

# Hydroformylation of propylene in supercritical CO<sub>2</sub> + H<sub>2</sub>O and supercritical propylene + H<sub>2</sub>O

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## Abstract

Hydroformylation of propylene has been carried out in supercritical CO<sub>2</sub> + H<sub>2</sub>O and in supercritical propylene + H<sub>2</sub>O mixtures using Rh(acac)(CO)<sub>2</sub> and triphenylphosphine trisulfonate trisodium salt (TPPTS), P(*m*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na)<sub>3</sub>, as catalyst. Visual observation of the reaction mixtures indicates that in both systems a single phase is present at supercritical temperatures and pressures so that the reaction occurs under homogeneous conditions. After reaction is complete, a biphasic system is formed when the pressure and temperature are reduced to ambient. This facilitates separation of the products in the organic phase and the rhodium catalyst in the aqueous phase. The rhodium concentration in the organic phase was found to be negligible ( $\sim 1.0 \times 10^{-6}$  mg/ml). Furthermore, compared with traditional hydroformylation technology, the supercritical reactions also show better activity and selectivity.

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**Keywords:** Supercritical reaction; Supercritical CO<sub>2</sub> + H<sub>2</sub>O; Supercritical propylene + H<sub>2</sub>O; Supercritical hydroformylation of propylene; Rhodium catalyst; TPPTS

## 1. Introduction

Hydroformylation, also called oxo synthesis, is a type of CO insertion. As a consequence of its tremendous industrial importance, the reaction has been widely studied [1,2]. In general rhodium-based homogeneous catalysts are used in this reaction because they are both active and selective. However, the cost of the catalysts is very expensive. Homogeneous catalysis is normally carried out using transition metal complexes dissolved in a suitable organic solvent, which serves as the reaction medium. One of the major problems in the current practice of homogeneous catalysis is the toxicity of the volatile organic solvents employed. Another problem is associated with the separation of the catalyst from the solvent, which results in loss of the expensive rhodium catalyst and contamination of the product. Many technologies have been developed in order to overcome these problems [3]. One such process involves the use of supported or heterogenized homogeneous catalysts. Although this can lead to reduced

rhodium losses, the catalysts suffer from reduced catalytic activity [4].

Supercritical fluids (SCFs) such as carbon dioxide (SCCO<sub>2</sub>) have been previously used as the reaction medium for hydroformylation. The most attractive feature of SCFs is that their properties such as density, polarity, viscosity, diffusivity, and overall solvent strength can be varied over a wide range by making relatively small changes in pressure and/or temperature. In addition, carbon dioxide is an environmentally benign solvent. Rathke et al. [5,6] and Erkey et al. [7] reported the hydroformylation of propylene in SCCO<sub>2</sub> using a cobalt-based catalyst. By means of high-pressure NMR studies, it was shown that the reaction proceeds cleanly in SCCO<sub>2</sub> and the ratio of linear to branched butyraldehyde (*n/i*) was higher than that obtained in conventional systems.

In this paper, we report our studies of the hydroformylation reactions of propylene in supercritical CO<sub>2</sub> + H<sub>2</sub>O and supercritical propylene + H<sub>2</sub>O as reaction media with water-soluble rhodium complexes as the catalyst. It was anticipated that these reaction systems would give a single phase under supercritical conditions, allowing the reactions to take place homogeneously, whereas, a biphasic system would be formed after a simple pressure swing at the end of the reaction. If these objectives are met,

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reaction rates should be fast because mass transfer constraints are eliminated, whilst phase separation of the products in the organic phase and the rhodium catalyst in the aqueous phase should also be very straightforward.

## 2. Experimental apparatus and procedures

CO<sub>2</sub> (99.995%), CO (99.99%) and H<sub>2</sub> (99.99%) were obtained from Beijing Reagent Company, and propylene (99.95%) from Yanshan Petrochemical Company. Rh(acac)(CO)<sub>2</sub> and TPPTS were synthesized according to literature procedures [8].

A schematic diagram of the experimental apparatus is shown in Fig. 1. The apparatus consists of a high pressure-viewing cell with silex windows immersed in a water or oil bath. The viewing cell has the advantage of allowing the reaction to be monitored visually by illumination through the silex windows. The total volume of the cell was 35.0 cm<sup>3</sup>. The contents of the cell were stirred with a magnetic stirring bar. The piston was sealed with a graphite gasket. The K type thermocouple used in this work was calibrated against an accurate mercury thermometer, with an error margin of ±0.05 K. The pressure was measured using a pressure transducer, which had been calibrated against a dead-weight gauge, with an error margin of ±0.01 MPa.

The high-pressure viewing cell was thoroughly cleaned before the experiment was started. The desired amounts of Rh(acac)(CO)<sub>2</sub> and TPPTS, and fixed amount of water (0.4 ml) and ethanol (0.4 ml) were loaded into the reactor before it was sealed. Helium was used to purge the reactor. The cell was then charged with propylene and CO<sub>2</sub> from dip-tubing cylinders, with the amounts controlled by pressure regulators. The cell was then charged with CO/H<sub>2</sub> (1:1) from a gas cylinder via the pressure control. The reactor was then heated to the desired temperature. The final pressure was adjusted when the desired temperature was reached and the temperature then kept constant for a set time.

The reaction was stopped by removing the cell from the temperature bath. After the temperature of the cell reached room temperature, the pressure of the system was slowly vented to the atmosphere.

An HP-1490 GC (GDX-104 column) equipped with FID was used for quantitative analysis of the organic product layer. A Shimadzu A 601 atomic absorption spectrometer was used to determine the rhodium concentration in the organic product layer.

## 3. Results and discussion

There is relatively little data in the literature [9,10] pertaining to critical mixtures of CO<sub>2</sub>, CO, H<sub>2</sub> and propylene and it is therefore difficult to predict the phase behavior of such reaction mixtures. In this study, the temperatures for all of the reactions were set far above the critical temperature of CO<sub>2</sub> and/or propylene. Therefore, all of the reactions should take place under homogeneous conditions. This was confirmed by monitoring the reaction process visually through the silex windows of the high pressure-viewing cell. No phase boundaries were observed under supercritical reaction conditions.

In all of the reactions, constant amounts (0.4 ml) of water and ethanol were introduced into the reaction mixture. This small amount of water does not significantly affect the critical properties of the reaction systems, but it is sufficient to dissolve the rhodium phosphine catalyst (solubility in water 1100 g/l at 20 °C) [11].

### 3.1. Hydroformylation of propylene in supercritical CO<sub>2</sub> + H<sub>2</sub>O

The activity and selectivity of a propylene hydroformylation catalyst can be expressed either in terms of its turnover number (TON) and the ratio of linear to branched butyraldehyde (*n/i*) in the product mixture, or in the yield of *n*-butyraldehyde, which is the combination of the *n/i* and the TON. The influence of varying the reaction temperature, rhodium concentration, and the molar ratio of rhodium to phosphine on the TON and *n/i* ratio, or on the yield of *n*-butyraldehyde in supercritical CO<sub>2</sub> + H<sub>2</sub>O were investigated.

#### 3.1.1. Effect of varying reaction temperature

As shown in Fig. 2, an increase in temperature in the range 50–65 °C, the yield of *n*-butyraldehyde attained a maximum

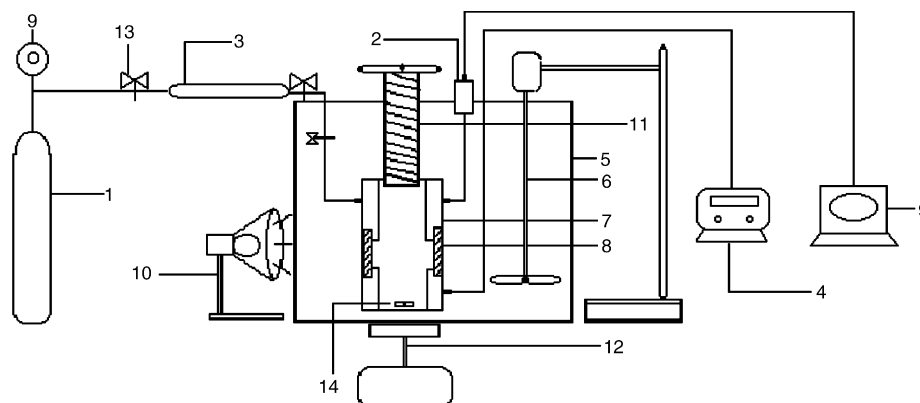


Fig. 1. Flow chart of the experimental apparatus: (1) CO<sub>2</sub> tank, (2) pressure sensor, (3) weighing vessel, (4) temperature control and display, (5) water or oil bath, (6) stirrer, (7) viewing cell, (8) silex window, (9) pressure gauge, (10) light source, (11) piston, (12) stirrer plate, (13) valve, (14) magnetic stirrer bar.

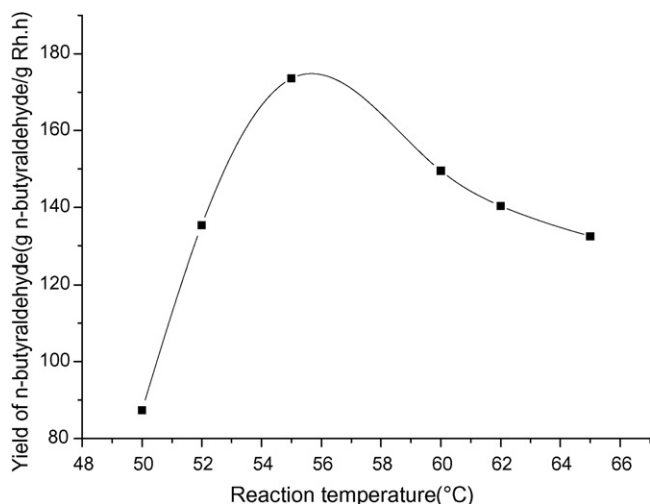


Fig. 2. Effect of varying temperature on the yield of *n*-butyraldehyde for hydroformylation in supercritical CO<sub>2</sub> + H<sub>2</sub>O under the following conditions: Rh concentration, 25 ppm; P/Rh, 20; propylene (2 g); CO<sub>2</sub> (13 g); H<sub>2</sub>O (0.4 ml); ethanol (0.4 ml); CO/H<sub>2</sub> (1:1) (3.5–4 MPa); reaction pressure, 12.0–14.0 MPa; reaction time, 6 h; reaction temperature, 50–65 °C.

of 174 g *n*-butyraldehyde/g Rh h at 56 °C, which affords the optimum combination of TON and *n/i* ratio. An increase in temperature leads to an increase in TON but a decrease in *n/i* ratio. This can be expected to reduce the number of phosphine ligands coordinated to the rhodium center, which may induce the decrease in *n/i* ratio.

### 3.1.2. Effect of varying Rh concentration

The effects of varying Rh concentration on the TON and *n/i* ratio are illustrated in Fig. 3. Both TON and *n/i* ratio increase with increasing Rh concentration at low concentrations, but no further increase is observed above ~20 ppm. Therefore, Rh concentrations in the range 15–20 ppm are appropriate for this system.

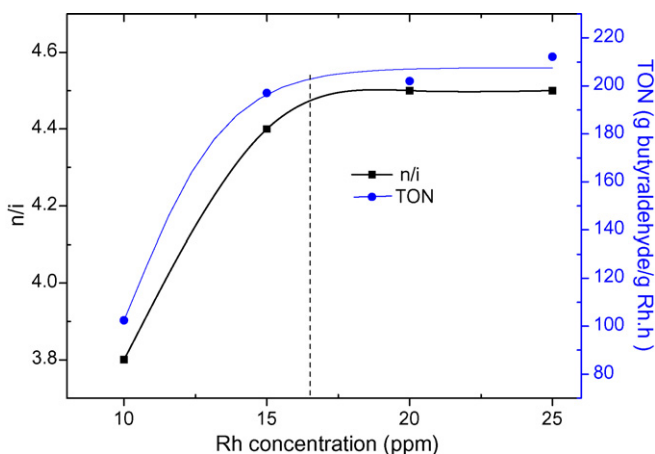


Fig. 3. Effect of varying Rh concentration on TON and *n/i* ratio for hydroformylation in supercritical CO<sub>2</sub> + H<sub>2</sub>O under the following conditions: P/Rh, 20; propylene (2 g); CO<sub>2</sub> (13 g); H<sub>2</sub>O (0.4 ml); ethanol (0.4 ml); CO/H<sub>2</sub> (1:1) (3.5–4 MPa); reaction pressure, 12.0–14.0 MPa; reaction time, 6 h; reaction temperature, 55 °C; Rh concentration, 10–25 ppm.

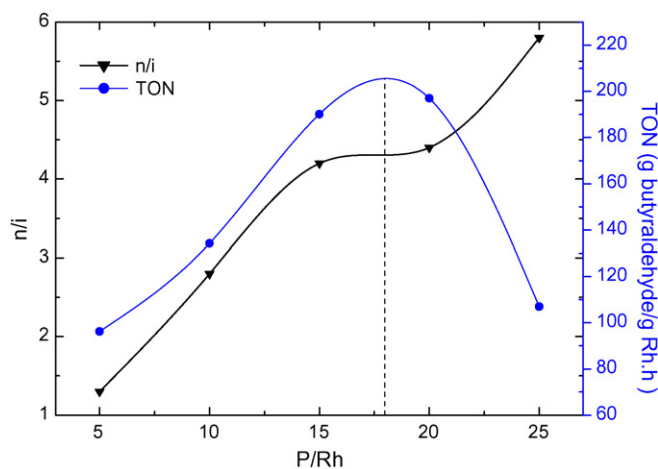


Fig. 4. Effect of varying the molar ratio of phosphine to rhodium on TON and *n/i* ratio for hydroformylation in supercritical CO<sub>2</sub> + H<sub>2</sub>O under the following conditions: Rh concentration, 15 ppm; propylene (2 g); CO<sub>2</sub> (13 g); H<sub>2</sub>O (0.4 ml); ethanol (0.4 ml); CO/H<sub>2</sub> (1:1) (3.5–4 MPa); reaction pressure, 12.0–14.0 MPa; reaction time, 6 h; reaction temperature, 55 °C; P/Rh, 5–25.

### 3.1.3. Effect of the varying the molar ratio of phosphine/rhodium

The effects of varying the P/Rh molar ratio on the TON and *n/i* ratio are shown in Fig. 4. The TON reaches a maximum value at P/Rh = 17, whereas, the *n/i* ratio increases monotonically with increasing P/Rh ratio.

It is well known that the presence of a large excess of phosphine ligands (high P/Rh ratios) favors the formation of *n*-butyraldehyde due to steric effects, resulting in large values of the *n/i* ratio in the product. On the other hand, very high P/Rh ratios can lead to poisoning of the active centers of the catalyst and thus reduce the activity [3]. The results suggest that a P/Rh molar ratio in the range 15–20 is suitable in our reaction system.

## 3.2. Hydroformylation of propylene in supercritical propylene + H<sub>2</sub>O

Hydroformylation of propylene in the supercritical propylene + H<sub>2</sub>O system was also studied. In this case, the propylene acts as both the supercritical medium and as a reactant. As for the case of the supercritical CO<sub>2</sub> + H<sub>2</sub>O system, the influence of varying temperature, Rh concentration and P/Rh ratio on the TON and *n/i* ratio or on the yield of *n*-butyraldehyde were investigated.

As shown in Fig. 5, the dependence of the yield of *n*-butyraldehyde on the reaction temperature in the supercritical propylene + H<sub>2</sub>O systems is very similar to that in the supercritical CO<sub>2</sub> + H<sub>2</sub>O system (see Fig. 2). Since the critical temperature of propylene is higher than that of CO<sub>2</sub>, the supercritical propylene + H<sub>2</sub>O system requires higher temperatures than those for the supercritical CO<sub>2</sub> + H<sub>2</sub>O system. A optimum temperature of 122 °C affords the maximum yield of *n*-butyraldehyde (475 g *n*-butyraldehyde/g Rh h). This is 66 °C higher than that required for the supercritical CO<sub>2</sub> + H<sub>2</sub>O system.

Fig. 6 illustrates the effect of varying Rh concentration on the TON and *n/i* ratio for hydroformylation in supercritical

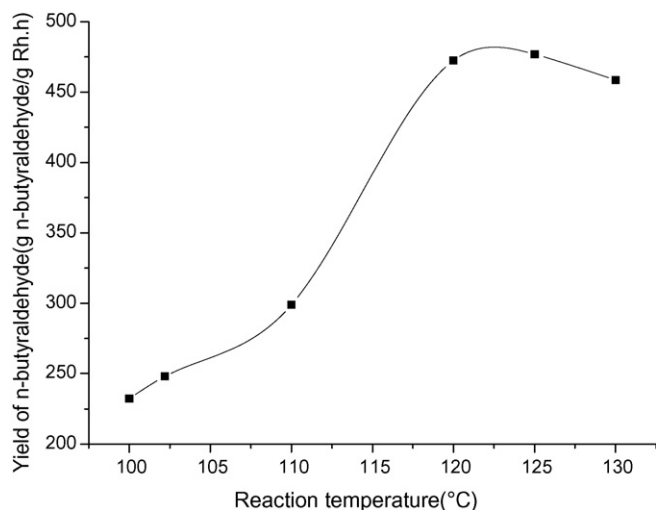


Fig. 5. Effect of varying temperature on the yield of *n*-butylaldehyde for hydroformylation in supercritical propylene + H<sub>2</sub>O under the following conditions: Rh concentration, 20 ppm; P/Rh, 20 ppm; propylene (13 g); H<sub>2</sub>O (0.4 ml); ethanol (0.4 ml); CO/H<sub>2</sub> (1:1) (3.5–4 MPa); reaction pressure, 6.0–10.0 MPa; reaction time, 4 h; reaction temperature, 100–130 °C.

propylene + H<sub>2</sub>O. The results indicate that the optimal Rh concentration is about 30 ppm.

Fig. 7 illustrates the effect of varying P/Rh ratio on TON and *n*/*i* ratio for the supercritical propylene + H<sub>2</sub>O system. The values of TON and *n*/*i* ratio attain their maxima at P/Rh = 28 and P/Rh = 22, respectively. This suggests that the optimal P/Rh ratio is about 25.

### 3.3. Comparison of the supercritical processes with the traditional biphasic process

In this section, we compared the activity (as shown by TON) and selectivity (as shown by *n*/*i* ratio) of the supercritical CO<sub>2</sub> + H<sub>2</sub>O and supercritical propylene + H<sub>2</sub>O systems with

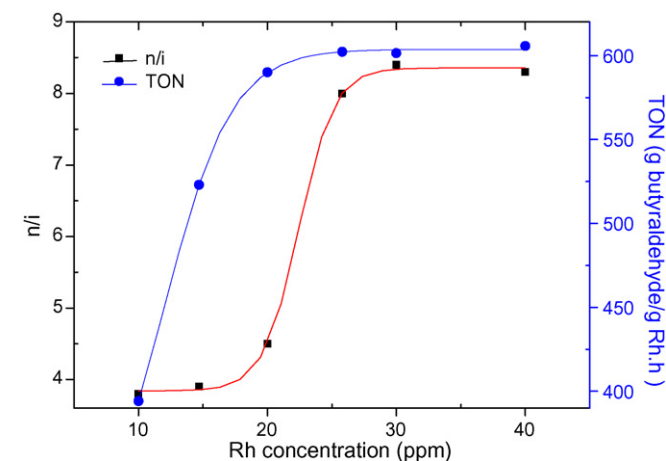


Fig. 6. Effect of varying Rh concentration on TON and *n*/*i* ratio for hydroformylation in supercritical propylene + H<sub>2</sub>O under the following conditions: P/Rh, 20; propylene (13 g); H<sub>2</sub>O (0.4 ml); ethanol (0.4 ml); CO/H<sub>2</sub> (1:1) (3.5–4 MPa); reaction pressure, 6.0–10.0 MPa; reaction time, 4 h; reaction temperature, 117 °C; Rh concentration, 10–40 ppm.

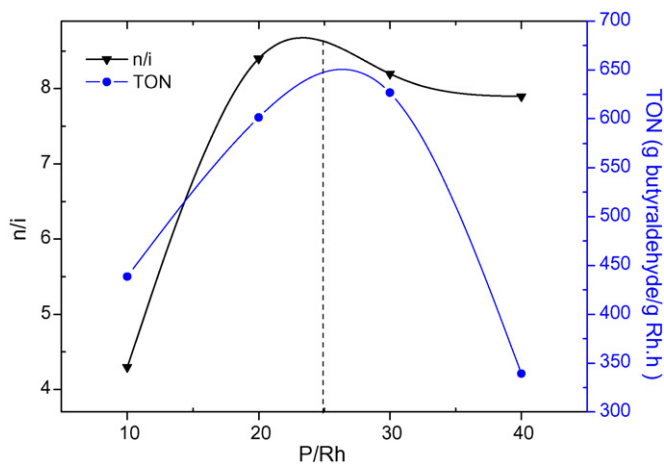


Fig. 7. Effect of varying the molar ratio of phosphine to rhodium on TON and *n*/*i* ratio for hydroformylation in supercritical propylene + H<sub>2</sub>O under the following conditions: Rh concentration, 30 ppm; propylene (13 g); H<sub>2</sub>O (0.4 ml); ethanol (0.4 ml); CO/H<sub>2</sub> (1:1) (3.5–4 MPa); reaction pressure, 6.0–10.0 MPa; reaction time, 4 h; reaction temperature, 117 °C; P/Rh, 10–40.

a traditional biphasic hydroformylation catalytic system. The results are shown in Table 1. The biphasic process takes place heterogeneously, with the products in the organic phase and the water-soluble rhodium catalyst in the aqueous phase. In contrast, the supercritical reaction occurs under homogeneous conditions with phase separation only occurring after the conclusion of the reaction, giving products in the organic phase and rhodium catalyst in the aqueous phase. Therefore, both the biphasic process and the supercritical processes have the advantage that separation of the reaction products from the catalyst can be accomplished easily.

As shown in Table 1, the TON and *n*/*i* ratio for the supercritical CO<sub>2</sub> + H<sub>2</sub>O system are respectively 250% and 130% of the corresponding values for the biphasic process. Employing homogeneous conditions allows the reaction to be carried out under milder conditions leading to higher activity and selectivity. The advantages of the supercritical system are even more evident in the case of the propylene + H<sub>2</sub>O system, for which the TON and *n*/*i* ratios are respectively 790% and 440% of the corresponding values for the biphasic system.

Table 1  
Comparison of catalytic properties for biphasic and supercritical reaction systems

Reaction system	TON g aldehyde/(g Rh h)	<i>n</i> / <i>i</i> ratio
Biphasic <sup>a</sup>	76.3	3.2
Supercritical CO <sub>2</sub> + H <sub>2</sub> O <sup>b</sup>	190.1	4.3
Supercritical propylene + H <sub>2</sub> O <sup>c</sup>	601.4	8.4

<sup>a</sup> Ref. [4]; Rh concentration, 30 ppm; P/Rh, 50; propylene (2 g); H<sub>2</sub>O (5 ml); cyclohexane (5 ml); CO/H<sub>2</sub> (1:1) (3.5–4 MPa); reaction pressure, 4.0–6.0 MPa; reaction temperature, 100 °C; reaction time, 8 h.

<sup>b</sup> Rh concentration, 15 ppm; P/Rh, 20; CO<sub>2</sub> (13.0 g); propylene (2 g); H<sub>2</sub>O (0.4 ml); ethanol (0.4 ml); CO/H<sub>2</sub> (1:1) (3.5–4 MPa); reaction pressure, 12.0–14.0 MPa; reaction temperature, 55 °C; reaction time, 6 h.

<sup>c</sup> Rh concentration, 15 ppm; P/Rh, 20; propylene (13 g); H<sub>2</sub>O (0.4 ml); ethanol (0.4 ml); CO/H<sub>2</sub> (1:1) (3.5–4 MPa); reaction pressure, 6.0–10.0 MPa; reaction temperature, 117 °C; reaction time, 4 h.

Table 2  
Comparison of Rh loss in different reaction systems

Reaction system	Rh (mg/ml)
Homogeneous <sup>a</sup>	0.025
Supercritical <sup>b</sup>	$1.0 \times 10^{-6}$

<sup>a</sup> Ref. [4]; catalyst (Rh(acac)(CO)<sub>2</sub> + triphenylphosphine); Rh concentration, 25 ppm; P/Rh, 25; reaction temperature, 100 °C; solvent, cyclohexane; reaction time, 6 h.

<sup>b</sup> Reaction conditions, see footnote c in Table 1.

Our results show that the supercritical propylene + H<sub>2</sub>O system, in which the propylene acts as both supercritical medium and reactant, is superior to the CO<sub>2</sub> + H<sub>2</sub>O system in terms of both activity and *n/i* ratio. The reason for the higher TON in the former process is probably related its higher reaction temperature, while an explanation of the higher *n/i* ratio would require further mechanistic studies beyond the scope of this paper.

### 3.4. Comparison of rhodium losses in different systems

Rhodium loss is a major problem in traditional homogeneous catalysis. Rhodium loss can be expressed in terms of the rhodium concentration in the final product. Atomic absorption spectrometry was used to compare the rhodium concentration in the final product from a typical homogenous system with that in product obtained using the supercritical propylene + H<sub>2</sub>O system. The results are listed in Table 2.

As shown in Table 2, the rhodium concentration in the organic phase is four orders of magnitude lower in the case of the supercritical reaction, demonstrating its superiority over the homogeneous reaction system.

## 4. Conclusions

Hydroformylation of propylene in supercritical CO<sub>2</sub> + H<sub>2</sub>O or supercritical propylene + H<sub>2</sub>O mixtures avoids the use of an organic solvent, which is often employed in current industrial practice. Hydroformylation of propylene under supercritical conditions also shows superior activity (in terms of TON) and selectivity (in terms of the ratio of linear to branched butyraldehyde (*n/i*)) compared with traditional biphasic processes. The

supercritical propylene + H<sub>2</sub>O system gives higher activity than the supercritical CO<sub>2</sub> + H<sub>2</sub>O system, although the reaction temperature required for the former system is about 66 °C higher.

The most attractive feature of the supercritical system is that the reaction takes place homogeneously under supercritical conditions and the system only becomes biphasic at the end of process, with products in the organic phase and rhodium phosphine catalyst in the water phase. Therefore, separation of reaction products from catalyst can be accomplished in a simple way. Furthermore, the amount of rhodium catalyst in the organic phase is extremely low.

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