

# Carbonylation of ethanol using Ni–isoquinoline complex catalyst: Activity and selectivity studies

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## Abstract

The carbonylation of ethanol using  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ /isoquinoline catalyst system and aqueous HI as a promoter has been investigated. Effect of catalyst, ethanol and HI concentration, temperature, partial pressures of CO and  $\text{H}_2$ , N- or P-containing ligands and co-catalysts on the activity and selectivity has been studied. The Ni catalysts were found to be active only in the presence of N- or P-containing ligands. LiI and NaI were found to further enhance the catalytic activity without affecting the selectivity. Activity of Ni–isoquinoline–HI catalyst was found to be constant even after 4 recycles indicating high stability.

*Keywords:* Ethanol carbonylation; Nickel; Isoquinoline; Iodide

## 1. Introduction

The carbonylation of alcohols using homogeneous transition metal catalysts is an industrially important reaction as evidenced by the success of Monsanto process [1] for manufacture of acetic acid. Carbonylation of ethanol to propionic acid is also important since propionic acid has useful applications in the manufacture of polyester resins, food preservatives, insecticides and cosmetic products. Extensive research on this subject indicated that metal complexes consisting of Rh, Ir, Co and Ni catalyze this reaction, though much of the previous work has been concerned with Rh catalyzed carbonylation of methanol [2–4]. In an attempt to develop alternative catalyst system to Rh, promising re-

sults are indicated with  $\text{NiI}_2\text{-PPh}_3$  [5] and  $\text{NiCl}_2\text{-isoquinoline}$  [6] catalyst precursors. Rizkalla et al. [5] have studied the kinetics of methanol carbonylation using  $\text{NiI}_2\text{-PPh}_3$ . Further Kelkar et al. [7] have shown that metal iodide promoters are superior to aqueous HI in the carbonylation of ethanol and *n*-propanol using  $\text{Ni(Isoq)}_4\text{Cl}_2$  (Isoq = isoquinoline) as a catalyst. However, there is lack of information on the effect of various reaction conditions, ligands and co-catalysts using ligand modified Ni complex catalysts for carbonylation of ethanol.

In the present work we report the carbonylation of ethanol using Ni–isoquinoline catalyst system and aqueous HI as a promoter. Effect of various N- or P-containing ligands, co-catalysts and various reaction conditions has been investigated in detail. Recycle experiments have also

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been carried out to test the stability of the catalyst.

## 2. Experimental

### 2.1. Materials

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  supplied by SD Chemicals, India was used. Solvent propionic acid was obtained from SD Chemicals, India, while the reactants ethanol and ethyl iodide of AR quality were procured from BDH laboratories, Bombay. Aqueous HI was procured from Fluka, Switzerland. Carbon monoxide and hydrogen were used directly from cylinders. Ligands used in this work (Table 1) were procured from Fluka, Switzerland.

### 2.2. Experimental procedure

Carbonylation experiments were carried out in a  $3 \times 10^{-4} \text{ m}^3$  autoclave made of Hastelloy C-276, supplied by Parr Instruments, USA. This autoclave was provided with arrangements for sampling of liquid and gaseous components,

automatic temperature control and variable stirrer speed.

In a typical experiment,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  ( $2.1 \times 10^{-6} \text{ kmol}$ ), isoquinoline ( $16.8 \times 10^{-6} \text{ kmol}$ ), aq. HI ( $3.8 \times 10^{-5} \text{ kmol}$ ), ethanol ( $3.4 \times 10^{-4} \text{ kmol}$ ) and solvent propionic acid to make total volume  $1 \times 10^{-4} \text{ m}^3$  were charged to the reactor and the contents were flushed with nitrogen. The contents were flushed with CO again and heated to 498 K. Hydrogen was introduced up to 961.52 kPa and CO was introduced up to 2885 kPa. In order to monitor the consumption of CO at a constant pressure, a CO reservoir was used along with a constant pressure regulator. A liquid sample was withdrawn and the reaction was initiated by switching the stirrer on. The reaction was continued for 190 min. At the end of the reaction, the liquid as well as gas samples were analyzed for reactants and products by gas chromatography. GC analysis showed that the conversion of ethanol was 93.12% with 95.78% selectivity to propionic acid. Selectivity to ethane and ethylene formed as by-products were 2.32 and 1.2%, respectively.

Table 1  
Effect of ligands on the activity and selectivity

Sr. No.	Ligand	Time (min)	Conversion (%)	Selectivity			Average activity (kmol/kmol/h)
				propionic acid (%)	$\text{C}_2\text{H}_6$ (%)	$\text{C}_2\text{H}_4$ (%)	
1	NiI	190	03.00	0.00	—	—	00
2	isoquinoline	260	96.72	94.14	2.06	1.42	34
3	PPh <sub>3</sub>	250	89.13	95.04	2.85	0.06	33
4	PBu <sub>3</sub>	260	92.00	95.08	1.02	0.00	33
5	quinoline	270	96.23	93.24	0.00	0.00	33
6	2,4-lutidine	260	95.18	92.22	0.88	1.00	33
7	1,2-bis(diphenylphosphino)-ethane	230	85.65	91.02	2.54	3.02	33
8	3-picoline	280	94.82	96.62	2.10	1.46	32
9	2,6-lutidine	280	94.28	93.62	1.02	0.56	31
10	2-picoline	260	86.02	95.62	1.54	2.00	31
11	8-hydroxyquinoline	260	75.24	92.32	0.98	1.23	26
12	2,2'-bipyridine	260	11.73	95.22	1.42	0.00	04
13	P(OBu) <sub>3</sub>	250	5.00	90.50	0.00	0.00	02
14	P(OPh) <sub>3</sub>	250	0.00	0.00	0.00	0.00	00

Reaction conditions: concentration of catalyst:  $2.1 \times 10^{-2} \text{ kmol/m}^3$ ; catalyst:ligand: 1:2; concentration of ethanol:  $3.40 \text{ kmol/m}^3$ ; concentration of aq. HI:  $0.38 \text{ kmol/m}^3$ ; partial pressure of  $\text{H}_2$ : 961.52 kPa; partial pressure of CO: 2885 kPa; temperature: 498 K; agitation speed: 550 rpm.

For carrying out recycle runs similar experimental procedure was followed. After the reaction was completed, the autoclave was cooled to room temperature and the gases were vented. The reaction mixture was transferred to a distillation flask. Light boiling fraction consisting of ethyl iodide and unreacted ethyl propionate was distilled out and stored separately. The product propionic acid was distilled. The residual solution containing catalyst and solvent propionic acid was cooled and charged to the reactor along with the light boiling fraction and fresh ethanol. The reaction was carried out as usual by pressurizing the autoclave with hydrogen and CO. This procedure was repeated four times.

The quantitative analysis of the carbonylation products was done by an external standard method using a HP 5840 gas chromatograph. The column used was 1/8" diameter and 8 feet long packed with 5% OV-17 on chromosorb W-AW 80-100 mesh. The gas phase was analyzed for ethane and ethylene by gas chromatography using 6 feet Poropak Q, 1/8" column.

### 3. Results and discussion

A few preliminary experiments were carried out on carbonylation of ethanol using  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ /isoquinoline as a catalyst system with aqueous HI as a promoter to examine the principal products and material balance. Propionic acid was the only carbonylation product with gaseous ethane and ethylene as side products.  $\text{CO}_2$  formation was < 1%, indicating that water-gas shift reaction was minimum under reaction conditions. In most experiments, the selectivity of propionic acid was above 95%, the rest being ethane and ethylene. Several experiments were carried out to study the role of ligands, co-catalysts and reaction conditions on the activity and selectivity. In all the experiments propionic acid was used as a solvent, since carboxylic acids were found to be the best solvents for this reaction [7]. The conversion,

average activity expressed as turn over number and selectivity are defined as:

Conversion (%)

$$= \frac{\text{reactant consumed (kmol)}}{\text{reactant charged (kmol)}} \times 100 \quad (1)$$

Selectivity (%)

$$= \frac{\text{carboxylic acid formed (kmol)}}{\text{reactant consumed (kmol)}} \times 100 \quad (2)$$

Turn-over No. (kmol/kmol/h)

$$= \frac{\text{carboxylic acid formed (kmol)}}{(\text{catalyst (kmol)})(\text{reaction-time (h)})} \quad (3)$$

#### 3.1. Effect of ligands

The results on the effect of various N- or P-containing ligands at 498 K are presented in Table 1. It was observed that  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  alone was inactive for the carbonylation of ethanol and precipitation of Ni metal occurred at the end of the reaction (See run 1, Table 1). A highly active and selective catalyst was formed when N- or P-containing ligand was used. For most of the ligands tested activity was very good with small variation depending on the type of ligand used. Tributyl phosphite and N,N'-bipyridine gave poor activities while triphenyl phosphite showed no activity. The activity of catalyst varied in a decreasing order with ligands as follows: isoquinoline >  $\text{PPh}_3$  =  $\text{PBu}_3$  = quinoline = 2,4-lutidine = 1,2-bis(diphenylphosphino) ethane > 3-picoline > 2,6-lutidine = 2-picoline > 8-hydroxyquinoline > 2,2'-bipyridine >  $\text{P}(\text{OBu})_3$  >  $\text{P}(\text{OPh})_3$ .

The exact role of ligands in Ni catalyzed carbonylation of alcohols is not well studied and there are only a few reports on the mechanism of the ligand modified Ni catalysts in the carbonylation of alcohols [5,8,10]. Rizkalla has proposed a speculative mechanism for the carbonylation of methanol with  $\text{NiI}_2/\text{PPh}_3$  catalyst system [5]. An active catalytic species of the

Table 2  
Screening of nickel complexes for carbonylation of ethanol

Sr. no.	Catalyst	Time (min)	Conversion (%)	Selectivity			Average activity (kmol/kmol/h)
				propionic acid (%)	C <sub>2</sub> H <sub>6</sub> (%)	C <sub>2</sub> H <sub>4</sub> (%)	
1	NiCl <sub>2</sub> · 6H <sub>2</sub> O + Isoq	190	93.12	95.78	2.32	1.20	46
2	Ni(acac) <sub>2</sub> + Acac	185	92.06	94.84	2.06	1.06	46
3	Ni(OAc) <sub>2</sub> + Isoq	200	97.06	96.34	1.62	0.24	45
4	NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> + PPh <sub>3</sub>	190	93.26	92.40	3.02	2.45	44

Reaction conditions: concentration of catalyst:  $2.1 \times 10^{-2}$  kmol/m<sup>3</sup>; concentration of ligand:  $1.68 \times 10^{-1}$  kmol/m<sup>3</sup>; concentration of ethanol: 3.40 kmol/m<sup>3</sup>; concentration of aq. HI: 0.38 kmol/m<sup>3</sup>; partial pressure of H<sub>2</sub>: 961.52 kPa; partial pressure of CO: 2885 kPa; temperature: 498 K; agitation speed: 550 rpm; Isoq = isoquinoline.

type Ni(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> or Ni(CO)<sub>3</sub>PPh<sub>3</sub> has been proposed. However, from the work of Gauthier-Lafaye and Perron [8] it is indicated that phosphines are alkylated rapidly in the presence of excess methyl iodide. It is highly unlikely that phosphine coordinated Ni complex will be present under reaction conditions to catalyze carbonylation. It is also shown that there is no change in the reaction rate when a quaternary phosphine is used instead of the free phosphine [8]. Recently, Nelson et al. [9] have shown that [Ni(CO)<sub>3</sub>I]<sup>-</sup> is the catalytically active species in the carbonylation of methyl acetate using Ni catalyst, by in-situ IR spectroscopy. Drawing analogy from this work, a probable mechanism for the carbonylation of methanol has been proposed with [Ni(CO)<sub>3</sub>I]<sup>-</sup>

as the active species [10]. It is quite likely that the quaternized N- or P-containing ligand stabilizes anionic Ni complex, by forming an ion pair. The increased concentration of the active catalytic species is a probable explanation for a very high activity observed when ligands are used. Such ion pairs have also been proposed by Braca et al. [11] in the homologation of methyl acetate with Ru complex catalysts. The observed variation in activity may be due to the extent of quaternization of the ligand.

### 3.2. Effect of catalyst precursors

The effect of different types of Ni salts as catalyst precursors was studied at 498 K and the results are presented in Table 2. It was observed

Table 3  
Effect of co-catalysts on the activity and selectivity

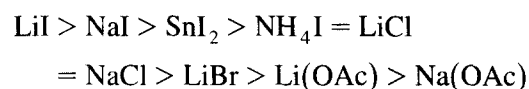
Sr. No.	Co-catalyst	Time (min)	Conversion (%)	Selectivity			Average activity (kmol/kmol/h)
				propionic acid (%)	C <sub>2</sub> H <sub>6</sub> (%)	C <sub>2</sub> H <sub>4</sub> (%)	
1	NiI	190	93.12	95.78	2.32	1.20	46
2	NiI + HI	150	85.36	93.58	2.56	2.03	52
3	LiI	150	96.23	95.97	1.58	1.00	60
4	NaI	150	96.13	94.42	0.65	0.06	59
5	SnI <sub>2</sub>	155	99.79	95.65	0.56	0.24	54
6	NH <sub>4</sub> I	150	92.28	90.62	0.82	0.00	53
7	LiCl	150	84.28	96.62	0.68	0.00	53
8	NaCl	150	88.62	92.32	0.98	1.23	53
9	LiBr	150	76.42	96.42	0.85	0.00	48
10	Li(OAc)	150	52.28	73.52	1.02	0.56	32
11	Na(OAc)	150	48.24	93.08	1.54	1.02	29

Reaction conditions: concentration of catalyst:  $2.1 \times 10^{-2}$  kmol/m<sup>3</sup>; concentration of isoquinoline:  $1.68 \times 10^{-1}$  kmol/m<sup>3</sup>; catalyst:co-catalyst ratio: 1:2; concentration of ethanol: 3.40 kmol/m<sup>3</sup>; concentration of aq. HI: 0.38 kmol/m<sup>3</sup>; partial pressure of H<sub>2</sub>: 961.52 kPa; partial pressure of CO: 2885 kPa; temperature: 498 K; agitation speed: 550 rpm.

that irrespective of the type of Ni precursor used, the average activity as well as the selectivity to propionic acid was the same. This indicates that the active catalyst could be similar in nature in all these cases.

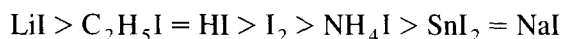
### 3.3. Effect of co-catalysts

The effect of co-catalysts consisting of metal halides or salts on the average activity and selectivity was also studied at 498 K. In all the experiments, co-catalyst:catalyst ratio was kept constant at 2 (Table 3). The activity of the catalyst was enhanced with LiI and NaI as co-catalysts. Other co-catalysts such as NH<sub>4</sub>I, LiCl, LiBr, and NaCl exhibited a slightly lower activity (53–54 kmol/kmol/h). In most of the cases the selectivity was very high (> 95%). In order to confirm that the enhancement in the activity was not due to the I<sup>-</sup> present in the alkali metal iodides, a reaction was carried out with excess HI (equimolar to alkali metal iodides added) which indicated that the average activity with LiI and NaI was higher (compare run No. 2 with 3 and 4 in Table 3). Thus, LiI and NaI exhibit synergistic behaviour with Ni complex catalyst. The activity for different co-catalysts varied in a decreasing order as follows:



### 3.4. Effect of iodide promoters

After confirming the synergistic role of LiI and NaI, the possibility of utilizing LiI or NaI for supplying iodide (instead of ag. HI or ethyl iodide) to form active catalyst as well as alkyl iodide formation during the course of a reaction was tested. For this purpose reactions were carried out using various iodide promoters such as HI, ethyl iodide, SnI<sub>2</sub>, LiI, NaI, KI, NH<sub>4</sub>I and I<sub>2</sub> at 498 K. The results are presented in Table 4. Reaction proceeds smoothly with LiI as a promoter with high activity (52 kmol/kmol/h) and selectivity (> 95%) even in the absence of HI or ethyl iodide. The activity was found to be slightly higher than the reaction with ethyl iodide as well as HI as a promoter (compare run No. 1 with 2 and 4 in Table 4). The activity with I<sub>2</sub> was found to be comparable with HI and ethyl iodide as the promoters. With other metal iodide promoters such as NaI, KI and SnI<sub>2</sub>, poor conversion (17 to 60%) and lower activity (0–8 kmol/kmol/h) was observed. The activity varied with promoters in a decreasing order as follows:



As reported in our previous communication [7], LiI was found to be a better promoter

Table 4  
Effect of iodide promoters on the activity and selectivity

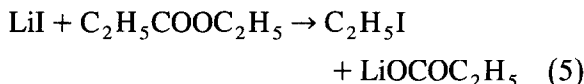
Sr. No.	Promoter	Time (min)	Conversion (%)	Selectivity			Average activity (kmol/kmol/h)
				propionic acid (%)	C <sub>2</sub> H <sub>6</sub> (%)	C <sub>2</sub> H <sub>4</sub> (%)	
1	LiI	176	96.76	96.65	1.68	1.02	52
2	C <sub>2</sub> H <sub>5</sub> I	190	88.22	88.25	7.02	1.34	40
3	HI	178	81.50	89.83	7.86	1.87	40
4	I <sub>2</sub>	200	78.37	96.34	1.86	2.14	37
5	NH <sub>4</sub> I	200	60.63	93.64	3.72	0.38	32
6	SnI <sub>2</sub>	200	22.26	75.77	11.22	10.59	08
7	NaI	200	17.03	94.12	4.38	1.32	08
8	KI	200	0.12	0.00	0.00	0.00	00

Reaction conditions: concentration of catalyst:  $2.1 \times 10^{-2}$  kmol/m<sup>3</sup>; concentration of isoquinoline:  $1.68 \times 10^{-1}$  kmol/m<sup>3</sup>; concentration of ethanol: 3.40 kmol/m<sup>3</sup>; concentration of promoter: 0.60 kmol/m<sup>3</sup>; partial pressure of H<sub>2</sub>: 961.52 kPa; partial pressure of CO: 2885 kPa; temperature: 498 K; agitation speed: 550 rpm.

compared to aq. HI as well as ethyl iodide. High activity obtained with LiI compared to other metal iodide promoters as well as aq. HI and ethyl iodide may be due to increased concentration of active catalytic species  $[\text{Ni}(\text{CO})_3\text{I}]^-$  by stabilizing it as an ion pair as shown below [12]:



Also LiI restricts the formation of excess ethyl iodide, which can lead to side products ethane and ethylene. Ethyl iodide can form LiI and ethyl propionate as follows



For other metal iodides, the ethyl iodide formation will be slow due to higher stability of metal iodides [13]. Higher stability of metal iodides will also result in a lower concentration of active catalytic species  $[\text{Ni}(\text{CO})_3\text{I}]^-$ . Thus, the observed variation in the activity is a coupled effect of ethyl iodide formation in negligible quantity and stabilization of the active catalytic species. Polichnowski [13] has explained the influence of LiI in the carbonylation of methyl acetate with Rh catalyst on the basis of

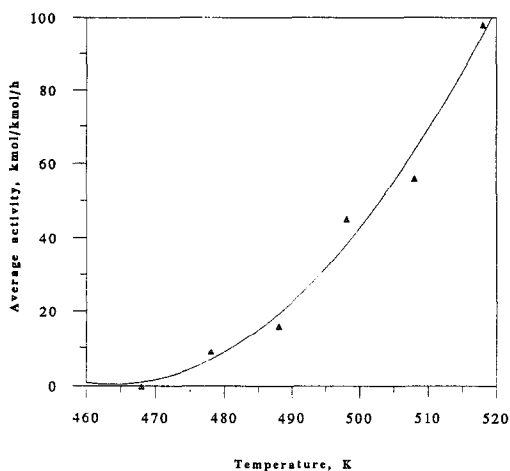


Fig. 1. Effect of temperature on average activity. Reaction conditions: concentration of ethanol:  $3.4 \text{ kmol/m}^3$ ; concentration of HI:  $0.38 \text{ kmol/m}^3$ ; concentration of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ :  $2.1 \times 10^{-2} \text{ kmol/m}^3$ ; concentration of isoquinoline:  $16.8 \times 10^{-2} \text{ kmol/m}^3$ ; partial pressure of CO: 2885 kPa; partial pressure of  $\text{H}_2$ : 961.52 kPa.

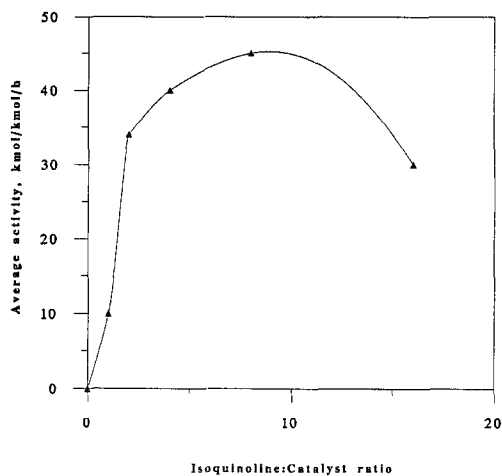


Fig. 2. Effect of isoquinoline:catalyst ratio on average activity. Reaction conditions: concentration of ethanol:  $3.4 \text{ kmol/m}^3$ ; concentration of HI:  $0.38 \text{ kmol/m}^3$ ; concentration of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ :  $2.1 \times 10^{-2} \text{ kmol/m}^3$ ; partial pressure of CO: 2885 kPa; partial pressure of  $\text{H}_2$ : 961.52 kPa; temperature: 498 K.

the formation of methyl iodide and lithium acetate.

### 3.5. Effect of temperature

The effect of temperature on the activity is shown in Fig. 1. Below 468 K, no reaction occurred indicating that certain minimum temperature is necessary for the initiation of the reaction. It was observed that the activity of catalyst increased with increase in temperature beyond 468 K but the selectivity was not affected.

### 3.6. Effect of isoquinoline:Ni ratio

The effect of isoquinoline:Ni ratio on the activity was studied in a range of 0–16. In all these experiments, the catalyst concentration was kept constant at  $2.1 \times 10^{-2} \text{ kmol/m}^3$ . The results are presented in Fig. 2. When isoquinoline was not used, the reaction did not proceed and precipitation of the catalyst as nickel metal and  $\text{NiI}_2$  was observed at the end of the reaction. IR analysis of the gas phase at the end of the reaction showed the presence of inactive

$\text{Ni}(\text{CO})_4$  [14]. This explains the catalyst deactivation and precipitation of nickel metal by decomposition of  $\text{Ni}(\text{CO})_4$  at the end of the reaction. However, in the presence of isoquinoline, active catalyst was obtained with high selectivity (95%) and the precipitation of nickel was not observed. At low isoquinoline: catalyst ratio ( $< 4$ ) the formation of  $\text{Ni}(\text{CO})_4$  and  $\text{NiI}_2$  dominates leading to lower average activity (Fig. 2). As the concentration of isoquinoline is increased further, formation of  $\text{Ni}(\text{CO})_4$  begins to decrease, with increase in the formation of active Ni complex concentration. At a isoquinoline:catalyst ratio of 8, precipitation of the catalyst was not observed. With further increase in isoquinoline concentration, the average activity of the catalyst decreased.

As explained earlier, the role of isoquinoline may be to stabilize the active catalytic species  $[\text{Ni}(\text{CO})_3\text{I}]^-$  by formatting an ion pair after quaternization. As isoquinoline:Ni ratio is increased, the formation of ion pair increases thereby reducing quantity of inactive catalytic species,  $\text{Ni}(\text{CO})_4$  and  $\text{NiI}_2$ . This results in increase in catalytic activity. At very high ratios ( $> 16$ ) probably some inactive species is formed resulting in lower activity.

### 3.7. Effect of catalyst concentration

The effect of catalyst concentration on the activity was studied at a constant ligand concentration of  $1.68 \times 10^{-1} \text{ kmol/m}^3$  and the results are presented in Table 5. The activity expressed as  $\text{kmol/kmol/h}$  was found to decrease with increase in catalyst concentration. It is expected

Table 5  
Effect of catalyst concentration on average activity and initial rate

Sr. No.	Catalyst concentration ( $\times 10^2 \text{ kmol/m}^3$ )	Average activity ( $\text{kmol/kmol/h}$ )		Initial rate ( $\times 10^4 \text{ kmol/m}^3/\text{s}$ )	
		498 K	508 K	498 K	508 K
1	1.05	48	86	1.72	2.5
2	2.1	45	63	3.5	5
3	4.2	19	34	4.3	8.65

Reaction conditions: concentration of isoquinoline:  $1.68 \times 10^{-1} \text{ kmol/m}^3$ ; concentration of ethanol:  $3.40 \text{ kmol/m}^3$ ; concentration of HI:  $0.38 \text{ kmol/m}^3$ ; partial pressure of  $\text{H}_2$ : 961.52 kPa; partial pressure of CO: 2885 kPa; agitation speed: 550 rpm.

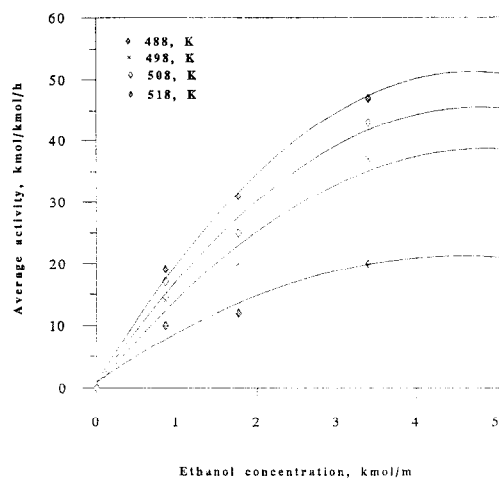


Fig. 3. Effect of initial ethanol concentration on average activity. Reaction conditions: concentration of HI:  $0.38 \text{ kmol/m}^3$ ; concentration of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ :  $2.1 \times 10^{-2} \text{ kmol/m}^3$ ; concentration of isoquinoline:  $16.8 \times 10^{-2} \text{ kmol/m}^3$ ; partial pressure of CO: 2885 kPa; partial pressure of  $\text{H}_2$ : 961.52 kPa.

that the activity of the catalyst should be constant with variation of its concentration, however, in this case the initial rate of reaction (see Table 5) was not found to be linearly dependent on catalyst concentration and hence a drop in activity. A possible reason for this may be the solubility limitations of the catalyst at higher concentrations.

### 3.8. Effect of ethanol concentration

The effect of ethanol concentration is shown in Fig. 3. The activity increases with increase in ethanol concentration upto  $4 \text{ kmol/m}^3$ . With further increase the activity was found to be independent of ethanol concentration (Fig. 3). In all the cases the selectivity to propionic acid

was  $> 95\%$ . At higher concentrations of ethanol, the concentration of water also increases at the start of the reaction (by esterification of ethanol) and hence, the observed trend is a combined result of changes in ethanol and water concentrations. In order to study the effect of water, a few experiments were carried out with addition of water in the beginning of the experiments, the results of which are presented below.

### 3.9. Effect of water concentration

The effect of water concentration was studied at 498 K and the results are presented in Fig. 4. It was observed that the activity decreased with increase in water concentration without affecting the selectivity, similar to the earlier studies on methanol carbonylation [5].

### 3.10. Effect of iodide promoter concentration

The effect of concentration of iodide promoters such as HI and ethyl iodide on the activity and selectivity was studied in a concentration range of 0.19 to 1.506  $\text{kmol/m}^3$ . The activity

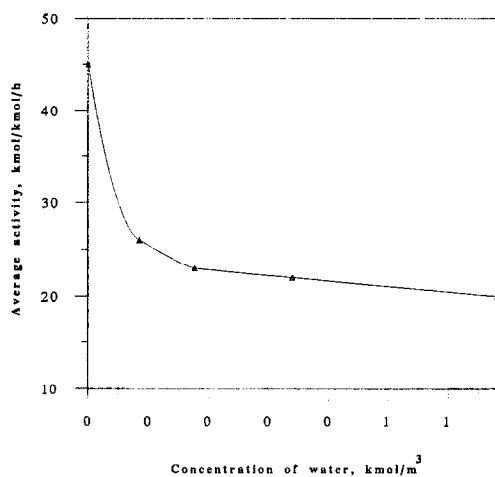


Fig. 4. Effect of water concentration on average activity. Reaction conditions: concentration of ethanol:  $3.4 \text{ kmol/m}^3$ ; concentration of HI:  $0.38 \text{ kmol/m}^3$ ; concentration of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ :  $2.1 \times 10^{-2} \text{ kmol/m}^3$ ; concentration of isoquinoline:  $16.8 \times 10^{-2} \text{ kmol/m}^3$ ; partial pressure of CO: 2885 kPa; partial pressure of  $\text{H}_2$ : 961.52 kPa; temperature: 498 K.

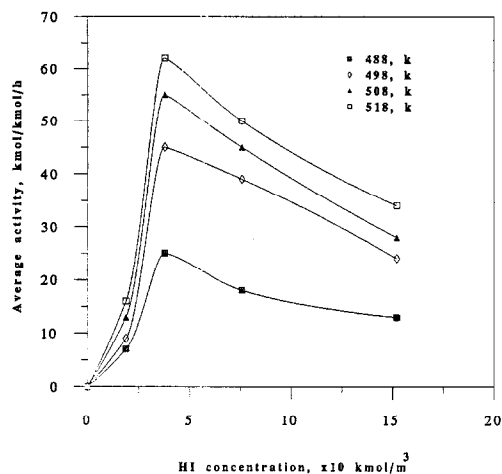
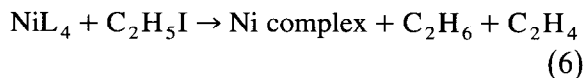


Fig. 5. Effect of HI concentration on average activity. Reaction conditions: concentration of ethanol:  $3.4 \text{ kmol/m}^3$ ; concentration of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ :  $2.1 \times 10^{-2} \text{ kmol/m}^3$ ; concentration of isoquinoline:  $16.8 \times 10^{-2} \text{ kmol/m}^3$ ; partial pressure of CO: 2885 kPa; partial pressure of  $\text{H}_2$ : 961.52 kPa.

increases with increase in HI concentration upto  $0.4 \text{ kmol/m}^3$  and with further increase, the activity drops sharply (Fig. 5). At lower HI concentration ( $0.19 \text{ kmol/m}^3$ ) inactive  $\text{Ni}(\text{CO})_4$  is formed. With increase in HI concentration (upto  $0.4 \text{ kmol/m}^3$ ) inactive nickel carbonyl formation is not observed (as indicated by IR analysis of the gas phase) thus increasing the active catalyst concentration. However, with further increase in HI concentration, the activity drops substantially due to formation of the side products such as ethane and ethylene. The formation of ethane and ethylene is known to take place by oxidative addition of ethyl iodide (formed from ethanol and HI) to Ni complex as shown below [15]:



With increase in HI concentration, ethyl iodide formation increases substantially leading to increased formation of ethane and ethylene. Thus, at higher HI concentration ( $1.506 \text{ kmol/m}^3$ ) no absorption of CO was observed even though propionic acid was formed along with ethane and ethylene. The results on the



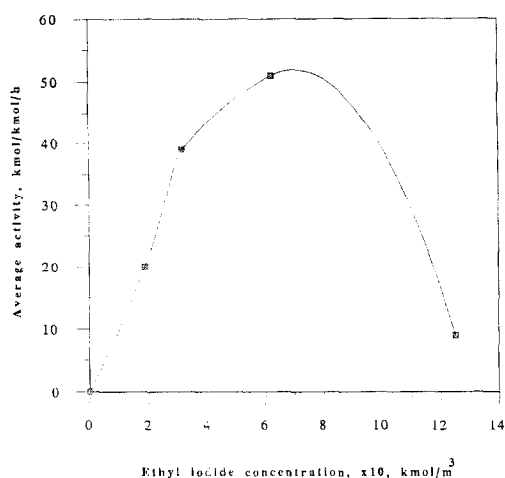


Fig. 6. Effect of ethyl iodide concentration on average activity. Reaction conditions: concentration of ethanol:  $3.4 \text{ kmol/m}^3$ ; concentration of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ :  $2.1 \times 10^{-2} \text{ kmol/m}^3$ ; concentration of isoquinoline:  $16.8 \times 10^{-2} \text{ kmol/m}^3$ ; partial pressure of CO: 2885 kPa; partial pressure of  $\text{H}_2$ : 961.52 kPa; temperature: 498 K.

selectivity behavior are presented in Table 6, which indicate that the activity, conversion and selectivity decrease as the concentration of HI increases. Therefore, for all further work, HI concentration of  $0.38 \text{ kmol/m}^3$  was used. Similar trend was also observed when ethyl iodide was used as a promoter (see Fig. 6).

### 3.11. Effect of hydrogen partial pressure

The effect of hydrogen partial pressure on the activity was studied in a range of 0 to 3297 kPa, and in a temperature range of 488–518 (Fig. 7). In all these experiments, the CO partial pressure was kept constant at 2885 kPa. The activity was found to increase with increase in hydrogen partial pressure upto 2061 kPa. Beyond this the

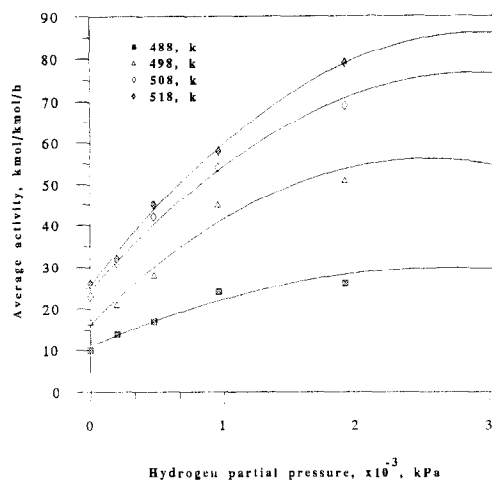


Fig. 7. Effect of  $\text{H}_2$  partial pressure on average activity. Reaction conditions: concentration of ethanol:  $3.4 \text{ kmol/m}^3$ ; concentration of HI:  $0.38 \text{ kmol/m}^3$ ; concentration of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ :  $2.1 \times 10^{-2} \text{ kmol/m}^3$ ; concentration of isoquinoline:  $16.8 \times 10^{-2} \text{ kmol/m}^3$ ; partial pressure of CO: 2885 kPa.

average activity was independent of hydrogen partial pressure (Fig. 7). There is no evidence at this stage to explain the exact role of hydrogen, however, as suggested by Rizkalla [5] hydrogen may accelerate the reduction of Ni(II) species to active Ni(0) species. From practical point of view, the hydrogen effect as a promoter is very useful.

### 3.12. Effect of CO partial pressure

The effect of CO partial pressure on the activity was studied in a range of 961 to 4259 kPa at different temperature (488–508 K). In all these experiments, partial pressure of hydrogen

Table 6  
Effect of HI concentration on the activity and selectivity to propionic acid

Sr. No.	HI concentration ( $\text{kmol/m}^3$ )	Time (min)	Conversion (%)	Selectivity <sup>a</sup> (%)	Average activity ( $\text{kmol/kmol/h}$ )
1	0.19	140	8.67	84.80	9
2	0.38	190	92.7	94.78	45
3	0.76	190	87.33	87.60	39
4	1.52	190	59.78	78.74	24

Reaction conditions: concentration of catalyst:  $2.1 \times 10^{-2} \text{ kmol/m}^3$ ; concentration of isoquinoline:  $1.68 \times 10^{-1} \text{ kmol/m}^3$ ; concentration of ethanol:  $3.40 \text{ kmol/m}^3$ ; partial pressure of  $\text{H}_2$ : 961.52 kPa; partial pressure of CO: 2885 kPa; temperature: 498 K; agitation speed: 550 rpm.

<sup>a</sup> Lower selectivity due to formation of ethane and ethylene.

was kept constant at 961 kPa. Activity of the catalyst first increases with increase in CO partial pressure upto 2885 kPa, and remains constant with further increase in CO partial pressure (Fig. 8). It is known from the earlier work on the carbonylation of methanol [5] that precipitation of catalyst in the form of  $\text{NiI}_2$  takes place at lower CO partial pressure. Thus, higher CO partial pressure is required for the formation of active nickel carbonyl species. The observed trends of increase in average activity with increase in CO partial pressure can be explained on the basis of increase in the concentration of active nickel carbonyl complex  $[\text{Ni}(\text{CO})_3\text{I}]^-$  (upto 2885 kPa). With further increase in CO partial pressure, average rate is independent of CO partial pressure, indicating that all Ni is converted to active catalytic species.

### 3.13. Catalyst recycle studies

Catalyst recycle experiments were carried out with the aim of studying the stability and reusability of the catalyst. The recycle experiments were carried out as described in the experimental section and the results are presented in Table 7. It was observed that the activity of

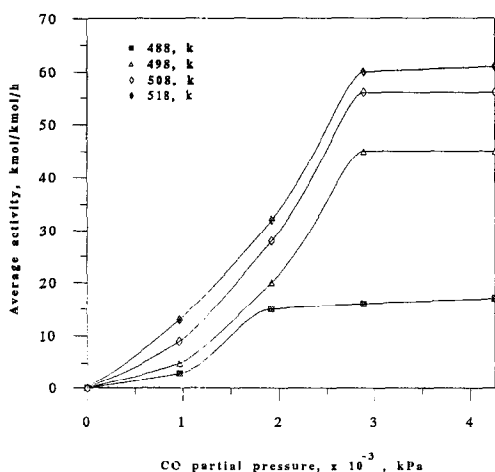


Fig. 8. Effect of CO partial pressure on average activity. Reaction conditions: concentration of ethanol:  $3.4 \text{ kmol/m}^3$ ; concentration of HI:  $0.38 \text{ kmol/m}^3$ ; concentration of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ :  $2.1 \times 10^{-2} \text{ kmol/m}^3$ ; concentration of isoquinoline:  $16.8 \times 10^{-2} \text{ kmol/m}^3$ ; partial pressure of  $\text{H}_2$ : 961.52 kPa.

Table 7  
Results on the catalyst recycle experiments

Sr. No.	Recycle No.	Average activity
1	0	46
2	1	46
3	2	45
4	3	44
5	4	42

Reaction conditions: concentration of catalyst:  $2.1 \times 10^{-2} \text{ kmol/m}^3$ ; concentration of isoquinoline:  $1.68 \times 10^{-1} \text{ kmol/m}^3$ ; concentration of HI:  $0.38 \text{ kmol/m}^3$ ; concentration of ethanol:  $3.40 \text{ kmol/m}^3$ ; partial pressure of  $\text{H}_2$ : 961.52 kPa; partial pressure of CO: 2885 kPa; temperature: 498 K; agitation speed: 550 rpm.

catalyst is retained even after four recycles with high selectivity ( $> 92\%$ ). Thus, the catalyst system was found to be very stable and was not deactivated even after four recycle runs when HI was used as a promoter.

## 4. Conclusions

Carbonylation of ethanol was studied using  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  as a catalyst precursor and isoquinoline as a ligand. Following observations were made:

(a) N- or P-containing ligands are necessary for catalytic activity. (b) Metal iodides such as LiI and NaI used as co-catalysts enhance the activity of the catalyst without affecting selectivity. (c) Ethane and ethylene are formed as side products, leading to lower selectivity to propionic acid. (d) With increase in aqueous HI concentration activity as well as selectivity are decreased due to increased formation of ethane and ethylene. (e) Catalyst activity is retained even after 4 recycles.

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