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NOTE

Carbonylation of Methanol Using Nickel Complex Catalyst: A Kinetic Study[1]

The carbonylation of alcohols to give carboxylic acids is of commercial importance, as evidenced by the Monsanto process for the manufacture of acetic acid (1). Several transition metal complexes consisting of Co, Rh, Ir, Ru, and Ni are known to catalyze the carbonylation of alcohols, but Rh was found to be the most active and selective catalyst (2). Recent reports (3–7) described Ni catalyzed carbonylation of methanol at lower temperatures and pressures giving high activity and selectivity. This development is particularly important as it will provide a cheaper and alternative catalyst to rhodium. For NiI_2–PPh_3 (3) and $Ni(PPh_3)_2(CO)_2$–PPh_3 (6) catalysts with methyl iodide as a promoter, methanol conversion of 98% with a selectivity of 75 to 90% has been reported. Further, Kelkar *et al.* (5) have reported that $Ni(isoq)_4Cl_2$ as a catalyst is highly active with 99% conversion and 90–98% selectivity for carbonylation of methanol as well as higher alcohols. Rizkalla (6) has also investigated the influence of catalyst, methyl iodide, methanol, and water concentrations and partial pressure of CO and hydrogen on the rate of reaction for NiI_2–PPh_3 system; however, this study was limited to only one temperature (453 K) and no rate equation has been proposed. For the Ni–isoquinoline catalyst system, no information on the kinetics and mechanism is available in the previous literature. Considering the potential importance of the $NiCl_2 \cdot 6H_2O$–isoquinoline catalyzed carbonylation of methanol as an alternative process of the future, a detailed investigation of the reaction kinetics would be most useful. Hence, the present work was undertaken to study the intrinsic kinetics of the reaction using the Ni–isoquinoline catalyst system and to develop a rate equation. Applicability of the rate model in predicting the concentration–time profiles in a batch reactor is also demonstrated.

Carbonylation experiments were carried out in a 3×10^{-4} m^3 autoclave (Hastelloy C-276, supplied by Parr Instruments Co., USA) as described elsewhere (8). In a typical experiment, nickel chloride hexahydrate (2.1×10^{-6} kmol), isoquinoline (16.8×10^{-6} kmol), methanol (4.94×10^{-4} kmol), methyl iodide (8.0×10^{-5} kmol), and acetic acid (1.27×10^{-3} kmol) were charged to the reactor. The contents were flushed first with nitrogen and then with CO and heated to 498 K. After the temperature was attained, hydrogen was introduced to a partial pressure of 961.52 kPa and CO to a partial pressure of 2885.27 kPa. A liquid sample was withdrawn, and the reaction was initiated by switching the stirrer on. In order to carry out the reaction at a constant pressure, CO was supplied from a reservoir through a constant pressure regulator as it was consumed due to reaction. The pressure in the reservoir was recorded using a pressure transducer and a recorder system to follow the progress of the reaction. The reaction was carried out until CO absorption stopped completely, indicating complete conversion of methyl acetate. The GC analysis of the liquid sample drawn after heating the reactor to 498 K indicated that almost all the charged methanol was converted to methyl acetate quantitatively; hence methyl acetate was considered as the substrate for carbonylation reaction. At the end of the reaction, GC analysis of the liquid and gas phase was carried out which indicated nearly complete conversion of methyl acetate with 99% selectivity to acetic acid. Traces (<0.5%) of methane were detected in the gas phase. Orsat analysis of the gas phase showed <1% of CO_2 formation (by water–gas shift reaction). The quantitative analysis of the carbonylation products was done by an external standard method using HP 5840 gas chromatograph. The column used was 1/8 in. diameter and 8 ft. long packed with 5% OV-17 on chromosorb W-AW 80–100 mesh. The gas phase was analyzed for methane and dimethyl ether by gas chromatography using a 6 ft. long Porapak Q column. Since selectivity to acetic acid based on CO and methanol was very high, CO absorption vs time data for low conversions (<10%) were used for initial rate calculations.

Preliminary experiments were carried out using the $NiCl_2 \cdot 6H_2O$–isoquinoline catalyst system with methyl iodide and hydrogen as promoters. Acetic acid was found to be the best solvent for this reaction, since methanol was completely converted to methyl acetate, which was stable at 498 K. With other solvents, dimethyl ether formation led to a rise in the pressure, and the conversion and selectivity to acetic acid was very poor. Further work was therefore carried out using acetic acid as a solvent. These experiments were performed at 498 K with hydrogen partial pressure of 961.52 kPa and CO partial pressure of 2885.27 kPa.

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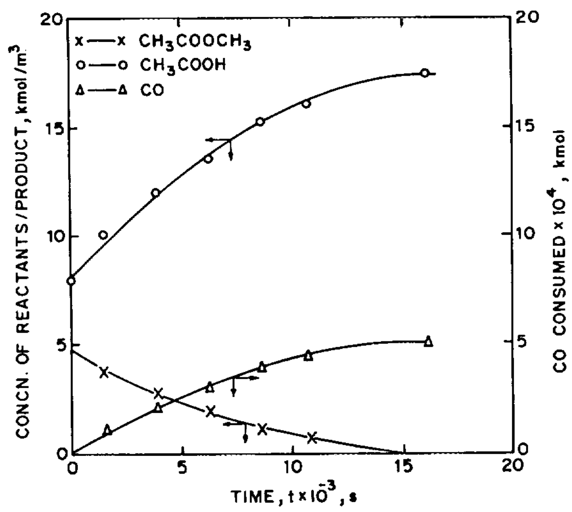

FIG. 1. Concentration–time profile for carbonylation of methanol at 488 K. Reaction conditions: concentration of $NiCl_2$, 2.10 × 10^{-2} kmol/m^3; concentration of isoquinoline, 16.8 × 10^{-2} kmol/m^3; concentration of CH_3I, 0.8 kmol/m^3; partial pressure of CO, 2885.27 kPa; and partial pressure of H_2, 961.52 kPa.

At the end of the reaction, methyl acetate conversion as well as selectivity to acetic acid was >98%. A typical plot showing the reactant consumed and products formed as a function of time is presented in Fig. 1. The gas-phase analysis showed 1 to 1.5% methane formation. It was observed that the reproducibility of the carbonylation experiments was within ±5–7% error.

The various reactions involved during carbonylation are

$$CH_3OH + CH_3COOH \leftrightarrow CH_3COOCH_3 + H_2O \quad [1]$$

$$CH_3COOCH_3 + HI \leftrightarrow CH_3I + CH_3COOH \quad [2]$$

$$CH_3I + CO \xleftrightarrow{\text{catalyst}} CH_3COI \quad [3]$$

$$CH_3COI + H_2O \rightarrow CH_3COOH + HI. \quad [4]$$

For the present case, charged methanol was almost completely converted to methyl acetate and water by the time the reaction temperature was attained. Hence, the overall reaction can be represented as

$$CH_3COOCH_3 + CO + H_2O \xrightarrow[\text{HI}]{\text{catalyst}} 2CH_3COOH. \quad [5]$$

In order to understand the intrinsic kinetics of carbonylation of methanol using the $NiCl_2 \cdot 6H_2O$–isoquinoline catalyst system, the effect of concentration of $NiCl_2$, methyl iodide, methyl acetate, water, and partial pressure of CO and hydrogen on the rate of reaction was studied in a temperature range of 478–508 K. In these experiments CO consumed as a function of time was monitored from the observed pressure drop (in the reservoir) vs time data. The reaction rates were calculated from these data in the initial region (<10% conversion of methyl acetate).

The effect of $NiCl_2 \cdot 6H_2O$ concentration on the rate of reaction is shown in Fig. 2. The rate was found to be 0.89th order with catalyst concentration. The effect of agitation speed on the rate of carbonylation was studied for higher concentrations of $NiCl_2 \cdot 6H_2O$ which indicated that the rate is independent of agitation speed, and hence mass transfer is not a rate limiting process. Further, a quantitative criteria (9) was also used to evaluate the significance of gas–liquid mass transfer based on the comparison of the observed rate with the maximum possible rate of mass transfer. Accordingly, a factor ϕ defined as (R_A/k_LaA^*) should be less than 0.1 for kinetic control. The values of k_La, the gas to liquid mass transfer coefficient, reported (10) for the same equipment were used. The solubility of CO in the reaction medium was calculated from a correlation (11) proposed earlier for CO–acetic acid–water system. For the data at different catalyst concentrations, ϕ values were found to be in a range of 8.9 × 10^{-3} to 7.8 × 10^{-2}, indicating that the mass transfer resistance is negligible and the reaction occurs essentially in the kinetically controlled regime.

The effect of concentration of methanol (charged) on the rate of reaction is shown in Fig. 3 for 478–508 K. In these experiments, initial methanol concentration was actually varied, which was almost completely converted to methyl acetate and water before the carbonylation run was started. It was observed that the rate first increases with an increase in methanol concentration and shows no dependence on the concentration of methanol in the higher

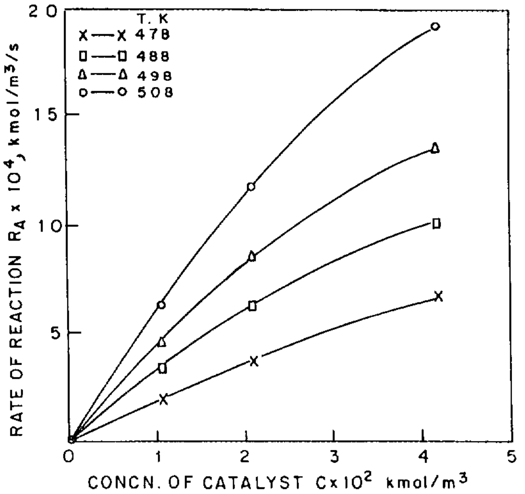

FIG. 2. Effect of catalyst concentration on rate of carbonylation. Reaction conditions: concentration of methanol, 4.94 kmol/m^3; concentration isoquinoline, 16.8 × 10^{-2} kmol/m^3; concentration of CH_3I, 0.80 kmol/m^3; partial pressure of CO, 2885.27 kPa; partial pressure of H_2, 961.52 kPa.

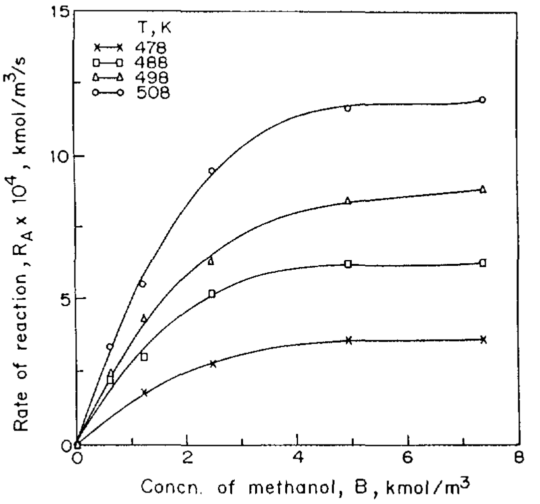

FIG. 3. Effect of methanol concentration on rate of carbonylation. Reaction conditions: concentration of $NiCl_2 \cdot 6H_2O$, 2.1×10^{-2} kmol/m³; concentration of isoquinoline, 16.8×10^{-2} kmol/m³; concentration of CH_3I, 0.80 kmol/m³; partial pressure of CO, 2885.27 kPa; partial pressure of H_2, 961.52 kPa.

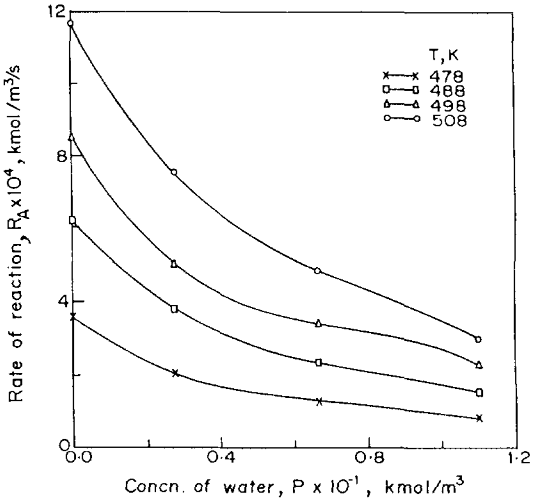

FIG. 4. Effect of water concentration on rate of carbonylation. Reaction conditions: concentration of methanol, 4.94 kmol/m³; concentration of $NiCl_2 \cdot 6H_2O$, 2.1×10^{-2} kmol/m³; concentration of isoquinoline, 16.8×10^{-2} kmol/m³; concentration of CH_3I, 0.80 kmol/m³; partial pressure of CO, 2885.27, kPa; partial pressure of H_2, 961.52 kPa.

range (>4.94 kmol/m³). In this case it is important to note that with an increase in methanol concentration, the methyl acetate as well as water concentrations increase, and hence the observations reported in Fig. 3 are a result of the combined influence of a change in the concentrations of methyl acetate and water. In evaluation of rate parameters, this variation has been taken into account. In order to check the effect of water concentration independently, a few experiments were carried out in which only the water concentration was varied (water was added at the beginning of the reaction) keeping all other conditions constant. The results are shown in Fig. 4 and clearly indicate inhibition of the rate of carbonylation in the presence of water.

The effect of methyl iodide concentration is shown in Fig. 5 for 478–508 K and indicates a first order dependence. The effect of CO partial pressure on the rate of reaction is shown in Fig. 6 for different temperatures (478–508 K). The initial rate of reaction was found to be linearly dependent on CO at lower pressures, but at higher pressures, the rate was independent of CO (Fig. 6). The effect of hydrogen (promoter) partial pressure on the initial rate of reaction is shown in Fig. 7. It was observed that the rate increases with increase in hydrogen partial pressure. The actual role of hydrogen is not yet clearly understood. It is quite likely that hydrogen enhances the formation of an active catalytic species $[Ni(CO)_3I]^-$ during the catalytic cycle.

The rate data were found to be represented by the following form of rate equation:

$$R_A = \frac{k_0 A^* B_\iota C^{0.89} E(1 + 0.0014 D^{0.9})}{(1 + K_A A^*)(1 + K_B B_\iota)(1 + K_P P_\iota)^2}. \qquad [6]$$

The values of rate parameters k_0, K_A, K_B, and K_P evaluated by using the optimisation routine of Marquardt (12) are presented in Table 1. The average error between the predicted and experimental rates was found to be ±6–8%. The activation energy calculated from the Arrhenius relation of ln k_0 vs $1/T$ was found to be 5.88×10^4 kJ/kmol.

In order to verify the applicability of the kinetic model under a wide range of conditions integral batch reactor

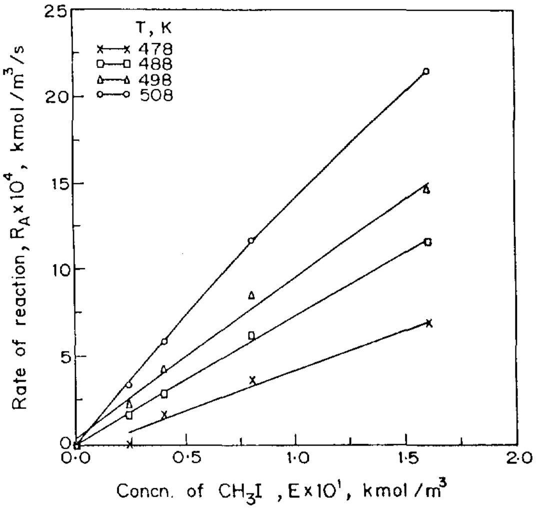

FIG. 5. Effect of methyl iodide concentration on rate of carbonylation. Reaction conditions: concentration of methanol, 4.94 kmol/m³; concentration of $NiCl_2 \cdot 6H_2O$, 2.1×10^{-2} kmol/m³; concentration of isoquinoline, 16.8×10^{-2} kmol/m³; partial pressure of CO, 2885.27 kPa; partial pressure of H_2, 961.52 kPa.

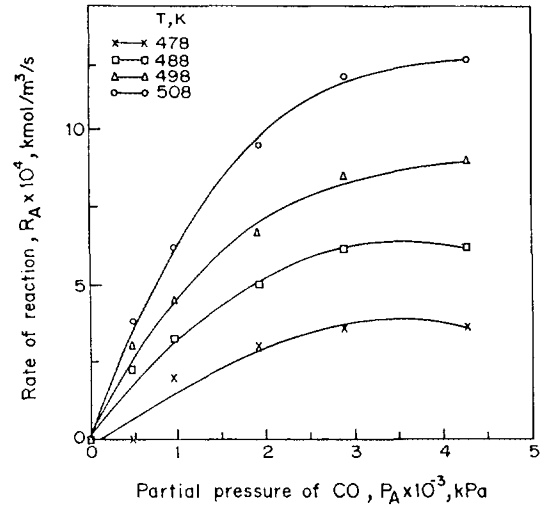

FIG. 6. Effect of partial pressure of CO on rate of carbonylation. Reaction conditions: concentration of methanol, 4.94 kmol/m³; concentration of $NiCl_2 \cdot 6H_2O$, 2.1 × 10^{-2} kmol/m³; concentration of isoquinoline, 16.8 × 10^{-2} kmol/m³; concentration of CH_3I, 0.80 kmol/m³; partial pressure of H_2, 961.52 kPa.

data were also obtained. In these experiments, the variation of concentration of reactants (methyl acetate and water) and of product (acetic acid) as a function of time was observed (see Fig. 1). The variation of concentration of methyl acetate, water, and acetic acid at constant catalyst and methyl iodide concentrations and hydrogen partial pressure can be represented by

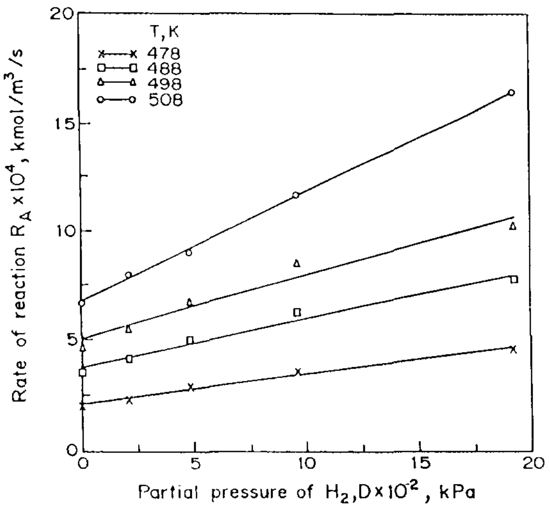

FIG. 7. Effect of partial pressure of hydrogen on rate of carbonylation. Reaction conditions: concentration of methanol, 4.94 kmol/m³; concentration of $NiCl_2 \cdot 6H_2O$, 2.1 × 10^{-2} kmol/m³; concentration of isoquinoline, 16.8 × 10^{-2} kmol/m³; concentration of CH_3I, 0.80 kmol/m³; partial pressure of CO, 2885.27 kPa.

TABLE 1

Rate Constants for Carbonylation of Methanol to Acetic Acid

Temp (K)	k_0 ($kmol^{-2.89}$ $m^{8.67}$ s^{-1})	K_A (m³/kmol)	$K_B \times 10^{-3}$ (m³/kmol)	K_P (m³/kmol)
478	0.0912	13.91	1.18	0.131
488	0.1330	12.86	9.00	0.110
498	0.1680	12.45	8.46	0.100
508	0.2200	11.97	7.85	0.097

Note. $a = 0.0014$; $b = 0.9$.

$$\frac{-dB_t}{dt} = \frac{k'A^*B_t}{(1 + K_A\mathrm{A}^*)(1 + K_BB_t)(1 + K_PP_t)^2} \qquad [7]$$

$$\frac{-dP_t}{dt} = \frac{kA^*B_t}{(1 + K_AA^*)(1 + K_BB_t)(1 + K_PP_t)^2} \qquad [8]$$

$$\frac{dF_t}{dt} = \frac{2kA^*B_t}{(1 + K_AA^*)(1 + K_BB_t)(1 + K_PP_t)^2}. \qquad [9]$$

The initial conditions are

$$\text{at } t = 0, \quad B_1 = B_{10};\ P_1 = \mathrm{P}_{10};\ \text{and } F_1 = F_{10}$$

The initial concentration of water P_{10}, represents water formed in esterification plus the extra quantity added if any. B_1, P_1, and F_1 represent concentrations (kmol/m³) of methyl acetate, water, and acetic acid, respectively. The solubility of CO varies with change in the concentrations of methyl acetate, acetic acid, and water and hence with time. The Henry's law constant H was evaluated from the correlation proposed by Dake and Chaudhari (11). The vapour pressure of reaction medium also changes with variation in the concentrations. The appropriate corrections for the change in A^* were made in the above analysis.

In order to predict the concentration–time data in a batch reactor, Eqs. [7] to [9] with appropriate corrections for change in A^* with concentrations were solved numerically by using the Runge–Kutta method. For this purpose, the rate parameters determined based on initial rate data (see Table 1) were used. The experimental and predicted concentration–time profiles are preseted in Fig. 8. The agreement was found to be excellent which suggests that the rate model proposed here can be reliably used for design and scale up purposes.

Ni-catalyzed carbonylation has been studied by various authors; however, the nature of active catalytic species in the catalytic cycle has not been thoroughly investigated. Rizkalla (6) has described a speculative mechanism for carbonylation of methanol with a NiI_2–PPh_3 catalyst system in which the active species of the type $Ni(CO)_2(PPh_3)_2$ or $Ni(CO)_3PPh_3$ has been suggested. Gauthier and Perron

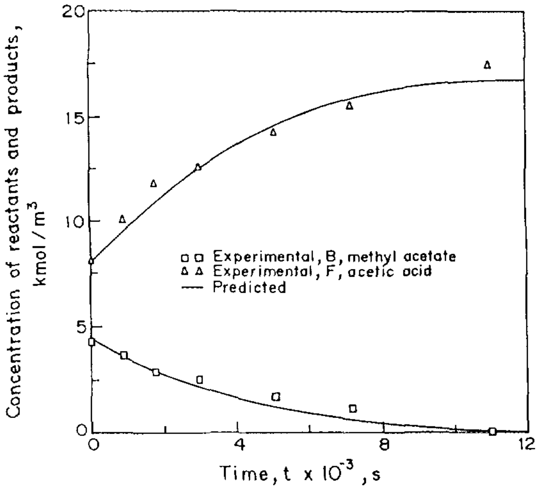

FIG. 8. Typical concentration vs time plot at 498 K. Reaction conditions: concentration of methanol, 4.94 kmol/m^3; concentration of $NiCl_2 \cdot 6H_2O$, 2.1×10^{-2} kmol/m^3; concentration of Isoquinoline, 16.8×10^{-2} kmol/m^3; concentration of CH_3I, 0.80 kmol/m^3; partial pressure of CO, 2855.27 kPa; partial pressure of H_2, 961.52 kPa; reaction volume, 10^{-4} m^3.

(14) have shown in their study that quaternary phosphonium salts were also effective as ligands for this reaction without any change in reaction rate, indicating that the nickel phosphine complex proposed by Rizkalla (6) may not be the catalytic intermediate in carbonylation of methanol.

Nelson and co-workers (13) have studied the carbonylation of methyl acetate in detail using a nickel catalyst with LiI and methyl iodide as promoters and pyrrolidinone as a solvent. They have identified $[Ni(CO)_3I]^-$ as the active catalytic species by *in situ* IR spectroscopy. Drawing analogy from these results, a catalytic cycle for carbonylation of methanol has been proposed with $[Ni(CO)_3I]^-$ as the active catalytic species (13). This mechanism explains the role of hydrogen and carbon monoxide. Hydrogen is necessary for reduction of Ni^{2+} species to active Ni(0), and appropriate CO pressure should be maintained to keep the catalyst in active form. However, the role of ligand is not understood by this mechanism. The ligand may be necessary for stabilising the active species ($[Ni(CO)_3I]^-$) since N- and P-containing ligands are necessary for the catalytic activity. Also, the promoting effect of quarternised phosphonium salt indicates that this ligand may help in stabilising $[Ni(CO)_3I]^-$. Alternatively, isoquinoline can replace one CO ligand from the species $[Ni(CO)_3I]^-$ to form complex of the type $[Ni(Isoq)_x(CO)_{3-x}I]^-$ (Isoq = isoquinoline). This can explain the necessity of isoquinoline for catalytic activity. However, further work is necessary to characterise the catalytically active species and to understand the role of isoquinoline completely.

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