

# Kinetics and Dynamics of Heterogeneous Hydroformylation Rh Catalyst

Mark A. Brundage, Steven S. C. Chuang, and Michael W. Balakos  
Department of Chemical Engineering,  
The University of Akron,  
Akron, OH 44325-3906, U.S.A.

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Heterogeneous CO/H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> reaction of 4 wt% Rh/SiO<sub>2</sub> catalyst was studied using steady-state pulse transient method coupled with *in situ* infrared spectroscopy. The dynamic responses measured at various partial pressures of reactants show that the CO/H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> reaction can accurately be described by a Langmuir-Hinshelwood-Hougen-Watson (LHHW) model with the hydrogenation of adsorbed C<sub>2</sub>H<sub>3</sub>CO as the rate-determining step for propionaldehyde formation and the hydrogenation of adsorbed C<sub>2</sub>H<sub>5</sub> as the rate-determining step for ethane formation. The kinetic model also accurately describes the adsorption isotherm of acyl intermediates measured by the pulse isotopic transient and adsorption isotherm of CO measured by IR spectroscopy. This study also demonstrates that the measurement of coverage of adsorbates by isotopic tracer pulsing and *in situ* infrared spectroscopy provides direct experimental evidence to confirm a postulated mechanism and rate law.

## INTRODUCTION

The determination of reliable rate expressions is paramount in the design and modeling of heterogeneously catalyzed processes. Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics of heterogeneous catalytic reactions has been studied for many years (1-7). However, the formalism has been the subject of much discussion and criticism. Most of the criticisms in the LHHW formalism are results of the inability to measure the coverage of adsorbates and reaction intermediates as a function of partial pressure of reactants and to identify the rate-determining step during the reaction (8,9). The objectives of this paper are to combine isotopic transient and *in situ* IR methods to study heterogeneous CO/H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> reaction and to test a LHHW model that can describe the overall kinetics for its ability to describe the adsorption isotherms of surface intermediates. Kinetic equations were derived from LHHW formalism with the postulation of a rate-determining step for both propionaldehyde and ethane formation. *In situ* IR coupled with transient isotopic tracing was used to observe the coverage of adsorbed species during the reaction and compared to the coverage predicted by the LHHW model.

## EXPERIMENTAL

A 4 wt% Rh/SiO<sub>2</sub> catalyst was prepared from RhCl<sub>3</sub>·3H<sub>2</sub>O solution by the incipient wetness impregnation method. After impregnation, the catalyst was dried overnight in air at 300 K and then reduced in flowing hydrogen at 673 K for 16 hr. The exposed metal atoms was determined to be 122 μmol/g by H<sub>2</sub> pulse chemisorption at 303 K assuming an adsorption stoichiometry of H<sub>ads</sub>/Rh = 1.

The apparatus used in this study is similar to that previously reported (10). Four independent quantities, including the rates of propionaldehyde and ethane formation and the surface converges of adsorbed CO and adsorbed acyl species, were measured as a function of partial pressure of reactants during steady-state condition. The coverage of intermediates during ethylene hydroformylation was determined from the dynamic response of C<sub>2</sub>H<sub>5</sub><sup>13</sup>CHO to a <sup>13</sup>CO pulse input. The coverage of adsorbed CO was measured by *in situ* IR spectroscopy.

## RESULTS

### Steady-State Measurements

The steady-state rate of formation of ethane and propionaldehyde during heterogeneous hydroformylation (CO/H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> reaction) on 4 wt% Rh/SiO<sub>2</sub> was measured by a gas chromatograph at 0.1 MPa. The main products in the reaction are ethane and propionaldehyde. Other minor hydrocarbon products include methane, propylene, butene, and butane. To determine the dependence of the reaction rates on the partial pressures of reactants, the rates were measured as the partial pressures of reactant at a total pressure of 0.1 MPa and 513 K. The flow rate of He was varied to maintain a constant total flowrate of 120 cm<sup>3</sup>/min. Both ethane and propionaldehyde formation rates are negative order in CO partial pressure while positive order in both hydrogen and ethylene.

The *in situ* IR spectra during the experiments of varying partial pressures are shown in Figure 1. The top spectra in Figure 1 show the variation of the spectra with CO partial pressure. The spectra at partial pressure of 0.083 MPa exhibit a linear CO band at 2037 cm<sup>-1</sup>; a small bridged CO band at 1885 cm<sup>-1</sup>; propionaldehyde band at 1740 cm<sup>-1</sup>; and gaseous ethylene and ethane bands between 1900 and 3300 cm<sup>-1</sup> (11,12). The intensity and the wavenumber of adsorbed CO show stronger dependence on P<sub>CO</sub> than P<sub>H<sub>2</sub></sub> and P<sub>C<sub>2</sub>H<sub>4</sub></sub>.

### Dynamic Measurements

The transient response of C<sub>2</sub>H<sub>5</sub><sup>13</sup>CHO and the IR spectra to 10 cm<sup>3</sup> pulse of <sup>13</sup>CO into the <sup>12</sup>CO feed to the reactor was recorded during the steady-state experimental runs. Figure 2 is the transient response of Ar, <sup>13</sup>CO, and C<sub>2</sub>H<sub>5</sub>CHO measured by mass spectrometry under the conditions of 0.1 MPa, 513 K and CO/H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/He = 1/1/1.

Infrared spectra taken during the pulse of  $^{13}\text{CO}$  in the CO feed show that the gas phase CO and adsorbed CO exchange with their isotopic counterparts at a rate much faster than the scanning rate of the IR. No other feature in the IR spectra changed during the course of the experiment, including those attributed to gaseous ethylene.

From the transient response, the average residence time of  $^{13}\text{CO}$  adsorbed on the catalyst surface can be obtained by (10,13)

$$\tau_{^{13}\text{CO}} = \int_0^{\infty} t E_{^{13}\text{CO}}(t) dt \quad (1)$$

Since the gaseous CO and adsorbed CO exchange rapidly, the gaseous  $^{13}\text{CO}$  response measured by mass spectrometry can be used as the response for the adsorbed  $^{13}\text{CO}$ . The average residence time of all intermediate species leading to the formation of  $^{13}\text{C}$  propionaldehyde from adsorbed  $^{13}\text{CO}$  can be expressed as

$$\tau_{\text{C}_2\text{H}_5^{13}\text{CHO}} = \int_0^{\infty} t E_{\text{C}_2\text{H}_5^{13}\text{CHO}}(t) dt - \tau_{^{13}\text{CO}} \quad (2)$$

Figure 3 shows the deuterated propionaldehydes response to a  $10 \text{ cm}^3$  pulse of  $\text{D}_2$  into the  $\text{H}_2$  flow during steady-state ethylene hydroformylation (14). The lag of the deuterated propionaldehydes response with respect to that of  $\text{D}_2$  indicates that the hydrogenation of acyl intermediates is a rate-determining step.

## DISCUSSION

The mechanism for the formation of propionaldehyde from  $\text{CO}/\text{H}_2/\text{C}_2\text{H}_4$  reaction has been postulated from analogy with the homogeneous hydroformylation reaction (12,15). The general accepted mechanism of the reaction is shown in Table 1 (12). The approach for kinetic analysis of a heterogeneous catalytic reaction involves the postulation of a rate-determining step and express the rate in terms of the concentrations of the reaction intermediates in that step. The concentrations of the intermediates must then be related to the gas phase concentration of the reactants and products (adsorption isotherms). The simplest theoretical expression for an adsorption isotherm is the Langmuir isotherm, on which the LHHW formalism is based.

Different rate-determining steps, RDS, yield different forms of the rate equations so that they can be distinguished from each other. The best fit of the data is when step 6 in Table 1 is considered as the RDS for propionaldehyde formation. Step 6 as the RDS is supported by  $\text{D}_2$  pulse studies as shown in Figure 3. The relation between  $\text{TOF}_{\text{C}_2\text{H}_5\text{CHO}}$ ,  $\text{TOF}_{\text{C}_2\text{H}_6}$ ,  $\theta_{\text{C}_2\text{H}_5\text{CO}}$ , and  $\theta_{\text{CO}}$ , and partial pressure of the reactants can be derived from LHHW formalism with step 6 as RDS, as shown below.

$$\theta_{\text{C}_2\text{H}_5\text{CO}} = \frac{\sqrt{K_1 K_2 K_3 K_4 K_5 P_{\text{CO}}} \sqrt{P_{\text{H}_2}} P_{\text{C}_2\text{H}_4}}{1 + K_2 P_{\text{CO}} + \sqrt{K_1 P_{\text{H}_2}} + K_3 P_{\text{C}_2\text{H}_4}} \quad (3)$$

$$\theta_{\text{CO}} = \frac{K_2 P_{\text{CO}}}{1 + K_2 P_{\text{CO}} + \sqrt{K_1 P_{\text{H}_2}} + K_3 P_{\text{C}_2\text{H}_4}} \quad (4)$$

$$\text{TOF}_{\text{C}_2\text{H}_5\text{CHO}} = \frac{k_6 K_1 K_2 K_3 K_4 K_5 P_{\text{CO}} P_{\text{H}_2} P_{\text{C}_2\text{H}_4}}{(1 + K_2 P_{\text{CO}} + \sqrt{K_1 P_{\text{H}_2}} + K_3 P_{\text{C}_2\text{H}_4})^2} \quad (5)$$

$$\text{TOF}_{\text{C}_2\text{H}_6} = \frac{k_1 K_1 K_3 K_4 P_{\text{H}_2} P_{\text{C}_2\text{H}_4}}{(1 + K_2 P_{\text{CO}} + \sqrt{K_1 P_{\text{H}_2}} + K_3 P_{\text{C}_2\text{H}_4})^2} \quad (6)$$

The above rate law and isotherm equations derived from LHHW were found to accurately describe the rate and isotherm data.

## CONCLUSION

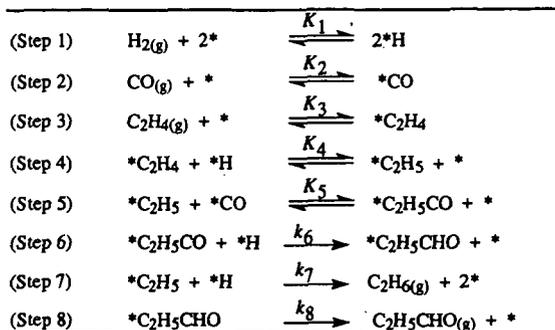
Four independent quantities,  $\text{TOF}_{\text{C}_2\text{H}_5\text{CHO}}$ ,  $\text{TOF}_{\text{C}_2\text{H}_6}$ ,  $\theta_{\text{C}_2\text{H}_5\text{CO}}$ , and  $\theta_{\text{CO}}$  were measured as a function of partial pressure of reactants during steady-state ethylene hydroformylation over  $\text{Rh}/\text{SiO}_2$ . The results of this study demonstrate that the coverage of acyl intermediate determined from the dynamic response of an isotopic tracer is quantitatively consistent with that calculated from LHHW formalism; the coverage of  $^*\text{CO}$  measured from IR spectroscopy is qualitatively consistent with that obtained from LHHW formalism. This study also shows that the measurement of coverage of adsorbates by both transient and IR techniques provides essential information to verify a proposed mechanism and kinetic model.

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Table 1. The Proposed Mechanism for Heterogeneous Hydroformylation of Rh/SiO<sub>2</sub>.



$K_i$  is the equilibrium adsorption parameter,  $i=1,2,\dots$   
 $k_{i+}$  is the forward rate constant;  $k_{i-}$  is the backward rate constant.

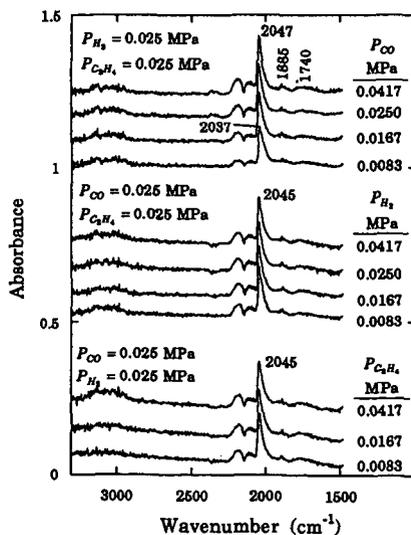


Figure 1. *In Situ* IR spectra of heterogeneous ethylene hydroformylation on 4 wt% Rh/SiO<sub>2</sub> at 513 K and 0.1 MPa at varying partial pressures of reactants.

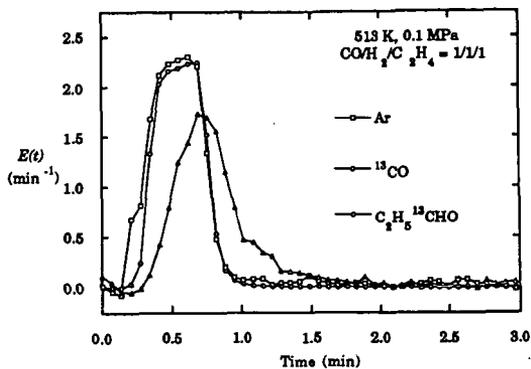


Figure 2. The Transient response of Ar,  $^{13}\text{CO}$ , and  $\text{C}_2\text{H}_5^{13}\text{CHO}$  to a  $1\text{ cm}^3$  pulse of  $^{13}\text{CO}$  in a  $^{12}\text{CO}$  flow during ethylene hydroformylation on 4 wt% Rh/SiO<sub>2</sub> at 513 K and 0.1 MPa.

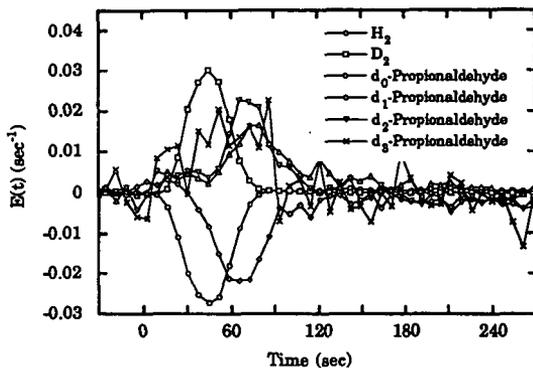


Figure 3. Transient Response of Deuterated Propionaldehydes to a  $10\text{ cm}^3$  pulse of  $\text{D}_2$  into a  $\text{H}_2$  flow during ethylene hydroformylation on 4 wt% Rh/SiO<sub>2</sub> at 513 K and 0.1 MPa.