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# Catalytic hydrocarboxylation of acetylene to acrylic acid using $Ni_2O_3$ and cupric bromide as combined catalysts

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ABSTRACT

A non-petroleum route to produce acrylic acid was investigated through hydrocarboxylation of acetylene with CO and water in the presence of $Ni_2O_3$ and cupric bromide as combined catalysts. The activity of $Ni_2O_3$ was compared with various homogeneous catalysts; the effect of initial total pressure, reaction temperature, molar ratio of $CO/C_2H_2$, the volume ratio of solvent/water, the catalyst amount and the role of promoters have been studied in detail. It was found that the acrylic acid space-time-yield as high as 764.6 mol AA/(mol Ni h) was obtained under the optimal experimental conditions. The $Ni_2O_3$ catalyst could be reused at least five times without obvious loss of activity. The characterization of recovered catalysts by XRD, XPS, SEM and TG–DTG revealed that the state of nickel remains unchanged during the reaction, and there are three types of soft coke deposited on the surface of the catalyst. The catalysts can be regenerated through calcination within 400 °C according to TG curve.

## 1. Introduction

Acetylene, known as "the mother of Organic Synthesis", is one of the most important raw materials for production of chemical products and carbon materials [1–3]. Due to its thermodynamic active state, it is easy to undergo different kinds of reaction, such as dimerization, vinylation, ethynylation, oligomerization and carbonylation. In the last century, acetylene-based routes for the commodity chemicals had been operated on an industrial scale [4], but the global availability of cheaper petroleum made the move of organic chemical industry from coal chemistry to petrochemical process, and thus both industry and academic lost their interest in the studies on the reaction of acetylene [1,5,6].

Recently, the increase in the oil price and the desire for feedstock diversification pushes the development of "non-petroleum route" for the production of bulk chemicals. The acetylene, derived from coal, natural gas or shale gas, has been again reconsidered as a potential feedstock for the chemical industry [7,8]. Note that large quantities of CO were produced during the generation of acetylene by calcium carbide process or cracking processes. It is significant and valuable to study the reaction of CO with acetylene and water to synthesize the acrylic acid (Scheme 1) – a high value-added bulk commodity that has wide application in the manufacture of acrylate, polymers, plastics and numerous other industrial and consumer products [9]. Such an acetylene-based process, independent of oil derived feedstocks, has received more and more attention [2,3].

The traditional homogeneous catalyst systems were previously studied and reviewed briefly [10–13], and it is sure that many of the recent studies would still focus on the design and application of a highly effective nickel-based heterogeneous catalyst for this Reppe carbonylation process [3]. It is previously reported that nickel-exchanged zeolites were able to efficiently catalyze the hydrocarboxylation of acetylene, and besides them we find that nickel oxides used as primary catalyst also show amazing reactivity.

Herein we first employed the $Ni_2O_3$ and cupric bromide as catalyst systems for the acetylene hydrocarboxylation. The catalytic performance of $Ni_2O_3$ was compared with all kinds of homogenous catalysts. The influence of reaction conditions and the recyclability of catalyst were studied in detail. Lastly, the fresh and recovered catalysts were characterized by XRD, XPS, SEM and TG technologies.

## 2. Experiment

### 2.1. Materials

Carbon monoxide of 99.95% purity was purchased from Nanjing Sutan Gases Co., Ltd. Acetylene was supplied by Shanghai Sunqiao-Longsheng Gases Co., Ltd. Distilled water was used as the liquid reactant.

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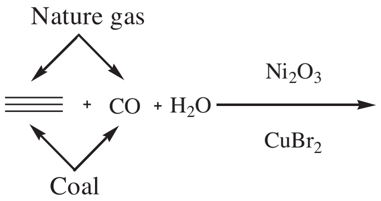

**Scheme 1.** Hydrocarboxylation of acetylene with CO and water to acrylic acid.

$Ni_2O_3$, $NiCl_2$, $Ni(NO_3)_2$, $Ni(OAc)_2$, $CuBr_2$, $CuCl_2$, CuI, CuCl, CuBr, and CuO were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China); the $NiBr_2$, triphenylphosphine ($PPh_3$) and methanesulfonic acid (MSA) were purchased from Aladdin Chemical Reagent Co. Ltd. All of the reagents were analytical grade and were used without further purification.

### 2.2. Characterization

The crystal structures of catalyst were characterized by X-ray diffractometer (XRD, Bruker D8, Germany) equipped with an atmosphere and temperature control stage and using Cu Kα radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 100 mA. The scanning ranged from 10° to 80° ($2\theta$), 0.02 step, and 1 s/step.

The morphology of fresh and reacted catalysts was obtained using a Nova Nano SEM450. The thermo-gravimetric analysis (TGA) was used to evaluate the coke amount and coke species. The samples were loaded on a platinum microcrucible and heated up to 800 °C at 10 °C/min with flowing air at 100 ml/min, recording continuously the weight of each sample.

To identify the chemical state of nickel, XPS spectra of the reacted catalysts were obtained by using a Perkin–Elmer PHI 5000C ESCA system equipped with Al Kα radiation (1486.6 eV). All binding energies were corrected by the C 1s line at 284.6 eV.

### 2.3. Hydrocarboxylation procedure and product analysis

The catalytic hydrocarboxylation of acetylene was performed in a 0.5 L Parr autoclave made of stainless steel-316 having facilities for gas inlet and outlet, a rupture disk as a safety measure in case of excessive pressure build-up, intermediate sampling, temperature-controlled heating, and variable agitation speed.

In a typical experiment, 0.1 g of $Ni_2O_3$, 0.03 g of promoters, $H_2O$ (15 ml), and acetone (150 ml) were successively added into the reactor, after which the reactor was purged with $N_2$ for several times and subsequently pressurized with acetylene to 0.4 MPa and then to 4 MPa of initial total pressure with CO (both controlled by mass flow meter, and the molar ratio of $CO/C_2H_2 = 1.5$) at room temperature. The reaction mixture was then heated to 235 °C unless otherwise stated and the reaction proceeded for 15 min with stirring at 800 rpm. After the reaction, the autoclave was quickly cooled to room temperature and the tail gas was collected with wet gas flow meter. The residue gas and liquid were analyzed with gas chromatography. For recycling experiments, the catalyst used in the previous run was separated by filtration and washed with acetone for several times and reused after drying under vacuum. The detailed schematic drawing of the reactor can be found elsewhere [13].

The conversion of acetylene, the selectivity and yield to acrylic acid, and the space-time-yield (STY: moles of acrylic acid (AA) produced per moles of Ni and hour) are defined as follows:

$$\text{Conversion} = \frac{n_0 - n_1}{n_0} \times 100\%, \qquad \text{Selectivity} = \frac{n_p}{n_0 - n_1} \times 100\%,$$

$$\text{Yield} = \frac{n_p}{n_0} \times 100\%, \qquad \text{STY} = \frac{\text{mol AA}}{\text{mol Ni} \cdot \text{h}} \times 100\%$$

where, $n_0$, amount of acetylene for feedstock before reaction; $n_1$, amount of acetylene for residue after reaction; $n_\text{p}$, amount of acetylene for forming acrylic acid; mol AA, the molar content of acrylic acid produced during reaction; mol Ni, the molar content of nickel contained in the catalysts for input before reaction; h, the reaction time (hour).

## 3. Results and discussion

### 3.1. Comparison of catalytic performance of various nickel catalysts

The nickel complexes or bivalent nickel salts have been proved to be an effective catalyst in the reaction of acetylene with carbon monoxide and a reactive hydrogen compound to yield acrylic acid derivatives [5,14–18]. Many patents disclosed these homogeneous catalysts but lacked detailed studies. It is firstly found that the $Ni_2O_3$ shows unique catalytic activity as a heterogeneous catalyst in the presence of copper salts for the hydrocarboxylation of acetylene.

The catalytic performance of $Ni_2O_3$ was compared with NiO and other common homogeneous catalysts, including $NiBr_2$, $NiCl_2$, $Ni(NO_3)_2$, and $Ni(OAc)_2$; the results are shown in Table 1. At the identical reaction conditions (4 MPa of intimal total pressure, 235 °C of reaction temperature, $CuBr_2$ as promoter), the $Ni_2O_3$ (entry 1) gave the best average activity with 764.6 mol AA/(mol Ni h). The order of reactivity of other catalysts was found to be $Ni(OAc)_2$ (entry 13) > $NiCl_2$ (entry 10) ≈ $NiBr_2$ (entry 8) > NiO (entries 6 and 7) > $Ni(NO_3)_2$ (entry 12) > $Ni(OAc)_2/PPh_3$/MSA (entry 15). It should be noted that the $Ni(OAc)_2$ is very unstable and it is easy to decompose to NiO or nickel metal during the reaction at the elevated temperatures and pressure. If $PPh_3$ and MSA were added as ligand, the $Ni(OAc)_2$ would become stable due to the coordination effect [10], but this catalyst system produced relatively lower yield under the present conditions. As is pointed in the previous study [13], a complex catalyst system tends to result in the coke deposition. In the industrial process for the hydrocarboxylation of acetylene to acrylic acid (BASF process), the nickel halide, especially for nickel bromide, had been chosen as primary homogeneous catalyst with a satisfactory result including a higher yield and less amount of coke [12]. In this study, the $NiCl_2$ gave an 707.3 mol AA/(mol Ni h) of STY, which is similar to that obtained when $NiBr_2$ was used as catalyst, but it produced more coke than $NiBr_2$. Interestingly, two repeated experimental runs demonstrated that the $Ni(NO_3)_2$ is not a suitable catalyst, which shows a very low catalytic activity with 286.6 mol AA/(mol Ni h). The NiO species would form during the regeneration process of $Ni_2O_3$ by calcination, so it is necessary to investigate the activity of NiO. Entries 4 and 5 compare the catalytic performance of two NiO catalysts, which is obtained by calcination of $Ni_2O_3$ and $Ni(OAc)_2$, respectively, at 550 °C for 240 min. The similar average activity (677.1 and 688.9 mol AA/(mol Ni h)) was found, but lower than that obtained by $Ni_2O_3$, suggesting the higher reactivity of $Ni^{3+}$.

Moreover, Table 1 also indicates that the initial total pressure and reaction temperature have a great influence on the catalytic activity. For both of $Ni_2O_3$ and other homogeneous catalysts, the average activity increased with the increase in the pressure; the similar trends were observed in our previous study. For the sake of reducing the decomposition of acetylene and the operational risk and cost, the initial total pressure was controlled within 4 MPa for the further experiments. As for the reaction temperature, the maximum activity was obtained at about 235 °C, and when reaction was performed at 200 °C, only a very small amount of acrylic acid was detected. If the temperature was selected at 220 °C, the total yield of acrylic acid is analogous to that obtained at 235 °C, but the reaction rate is relative lower due to the less amount of

**Table 1**
Comparison of catalytic activity of homogeneous and heterogeneous nickel catalysts.

| Entry | Catalyst | Reaction time (min) | Initial total pressure (MPa) | Reaction temperature (°C) | Average activity (mol AA/(mol Ni h)) |
|---|---|---|---|---|---|
| 1 | $Ni_2O_3$ | 15 | 4 | 235 | 764.6 |
| 2 | $Ni_2O_3$ | 15 | 3.5 | 235 | 556.9 |
| 3 | $Ni_2O_3$ | 15 | 4 | 250 | 760.7 |
| 4 | $Ni_2O_3$ | 20 | 4 | 220 | 558.8 |
| 5 | $Ni_2O_3$ | 30 | 4 | 200 | 69 |
| 6 | NiO(1)[a] | 15 | 4 | 235 | 677.1 |
| 7 | NiO(2)[b] | 15 | 4 | 235 | 687.9 |
| 8 | $NiBr_2$ | 15 | 4 | 235 | 699.6 |
| 9 | $NiBr_2$ | 15 | 3.5 | 235 | 545 |
| 10 | $NiCl_2$ | 15 | 4 | 235 | 707.3 |
| 11 | $NiCl_2$ | 15 | 3.5 | 235 | 545.6 |
| 12 | $Ni(NO_3)_2$ | 40 | 4 | 235 | 286.6 |
| 13 | $Ni(OAc)_2$ | 15 | 4 | 235 | 752.3 |
| 14 | $Ni(OAc)_2$ | 15 | 3.5 | 235 | 549.5 |
| 15 | $Ni(OAc)_2/PPh_3$/MSA[c] | 20 | 4 | 235 | 576.7 |

[a] The NiO(1) catalyst was prepared by calcination of $Ni_2O_3$ at 550 °C for 240 min.

[b] The NiO(2) catalyst was prepared by calcination of $Ni(OAc)_2$ at 550 °C for 240 min.

[c] The catalyst system was obtained according to literature [10]: 1.3 mmol $Ni(OAc)_2 \cdot 4H_2O$, 2.6 mmol $PPh_3$, 0.585 mmol $CuBr_2$, 1.3 mmol $CH_3SO_3H$(MSA).

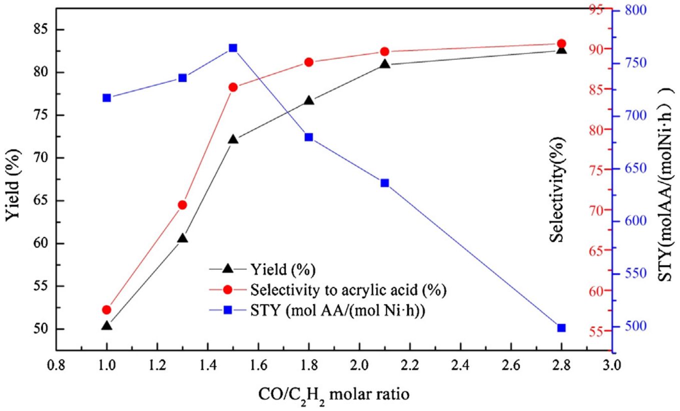

**Fig. 1.** Effect of $CO/C_2H_2$ molar ratio on the hydrocarboxylation of acetylene.

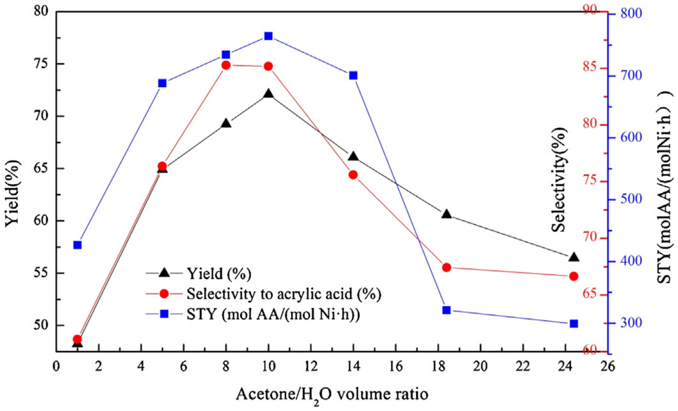

**Fig. 2.** Effect of volume ratio of acetone/$H_2O$ on the hydrocarboxylation of acetylene.

activated molecules. As the reaction proceeded, the rise in the reaction temperature would therefore enhance the reaction rate. However, when the reaction temperature is above 250 °C, the formation rate of acrylic acid also becomes lower, caused by the occurrence of side reaction such as decomposition of acetylene and polymerization of acrylic acid, etc. Hence, the optimal reaction temperature should be selected at about 230–235 °C.

### 3.2. *Effect of $CO/C_2H_2$ molar ratio*

The effect of molar ratio of CO to $C_2H_2$ on the hydrocarboxylation of acetylene is presented in Fig. 1. The reaction was performed at 4 MPa of initial total pressure and 235 °C of reaction temperature. It is clear that the yield and selectivity to acrylic acid were greatly affected by the molar ratio of $CO/C_2H_2$. As a $CO/C_2H_2$ molar ratio of 1, the yield of acrylic acid is just 50.3% and the selectivity to acrylic acid is also only 57.6%. On increasing the molar ratio of $CO/C_2H_2$ from 1 to 1.5, the yield and selectivity increase drastically and the STY goes through the maximum at molar ratio of 1.5. With further increase in the molar ratio, the yield and selectivity are still going up slightly and nearly stay at this level when the ratio exceeds 2.2, while the changes trend of STY is on the contrary. Theoretically, equal mole of CO and $C_2H_2$ in the feedstock would favor the reaction, but the acetylene reaction, in fact, takes place in the liquid phase and it is no doubt that the solubility of $C_2H_2$ is far higher than that of CO, thus the increase of partial pressure of CO would increase its solubility in the liquid and further increase the coordination effect of CO toward nickel center, causing increase in the activity. In the acetylene hydrocarboxylation process, acetone is used as the solvent, and the reaction rate is controlled primarily by the interfacial mass transfer of CO from gas to liquid. Moreover, for any acetylene process under high pressure there exists the possibility of an explosion or decomposition; it is a usual practice for safety by reducing the partial pressure of $C_2H_2$ [1,6,19]. Note that the amount of coke deposition of the reaction carried out under the equal mole of CO and $C_2H_2$ is larger than that of reaction performed at the lower partial pressure of $C_2H_2$, which is proved by the TG-DTG characterization shown in the next section. To obtain the higher STY, the moral ratio of CO to $C_2H_2$ is selected at 1.5 for this study.

### 3.3. *Effect of volume ratio of acetone/$H_2O$*

Nearly all of the acetylene reactions under pressure are performed in the liquid [20]. In this reaction, acetone is used as solvent and $H_2O$ is one of the reactants. The effect of volume ratio of acetone to $H_2O$ on the hydrocarboxylation of acetylene to acrylic acid is shown in Fig. 2. The yield, selectivity and STY enhanced drastically with increase in the acetone/$H_2O$ volume ratio. The highest yield of 72.1% and STY of 764.6 mol AA/(mol Ni h) were obtained at an acetone/$H_2O$ volume ratio of 10, the corresponding selectivity to acrylic acid is 85.2%. However, the activity decreased with further increase in the acetone/$H_2O$ volume ratio. For example, when 6.5 ml of water was mixed with 158.5 ml of acetone, resulting in 24.4 of acetone/$H_2O$ volume ratio, the STY decreased to about 314.3 mol AA/(mol Ni h). Two main reasons for this phenomenon are proposed as follows. On one hand, the solubility of CO and $C_2H_2$ in the water is very low and there are not enough gas reactant molecules that can

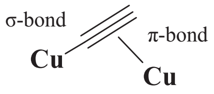

**Fig. 3.** Structure of copper–acetylene complexes.

work with catalysts if abundant water was added in the reaction system, thus causing the decrease in the reaction rate. Due to its poor solubility, the partial and total pressure of gas would increase and result in the increase of side reaction. On the other hand, water acts as a reactant, a certain amount of water can enhance the formation rate of Ni—H active species and meanwhile promote its attack to Ni-acyl complex and thus favors the formation of acrylic acid. The shortage of water is a disadvantage to the effective performance of catalytic cycle.

### *3.4. Comparison of catalytic activity with various copper salts as promoter*

It is found that nickel oxide alone does not effectively serve as a catalyst but a mixture of nickel oxide–copper salt works very well. The effect of copper salts as promoter on the hydrocarboxylation of acetylene was investigated at 235 °C, 4 MPa of initial total pressure, 1.5 of CO/$C_2H_2$ molar ratio and 10 of acetone/$H_2O$ volume ratio. As can be seen from Table 2, different copper salts showed varied catalytic activity. The catalytic activity of copper halides (entries 1–6) is significantly higher than that of the other copper salts (entries 7–9). When cupric acetate, cupric nitrate and cupric oxide were used as promoters, large quantities of resinous material were found sticking to the side of the autoclave, and almost no acrylic acid can be detected in the liquid, indicating the occurrence of polymerization of acetylene instead of its decomposition or hydrocarboxylation. It was observed that the employ of $CuCl_2$ as activator also resulted in the formation of resinous material. Among these copper halides, the cupric bromide and cuprous bromide gave the best catalytic activity. For the cuprous bromide, the biggest advantage is that it can be recovered and recycled with the nickel oxide catalyst after reaction, while the cupric bromide is difficult to be separated from the product due to its complete solubility in the liquid. An 80.1% of selectivity to acrylic acid was obtained when using CuI as promoter, but together with a lower STY due to the relative longer contact time to finish a reaction.

Cupric halide or cuprous halide has been accepted as the effective catalysts in activating acetylene to give complexes of the following composition [21]:

$$n\mathrm{CuX}_m + \mathrm{C_2H_2} \rightarrow [(\mathrm{CuX}_m)_n(\mathrm{C_2H_2})]$$

In these complexes, the copper is bonded to an acetylide as well in $\delta$-metal–carbon bonds as in $\pi$-metal–carbon bonds (Fig. 3). These copper–acetylene complexes may thermally decompose to release the acetylene or, further react with acetylene to form polymer or, insert into the Ni—H bond to form an alkyne–Ni-complex in the presence of nickel catalyst. The anion in the copper salt may play a special role in stabilizing the copper–acetylene complex and/or help to form a suitable spatial structure and finally would contribute to the insertion reaction.

### *3.5. Effect of cupric bromide*

As discussed above, the cupric salt plays an indispensable role in the hydrocarboxylation of acetylene to acrylic acid. Fig. 4 suggests that the conversion of acetylene increases drastically with the increase in cupric bromide concentration from 0 mM/l to 2.7 mM/l, and with further increase in concentration, the conversion increases slightly. The selectivity and STY are strongly affected by concentration of cupric bromide. Almost no acrylic acid was produced without adding cupric bromide, and a marked increase of selectivity and STY were found as the increase in amount of $CuBr_2$. The catalytic activity goes through a maximum when concentration of $CuBr_2$ is about 0.8 mM/l and the corresponding selectivity and STY is 85.2% and 764.6 mol AA/(mol Ni h), respectively. However, as pointed in the previous study, the cupric salt plays a double role in the carbonylation process; the relative high concentration of promoter would not increase the selectivity and STY but reversely leads to the decomposition of acetylene. Thus, the optimum concentration should be controlled at about 0.5–1.5 mM/l.

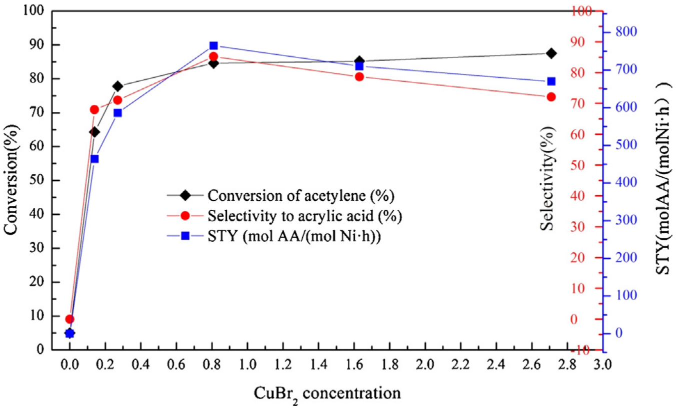

**Fig. 4.** Effect of $CuBr_2$concentration on the hydrocarboxylation of acetylene.

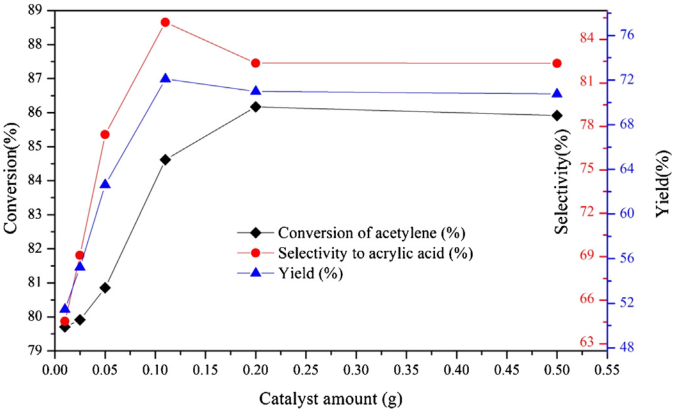

**Fig. 5.** Effect of catalyst amount on the catalytic activity.

### *3.6. Effect of catalyst amount on the hydrocarboxylation of acetylene*

The effect of the catalyst amount on the reaction is presented in Fig. 5. When the reaction was carried out in the absence of the nickel oxide, there was no acrylic acid in the liquid. After adding a small amount of catalyst, the conversion of acetylene, yield of acrylic acid and STY increased quickly. For example, in the presence of 0.01 g of the $Ni_2O_3$ catalyst, 80% of acetylene was converted. The yield of acrylic acid reached 51.4%, and the selectivity to acrylic acid increased to 64.5%. With further increase in the catalyst amount, the yield and selectivity increased first and then decreased slightly, while the conversion of acetylene increased and then changed a little. The highest acrylic acid yield of 72.1% was obtained under the conditions of 0.1 g $Ni_2O_3$, 0.03 g $CuBr_2$, 15 ml water, 150 ml acetone, 235 °C, 1.5 molar ratio of CO/$C_2H_2$, 4 MPa of initial total pressure, and 15 min of reaction time. For those reactions with a small amount of the catalyst, the initial reaction rate is low, and they produce low yields of acrylic acid due to the low concentration

**Table 2**
Comparison of catalytic performance of various copper salts as promoter.

| Entry | Promoter | Initial total pressure (MPa) | Selectivity (%) | Yield (%) | Average activity (mol AA/(mol Ni h)) |
|---|---|---|---|---|---|
| 1 | $CuBr_2$ | 4 | 85.2 | 72.1 | 764.6 |
| 2 | $CuCl_2$ | 4 | 55.9 | 48.2 | 511.6 |
| 3 | CuI | 4 | 80.1 | 65.3 | 346.3 |
| 4 | CuCl | 4 | 65.4 | 55.9 | 593.3 |
| 5 | CuBr | 4 | 82.2 | 69 | 731.4 |
| 6 | CuBr | 3.5 | 73.5 | 57.8 | 543.1 |
| 7 | $Cu(OAc)_2$ | 4 | 0 | 0 | 0 |
| 8 | $Cu(NO_3)_2$ | 4 | 0 | 0 | 0 |
| 9 | CuO | 4 | 0 | 0 | 0 |

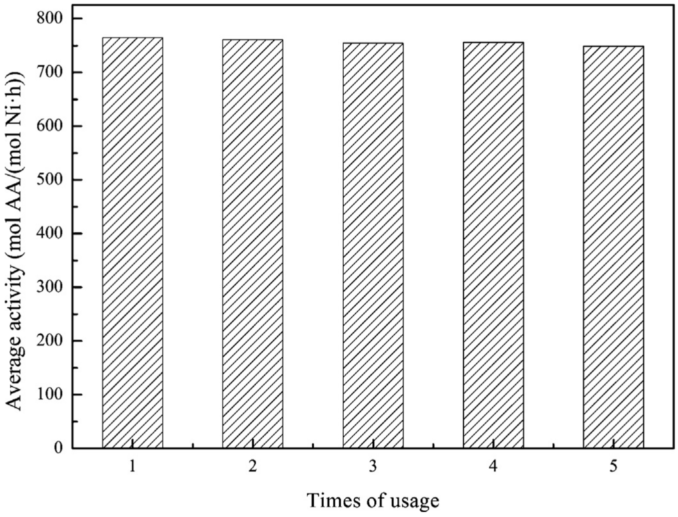

**Fig. 6.** Recycling test of $Ni_2O_3$.

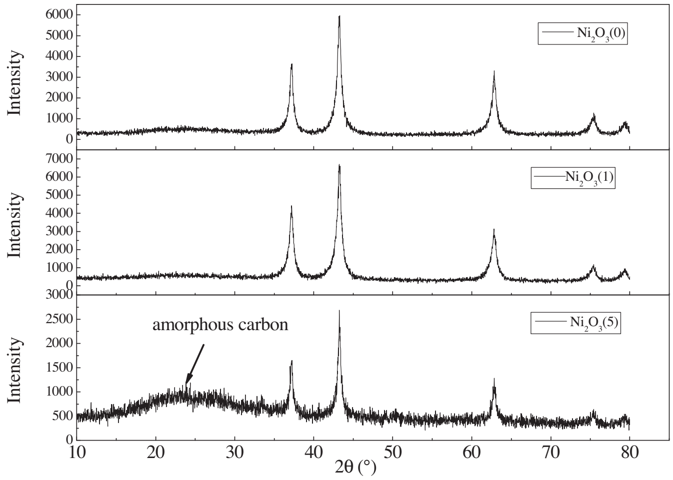

**Fig. 7.** XRD diffractograms of fresh and recovered catalyst: $Ni_2O_3(x)$, $x$ represents the times of usage for the same catalysts.

of active species available. Under the high temperature and high pressure, the long reaction time would result in side reaction of acetylene to form coke, polymer, acetaldehyde and possibly other compounds and will reduce the selectivity. At a higher catalyst concentration, the decomposition of acetylene to coke, however, would be favored under the Ni catalyst [22].

### 3.7. Recycling of the catalyst

The stability and reusability of catalysts are extremely crucial for prospective uses in a continuous tubular reactor and further applications in industrial process, since these features will reduce production costs. It is known that conventional homogeneous catalysts are difficult to isolate with the product and thus their recovery are not under consideration after the reactions.

To stand out the role of heterogeneous catalyst, the reusability of $Ni_2O_3$ catalyst in the conversion of acetylene with CO and water to acrylic acid was therefore investigated. The recycled catalyst was used for next run under identical reaction conditions; the result is shown in Fig. 6. Similar average activity was obtained during as many as five repeated reaction cycles, indicating that the $Ni_2O_3$ catalyst was not deactivated in the course of the catalytic

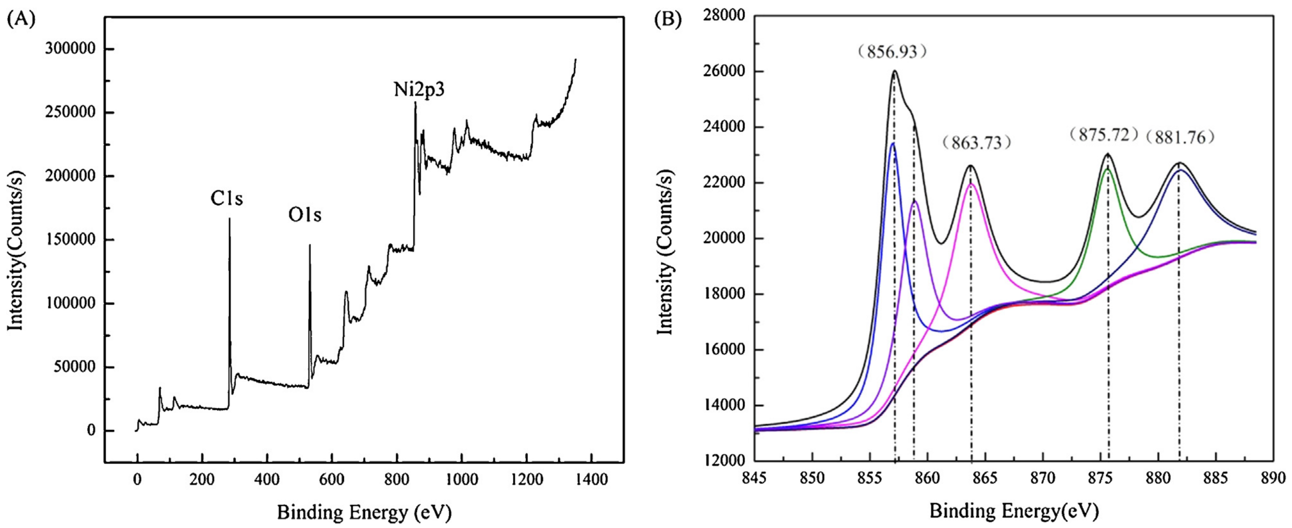

**Fig. 8.** XPS spectra resulted from wide scan of reacted catalyst (A) and high resolution of Ni 2p (B).

runs. To establish the longer-term behavior of these catalysts, the continuous reaction in a fixed bed reactor instead of autoclave will be performed in our subsequent work.

### 3.8. Characterization of catalyst

In order to study the state of catalysts after reaction, the fresh and recovered catalysts were characterized by XRD and XPS. As shown in Fig. 7, noticeable peaks of nickel oxide at $2\theta = 37.2°$, 43.24°, 62.82°, 75.46°, 79.32° were observed [23]. For the catalysts recovered from the first catalytic run, there is no obvious peaks change, indicating the state of nickel remains nearly unchanged during the reaction. While for the catalyst recovered after the fifth time of catalytic run cycle, the peak intensity clearly decreased and a new broad peak at $2\theta = 24°$ appeared, suggesting there exits amorphous carbon. That is to say, the decomposition of acetylene occurred after several times of reaction run, and it is the coke deposited on the catalyst that caused the decrease of peak intensity. Fig. 8(A) shows that the XPS spectra resulted from broad scan in the region of 0–1400 eV, while Fig. 8(B) reveals high resolution

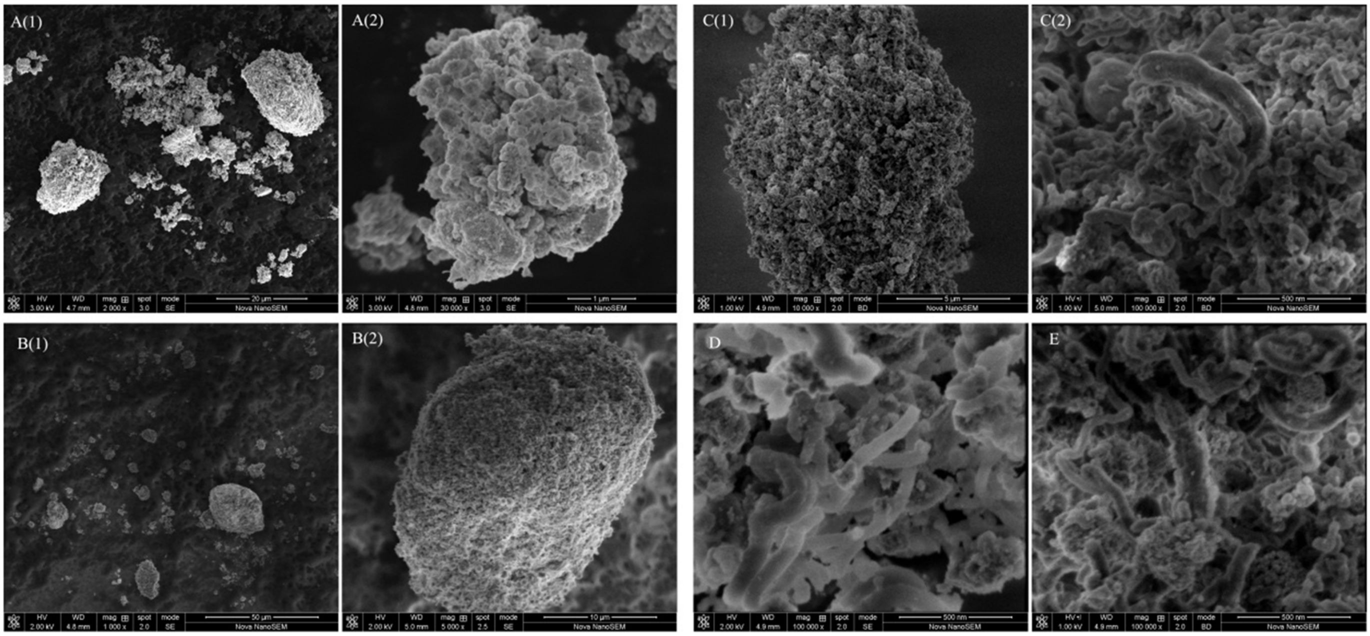

**Fig. 9.** SEM micrographs of fresh $Ni_2O_3$ catalyst (A(1), A(2)) and recovered catalyst under different reaction conditions: B(1), B(2) for the catalyst recovered after the first time of catalytic run; C(1), C(2) for the catalyst recovered after the fifth time of catalytic run; D for the catalyst recovered after reaction carried out under 0.1 g of $CuBr_2$($Ni_2O_3$/$CuBr_2$(0.1)); E for the catalyst recovered after reaction performed under equal molar ratio of $CO/C_2H_2$ ($CO/C_2H_2 = 1$).

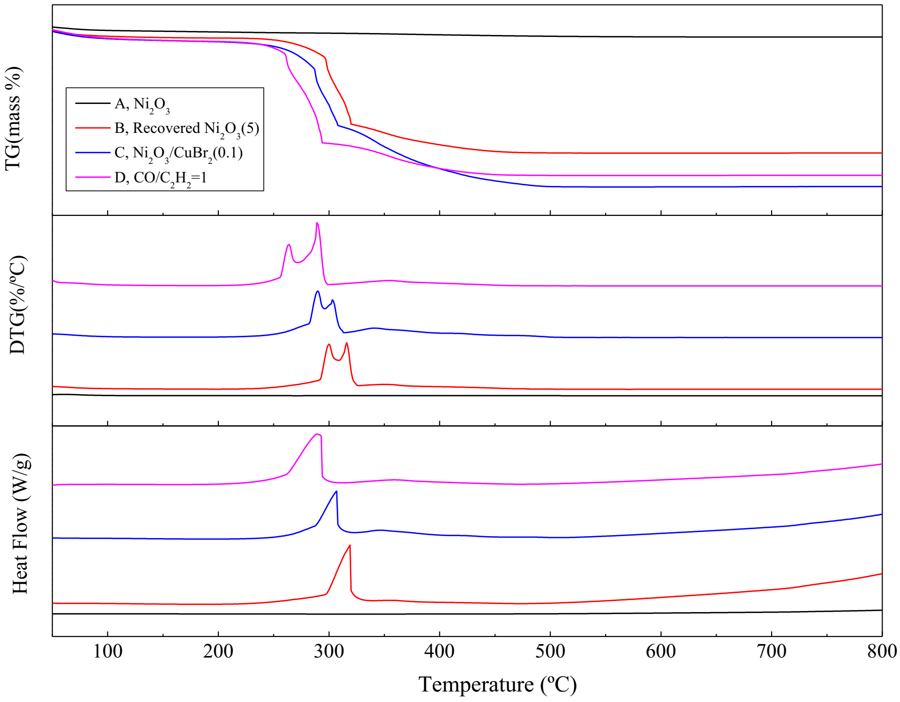

**Fig. 10.** TGA analysis of fresh and reacted catalysts: (A) fresh $Ni_2O_3$; (B) recovered $Ni_2O_3$(5); (C) recovered $Ni_2O_3$–$CuBr_2$ (0.1); (D) recovered $Ni_2O_3$–$CO/C_2H_2 = 1$).

XPS spectra obtained from the same reacted catalysts. The existence of Ni (2*p*) peak at E.B. of 856.93 eV (2*p*3/2) and 875.72 eV (2*p*1/2) could be attributed to the $Ni^{3+}$ in $Ni_2O_3$. According to the reports, the characteristic peak corresponded to $Ni^{3+}$ at Eb = 856 eV [24] or 856.83 eV [25] or 856.9 eV [26]. Moreover, the O (1*s*) spectra at a binding energy of 532 eV is attributed to the existence of $O^{2-}$ in $Ni_2O_3$ [25]. As is presented in Table 1, the $Ni_2O_3$ is more active than NiO due to its metallic property, it can be presumed that the $Ni_2O_3$ with higher binding energy would do a lot more to coordinate the CO and acetylene.

The SEM results of fresh and recovered catalysts are shown in Fig. 9. The as-received $Ni_2O_3$ grains have irregular shapes and different sizes. After recovered from the first catalytic run (B(1), B(2)), lots of fine particles appear and the shape becomes more regular. No obvious coke deposition is observed. While for the catalyst recovered from the fifth time of catalytic run (C(1), C(2)), a lot of carbon nanofibers with filamentous lines and helical structures are observed and they deposited on the surface of the $Ni_2O_3$ particles, agreeing with the results analyzed by XRD characterization. As discussed above, the more amount of cupric bromide and acetylene in the feedstock, the less the selectivity to acrylic acid would be obtained, which is proved again by the SEM results (Fig. 9(D and E)). It can be inferred that the activity would decline if the catalyst grains are completely covered by these carbon nanofibers.

The fresh and reacted catalysts were characterized by TG technology. The TG, DTG, and heat flow results from the temperature-programmed oxidation (TPO) of the various coked catalysts are shown in Fig. 10. The weight ratio in Fig. 10 equals the weight at each temperature point divided by the original sample weight. From the DTG result of those reacted catalysts, three obvious oxidation peaks were observed. It seems that three types of carbon were formed during the reaction. The oxidation peaks appear somewhat different from each other according to the specific reaction conditions, but all of them occur at low temperature zone. For example, the oxidation peaks of recovered $Ni_2O_3$(5) occurred at a temperature about 300 °C, 317 °C, and 353 °C, respectively. These three types of coke can be collectively referred to as soft coke, which can be removed at a relative lower temperature [27]. In other words, the reacted catalysts can be regenerated through calcination within 400 °C. From the view of coke amount, the high concentration of $CuBr_2$ in the liquid would boost the formation of coke followed by the reaction with equal molar ratio of $CO/C_2H_2$. The TG analysis agrees well with the finding in the XRD and SEM characterization.

## 4. Conclusion

It has been demonstrated that the $Ni_2O_3$ and cupric bromide can effectively catalyze the hydrocarboxylation of acetylene with carbon monoxide and water to produce the acrylic acid.

Careful comparison of the catalytic activity of $Ni_2O_3$ and various nickel-based homogeneous catalysts reveals that this heterogeneous catalyst gives the best activity with 72.1% of yield, 85.2% of selectivity and 764.6 mol AA/(mol Ni h) of STY when reacting 0.1 g $Ni_2O_3$, 0.03 g $CuBr_2$, 15 ml water, 150 ml acetone, 235 °C, 1.5 molar ratio of $CO/C_2H_2$, 4 MPa of initial total pressure, and 15 min reaction time. The $Ni_2O_3$ catalyst does not require any pre-treatment and it keeps a remarkable reusability in spite of some coke deposition after many times of recovery.

The catalytic activity was found strongly influenced by the reaction parameters such as initial total pressure, reaction temperature, molar ratio of $CO/C_2H_2$, the volume ratio of solvent/water and the catalyst amount. In addition, the copper salt plays an indispensable but double role in the hydrocarboxylation of acetylene. It will work with acetylene as well in $\delta$-metal–carbon bonds as in $\pi$-metal–carbon bonds. These copper–acetylene complexes are much easier to coordinate toward Ni center.

The XRD and XPS characterization indicates that the nickel oxide remains in its state unchanged during the whole reaction. The SEM, TG and XRD analyses of the reacted catalysts suggest the occurrence of coke with filamentous lines and helical structures deposited on the surface of the nickel oxide. The three types of coke occurred at a low temperature ranging from 250 °C to 400 °C and can be assigned to soft coke. Different reaction conditions will result in different coke amount, and it can be removed through calcination.

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