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A unique nickel-base nitrogen-oxygen bidentate ligand catalyst for carbonylation of acetylene to acrylic acid

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ARTICLE INFO	A B S T R A C T
Keywords:	A nickel-base nitrogen-oxygen bidentate ligand catalyst was prepared in-situ via the complexation method. Our
Carbonylation	results show that the ligand with nickel can form a chelate catalyst possessing a ring structure, which exhibits
Acrylic acid	good catalytic performance in the carbonylation reaction of acetylene to acrylic acid (AA). Furthermore, we
Nickel acetate	discovered that, under our optimized conditions, when 8-hydroxyquinoline (HQ) is used as the ligand [c(Ni
8-Hydroxyquinoline	$(OAc)_2 4H_2O) = 15 \times 10^{-6} \text{ mol } L^{-1}, n(HQ):n(Ni(OAc)_2 4H_2O) = 1:1, V(H_2O) = 7 \text{ mL}], 70.1\%$ conversion of
	acetylene and 92.4% the selectivity of AA is achieved at 200 °C with 8.0 MPa pressure for 30 min. Compared to
	traditional acetylene carbonylation catalysts and nickel-base phosphine ligand homogeneous complex catalysts,
	our catalytic system has unique advantages, including no copper, no halogen and no carbon deposition gener-
	ated during the reaction process. It displays high selectivity and no corrosion of equipment, suggesting that this

catalytic system possesses future industrial applications.

1. Introduction

Acrylic acid is a highly important and widely used chemical material, for water-borne coatings, polymer materials and as a dispersion agent [1]. Due to increased demand of absorbent resins in recent years, acrylic acid has been of growing interest. Acrylic acid is produced using numerous techniques which include the ketene method, acetylene carbonylation, oxidation of propane, oxidation of propylene, dehydration of glycerol oxidation, and dehydration of lactic acid. Unfortunately, due to their environmentally unfriendly synthetic processes, these methodologies have yet to be adapted into industry. At present, the partial oxidation of propylene and carbonylation of acetylene are the preferred routes for acrylic acid preparation. However, depletion of the world's oil has provoked a rapid increase in production costs of acrylic acid prepared via the oxidation of propylene. In the case of acetylene, generated from calcium carbide and carbon monoxide for the synthesis of acrylic acid, it belongs to the atomic economic reactions and plays a crucial role in the full utilization of resources. Therefore, it is an effective way in compensating for petrochemical raw materials shortage [2].

Initially, a nickel carbonyl catalyst was used for the carbonylation of acetylene to acrylic acid, but because of the catalysts high toxicity, weak acidic salts of nickel such as NiX₂, nickel acetate and nickel naphthenate were studied. However, their catalytic activity is greatly reduced, which can be overcome with the addition of copper and acid additives to the reaction system [3–6]. This type of approach is widely used in industrial production, but the catalytic system possesses some disadvantages, such as carbon deposition during the reaction process, low selectivity to acrylic acid, and corrosion of equipment.

In order to solve these problems, homogeneous complex catalyst systems were developed, as well as phosphine ligand based complexes. To date, numerous reports have investigated phosphine ligand based nickel complexes that display good catalytic activities [7–11]. Furthermore, in our previous work, nickel salts and triphenylphosphine are used as catalysts for acrylic acid synthesis, giving 90% selectivity under optimal conditions [12]. Palladium salts with diphenyl-2-pyridylphosphine ligands are also examined for methyl acrylate preparation, resulting in 99.7% selectivity under mild conditions [13,14].

Importantly, all the above mentioned homogeneous catalysts bear halogen and acidic proton moieties, which are seriously corrosion to equipment. The presence of copper ions can intensify acetylene decarburization and polymerization of acetylene and acrylic acid. These issues must be addressed before considering any industrial application by developing a novel catalyst without copper, halogen, and protonic

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acid groups. Due to the strong coordination ability of nitrogen ligands, they are ideal for incorporation into nickel based systems to catalyze the carbonylation of acetylene. Furthermore, considering the stability of nitrogen bound ligands, the catalytic system of other carbonylation reactions is used as reference [15–18]. Herein, a series of N-ligands with nickel salt are studied for the carbonylation of acetylene. We found that the prepared catalysts, consisting of a nitrogen-oxygen bidentate ligand and nickel salt, display enhanced catalytic performance under optimized conditions, compared with traditional nickel based systems. A plausible reaction mechanism is also proposed.

2. Experimental

2.1. Chemical reagents

All preparations were performed under laboratory atmosphere. All reagents and solvents employed were commercially available, of analytical grade and used without further purification. CO (> 98%) and C_2H_2 (> 99.95%) were purchased from the Southwest Research & Design Institute of the Chemical Industry.

2.2. General procedure

Tetrahydrofuran (60 mL), the specified amount of water and catalyst were charged into a 100 mL high pressure reactor and purged three times with N_2 . The specified amount of acetylene was dissolved in the solution with stirring for 20 min. The reactor was then pressurized with CO to 6.2 MPa. The reaction was carried out at 200 °C and 8.0 MPa, 1000 rpm stirring speed for the specified time, followed by water bath cooling of the reaction system to room temperature. The gases and liquid solution were analyzed by GC with TCD and FID, respectively.

2.3. Preparation of NiQ₂

0.25 g Ni(OAc)₂·4H₂O and 0.30 g 8-Hydroxyquinoline (HQ) were dissolved in 100 mL ethanol solution, respectively. The ethanol solution with HQ was added to the ethanol solution of nickel acetate, stirred for 20 min at 60 °C, filtered while hot, washed and dried, and then 8-hydroxyquinoline nickel complex (NiQ₂) was obtained.

2.4. Product analysis

Tail gas was analyzed by GC-3000B gas chromatography, using N₂ as the carrier gas with a TDX-01 Aglient's (1 m \times 2 mm, I.D.) chromatographic column. Column temperature: 130 °C, TCD temperature: 140 °C, vaporizing chamber temperature: 140 °C, current bridge current: 120 mA, signal polarity: +, carrier gas flow rate: 65 mL·min^{-1}.

Kettle liquid was analyzed by SC-14B gas chromatograph. Nitrogen was the carrier gas, with a hydrogen flame detector, and DB-FFAP Aglient's ($60 \text{ m} \times 0.34 \text{ mm} \times 0.5 \mu \text{m}$) chromatographic column. Temperature programmed retention: initial temperature 40 °C 2.5 min, 40 °C–220 °C/min. The detector temperature: 240 °C, the gasification chamber temperature: 240 °C.

3. Results and discussion

3.1. Effect of different ligands

The effect of quinolone ligands on the carbonylation reaction is summarized in Table 1 (entry 1–5). Optimum activity is obtained for the catalyst bearing HQ ligand, displaying 84.5% acrylic acid selectivity and 64.5% conversion of acetylene (entry 2). When the hydroxyl group of HQ ligand is replaced with an amino electron donating group (8aminoquinoline) (entry 4) or nitro electron withdrawing group (8nitroquinoline) (entry 3) rendered the catalyst inactive. Moreover, when the position of the hydroxyl group is changed on quinolone the catalyst is also inactive (entry 5). Hence, both the presence and position of the hydroxyl group is vital for catalytic performance.

The effect of pyridine ligands on the carbonylation reaction is correspondingly summarized in Table 1 (entry 6–11). When 2-(hydroxymethyl)pyridine or 2-picolinic acid derivative are employed as the ligand, good catalytic activity is observed, with 81.2% and 57% selectivity of AA and 63.9% and 72.6% conversion of acetylene, respectively (entry 9 and 11). In this case hydroxypyridine ligands, the hydroxyl group position did not have a substantial influence on the catalytic activity, however, the overall catalytic affect is not satisfactory (entry 6–8). In the comparison of HQ, 2-(hydroxymethyl)pyridine and 2-picolinic acid chemical structures, a common characteristic is detected. All nitrogen atoms are equal distance from the hydroxyl group (two carbon atoms), creating a stable chelate ring structure (Scheme 1) with the nickel salt, resulting in excellent catalytic effect (Scheme 2).

According to reports the key step in the acetylene carbonylation mechanism is the transition of carbonyl complexes adsorbed acetylene to acyl complexes via CO insertion reaction [19]. During the carbonylation process, L₁ and L₂ are substituted by carbonyl forming carbonyl complexes in CO atmosphere, upon adsorbing acetylene alkynes complexes are generated, and after the CO insertion reaction they transform to acyl complexes. When nitrogen-oxygen bidentate chelates are used as catalysts, the substituents on the ligands affect the electron cloud density on Ni through the five-membered ring. This eventually regulates the strength of C-O bonds and those complexes that can facilitate the conversion of carbonyl to acyl complexes exhibit enhanced catalytic activity. The experimental results show that catalyst activity is in the following order: HQ > 2-picolinic acid > 2-hydroxymethyl pyridine. Therefore, when N and O are close to the electron-absorbing or aromatic groups, they are beneficial to the conversion of carbonyl to acyl complexes.

However, other hydroxyl-substituted quinolones are inactive, whereas hydroxyl-substituted pyridines have certain activity, this may be attributed to the spatial structure. Ni can complex to N on one pyridine ligand and O on the other simultaneously. However, the described intermolecular coordinated complex is not as stable as the intramolecular ring structure, which shows moderate catalytic activity. Correspondingly, intermolecular coordination complex formation is impossible between Ni and 2,4-dihydroxyquinoline, because the quinoline ring is relatively larger, resulting in low catalytic activity.

Among the examined ligands, optimal catalytic performance is obtained when HQ is used as the ligand. Therefore, the catalytic performance of Ni(OAc)₂-HQ was investigated, and the process conditions optimized.

3.2. Effect of the preparation method on catalytic performance

Table 2 shows that the catalyst, which has 1:1 M ratio of ligand: Ni prepared in-situ (entry 2), has an 84.5% increase in selectivity compared with NiQ₂ (entry 4). When the molar ratio of ligand: Ni is 2:1(entry 3), the amount of AE increases, and the selectivity of AA reduces to ca. 5%. Importantly, the ligands can effectively prevent the formation of carbon deposits.

Furthermore, Table 2 compares catalysts bereft of ligands, with HQ and Ni(OAc)₂·4H₂O prepared in-situ and complexes prepared out-situ, catalyst AA selectivity increases of AA from 62.3% to 84.5%, the conversion of acetylene increases from 45.7% to 64%. This substantial increase is observed especially in the case of HQ and Ni(OAc)₂·4H₂O prepared together in-situ, which allows for reduction in the amount of ligand and AE, enhancing the selectivity of acrylic acid. Importantly, this has great significance in the promotion of further applications of acetylene as well as decreasing catalyst production costs in industrial.

3.3. Effect of Ni(OAc)₂·4H₂O concentrations

As shown in Fig. 1, the carbonylation reaction is inactive without

Table 1

Catalytic performance of Ni(OAc)2·4H2O with different ligands.

Entry	Ligand (HL)	Conversion of acetylene/%	ne/% Selectivity/%					
			AA	Acetone	Acetaldehyde	Acetic acid	Dimer	AE
1 2		45.7 64.5	62.3 84.5	4.9 2.6	12.9 3.4	15.2 2.7	3.4 5.6	0.4 1.0
3	ОН N	7.8	2.9	28.7	37.9	29.8	0.0	0.4
4	NO ₂	9.8	19.4	22.9	30.1	23.7	0.0	0.4
5	OH	10.3	24.4	21.8	28.7	22.5	0.0	0.5
6	HO' N Ü	37.2	53.4	10.5	13.9	10.9	2.4	5.2
7	OH OH	40	54.9	9.8	12.9	10.2	2.3	4.9
8	OH	36.4	50.7	10.8	14.2	11.2	2.5	5.4
9	OH OH	57	72.6	3.9	5.2	4.1	6.3	5.7
10		15.1	37.3	14.8	19.6	15.4	0.6	6.5
11	ОН	63.9	81.2	2.6	4.6	2.7	5.7	0.4

0

Reaction conditions: $n(Ni(OAc)_2 \cdot 4H_2O) = 0.001 \text{ mol}$, n(ligand) = 0.001 mol, V(THF) = 60 mL, $V(H_2O) = 5 \text{ mL}$, $m(C_2H_2) = 4 \text{ g}$, P = 8.0 MPa, $T = 200 \degree C$, r = 1000 rpm, t = 30 min.





catalyst, generating 9.8% acetylene via decarburization reaction, and producing a large amount of carbon deposition. When the concentration of catalyst (n(HQ): N(Ni(OAc)₂·4H₂O) = 1:1) is increased to 8×10^{-6} mol L⁻¹, the conversion of acetylene and selectivity of acrylic acid shows a significant increase to 65.6% and 83.1%, respectively. When the concentration is further increased to 15×10^{-6} mol·L⁻¹, the conversion and selectivity are 70.1% and 92.4%, respectively. Above this concentration, the conversion slowly increases to 72.5%, but the selectivity is greatly reduced to 81.3%, due to the occurrence of side reactions.

3.4. Effect of the amount of ligand

The effect of the amount of HQ on the carbonylation reaction is shown in Fig. 2. The conversion of acetylene is very low without HQ, only 55.3%. Increasing the concentration of HQ, the selectivity of acrylic acid increases rapidly. When the ratio of $n(HQ)/n(Ni(OAc)_2 · 4H_2O)$ is ca. 1.0, the selectivity of acrylic acid is 92.3%. HQ, an amphoteric compound, can undergo esterification with acrylic acid, whereas excessive HQ reduces the selectivity of acrylic acid.

3.5. Effect of H₂O

In the studied reaction, water is both raw material and a composition of mixed solvent with tetrahydrofuran, which absorbs acetylene and CO, followed by the carbonylation reaction in the liquid phase. The amount of water effects the relative concentration of raw materials and polarity of the solution, which influences acetylene and CO concentration in the liquid phase, and the reaction rate. The effect of water on the reaction is shown in Fig. 3. When 4 mL of water is used, which is in stoichiometric ratio with acetylene, the conversion of acetylene and selectivity of acrylic acid are rather low at 65.9% and 70%, respectively. An increase in water to 7 mL resulted in 70.1% conversion and 92.4% selectivity. Excess water promotes the reaction with acetylene, and the increase in by-product acetaldehyde production. Hence, the addition of 10 mL of water reduced the selectivity to acrylic acid to 83.1%.

3.6. Effect of reaction time

Effect of reaction time is shown in Fig. 4, the conversion of acetylene and selectivity of acrylic acid are 65.4% and 86%, respectively, at 20 min. The yield of acrylic acid is 56.2%, which shows that the catalytic activity is high. When the reaction is conducted for 30 min, the selectivity reaches a maximum of 92.4%, and conversion of 70.1%. Prolongation of the reaction time did not significantly increase acetylene conversion rate, but increases the amount of side reactions whilst decreasing the selectivity to 82.1%. Therefore, the optimal reaction time is 30 min.



Scheme 2. Proposed catalytic mechanism of acetylene carbonylation to AA catalyzed by Ni-HQ.

Table 2

Effect of the	preparation	method	on	catalytic	performance.
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Entry	Catalyst	Conversion of	Selectiv	/ity/%	Carbon
		acceptence / 10	AA	AE	deposition
1	^a Ni(OAc) ₂ ·4H ₂ O	45.7	62.3	-	Yes
2	^b Ni(OAc) ₂ ·4H ₂ O,HQ	64.5	84.5	1.0	No
3	°Ni(OAc)2·4H2O,HQ	63.7	78.7	5.2	No
4	^d NiQ ₂	63.9	79.8	4.6	No

^a $n(Ni(OAc)_2 \cdot 4H_2O) = 0.001 \text{ mol.}$

^b $n(Ni(OAc)_2 4H_2O) = 0.001 \text{ mol}, n(HQ) = 0.001 \text{ mol}.$

^c $n(Ni(OAc)_2 \cdot 4H_2O) = 0.001 \text{ mol}, n(HQ) = 0.002 \text{ mol}.$

^d $n(NiQ_2) = 0.001 \text{ mol.}$

3.7. Reaction mechanism

On the basis of the above experiments and reported mechanisms of nickel or palladium catalyzed hydroesterification of methylacetylene or



Fig. 1. Effect of catalyst concentrations on the carbonylation reaction. Reaction conditions: n(ligand): n(Ni(OAc)₂·4H₂O) = 1:1, V(THF) = 60 mL, V (H₂O) = 5 mL, m(C₂H₂) = 4 g, P = 8.0 MPa, T = 200 °C, r = 1000 rpm, t = 30 min.



Fig. 2. Effect of the amount of HQ on the carbonylation reaction. Reaction conditions: $n(Ni(OAc)_2 \cdot 4H_2O) = 0.001 \text{ mol}$, V(THF) = 60 mL, $V(H_2O) = 5 \text{ mL}$, $m(C_2H_2) = 4 \text{ g}$, P = 8.0 MPa, T = 200 °C, r = 1000 rpm, t = 30 min.

acetylene with carbon monoxide, the following mechanism is proposed [19–22]:

Under the reaction conditions, Ni(OAc)₂ forms a chelate with HQ acetic acid nickel chelate with HQ, and freed protons (1). Chelation in CO atmosphere (2) removes acetate ions formed HQ nickel carbonyl complexes, generating a ring shaped nickel hydride complexes active component in part of the proton acid (3). The complex adsorbs acetylene and undergoes additional reactions (4), followed by the insertion reaction of carbonyl complexes, allowing the acyl complexes to transform to the acyl complex. The acyl complex with one part of CO as ligand forms acrylic acid in the presence of water (8). At the same time, the catalyst is reduced to the ring nickel metal hydride complexes active components. Step (3) is the key step in the catalytic cycle, while step (6) is the rate-determining step.

4. Conclusions

Herein, we found that nitrogen ligands containing a hydroxyl group and a lone pair of electrons on the aromatic ring generates a ring



Fig. 3. Effect of H₂O on the carbonylation reaction. Reaction conditions: $n(Ni(OAc)_2 \cdot 4H_2O) = 0.001 \text{ mol}$, n(ligand) = 0.001 mol, m $(C_2H_2) = 4 \text{ g}$, P = 8.0 MPa, T = 200 °C, r = 1000 rpm, t = 30 min.



Fig. 4. Effect of reaction time on the carbonylation reaction. Reaction conditions: $n(Ni(OAc)_2:4H_2O) = 0.001$ mol, n(ligand) = 0.001 mol, V (THF) = 60 mL, V(H₂O) = 5 mL, $m(C_2H_2) = 4$ g, P = 8.0 MPa, T = 200 °C, r = 1000 rpm.

complex with nickel salt, resulting in good catalytic activities. Catalysts bearing 8-hydroxyquinoline as the ligand display good catalytic activity and higher acrylic acid selectivity. Importantly, the catalytic system has no copper, no halogen, no need for acidic protons and no carbon deposition occurring during the reaction process. Our approach has successfully solved the problems of the traditional acetylene carbonylation catalyst and phosphine ligand homogeneous complex catalysts, whilst maintaining excellent catalytic efficiency for the carbonylation of acetylene to acrylic acid, making it suitable for industrial production.

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