of yields started slowing down at about 413 K. This is due to that the higher temperature can lead to the decrease of carbon dioxide absorption on catalysts. Fig. 6 shows the selectivity of DMC base on

CH_3OH as a product at different temperatures. The major by-product is dimethoxyl methane (DMM) in this reaction. The selectivity decreased at higher temperatures in all the catalytic systems due to the decomposition of DMC. When temperature

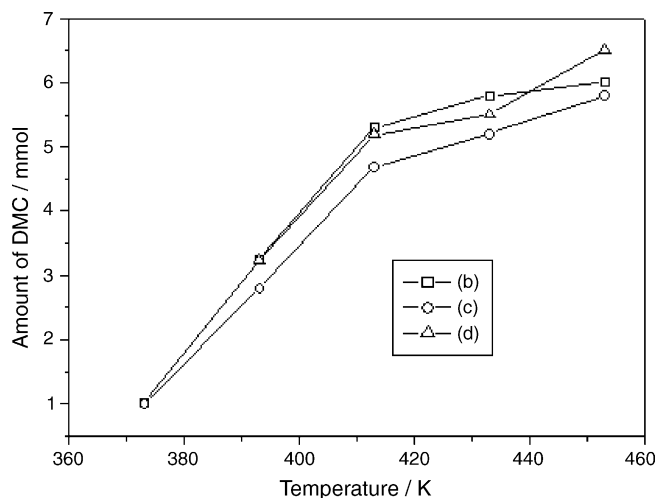


Fig. 5. Dependence of DMC formation on temperature over different Cu-Ni/VSO samples: (b), (c) and (d) depicted in Table 1.

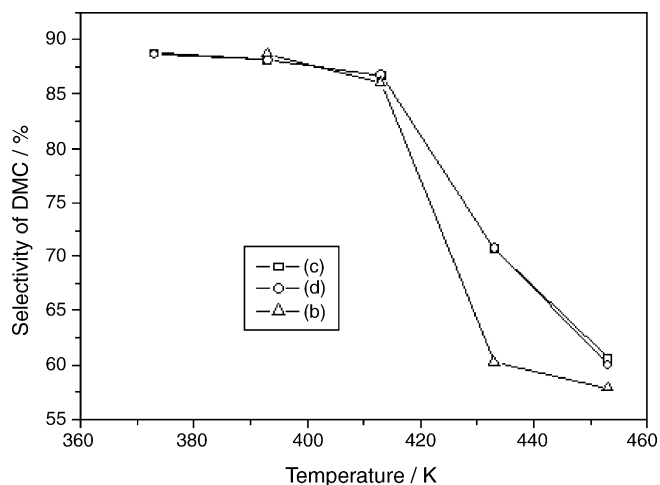


Fig. 6. The dependence of DMC selectivity on temperature over different Cu-Ni/VSO samples: (b), (c) and (d) depicted in Table 1.

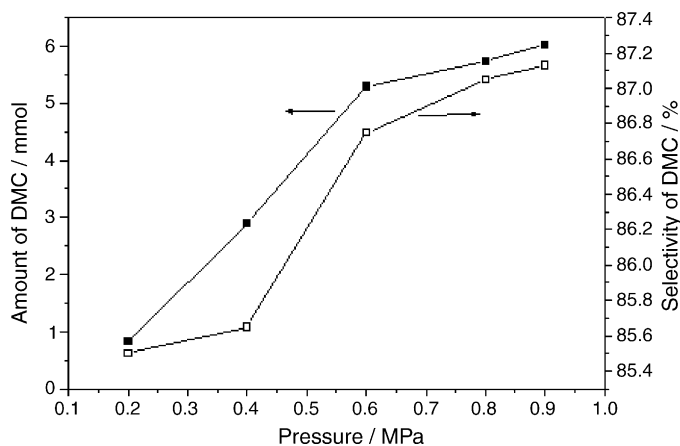


Fig. 7. The dependence of DMC formation and selectivity on pressure over Cu-Ni/VSO (c) depicted in Table 1.

was higher than 413 K, the selectivity decreased more dramatically, following an order of (b) > (c) \approx (d). In summarizing, the optimal temperature for the synthesis of DMC synthesis using the supported catalysts is about 413 K.

Fig. 7 shows the pressure dependence of the yield and selectivity of DMC base on CH₃OH with Cu-Ni/VSO (c) as the catalyst. Both the yield and selectivity of DMC increased with increasing pressure. The increasing trend leveled off when the pressure reached to about 0.6 MPa.

4. Conclusions

Based on the experimental results, the following conclusive remarks can be obtained:

- (1) A new V–O–Si bond was formed when V₂O₅ was supported onto SiO₂ as evidenced by the observation from the FTIR spectrum changes of VSO.
- (2) The crystal type of V₂O₅ remained unchanged on the surface of VSO, while it changed when CuO–NiO/VSO was reduced to Cu–Ni/VSO.
- (3) Based on the DRIFT spectra, methanol and CO₂ were activated upon being adsorbed onto the catalyst. This is of crucial importance for this catalytic reaction.
- (4) The crystallinity of the catalysts showed a slight influence on the DMC synthesis, and a higher crystallinity resulted in a higher yield of DMC.

- (5) An increase in reaction temperature led to a higher conversion of CH₃OH but a decrease in selectivity of DMC formation. The optimal conditions for both the high conversion of methanol and the good selectivity of DMC formation were the temperature of 413 K and the pressure of 0.6 MPa.

Acknowledgments

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