

# Nickel-catalyzed carbonylation of methyl acetate to acetic anhydride

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## Abstract

Liquid phase carbonylation of methyl acetate to acetic anhydride using nickel catalyst with methyl iodide promoter is reported. Effect of different catalyst precursors, total reaction pressure, hydrogen partial pressure, temperature, catalyst, lithium acetate and methyl iodide concentration, a variety of ligands on the activity and selectivity of nickel catalyst has been investigated. Additionally, FT-IR spectra of the reaction solution were studied and possible side reactions in the carbonylation were examined. Based on these observations, a proposed mechanism for the homogeneous nickel-catalyzed carbonylation of methyl acetate was discussed. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Nickel catalyst; Carbonylation; Acetic anhydride; Ligand; Mechanism

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## 1. Introduction

The new technology of carbonylation of methyl acetate to acetic anhydride marks the first important transfer for chemical materials from oil to coal and natural gas, and this process is one of the most successful examples of the industrialization of  $C_1$  chemistry. Compared with some ‘classic’ methods, for example, oxidation of acetaldehyde, the carbonylation method has significant advantages in cutting down energy consumption and in decreasing environmental pollution. Of all the catalysts having been studied, rhodium is found to be the most active and selective and so far, it is used in industry. However, rhodium is also one of the noble metals and is very rare on the earth, for this reason, it became more and more important for people to explore non-noble metal catalysts. Recent patents indicate that nickel catalyst is better than other non-noble metal catalysts in its higher activity and milder reaction conditions [1,2]. Kelkar et al. [3] have studied the influence of a few N- or P-containing ligands and reaction conditions on the activity of  $Ni(isq)_4Cl_2$  catalyst system. But this catalyst system is not completely satisfactory from the standpoint of activity and reaction rate, in addition, no information on the mechanism is available. Considering the potential importance of

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Ni-catalyzed carbonylation of methyl acetate as an alternative process of the future, we report the carbonylation of methyl acetate to acetic anhydride using  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  as catalyst precursor with MeI promoter in the present work. Effect of various reaction conditions, promoters as well as different types of ligands have been investigated in detail. Based on these results, a reasonable proposal for the mechanism of Ni-catalyzed methyl acetate is discussed.

## 2. Experimental

### 2.1. Materials

The complex  $(\text{Ph}_3\text{P})\text{Ni}(\text{CO})_3$ ,  $(\text{Ph}_3\text{P})_2\text{Ni}(\text{CO})_2$ ,  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$  were prepared respectively according to the literature [4,5].

1,2-Dimethyl pyridinium iodide (1,2-DMPyI), 1,4-dimethyl pyridinium iodide (1,4-DMPyI), 1,2,6-trimethyl pyridinium iodide (1,2,6-TMPyI) were prepared according to the literature [6]. 1,4-Dimethyl-2-aminopyridinium iodide (1,4-DM-2APyI), 1-methyl-2,2'-bipyridinium iodide (1M-2,2'-biPyI) were prepared according to the literature [7]. 1,2-Bis(diphenylphosphino)ethane (DPPE) were prepared according to the literature [8].

The catalyst precursor  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , all the other solid and liquid materials were commercial products and used without further purification.

Carbon monoxide and hydrogen with 99.9% purity were used directly from the cylinders.

### 2.2. Carbonylation procedure

The carbonylation experiments were carried out in a 250-ml zirconium autoclave, equipped with electric heating jacket, thermocouple and sealed mechanical stirrer driven by electromagnet. In a typical experiment, this autoclave was charged with calculated quantities of catalyst precursor, promoter(s), methyl acetate, solvent and ligand (if used). Then it was sealed, flushed with CO for 2–3 times. Hydrogen was introduced to a desired value and the contents were heated. After the desired reaction temperature was reached, the reactor was filled with CO up to required pressure and a liquid sample was withdrawn for gas chromatography (GC) analysis. The pressure was maintained constant by continuously introducing CO during the reaction. At the end of the reaction, the product mixture was cooled and analyzed by GC.

### 2.3. Analysis of gas chromatography

The analysis of liquid reaction mixture was carried out using a Shanghai temperature-programmed GC-8810 gas chromatograph with a TCD detector.  $\Phi 3 \times 3000$  mm PTFE column packed with GDX-203 stationary phase was used. The column temperature was from 90 to 160°C at a heating rate of 6°C/min. Carrier gas was hydrogen. Methane was analyzed by using TDX-01 as stationary phase.

### 2.4. FT-IR study

The spectra were recorded on a Bruker IFS-25 FT-IR spectrometer after 32 scans with a 2-cm<sup>-1</sup> resolution.

### 3. Results and discussion

In all the experiments the reactant AcOMe, acetic acid as well as carbonylation product acetic anhydride were used as solvents, since they were found to be the best solvent for the reaction and can be easily separated by distillation [7]. The AcOMe conversion, the reaction rate (expressed as space–time yield, STY) and catalytic activity (expressed as turn over number, TON) as well as selectivity to acetic anhydride are defined as:

$$\text{AcOMe conversion (\%)} = \frac{\text{AcOMe consumed (mol)}}{\text{AcOMe charged (mol)}} \times 100$$

$$\text{STY (mol/(1h))} = \frac{\text{increment of Ac}_2\text{O (mol)}}{(\text{reaction volume (l)})(\text{reaction time (h)})}$$

$$\begin{aligned} \text{TON (mol/(mol h))} &= \frac{\text{increment of Ac}_2\text{O (mol)}}{(\text{nickel catalyst (mol)})(\text{reaction time (h)})} \\ &= \frac{\text{STY (mol/(1h))}}{\text{nickel catalyst concentration (mol/l)}} \end{aligned}$$

$$\text{Ac}_2\text{O selectivity (\%)} = \frac{\text{increment of Ac}_2\text{O (mol)}}{\text{total increment of Ac}_2\text{O and HOAc (mol)}} \times 100.$$

When the nickel catalyst concentration was kept constant, the changing tendency of TON also stood for that of STY, so, we gave both TON and STY value only when studying the effect of nickel catalyst concentration.

#### 3.1. Effect of nickel catalyst precursors

The effect of different catalyst precursors on AcOMe carbonylation was studied. The results are presented in Table 1. It was observed that the carbonylation activities were almost the same, irrespective of the type of nickel catalyst precursors used. This indicated that the active species could be similar in nature in all these cases. In the following experiments, the simple two-valence nickel salt, Ni(OAc)<sub>2</sub>, was used as catalyst precursor.

Table 1  
Effect of nickel catalyst precursor on AcOMe carbonylation

Catalyst precursor	[Cat] (mol/l)	TON (mol/(mol h))	AcOMe conversion (%)	Selectivity (%)	
				AcOAc	AcOH
Ni(OAc) <sub>2</sub> + Ph <sub>3</sub> P	0.050	24.1	45.9	100	0
(Ph <sub>3</sub> P)Ni(CO) <sub>3</sub>	0.027	23.6	19.3	95.1	4.9
(Ph <sub>3</sub> P) <sub>2</sub> Ni(CO) <sub>2</sub>	0.050	24.2	50.7	100	0
(Ph <sub>3</sub> P) <sub>2</sub> NiCl <sub>2</sub>	0.050	27.3	56.4	100	0
(Ph <sub>3</sub> P) <sub>2</sub> NiCl <sub>2</sub>	0.016	25.2	16.9	94.4	5.6

Reaction conditions:  $P_1 = 5.5$  MPa,  $P_{H_2} = 1.3$  MPa,  $T = 443$  K,  $t = 2.5$  h, [AcOMe] = 5.08 mol/l, [AcOH] = 3.45 mol/l, [MeI] = 1.86 mol/l, [Ac<sub>2</sub>O] = 2.99 mol/l, [LiOAc] = 0.40 mol/l, stirring speed: 400 rpm.

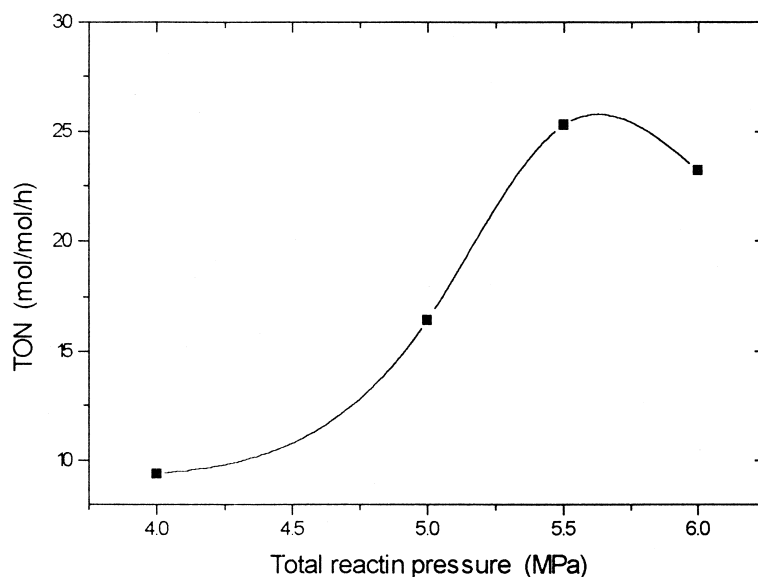


Fig. 1. Effect of total reaction pressure on AcOME carbonylation rate. Reaction conditions:  $P_{\text{H}_2} = 1.3$  MPa,  $T = 453$  K,  $t = 1$  h,  $[\text{Ni}(\text{OAc})_2] = 0.050$  mol/l,  $[\text{AcOME}] = 5.08$  mol/l,  $[\text{AcOH}] = 3.45$  mol/l,  $[\text{MeI}] = 1.86$  mol/l,  $[\text{Ac}_2\text{O}] = 2.99$  mol/l,  $[\text{LiOAc}] = 0.40$  mol/l, stirring speed: 400 rpm.

### 3.2. Effect of total reaction pressure

The effect of total reaction pressure on carbonylation is shown in Fig. 1. It was found that the activity of nickel catalyst and selectivity to acetic anhydride increased significantly with increase in total pressure up to 5.5 MPa. With further increase, the activity was independent of total pressure.

### 3.3. Effect of nickel catalyst concentration

Table 2 is the effect of nickel catalyst concentration. As might be anticipated, the reaction rate increased with rising concentration of nickel catalyst and it exhibited first-order dependence on nickel catalyst concentration.

Table 2  
Effect of nickel catalyst concentration on AcOME carbonylation

[Ni(OAc) <sub>2</sub> ] (mol/l)	STY (mol/(l h))	TON (mol/(mol h))	AcOME conversion (%)	Selectivity (%)	
				AcOAc	AcOH
0.010	0.40	38.6	7.7	86.7	13.3
0.020	0.82	40.1	17.9	88.5	11.5
0.030	1.24	40.5	21.4	95.8	4.2
0.036	1.40	39.0	28.4	95.5	4.5

Reaction conditions:  $P_1 = 6.0$  MPa,  $P_{\text{H}_2} = 1.3$  MPa,  $T = 453$  K,  $t = 1$  h,  $[\text{Ni}(\text{OAc})_2]:[\text{Ph}_3\text{P}] = 1:1$ ,  $[\text{AcOME}] = 5.08$  mol/l,  $[\text{AcOH}] = 3.45$  mol/l,  $[\text{MeI}] = 1.86$  mol/l,  $[\text{Ac}_2\text{O}] = 2.99$  mol/l,  $[\text{LiOAc}] = 0.40$  mol/l, stirring speed: 400 rpm.

### 3.4. Effect of lithium acetate concentration

The effect of lithium acetate promoter on methyl acetate carbonylation was studied. The results are presented in Fig. 2. It was observed that the activity increased markedly with augmentation of lithium acetate concentration at lower concentrations, then growth rate dropped at higher concentrations.

It was believed by Nelson et al. [9] that  $[\text{Ni}(\text{CO})_3\text{I}]^-$  was the active catalytic species in the nickel-catalyzed carbonylation of methyl acetate. In our study, we did observe two typical absorption bands in  $2029.7\text{ cm}^{-1}$  and  $2076.9\text{ cm}^{-1}$ , respectively, when FT-IR spectra of the reaction solution (with no ligand existed) were taken. These two bands were considered to belong to the C–O stretching vibrations in zero-valence nickel carbonyl complex  $\text{Li}^+[\text{Ni}(\text{CO})_3\text{I}]^-$ . We also found the two carbonyl bands disappeared when lithium acetate was not added to the reaction mixture. However, with the addition of equal molar potassium iodide in place of lithium acetate, the two bands reappeared (Fig. 3). The result indicated that lithium acetate and potassium iodide could enhance the formation of  $[\text{Ni}(\text{CO})_3\text{I}]^-$  by providing corresponding cations. Another role of lithium acetate was promoting the formation of acetic anhydride which was similar to the rhodium-catalyzed carbonylation of methyl acetate [10].

### 3.5. Effect of hydrogen partial pressure

The effect of hydrogen partial pressure ( $P_{\text{H}_2}$ ) was also studied. The results are presented in Table 3. It was found that the carbonylation did not proceed without hydrogen at 5.2 MPa. When hydrogen partial pressure was 0.8 MPa, a highly active and selective catalyst was formed. With further increase in hydrogen partial pressure, the activity was almost the same, while the selectivity to acetic anhydride decreased on the contrary. Carbon monoxide pressure was increased to 6.0 MPa in order to confirm whether hydrogen is crucial to the occurrence of carbonylation and it was observed that almost the same activity could be obtained at higher CO pressure without hydrogen.

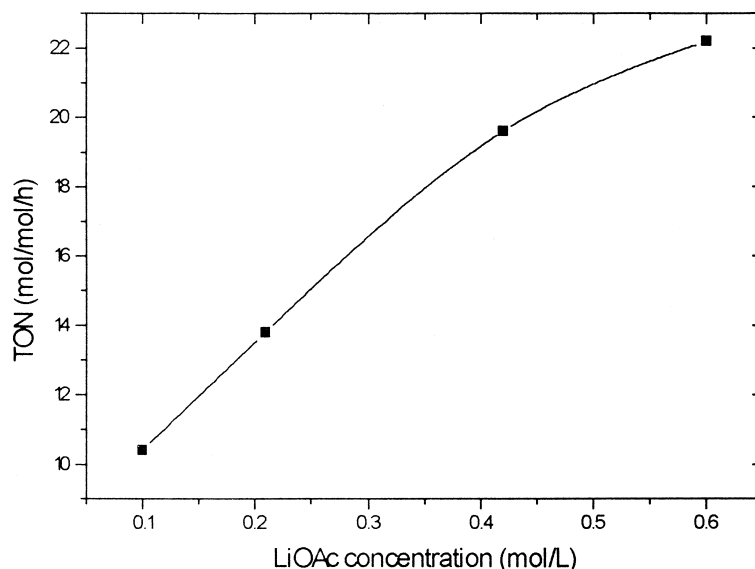


Fig. 2. Variation of carbonylation rate with lithium acetate concentration. Reaction conditions:  $P_1 = 5.2\text{ MPa}$ ,  $P_{\text{H}_2} = 1.3\text{ MPa}$ ,  $T = 443\text{ K}$ ,  $[\text{Ni}(\text{OAc})_2] = 0.053\text{ mol/l}$ ,  $[\text{AcOMe}] = 5.12\text{ mol/l}$ ,  $[\text{AcOH}] = 3.13\text{ mol/l}$ ,  $[\text{MeI}] = 2.97\text{ mol/l}$ ,  $[\text{Ac}_2\text{O}] = 2.42\text{ mol/l}$ ,  $t = 2.5\text{ h}$ , stirring speed: 300 rpm.

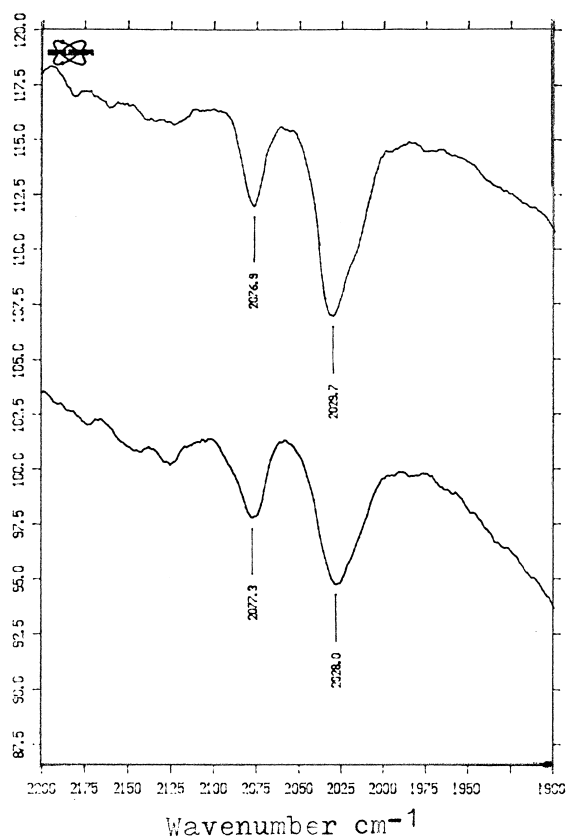


Fig. 3. FT-IR spectra of the active species in the reaction solution. The upper one with LiOAc promoter, the lower with KI promoter.

In the carbonylation, hydrogen possibly acted as reducing agent accelerating two-valence nickel salt convert to zero-valence nickel active species  $[\text{Ni}(\text{CO})_3\text{I}]^-$ .

### 3.6. Effect of ligands

#### 3.6.1. Effect of quaternary ammonium iodides

Six kinds of quaternary ammonium iodides were studied. The results are presented in Table 4. The activity of nickel catalyst improved with the addition of iodides. The activity sequence of  $\text{Me}_4\text{N}^+\text{I}^-$ ,

Table 3  
Effect of hydrogen partial pressure on AcOMe carbonylation

$P_{\text{H}_2}$ (MPa)	TON (mol/(mol h))	AcOMe conversion (%)	Selectivity (%)	
			AcOAc	AcOH
0	0	0	0	0
0.8	19.5	40.2	95.0	5.0
1.3	19.6	45.6	89.4	10.6
0 <sup>a</sup>	18.8	31.6	100	0

Reaction conditions:  $P_1 = 5.2$  MPa,  $T = 443$  K,  $t = 2.5$  h,  $[\text{Ni}(\text{OAc})_2] = 0.053$  mol/l,  $[\text{AcOMe}] = 5.12$  mol/l,  $[\text{AcOH}] = 3.13$  mol/l,  $[\text{MeI}] = 2.97$  mol/l,  $[\text{Ac}_2\text{O}] = 2.42$  mol/l,  $[\text{LiOAc}] = 0.42$  mol/l, stirring speed: 300 rpm.

<sup>a</sup> $P_{\text{CO}} = 6.0$  MPa.

Table 4  
Effect of quaternary ammonium iodides on AcOMe carbonylation

Ligand	TON (mol/(mol h))	AcOMe conversion (%)	Selectivity (%)	
			AcOAc	AcOH
–	14.4	21.3	92.9	7.1
Me <sub>4</sub> N <sup>+</sup> I <sup>-a</sup>	15.8	18.0	98.3	1.7
Et <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	27.3	41.4	100	0
Bu <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	23.7	39.9	100	0
1,2-DMPyI <sup>b</sup>	26.7	44.8	100	0
1,4-DMPyI	24.8	41.0	97.8	2.2
1,2,6-TMPyI <sup>c</sup>	27.2	37.0	100	0

Reaction conditions:  $P_1 = 5.5$  MPa,  $P_{H_2} = 1.3$  MPa,  $[Ni(OAc)_2] = [ligand] = 0.050$  mol/l,  $[AcOMe] = 5.08$  mol/l,  $[AcOH] = 3.45$  mol/l,  $[MeI] = 1.86$  mol/l,  $[Ac_2O] = 2.99$  mol/l,  $[LiOAc] = 0.40$  mol/l,  $T = 443$  K,  $t = 2.5$  h, stirring speed: 400 rpm.

<sup>a</sup> $t = 2.16$  h.

<sup>b</sup> $t = 2.67$  h.

<sup>c</sup> $[Ni(OAc)_2] = 0.043$  mol/l,  $[ligand] = 0.040$  mol/l.

Et<sub>4</sub>N<sup>+</sup>I<sup>-</sup> and Bu<sub>4</sub>N<sup>+</sup>I<sup>-</sup> was Et<sub>4</sub>N<sup>+</sup>I<sup>-</sup> > Bu<sub>4</sub>N<sup>+</sup>I<sup>-</sup> > Me<sub>4</sub>N<sup>+</sup>I<sup>-</sup> and it almost doubled when Et<sub>4</sub>N<sup>+</sup>I<sup>-</sup> was used. As for methyl(s)-substituted pyridinium iodides, the number and the position of substituted methyl group on pyridinium ring made little difference in their promotive effect.

The exact role of ligands in nickel-catalyzed carbonylation of methyl acetate is not well-understood and there is few report on the mechanism of the ligand modified nickel-catalyzed carbonylation of methyl acetate. FT-IR measurement of the reaction solution with Bu<sub>4</sub>N<sup>+</sup>I<sup>-</sup> as a ligand showed that the carbonyl absorption (in 2029.7 and 2075.0 cm<sup>-1</sup>, respectively) did not change much compared with that of no ligand existed, on this account, it was possible that quaternary ammonium iodides mainly had two roles: (1) enhanced the formation of the catalytic intermediate by providing I<sup>-</sup>; (2) providing coordinating cation for the active anion, thus stabilizing the active species. For Me<sub>4</sub>N<sup>+</sup>I<sup>-</sup>, Et<sub>4</sub>N<sup>+</sup>I<sup>-</sup> and Bu<sub>4</sub>N<sup>+</sup>I<sup>-</sup>, the stabilizing energy was different because of their different electronic and steric effect, as a result, the activity had different improvements.

### 3.6.2. Effect of phosphorus-containing ligands

The results on the effect of phosphorus-containing ligands are shown in Table 5. It was found that the activity rose with rising concentration of Ph<sub>3</sub>P. Bidentate phosphorus ligand Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (DPPE) had lower activity than Ph<sub>3</sub>P because of chelation with nickel catalyst, but the activity still increased compared with that of no ligands existed.

Table 5  
Effect of phosphorus-containing ligands on AcOMe carbonylation

Ligand	[Ligand] (mol/l)	TON (mol/(mol h))	AcOMe conversion (%)	Selectivity (%)	
				AcOAc	AcOH
–	–	14.4	21.3	92.9	7.1
Ph <sub>3</sub> P	0.025	19.0	35.2	97.3	2.7
Ph <sub>3</sub> P	0.050	24.1	45.9	100	0
Ph <sub>3</sub> P	0.075	30.5	51.0	100	0
Ph <sub>3</sub> P	0.100	34.8	54.7	100	0
DPPE	0.040	17.8	32.3	100	0

Reaction conditions:  $P_1 = 5.5$  MPa,  $P_{H_2} = 1.3$  MPa,  $T = 443$  K,  $t = 2.5$  h,  $[Ni(OAc)_2] = 0.050$  mol/l,  $[AcOMe] = 5.08$  mol/l,  $[AcOH] = 3.45$  mol/l,  $[MeI] = 1.86$  mol/l,  $[Ac_2O] = 2.99$  mol/l,  $[LiOAc] = 0.40$  mol/l, stirring speed: 400 rpm.

Table 6  
Effect of monodentate nitrogen-containing ligands on AcOMe carbonylation

Ligand	TON (mol/(mol h))	AcOMe conversion (%)	Selectivity (%)	
			AcOAc	AcOH
–	14.4	21.3	92.9	7.1
imidazole	22.9	36.6	100	0
<i>n</i> -Pr <sub>3</sub> N	21.9	34.8	100	0
pyridine	21.6	32.0	100	0
4-methyl-pyridine	22.0	37.8	100	0

Reaction conditions:  $P_t = 5.5$  MPa,  $P_{H_2} = 1.3$  MPa,  $T = 443$  K,  $t = 2.5$  h,  $[\text{Ni}(\text{OAc})_2] = [\text{ligand}] = 0.050$  mol/l,  $[\text{AcOMe}] = 5.08$  mol/l,  $[\text{AcOH}] = 3.45$  mol/l,  $[\text{MeI}] = 1.86$  mol/l,  $[\text{Ac}_2\text{O}] = 2.99$  mol/l,  $[\text{LiOAc}] = 0.40$  mol/l, stirring speed: 400 rpm.

It was reported that  $\text{Ph}_3\text{P}$  could be easily alkylated in the presence of excess methyl iodide [11], therefore, with increase in concentration of  $\text{Ph}_3\text{P}$ , the concentration of active species  $[\text{Ni}(\text{CO})_3\text{I}]^-$  stabilized by  $\text{Ph}_3\text{P}^+\text{MeI}^-$  will increase, this resulted in rise in catalytic activity.

### 3.6.3. Effect of monodentate nitrogen-containing ligands

The improvements of the activity were also observed when monodentate nitrogen-containing ligands were used. The results are presented in Table 6.

The effect of these ligands was similar to that of quaternary ammonium iodides because they could easily react with methyl iodide promoter in reaction media to form corresponding ammonium iodides.

### 3.6.4. Effect of bidentate N-containing ligands and their quaternary ammonium iodides

The effect of bidentate nitrogen-containing ligands is somewhat complex. 2-Amino-4-methyl-pyridine and 2,2'-bipyridine gave poor activities and selectivities to acetic anhydride, especially when their molar ratios with nickel salt were 1:1. The activity was slightly lower than that of no ligand existed with the quaternization of the nitrogen atom on pyridine ring in 2A4MPy; while the activity was still very poor with the quaternization of nitrogen atom on one of the pyridine ring in 2,2'-bipyridine. The results are presented in Table 7.

The main reason for bidentate organonitrogen ligands 2A4MPy, 2,2'-bipyridine giving poor activities was that these bidentate ligands reacted with the catalyst precursor- $\text{Ni}^{2+}$  species forming stable chelates and resulted in decreased concentration of the active species-zero valence carbonyl nickel complex. For 2,2'-bipyridine, the quaternization was relatively difficult possibly because of

Table 7  
Effect of bidentate N-containing ligands and their quaternary ammonium iodides on AcOMe carbonylation

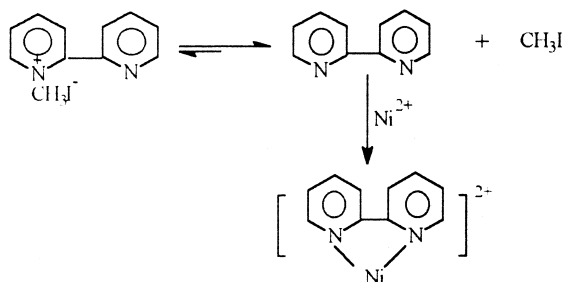
Ligand	TON (mol/(mol h))	AcOMe conversion (%)	Selectivity (%)	
			AcOAc	AcOH
–	14.4	21.3	92.9	7.1
2A4MPy <sup>a</sup>	9.0	13.9	92.4	7.6
2A4MPy	1.8	3.2	18.9	81.1
1,4-DM-2APyI	13.2	17.5	95.8	4.2
2,2'-bipyridine	2.5	4.8	22.6	77.4
1M-2,2'-biPyI	3.1	2.7	61.5	38.5

Reaction conditions:  $P_t = 5.5$  MPa,  $P_{H_2} = 1.3$  MPa,  $[\text{Ni}(\text{OAc})_2] = [\text{ligand}] = 0.050$  mol/l,  $[\text{AcOMe}] = 5.08$  mol/l,  $[\text{AcOH}] = 3.45$  mol/l,  $[\text{MeI}] = 1.86$  mol/l,  $[\text{Ac}_2\text{O}] = 2.99$  mol/l,  $[\text{LiOAc}] = 0.40$  mol/l,  $T = 443$  K,  $t = 2.5$  h, stirring speed: 400 rpm.

<sup>a</sup>[2A4MPy] = 0.04 mol/l.



steric hindrance (it was found that the reaction of 2,2'-bipyridine with MeI needed higher reaction temperature and longer time with lower productivity than that of 2A4MPy with MeI during the preparation of corresponding pyridinium iodides), as a result, the formed 1-methyl-2,2'-bipyridinium iodide inclined to get rid of MeI under carbonylation reaction conditions; on the other hand, five-membered chelate ring formed by 2,2'-bipyridine with  $\text{Ni}^{2+}$  was very stable. For the two reasons above, the quaternized bipyridine with nickel showed poor activity.



Since 1,4-DM-2APyI was much more stable than 1-methyl-2,2'-bipyridinium iodide in the carbonylation procedure, the nickel catalyst with 1,4-DM-2APyI still gave higher activity.

### 3.7. Effect of methyl iodide concentration

The effect of methyl iodide concentration was also studied. The results are shown in Fig. 4. It was observed that the activity (i.e., the reaction rate) was first-order dependent on methyl iodide concentration in the range of 0–3 mol/l.

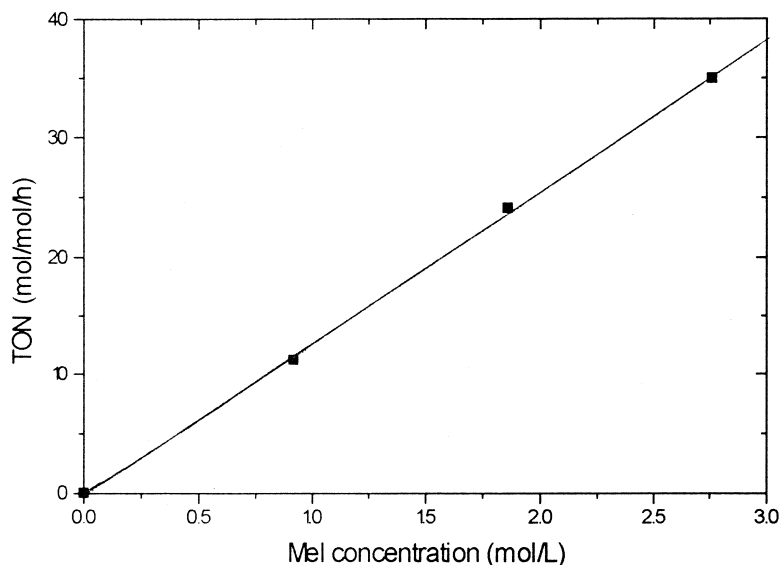


Fig. 4. Variation of carbonylation rate with methyl iodide concentration. Reaction conditions:  $P_1 = 5.5$  MPa,  $P_{\text{H}_2} = 1.3$  MPa,  $[\text{Ni}(\text{OAc})_2] = [\text{Ph}_3\text{P}] = 0.050$  mol/l,  $[\text{LiOAc}] = 0.40$  mol/l,  $\text{AcOMe}:\text{AcOH}:\text{Ac}_2\text{O} = 1.83:1.07:1$  (molar ratio),  $T = 443$  K,  $t = 2.5$  h, stirring speed: 400 rpm.

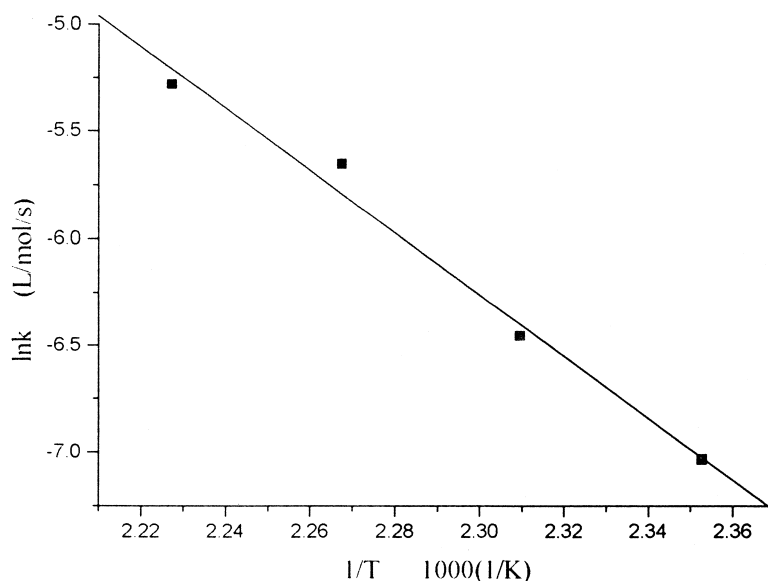


Fig. 5. The Arrhenius plot of Ni-catalyzed carbonylation of methyl acetate. Reaction conditions:  $P_t = 6.0$  MPa,  $P_{H_2} = 1.3$  MPa,  $[Ni(OAc)_2] = [Ph_3P] = 0.050$  mol/l,  $[AcOMe] = 5.12$  mol/l,  $[AcOH] = 3.13$  mol/l,  $[MeI] = 2.97$  mol/l,  $[Ac_2O] = 2.42$  mol/l,  $[LiOAc] = 0.42$  mol/l, stirring speed: 400 rpm.

### 3.8. Effect of reaction temperature

The effect of temperature on the carbonylation was studied in the temperature range from 420 to 450 K with  $Ph_3P$  as a ligand and the activation energy of the reaction was determined. All the reaction rates were calculated from analysis of reaction compositions after 1 h of reaction. The results are illustrated in Fig. 5. Apparent activation energy derived from the plot was 120.5 kJ/mol and the preexponential  $k_0$  was  $5.73 \times 10^{11}$  1/(mol s).

### 3.9. Mechanism for the Ni-catalyzed carbonylation

#### 3.9.1. Possible side reactions in the carbonylation

Under some reaction conditions, noticeable increment of acetic acid in liquid phase was observed. Where is this extra acetic acid from? In order to answer the question, we examined the reaction gas by GC. Methane was found to exist and its quantity related to the increment of acetic acid. The more methane formed, the more acetic acid increased. When increasing hydrogen partial pressure, more methane and acetic acid were generated. As a result, the selectivity to acetic anhydride decreased. In addition, it was found that no methane was produced when nickel catalyst precursor or methyl iodide or hydrogen or lithium acetate was not introduced into the carbonylation. Based on these observations, the following reactions may exist:



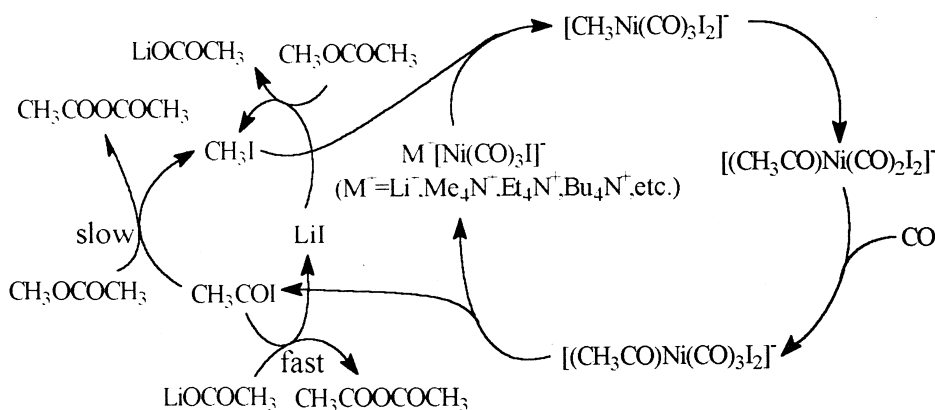


Fig. 6. Proposed mechanism for the nickel-catalyzed carbonylation of methyl acetate.

The total reaction was:



In addition, because of the above reaction (2) being reversible, especially in the presence of lithium acetate, it was found that there were some consumption of methyl iodide and acetic acid, and parallelly correspondent augmentations of methyl acetate, mainly in the reactions of longer time (> 1 h) in which methyl acetate had been mostly converted and the reaction system relatively abounded with acetic acid.

### 3.9.2. Mechanism for the carbonylation

A reasonable mechanism for nickel-catalyzed carbonylation of methyl acetate to acetic anhydride was proposed from above experimental results and drawing analogy from the same reaction catalyzed by rhodium [10] (Fig. 6).

The active species  $\text{M}^+[\text{Ni}(\text{CO})_3\text{I}]^-$  was formed in situ under reaction conditions, followed by the oxidative addition of methyl iodide promoter to form a six-coordinate alkyl-nickel (II) species. Rapid insertion of carbon monoxide into the methyl-nickel bond occurred to yield an acyl-nickel (II) complex. Finally, the reductive elimination of acetyl iodide regenerated the original active Ni(0) species. The desired carbonylation product acetic anhydride was obtained either by reaction of acetyl iodide with methyl acetate or by reaction of acetyl iodide with lithium acetate. Since the latter was much quicker, the reaction rate increased significantly in the presence of lithium acetate. It was believed that the oxidative addition of methyl iodide to  $[\text{Ni}(\text{CO})_3\text{I}]^-$  was the rate-determining step, since the carbonylation rate exhibited first-order dependence on nickel and methyl iodide concentrations.

## 4. Conclusions

The carbonylation of methyl acetate to acetic anhydride was studied using diverse nickel catalyst precursors with methyl iodide promoter.

Following observations were made essentially with  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  as the catalyst precursor: (a) the reaction rate exhibited first-order dependence on nickel catalyst and methyl iodide concentrations;

(b) hydrogen improved effectively the activity of nickel catalyst, and lithium acetate accelerated the formation of acetic anhydride; (c) under some circumstances, methane in gas phase accompanied with HOAc in liquid phase are formed as side products, leading to lower selectivity to acetic anhydride; (d) quaternary ammonium iodides obviously increased the reaction activity which was related to the electronic and steric effect of iodides; (e) monodentate N- and P-containing ligands also improved the activity of nickel catalysts; (f) effect of multidentate ligands were dependent on their coordinating atoms, electronic and steric effect. Of all the ligands studied, the activities of chelate ligands are usually lower than those of corresponding non-chelate ligands.

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