Optimal Performance for both CuO and NiO as Ametal Oxide Nanoparticles Catalyst in the Carbonylation the Glycerol with Carbon Dioxide to Produce Glycerol Carbonate

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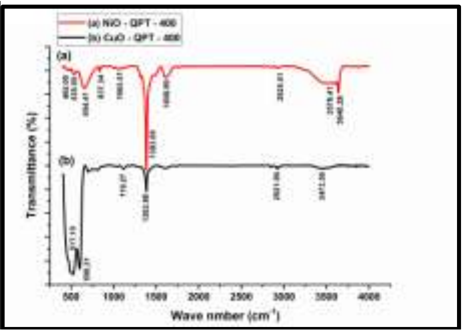
Graphical abstract



Highlights

1) The quick traditional precipitation (QPT) was a new route for the preparation of metal oxide nanoparticles catalyst was developed by strategy in this work.
2) This is the first report about formed (CuO-QPT-400) and (NiO-QPT-400) nanoparticles catalyst for glycerol carbonate production.
3) (CuO-QPT-400) was worked as a best and new as a metal oxide nanoparticle catalyst to produce glycerol carbonate by the carbonylation of Glycerol with Carbone Dioxide.

Abstract: ***Two types of metal oxide nanoparticle catalysts Nickel oxide (NiO) and Copper oxide (CuO) are prepared by new method which was quick precipitation (QPT) methodat calcination temperature of 400°C for 4h and used for the synthesis of glycerol carbonate GC ($C_4H_6O_4$) from the direct reaction by the carbonylation of Glycerol GL ($C_3H_8O_3$) with Carbone Dioxide. The quick precipitation (QPT) was a new and important route for the preparation of nanoparticles catalyst and it was developed by strategy in this work. The effects of performance of (NiO and CuO) nanoparticle catalysts on the conversion of glycerol GLyield of glycerol carbonate, selectivity of glycerol carbonate and Turnover frequencyare researched. XRD, FT-IRand SEM are used for the characterization of the prepared metal oxide catalysts. It is found that the best metal oxide nanoparticles catalyst in GL carbonylation reactionis CuO prepared by quick precipitation (QPT) method at calcination temperature of 400°C for 4h. Under 150 °C, 4MPa (≈ 40 bar.), 5h, and CuO catalyst amount 37.6% (based on ratio of glycerol weight) by using2-pyridinecarbonitrate ($C_6H_4N_2$) as dehydrating agent and dimethylformamide (DMF)(C_3H_7NO) as solvent, the glycerol conversion, glycerol carbonate yield and selectivity are 48.64%, 38.88%, and 79.94%, respectively, and the turnover frequency (TOF) valueof the catalyst can reach 0.2061h^{-1},and the catalysts could be easily regenerated by washing with methanol and water after a reaction and then dried at 60 °C overnight after that calcination at 400°C for 4h without loss of activity after five recycling times.***

Keywords: glycerol ;glycerol carbonate ;carbon dioxide ; metal oxidenanoparticle catalyst ; CuO nanoparticle catalyst ; carbonylation ; La_2O_3; DMF.

1. Introduction

In recent decade, as aclean and renewable fuel, the biodiesel has attracted a great deal of interest in the whole world. Huge amounts of glycerol (GL)($C_3H_8O_3$) are produced as a by-product of the biodiesel manufactures. Because of rapidly increasing production of global biodiesel in a great quantity, it becomes a research and study focus to transform GL to value-added chemicals. It is predicted that the global production capacity of biodiesel will reach 50 million tons a year in 2020 [1-5]. In the industry, the biodiesel is mainly produced by the transesterification of animal or vegetable oil with methanol. In the process, glycerol (GL)is also rapidly produced as a main by-product at a rate of 10% of biodiesel production, resulting in a large surplus over traditional requirements in the chemical industry [6, 7]. Therefore, more and more attention are drawn on transforming GL to high value-added products, such as acrolein,1,3-propanediol, polyglycerols, and glycerol carbonate (GC) ($C_4H_6O_4$). GC has many potential applications due to its low toxicity, high boiling point, and good biodegradability. It can be used as surfactant, adhesive, and paint as well as a component in gas separation membranes. GC also can serve as a useful solvent in lithium-ion batteries and a monomer for polymers such as polyesters, polycarbonates, polyurethanes, and polyamides[8-15].

In the last years, the broad and suitable availability of glycerol at low prices, together with the need of new and good economic synthetic routes for chemicals starting from non-petrochemical sources, have created a huge interest in glycerol molecule as a building block, mainly because of the very broad spectrum of its valuable derivatives [7].

GC can be synthesized from GL via several routes, which can be divided into two categories: indirect and direct routes, according to different carbonyl sources. GC can be indirectly synthesized by the transesterification of GL with other organic carbonates and urea. However, carbonates such as dimethyl or diethyl carbonate would be relatively expensive chemicals leading to less commercial benefit for the transesterification of GL with them [16-18]. Meanwhile, ammonia is produced in the glycerolysis of urea, which need to low-pressure reaction condition to remove the ammonia gas [19-22]. Compared with the indirect route, the direct synthesis of GC by GL carbonylation with CO_2 is more interesting and its atom utilization is as high as 87% [23, 24]. Moreover, this reaction is regarded as a green process in which two cheap raw reactants, GL, a by-product of biodiesel production, and CO_2, a primary greenhouse gas, can be converted to a value-added chemical, GC.

Up to now, a series of catalysts were used to catalyze the carbonylation of GL with CO_2, such as basic ion-exchange resin, CeO_2-Al_2O_3 or CeO_2-Nb_2O_5, tin complexes, Cu/La_2O_3, $La_2O_2CO_3$/ZnO and so on [25-28]. However, a low GL conversion was obtained over these catalysts because of thermodynamic limitation. Vieville et al. used GL and supercritical carbon dioxide as reactants by using basic ion-exchange resin as a catalyst to obtain GC, but the reaction did not occur [25]. Dibenedetto et al. employed CeO_2-Al_2O_3 and CeO_2-Nb_2O_5 as catalyst using tetra (ethylene glycol) dimethyl ether as the solvent, and the conversion of GL only reach 2.5% after 15 h reaction [26]. Recently, in order to overcome the thermodynamic limitation, some agents, such as acetonitrile and 2-cyanopyridine, were used as dehydrant in the carbonylation of GL with CO_2 and a little enhanced GL conversion was obtained [27]. Despite of these progresses, the conversion of GL is still relatively low and it is a challenge to develop new effective catalytic system. 13X type of zeolite and acetonitrile were employed for this purpose with both Cu/La_2O_3 [22], Bu_2SnO [7] and achieved to a good result. Despite of all these improvements, the conversion of GL is still relatively low and it is a challenge to improve and develop new effective catalytic system.

To produce GC from GL with dimethyl carbonate (DMC) by transesterification of GL process can be obtained high conversion and high yield by using a suitable catalyst such as alkali metal or carbonate or hydroxide (for example, K_2CO_3, KOH, NaOH), Ma/Al/Zr mixed oxide, Mg/Al hydrotalcite, calcium diglyceroxide, alkaline earth metal oxide (CaO) and others [23–28].

In general nanoparticle metal oxide heterogeneous catalysts are a technologically very important as acid-base and unique redox properties such as (La_2O_3, CeO_2, NiO, CuO and $Co_3O_4$and others) [29].

Metal oxide nanoparticle is an important kind of catalysts with a high surface area and a high catalyst activity. In more and more reactions, metal oxide nanoparticle works as a catalyst showing very good performance [30-32]. For instance, Paulose et al. prepared nanoparticles copper oxide (CuO) dispersed on alumina by sol-gel method and found the catalyst shows high catalytic activity for the thermal decomposition of ammonium perchlorate [32]. Shokrani et al. also synthesized CuO-based as nanocatalyst by urea-nitrates combustion method and found that the nanocatalyst has a well practicability for hydrogen production via steam reforming of methanol [33].

Kankanit Phiwdang et al. [34], reported that the Catalyst preparation CuO nanostructures catalysts by traditional Precipitation (PT) method using copper chloride (CuCl2) and copper nitrate ($Cu(NO_3)_2.3H_2O$). First, each precursor was dissolved in 100 ml deionized water to form 0.1 M concentration. NaOH solution (0.1 M) was slowly dropped under vigorous stirring until pH reached to 14. Black precipitates were obtained and repeatedly washed by deionized water and absolute ethanol for several times till pH reached 7. Subsequently, the washed precipitates were dried at 80 °C for 16 h. Finally, the precursors were calcined at (400-500) °C for 4h.

XiangYi Deng et al. [35] they've been able to prepare the NiO nanoparticles catalyst as follows: 150 ml $NiCl_2.6H_2O$ solution (0.1-0.5 M) NH_3 solution was added slowly (approximately 30–60 min) under vigorous stirring (500–800 rpm) at room temperature. Distilled water was used as a solution agent. The solution was kept under stirring for 20–30 min after the precipitation addition. The pH of the solution was determined using a pH meter. The resulting precipitates were filtered, and washed with distilled water and alcohol. After dried at 105 ^oC for 1 h, the precipitates were heated at 400 ^oC for (1- 4) h.

In present work, we employed two type of metal oxide Nanoparticle (CuO and NiO) as the catalyst for the synthesis of GC from GL and CO2 in the presence of (2-pyridinecarbonitrate) which was used as a dehydration agent to pull water from the middle of the chemical reaction as side product and shift the chemical equilibrium to the GC production side and solvent of CO_2(Dimethylformamide (DMF)). The important objective of this work was to select the best one of two type of metal oxide Nanoparticle (NiO and CuO), and develop a new effective catalytic system (carbonylation system) to increase the reaction rate and selectivity of the carbonylation of GL. The quick precipitation (QPT) was a new route for the preparation of Nanoparticles metal oxide catalyst was developed by strategy in this research. The stability and activity of the suitable catalysts were studied in detail. From our knowledge, this is the first work of the application of prepared (Nano particles metal oxide)-based catalyst for using in the carbonylation of GL reaction for GC production.

2. Experimental Section

2.1. Chemicals

Nickel(II)nitrate hexahydrate[$Ni(NO_3)_2.6H_2O$] ≥ 90% purity, Copper(II) nitrate trihydrate [($Cu(NO_3)_2.3H_2O$]99% purity, (25 wt.%) ammonia solution (NH_3), Glycerol GL($C_3H_8O_3$)99% purity and N.NDimethylformamide(DMF) (C_3H_7NO) 99% purity were bought from Sinopharm Chemical Reagent Co., Ltd.,Beijing-China. 2-pyridinecarbonitrate($C_6H_4N_2$)was purchased from Aladdin Industrial Corporation Co., Shanghai-China. Carbon dioxide (CO_2) 99.9% purity was supplied by Sichuan Tianyi Science & Technology Co., Ltd., Sichuan-China. All these chemicals were used without further purification.

2.2. Catalyst preparation method.

The quick precipitation (QPT) method was a new route for the preparation of metal oxide nanoparticles catalysts, the amounts of materials depended on the stoichiometric of materials to prepared the metal oxide nanoparticles catalysts:

2.2.1. (CuO) nanoparticles catalystspreparation:

300ml of Copper(II) nitrate trihydrate [($Cu(NO_3)_2.3H_2O$] 0.25mol/L solution was put into a 500ml Boiling Flask and heated to 80°C with constant stirring (500 rpm) by using oil bath. The color of the mixture was bright (saturated case) about 3h. About 100 mL of 25% NH_3 (1mol/L) solution (1M) was rapidly added into the mixture at two batch, and a Nanoparticle suspension was formed, the suspension was kept at 60 °C for 1h and keeping the pH value (10 ± 1). An amount of black precipitate was filtered and washed with deionized water for five times, and after that dried at 60◦C in vacuum dryer for 2h, and then grinned to (100) mesh scale, followed by calcination at 400◦C for 4 h in air. The obtained product was denoted as (CuO-PT-400). The sample was calcined at different temperatures were named as [CuO- PT-T (T means the calcination temperature)].

2.2.2. (NiO) nanoparticles catalystspreparation:

300ml of Nickel(II)nitrate hexahydrate [$Ni(NO_3)_2.6H_2O$] 0.25mol/L solution was put into a 500ml Boiling Flask and heated to 80°C with constant stirring (500 rpm) by using oil bath. The color of the mixture was bright (saturated case) about 3h. About 100 mL of 25% NH_3 (1mol/L) solution (1M) was rapidly added into the mixture at two batch, and a Nanoparticle suspension was formed, the suspension was kept at 60 °C for 1h and keeping the pH value (10 ± 1). An amount of black precipitate was filtered and washed with deionized water for five times, and after that dried at 60◦C in vacuum dryer for 2h, and then grinned to (100) mesh scale, followed by calcination at 400◦C for 4 h in air. The obtained product was denoted as (NiO-PT-400). The sample was calcined at different temperatures were named as [NiO-PT-T (T means the calcination temperature)].

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of the catalysts were measured on a X'Pert PRO using Cu Kα radiation at 30 kV and 15 mA, over a 2θ range of 5-90^o with a step size of 0.0167^o at a scanning speed of 8min^{-1}.

Bruker VERTEX 70 FT-IR spectrometers was used to obtained the FT-IR spectra of samples using KBr pellet technique, with 2 cm^{-1} resolution over the wavenumber range (4000–400) cm^{-1}.

The morphology of the particles was observed by use of a scanning electron microscope (SEM, TESCAN VEGA3) with 20.0 kV of an accelerating voltage.

2.4. Reaction procedure.

Glycerol carbonate (GC) was obtained from the carbonylation of glycerol (GL) and CO_2 over nanoparticles catalysts.As shown in scheme 1.

Scheme 1: Carboxylation of glycerol and CO_2 over nanoparticles metal oxide catalysts

The tests of the catalytic activities of the nanoparticles metal oxide catalysts were carried out in a stainless-steel autoclave reactor system with an inner volume of 200ml and it has thermostat with an electric heating jacket, pressure gauge and agitator, the autoclave reactor was one of the most important chemical engineering equipment and its operation is not easy, it requires attention and caution when operating, because it works under conditions of high temperature and high pressure. After ascertaining the validity of the autoclave system (fig.1.), the typical procedure is as follows: 40mmol glycerol (GL), 37mmol% Cat./GL, 16 g of Dimethylformamide (DMF) 6 g of 2-pyridinecarbonitrate , were added into the autoclave together, and then the reactor was sealed, purged with N_2 or CO_2 for 3 times and then pressurized with CO_2 to 4 MPa. Subsequently, the autoclave was heated to the reaction temperature (150 ^{o}C) and maintained for certain reaction time (5h) under vigorous stirring. After reaction, the reactor was cooled to room temperature and depressurized, the product mixture was taken out from the autoclave reactor to centrifugal filtration 5000 rpm for 6 min to separation the solid catalyst and liquid products, after that take all liquid product to analyzing.

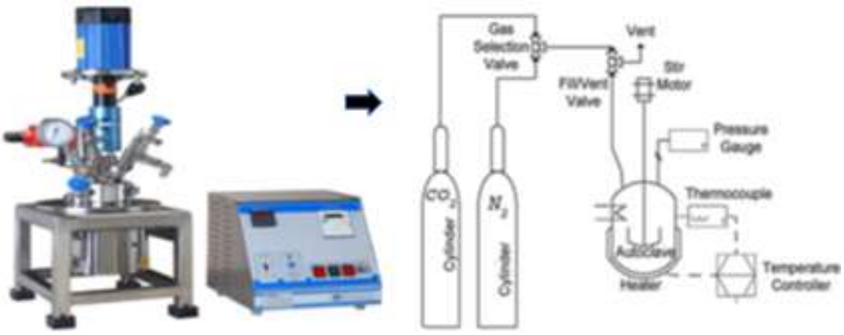


Figure 1: Autoclave reactor system

2.5. Liquid product analysis

All the components in liquid product were analyzed by the gas chromatograph (Fuli 9790-II) equipped with a flame ionization detector (FID) and a capillary column DM-FFAP (30 m long, 0.25 mm id). The internal standard method was used. Hydrogen (H_2) nitrogen (N_2) (99.999% pure) and air (20.8% O_2, 79.2% N_2), were supplied by (Sichuan Tianyi Science & Technology Co., Ltd., Sichuan, China), air and N_2 were used as the carrier gas with a flow rate of 30 mL/min at 0.4 MPa and H_2 at 0.25MPa. The temperatures of the injector and the detector were 250 C and 270 ^{o}C, respectively. The temperature of the column was programmed to have a 2min initial hold at 70 ^{o}C, a 15 ^{o}C/min ramp from 70 ^{o}C to 250 ^{o}C and a 15 min hold at 250 ^{o}C. A good peak separation was achieved under these conditions for all components. n- Butanol was used as the internal standard to determine Methanol, while tetra ethylene glycol was used as the internal standard to determine GL and GC. Added about 1g methanol to liquid product sample for diluting before injecting into gas chromatograph (Fuli 9790-II), the mass of all sample was (mass of samples + mass of ethanol) to determining the mass of GL and GC output with product.

The conversion of GL, X_{GL}, and the yield of GC, Y_{GC}, and selectivity of GC, S_{GC} and theTurnover frequency (TOF) were calculated according to the following equations:

$$Conversion(X_{GL}) = \frac{n_{GL.in} - n_{GL.out}}{n_{GL.in}} \times 100 \qquad (1)$$

$$yield\ (Y_{GC}) = \frac{n_{GC.out}}{n_{GL.in}} \times 100 \qquad (2)$$

$$Selectivity\ (S_{GC}) = \frac{Y_{GC}}{X_{GL}} \times 100 \qquad (3)$$

$$TOF\ (Turnover\ frequency) = \frac{n_{GC.\ out}}{n_{cat\ .} \times time\ (h)} \qquad (4)$$

Where $n_{GL.in}$ the number of initial moles of GL, $n_{GL.out}$ is the number ofmoles of GL output (unreacted), $n_{GC.out}$ is the number of moles of GC product and $ncat.$ is the number of moles of catalyst.

A catalyst's turnover frequency number, or turnover number per time unit, characterizes its level of activity. So, the TOF is the total number of moles transformed into the desired product by one mole of active site per hour. The large one of the TOF that means more active catalyst.

3. Result and Discussion

The synthesis of GC from GL and CO_2 by carbonylation reaction over metal oxide nanoparticles catalyst in the presence of (2-pyridincarbonitrate), which was used as a dehydration agent to pull water from the middle of the chemical reaction as byproduct to produced 2-picolinamide ($C_6H_6N_2O$) and shift the chemical equilibrium to the GC production side and solvent of CO_2 Dimethylformamide (DMF). As shown in mechanism of carboxylation reaction in scheme 2. The conditions of reaction were (150 ^{o}C temperature, 5h time, and 4MPa initial pressure of CO_2 and 500 rpm of mixing. The gas chromatogram of the reaction mixture is given in Fig. 2 it can be found a good peak separation is achieved for all components.

Scheme2. Mechanism of carboxylation of glycerol by CO_2 and dehydration over nanoparticles metal oxide catalysts as the coupling reaction.

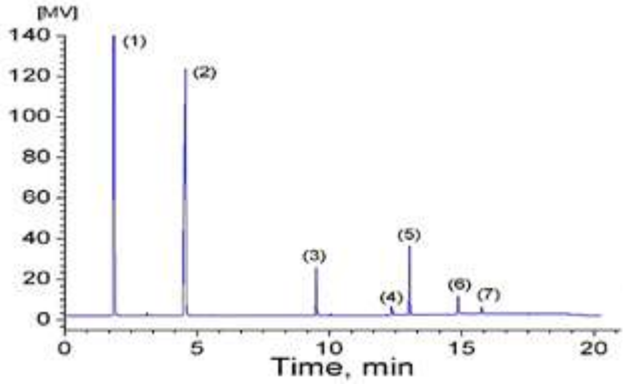


Figure 2: The gas chromatogram of the reaction mixture ((1) methanol, (2) DMF, (3) 2-pyridincarbonitrate, (4) GL, (5) 2-picolinamide, (6) tetra ethylene glycol, (7) GC

3.1. Effect of type of nanoparticles metal oxide catalyst

Two types of metal oxide nanoparticle catalysts(CuO-QPT-400) and (NiO-QPT-400) were used incarbonylation of GLwithCO_2 to produce GC andtheir catalytic performancesand presented in Table1.Among two catalysts, the (CuO-QPT-400) nanoparticle has the highest catalytic performance; in contrast, NiO-QPT-400 shows the lowest activity for the reaction of GL with CO_2. Over (CuO-QPT-400) catalyst, the GL conversion (X_{GL}), GD yield (Y_{GC}), and GD selectivity (S_{GC}) and the Turnover frequency (TOF) were determined by equations (1, 2, 3, 4) and we could reach 48.64%, 38.88%, and 79.94%, respectively, while the TOF value reach 0.2061 h^{-1} as shown in table1.The results mean (CuO-QPT-400) nanoparticle is a good catalyst for carbonylation of GLwithCO_2.

Table 1: The catalytic performances of the metal oxide nanoparticle catalysts inthe carbonylation of GLwithCO_2 to produce GC[a]

Cat.	X_{GL}/%	Y_{GC}/%	S_{GC}/%	TOF/h^{-1} [b]
CuO-QPT-400	48.64	38.88	79.94	0.2061
NiO-QPT-400	34.01	6.21	18.26	0.0263

[a] Reaction condition: 40 mmol GL, 37.7mmol % Cat./GL, 5 g of 2-pyridinecarbonitrate,15g DMF, 150°C, 4 MPa CO_2 and 5h.

[b] TOF:Turnover frequency (h^{-1}).

The catalyticperformances were presented in Table1. Show high conversion of GL., optimal yield of GC, optimal selectivity of GC. And optimal TOF with (CuO-QPT-400) Nano catalyst when compared with (NiO-QPT-400) and ranked as:

(CuO-QPT-400)>(NiO-QPT-400)

And the (CuO-QPT-400) was more activity than (NiO-QPT-400) catalysts because it has more TOF.

3.2 Catalyst characterization

3.2.1 XRD

Fig.3 shows the XRD patterns of (CuO and NiO) nanoparticles catalysts calcined at temperature (400 °C) for 4h. The samples present a typical band of CuO phase with monoclinic crystal system Ref. Code(00-048-1548) (at 2θ = 32.5°, 35.5°, 38.8°, 46.2°, 48.8°, 51.4°, 53.5°, 58.3°, 61.5°, 66.3°, 68.13°, 72.5°, 75.1°, 80.1°, 82.5°, 83.1°, 83.6° and see PDF-2….e2004-163835) also a typical band of NiO phase with monoclinic crystal system Ref. Code(00-044-1159) (at 2θ = 19.181°, 33.01°, 38.484°, 51.891°, 59.015°, 62.655°, 70.249° and see PDF-2….e2004-163835) In Fig. 3, it is also found that for CuO-QPT-400 sample, indicating the gradual bulk sintering and growth of crystallite size of CuO-QPT-400. All the catalysts show clear and sharp peaks of CuO-QPT-400 more than NiO-QPT-400 and the diffraction intensity of crystal face (111) is more than of crystal face (110), in contrast, for NiO-QPT-400, the diffraction intensity of crystal face (2 0 0, 2 2 0, 2 2 0, 3 1 1 and 2 2 2) is more than of crystal face (111). The width of the diffraction lines is produced using the smaller grains. The diffraction peaks of nanoparticlesNiO-QPT-400 were broader, which indicates the presence of small particles in the former catalysts and show the particle size is fineandall the Ni-based metaloxides samples obtained by calcination at 400◦C exhibitthe diffraction peaks of NiO crystals located at (2θ) around 38.484°, 51.891°, 59.015°, 62.655°and 70.249°, which are attributed to the (1 1 1),(2 0 0), (2 2 0), (3 1 1) and (2 2 2) reflections, respectively. It means that the effectiveness of the NiO-QPT-400 was a little and less than CuO-QPT-400, which is accordant with the order of the catalytic activity for these catalysts (Table 1, except with CuO-QPT-400), meaning that the crystal face (111) for CuO-QPT-400 nanoparticles catalyst may be have more active site for the carbonylation of GL with CO_2.

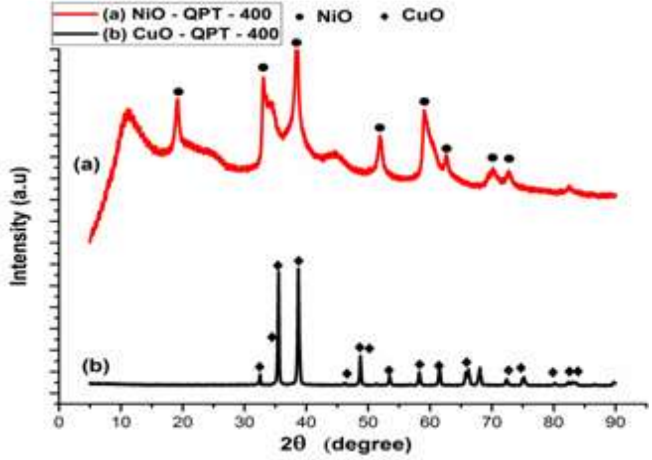


Figure 3: XRD patterns of the nanoparticle catalysts: (a)NiO-QPT-400, (b) CuO-QPT-400.

3.2.2 FT-IR

The FT-IR analysis results are depicted in Fig. 4 for CuO-QPT-400 nanoparticles catalyst with different calcination temperature. For all samples the peak positions are approximately similar indicatingthey have the same surface functional groups. The peaks appearing at 517 and 598 cm^{-1} are attributed to (Cu-O) stretching modes.

The FT-IR analysis results are depicted in Fig.4 for CuO-QPT-400 nanoparticles with (400 °C)calcination temperature. For all samples the peak positions are approximately similar indicating they have the same surface functional groups. The peaks at 1384 cm^{-1} may be assigned to (O-H) bending vibrations combined with copper atoms. Furthermore, peaks at around 3460 cm^{-1} show the existence of the hydroxide group.A FT-IR transmission spectrum of the suggested nanoparticles catalystNiO-QPT-400 is shown.Generally speaking, owing to their inter-atomic vibrations, metaloxides (e.g., nickel oxide) have absorption bands lower than800 cm^{-1}. Ni-O stretching vibration mode has a spectral peakat around 465.09 cm^{-1}, and thus the calcined nickel oxides at400 ^{o}C are of pure inorganic type. However, during the preparationof nickel oxide nanoparticles catalyst, no organic species were introduced. Theadsorbed water on the nickel oxide nanoparticles catalyst is associated with threepeaks at 3640.28, 1608.89 and 1383.09 cm^{-1}. The peak at 1630 cm^{-1} is theO-H bending band, whereas the wide band at 3640.28 cm^{-1} is mostlythe O-H stretching vibration mode. Therefore, a FT-IR spectrum is inagreement with XRD pattern. The FT-IR result suggests the formation of CuO compound and is consistent with the XRD.

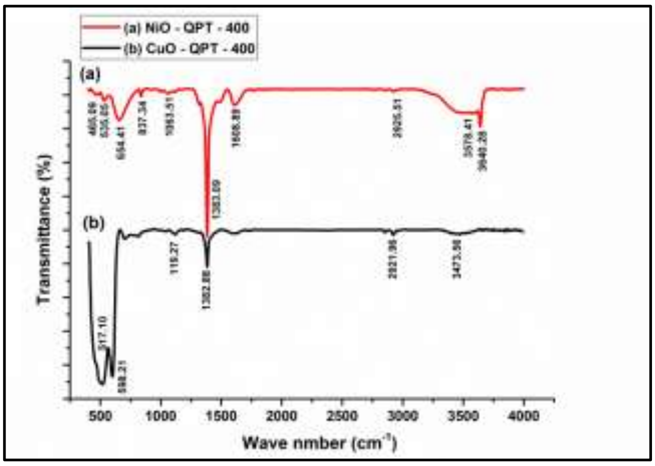


Figure 4: FT-IR spectra of nanoparticles catalysts: (a)NiO-QPT-400, (b) CuO-QPT-400

3.2.3 SEM

The Morphology of (NiO-QPT-400) and (CuO-QPT-400) nanoparticles catalyst prepared with quick precipitation method (QPT) was examined by scanning electron microscope (SEM).

The SEM images of the catalysts are shown in Fig.5 (a, b). It can be seen that all samples present aggregates of variable morphology and size. The nanoparticles for (CuO-QPT-400) catalyst Fig.5(a) was a best one because of particles size distribution was homogenous (160nm – 320nm) and high surface area and good dispersion and It shows that higher tendency of agglomerations but the nanoparticles for (NiO-QPT-400) catalyst Fig.5(b) are obviously the particles size distribution of (1.163µm – 921.5nm) that means this particles size distribution not homogenous and a little surface area and the (NiO-QPT-400) is formed through the accumulation of small particles, it was consisted of loose and tiny floc and tightly gathered with a large lump and a little stripe structure.Fig.3.5 (b) illustrates the scanning electron microscopic (SEM) imagesof nanostructure nickel oxide calcined at 400 °C for 4 h. Themicroscopic study indicated that all the particles were sphericalin shape with low agglomeration.It means, among these samples, CuO-PT-400 has the optimal particles with the smallest size and the most uniform shape, resulting in the best catalytic activity.The SEM result suggests the formation of (CuO-PT-400)nanoparticles catalyst and is consistent with the XRD, which is accordant with the order of the catalytic activity for these catalysts (Table 1, except with CuO-QPT-400).

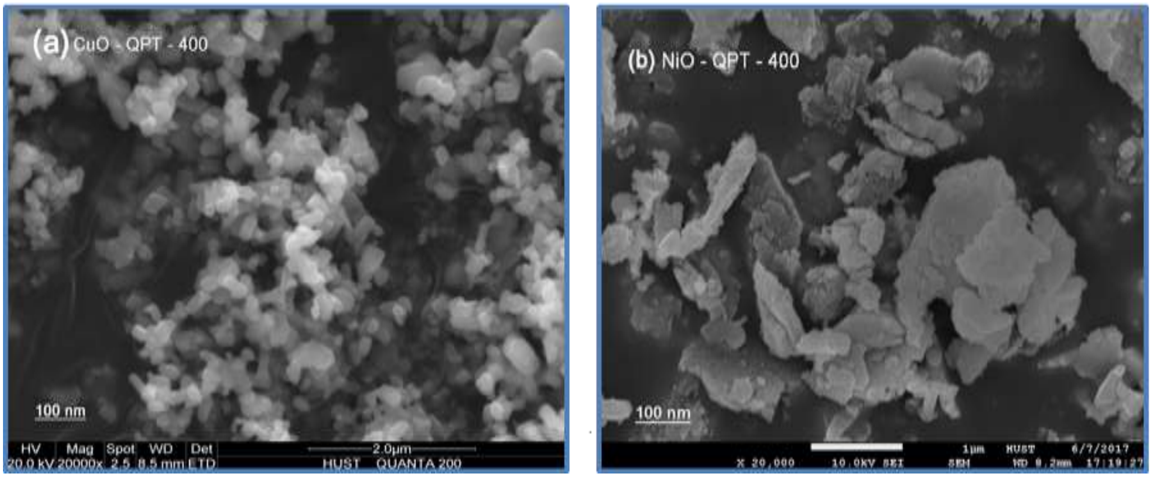


Figure 5: SEM a scanning electron microscope images of the fresh nanoparticles catalysts (a) CuO-QPT-400 and (b) NiO-QPT-400

3.3 Stability of the CuO-QPT-400 nanoparticle catalyst.

When choose the best one which is CuO-QPT-400nanoparticles catalyst is very important to complete all the functions of using the catalyst and one of these functions is recyclability of catalyst several times at least five times, the used catalysts were recovered. The stability of CuO-QPT-400 was also researched and the result is shown in Fig. 6.It is found that at the fourth recycling, the activity of CuO-QPT-400 hardly decreases and the GL conversion and GC yield can also reach 46.09% and 37.71%, respectively. At the fifth recycling, the GL conversion and GC yield reach 46.10% and 35.86%, respectively, indicating that the activity of CuO-QPT-400 slightly decreases.In order to ascertain the reason of the decrease of the catalytic activity for the CuO-QPT-400 catalyst, the recovered CuO-QPT-400 in the fifth recycling was also characterized by XRD and FT-IR.Fig.7.(a) shows that the crystalline structure of recovered CuO-QPT-400 is changed, and it has a strong cubic Cu phase (2θ= 43.5^{o}, 50.65^{o}, see PDF 00-001-1242).Fig.8.(a) shows that in the FT-IR spectra of recovered CuO-QPT-400, the characteristic peaks attributed to Cu-O stretching mode (at 517 and 598 cm^{-1}) are vanished. These results imply that generation of Cu phase is responsible for the deactivation of the CuO-QPT-400 catalyst. Interestingly, when the recovered CuO-QPT-400 is calcined at 400 °C, its main phase can be converted back into the monoclinic CuO again (Fig. 7 (b), Fig. 8 (b)).

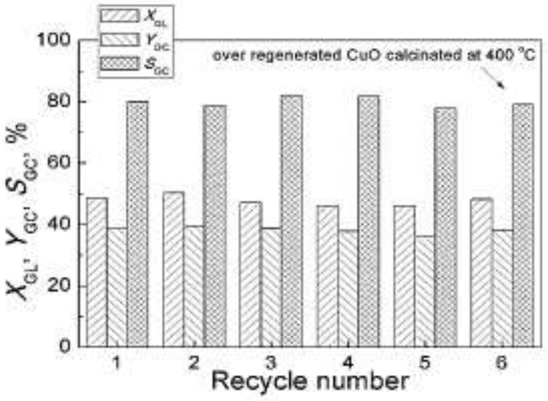


Figure 6: The stability of CuO-QPT-400 nanoparticle catalyst on the reaction of GL with CO_2(Reaction condition: 40 mmol GL, 37.7mmol % Cat./GL, 5 g of 2-pyridinecarbonitrate,15g DMF, 150°C, 4 MPa CO_2, 5 h).

Meanwhile, the regenerated catalyst CuO-QPT-400 was used to the reaction of GL and CO_2 and also can produce GL conversion of 48.25% and GC yield of 38.10% (Fig. 6). It indicates that the recovered catalyst CuO-QPT-400 can be easily regenerated by calcining at 400 °C after washing in methanol three times. Furthermore, the Cu concentration in the reaction mixture in the first run was also measured by inductively coupled plasma-mass spectrometry (ICP-MS) and the result only was 45.12 μg/L, indicating that the leaching of CuO almost can be neglected.

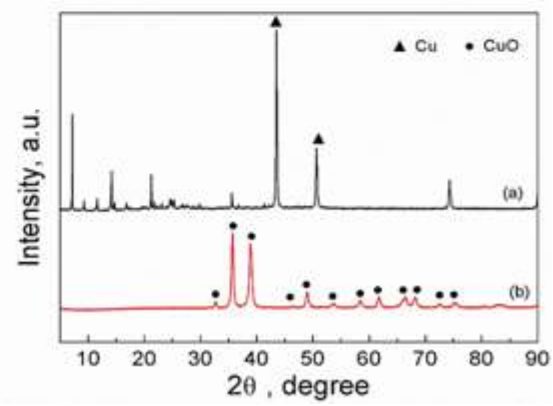


Figure 7: XRD patterns of the CuO nanoparticle catalysts: (a) the recovered CuO-QPT-400 catalyst after the fifth recycling; (b) the recovered CuO-QPT-400 catalyst regeneration by again calcination at 400 °C.

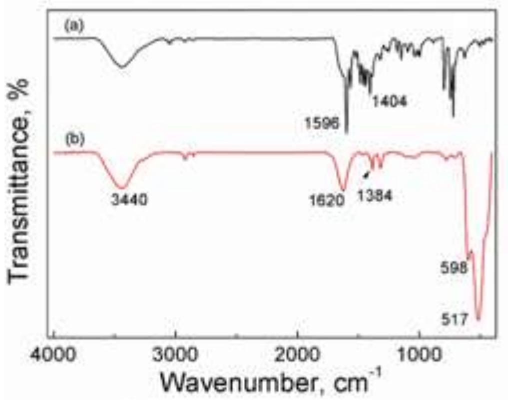
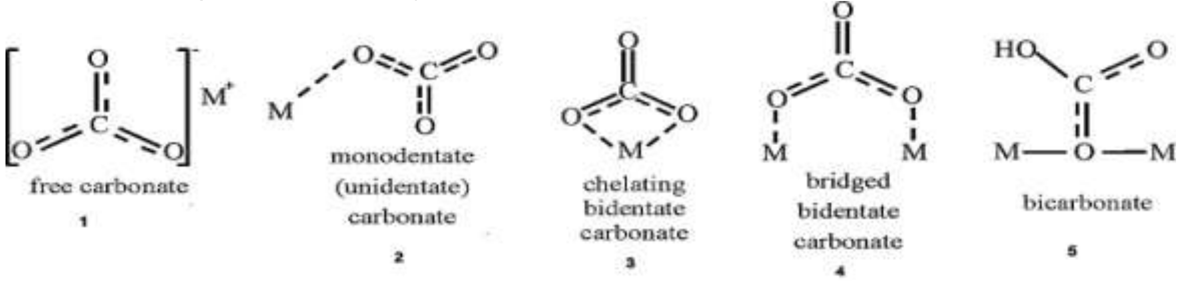


Figure 8: FT-IR spectra of CuO nanoparticles catalysts: (a) the recovered CuO-QPT-400 catalyst after the fifth recycling; (b) the recovered CuO-QPT-400 catalyst regeneration by again calcination at 400 °C.

4. The possible mechanisms of glycerol carbonate synthesis at carboxylation reaction over (CuO-QPT-400) nanoparticles catalyst

In order to understand the reaction mechanism, in chemical engineering processes this reaction was heterogeneous reaction because the reactants at difference phase, glycerol (GL) is liquid, CO_2 is gas and (CuO – QPT – 400) nanoparticles catalyst was solid. Poor conversion and mass-balance of glycerol were gained when no solvent was applied. To improving the reaction rates should be dissolve CO2 in middle of the reaction until it reaches the surface of the catalyst. Supercritical carbon dioxide ($ScCO_2$) at (7.5 MPa, 150 °C) is considered to be a highly attractive modern solvent compared to traditional organic solvents, the solvent employed in this study, DMF gave the maximum yield of glycerol carbonate, indicating that the solvent effect in our CuO/2-cyanopyridine system was one of the important factors responsible for the much better catalytic performance. Solvents usually show some effects on reaction rates, chemical equilibrium as well as reaction mechanisms in organic reactions. It had been proposed that for GL reacting with CO_2 to form GC over CuO surface in the presence of 2-pyridinecarbonitrate and DMF, nucleophile attack of the other OH group to the carbonyl carbon in carbonate species, which led to the production of cyclic carbonate and water, was one of the important steps in the proposed reaction mechanism. Since the nucleophilicity of the reactants was affected in dipolar aprotic solvent [36], the step mentioned above could be enhanced in DMF. On the other hand, the solubility of CO_2 in the solvents might also be an important factor besides the polarity and aprotic properties of the solvents. The basic nature of DMF may favor the dissolving and adsorption of CO_2. In fact, the solubility of CO_2 in DMF is 31.1 mol% at 40◦C and 4.5 MPa(45bar) [37]. Therefore, high solubility of CO_2in DMF might be favorable to increase the concentration of CO_2on the surface of the catalysts, consequently benefiting to the reaction. The CO_2 adsorption modes identified in previous work are shown in **Scheme3** [38-40]. The formation of different species might stem from different basic sites: e.g. (1). Free carbonate (FC) (2). Monodentate (unidentate) carbonate (MC), adsorbed on oxygen ions with the lowest coordination number, can be attributed to strongly basic sites, (3).Chelating bidentate carbonate (CBC) and (4).Bridged bidentate carbonate (BBC) adsorbed on (**M^+ – O_2^-**) pairs can be assigned to moderately basic sites Moreover, the weakly basic sites may be associated with the surface hydroxyl groups (OH^-) over which the CO_2 adsorption species is present in the form of (5). Bicarbonate [39].



Scheme 3: Types of species of CO2 adsorption

The cyclic carbonate was formed through the insertion of activated CO_2 to metal alkoxides followed by intermolecular nucleophile attack of alkoxy groups to carbonyl carbon atoms. In our experiment, the bridged bidentate carbonate was the main adsorption mode at 150 °C (reaction temperature) on the catalysts. Therefore, the activated CO_2 may be in the form of a bridged bidentate carbonate that inserts into the copper glycerolate to form a cyclic metal carbonate (as in **Scheme 4**) followed by intermolecular rearrangement to produce glycerol carbonate. The copper glycerolate reaction with CO_2 and theoretical calculations indicate that the proposed reaction mechanism is reasonable, that the A species produced by the insertion of activated CO_2 to copper glycerolate is stable and that the process happens spontaneously. The process of glycerol carbonate formation by the intermolecular rearrangement of the A species is the rate-determining step. Glycerol carbonate was obtained from the carbonylation of glycerol and CO_2 over CuO Nano catalysts with the hydrolysis of 2-pyridinecarbonitrate as the coupling reaction. As shown in Scheme 4, in the CuO/2-pyridinecarbonitrate system, glycerol reacts with CO_2 over CuO catalyst surface to produced glycerol carbonate and H_2O, while the formed H_2O reacts with 2-pyridinecarbonitrate (2-cyanopyridine) to produced (2 – picolinamide) and removed H_2O from the reaction system to pull water from the middle of the chemical reaction as side product and shift the chemical equilibrium to the GC production side and the chemical reaction bath doesn't return back to reverse direction to produce GL [7, 41, and 42].

Scheme 4: The reaction roadmap and the mechanism of insertion of activated CO_2 to copper glycerolate to form glycerol carbonate(Reaction condition: 40mmol glycerol, 37.7 mmol % Cat./GL, 5 g of 2-pyridinecarbonitrate, 15 g of DMF, 150 ^oC and 4 MPa CO_2 for 5h)

5. Conclusion

CuO nanoparticle was synthesized by new method it is quick precipitation (QPT). It showed the best one and excellent catalytic optimal performance among two type of nanoparticles metal oxide catalyst (NiO-QPT-400 and CuO-QPT-400) in the carbonylation of glycerol and CO_2 with 2-cyanopyridine as a dehydrating agent. The active site of CuO-QPT-400 catalyst may be crystal face (111). The incredibly yield of glycerol carbonate GC (can reach about 40%) had strong relevance with the efficient hydration of 2-pyridinecarbonitrate (2-cyanopyridine) and solvent effect of DMF and (400) ^oC was a good calcination temperature. The proper reaction conditions were (5.0- 7.0) g2-pyridinecarbonitrate (3 times of stoichiometric value), 150 ◦C, 4 MPa and 5 h. The active site of the CuO catalyst is all CuO surface. The catalyst not only has higher surface area, but also higher mechanical strength, and is suitable for the industrial reactor. The stability research for CuO nanoparticle shows that the catalyst can be reused five times with little loss of activity and can be easily regenerated by calcination at 400 ^oC after washing in methanol three times. In our future work, the suitable support for this catalyst and mixed this catalyst with another suitable nanoparticles metal oxide catalyst will be investigated and reported in due course.

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