

第二届催化动态分析技术
及应用学术交流会

论 文 汇 编

一九九四年八月 · 太原

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Dynamics and Kinetics of CO/H₂/C₂H₄ Reaction

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ABSTRACT: Heterogeneous CO/H₂/C₂H₄ reaction on a 4 wt% Rh/SiO₂ 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/H₂/C₂H₄ reaction can be accurately described by a Langmuir-Hinshelwood-Hougen-Watson (LHHW) model with the hydrogenation of adsorbed C₂H₅CO as the rate-determining step for propionaldehyde formation and the hydrogenation of adsorbed C₂H₅ 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 the adsorption isotherm of CO measured by IR spectroscopy. The study establishes the relationship between the dynamic response of propionaldehyde and the overall kinetics of CO/H₂/C₂H₄ reaction. 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. The kinetics of heterogeneous catalytic reactions has been studied for many years (1-5). Hougen and Watson (1,6) first extended the Langmuir theory of adsorption and applied it to the rates of catalytic reactions. The type of rate equations derived from this approach is now commonly called Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics (7).

Despite the wide use of LHHW kinetics, 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

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isotopic transient and *in situ* IR methods to study heterogeneous CO/H₂/C₂H₄ 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 the 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/SiO₂ catalyst was prepared by incipient wetness impregnation method. An aqueous solution of RhCl₃·3H₂O (Alfa Products) was impregnated into a large pore SiO₂ support (Strem Chemicals, surface area of 350 m²/g) and then reduced in flowing hydrogen at 673 K for 16 hr. The H₂ uptake of the catalyst was measured at 303 K by pulse adsorption method and was found to be 122 μmol/g. This corresponds to a dispersion of 0.62 and a crystallite size of 15 Å, assuming an adsorption stoichiometry of H_{ads}/Rh = 1 and a cubic shape of Rh crystallites.

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 coverages 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 C₂H₅¹³CHO to a ¹³CO 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/H₂/C₂H₄ reaction) on 4 wt% Rh/SiO₂ were measured by gas chromatography at 0.1 MPa. The main products of the reaction are ethane and propionaldehyde. Other minor hydrocarbon products include methane, propylene, butene, and butane which make up 0.4 % of the products at 483 K and increases to 5.5 % at 573 K. 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 flowrate of He was varied to maintain a constant total flowrate of 120 cm³/min. Figure 1 are log-log plots of the TOF for ethane and propionaldehyde formation versus the partial pressures of CO,

H₂, and C₂H₄. 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 2. The top spectra in Figure 2 shows the variation of the spectra with CO partial pressure. The spectra at a partial pressure of 0.0083 MPa exhibits a linear CO band at 2037 cm⁻¹; a small bridged CO band at 1885 cm⁻¹; propionaldehyde band at 1740 cm⁻¹; and gaseous ethylene and ethane bands between 2900 and 3300 cm⁻¹ (11,12). The intensity and the wavenumber of adsorbed CO show stronger dependence on P_{CO} than P_{H_2} and $P_{C_2H_4}$.

Dynamic Measurements

The transient response of C₂H₅¹³CHO and the IR spectra to a 10 cm³ pulse of ¹³CO into the CO feed to the reactor were recorded during the steady-state experimental runs. Figure 3 is the transient response of Ar, ¹³CO, and C₂H₅¹³CHO measured by mass spectrometry under the conditions of 0.1 MPa, 513 K, and CO/H₂/C₂H₄/He = 1/1/1/1. For comparison, the response is normalized to $E(t)$ and is defined as

$$E(t) = \frac{C(t)}{\int_0^\infty C(t) dt} \quad [1]$$

Infrared spectra taken during the pulse of ¹³CO 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. The same conclusions can be drawn for all the spectra recorded during all the transient experiments.

From the transient response, the average residence time of the ¹³CO adsorbed on the catalyst surface can be obtained by (10,13)

$$\tau_{^{13}CO} = \int_0^\infty t E_{^{13}CO}(t) dt \quad [2]$$

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

$$\tau_{C_2H_5^{13}CHO} = \int_0^\infty t E_{C_2H_5^{13}CO}(t) dt - \tau_{^{13}CO} \quad [3]$$

It has been recently shown (11) that a good estimate of the surface coverage of all intermediate species leading to the formation of propionaldehyde from adsorbed CO can be estimated by

$$\theta_{C_2H_5CO} = \tau_{C_2H_5^{13}CHO} \cdot TOF_{C_2H_5CHO} \quad [4]$$

Equations [2]-[4] were used to obtain $\theta_{C_2H_5CO}$ from the transient responses of the ^{13}C labeled gaseous CO and propionaldehyde at various partial pressure of reactants and the results are shown as the symbols in Figure 4. Figure 4 is the adsorption isotherms of the intermediate species in propionaldehyde formation during the reaction. The surface coverage of intermediates shows a Langmuir isotherm-type dependence on CO and H_2 partial pressures under the conditions of the reaction. The surface coverage of intermediates exhibits a linear dependence on the partial pressure of C_2H_4 under these conditions.

DISCUSSION

Reaction Mechanism

The mechanism for the formation of propionaldehyde from CO/ H_2 / C_2H_4 reaction has been postulated from analogy with the homogeneous hydroformylation reaction (12,14). The generally 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. The underlying assumptions of the Langmuir isotherm include (9): (i) monolayer coverage; (ii) uniformly energetic adsorption sites; and (iii) no interaction between adsorbed molecules. Assumption (i) is generally valid for heterogeneous catalysis. The structure-insensitive nature of hydroformylation (11) makes assumption (ii) applicable to this study. Although surface interactions can not be ignored, assumption (iii) is also considered in the LHHW formalism in this study to derive the rate laws for product formation and isotherm equations for adsorbates.

Different rate-determining steps, RDS, yield different forms of 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. The relation

between $TOF_{C_2H_5CHO}$, $TOF_{C_2H_6}$, $\theta_{C_2H_5CO}$, and θ_{CO} , and partial pressure of reactants can be derived from LHHW formalism with step 6 as RDS as shown below.

$$\theta_{C_2H_5CO} = \frac{\sqrt{K_1 K_2 K_3 K_4 K_5 P_{CO}} \sqrt{P_{H_2} P_{C_2H_4}}}{1 + K_2 P_{CO} + \sqrt{K_1 P_{H_2}} + K_3 P_{C_2H_4}} \quad [5]$$

$$\theta_{CO} = \frac{K_2 P_{CO}}{1 + K_2 P_{CO} + \sqrt{K_1 P_{H_2}} + K_3 P_{C_2H_4}} \quad [6]$$

$$TOF_{C_2H_5CHO} = \frac{k_6 K_1 K_2 K_3 K_4 K_5 P_{CO} P_{H_2} P_{C_2H_4}}{(1 + K_2 P_{CO} + \sqrt{K_1 P_{H_2}} + K_3 P_{C_2H_4})^2} \quad [7]$$

$$TOF_{C_2H_6} = \frac{k_7 K_1 K_3 K_4 P_{H_2} P_{C_2H_4}}{(1 + K_2 P_{CO} + \sqrt{K_1 P_{H_2}} + K_3 P_{C_2H_4})^2} \quad [8]$$

In this study, the variation of $TOF_{C_2H_5CHO}$, $TOF_{C_2H_6}$, $\theta_{C_2H_5CO}$, and θ_{CO} with the partial pressure of reactants are measured. Both overall kinetics (LHHW equations) and isotherm equations for adsorbed C_2H_5CHO and adsorbed CO derived from the proposed mechanism are tested by comparison with the experimental results.

Figure 5 is a plot of the experimentally measured TOF vs. the TOF calculated from the LHHW model, i.e., Eq [7] and [8], and shows a good fit for both ethane and propionaldehyde formation over a wide range of rates. The parameters obtained are $K_2 = 322 \text{ MPa}^{-1}$, $\sqrt{K_1} = 910 \text{ MPa}^{-1/2}$, and $K_3 = 0.0263 \text{ MPa}^{-1}$ and $k_6 K_1 K_2 K_3 K_4 K_5 = 139000 \text{ min}^{-1} \text{ MPa}^{-3}$. The measured isotherms of the adsorbed intermediates shown in Fig. 4 obtained during the reaction were used to test the goodness of fit to the isotherms (Eqs. [5] and [6]). The parameters in the adsorption group appearing in rate equations [7] and [8] are the same as those for the isotherm of $\theta_{C_2H_5CO}$ (Eq. [5]). Thus, Eq [5] can be written with the values of adsorption parameters as the following.

$$\theta_{C_2H_5CO} = \frac{\sqrt{K_1 K_2 K_3 K_4 K_5 P_{CO}} \sqrt{P_{H_2} P_{C_2H_4}}}{(1 + 321.8 P_{CO} + 9.101 \sqrt{P_{H_2}})} \quad [9]$$

Using equation [9] to fit the measured isotherms by least squares approximation, the parameter $\sqrt{K_1 K_2 K_3 K_4 K_5}$ is estimated to be $1562 \text{ MPa}^{-5/2}$ with $\Delta\% = 9.95\%$. The measured $\theta_{C_2H_5CO}$ agrees well with the fitted isotherms as can be seen in Figure 4 where the solid line is equation [9] and the symbols are the measured $\theta_{C_2H_5CO}$.

The integrated area under the IR intensity of the linear CO band, which is proportional to the surface coverage of *CO , is compared to the CO coverage

obtained from Equation [6]. Including the estimated parameters and neglecting $K_3 P_{C_2H_4}$, equation [6] can be written as

$$\theta_{CO} = \frac{321.8 P_{CO}}{(1 + 321.8 P_{CO} + 9.101 \sqrt{P_{H_2}})} \quad [10]$$

Assuming that the integrated areas under the linear CO IR bands in Figure 2 are proportional to the concentration of *CO on the surface, θ_{CO} in Equation [10] at a specified P_{CO} and P_{H_2} multiplied by a proportionality constant should fit the area under the linear CO band taken under the same partial pressure. Figure 6 shows the data points taken from area under the linear CO band and equation [10] (solid line) multiplied by a factor of 12.96 cm^{-1} . Since the LHHW rate equations and isotherm equations, Eq [7]-[10] are successfully tested by two sets of independent data, i.e., TOF vs. P_i and θ_i vs. P_i data, the model is likely to be the "correct" one which may accurately describe the reaction.

The value of the adsorption parameters in the model equations give insight into the surface coverages of adsorbed species during the reaction. The parameter K_2 is much larger than both K_1 and K_3 , indicating that *CO is the most abundant surface species. The surface coverages of *C₂H₄, *C₂H₅, *C₂H₅CO, and *C₂H₅CHO are insignificant in the site balance under the conditions of this study, as evidenced from the rate law of ethane and propionaldehyde formation and the adsorption isotherms depending mainly on P_{CO} and P_{H_2} in the denominator. The surface coverage of the *C₂H₅CO was measured to be on the order of 0.007 to 0.026. This result also justifies the assumption of negligible surface coverage of this intermediate in the adsorption group of the LHHW rate equations.

The dominance of K_2 , the adsorption equilibrium parameter for CO adsorption, may diminish the role of adsorbate interactions in the adsorption isotherm equations for the description of the dependence of surface coverage on reaction conditions. The lack of adsorbate interactions can also be seen from the invariance in the wavenumber of linear *CO with various partial pressures of hydrogen and ethylene in the IR spectra in Figure 1. Due to the dominance of K_2 and lack of pronounced adsorbate interactions, the assumptions of no interaction between adsorbates appears to be valid for the derivation of the LHHW model for hydroformylation on the Rh/SiO₂ catalyst.

CONCLUSIONS

Four independent quantities, $TOF_{C_2H_5CHO}$, $TOF_{C_2H_6}$, $\theta_{C_2H_5CO}$, and θ_{CO} , were measured as a function of partial pressure of reactants during steady-state ethylene hydroformylation over Rh/SiO₂. The results of this study demonstrate that the coverage of acyl intermediates determined from the dynamic response of an isotopic tracer is quantitatively consistent with that calculated from the LHHW formalism; the coverage of adsorbed *CO measured from IR spectroscopy is qualitatively consistent with that obtained from the LHHW formalism. Although the assumptions for the Langmuir isotherm does not account for interactions between adsorbates, the proposed mechanism and LHHW equations satisfactorily describe the kinetics, reaction pathway, and rate-determining steps for ethane and propionaldehyde formation. 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 on Rh/SiO₂.

(Step 1)	$H_2(g) + 2*$	$\xrightleftharpoons{K_1} 2*H$
(Step 2)	$CO(g) + *$	$\xrightleftharpoons{K_2} *CO$
(Step 3)	$C_2H_4(g) + *$	$\xrightleftharpoons{K_3} *C_2H_4$
(Step 4)	$*C_2H_4 + *H$	$\xrightleftharpoons{K_4} *C_2H_5 + *$
(Step 5)	$*C_2H_5 + *CO$	$\xrightleftharpoons{K_5} *C_2H_5CO + *$
(Step 6)	$*C_2H_5CO + *H$	$\xrightarrow{k_6} *C_2H_5CHO + *$
(Step 7)	$*C_2H_5 + *H$	$\xrightarrow{k_7} C_2H_6(g) + 2*$
(Step 8)	$*C_2H_5CHO$	$\xrightarrow{k_8} C_2H_5CHO(g) + *$

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.

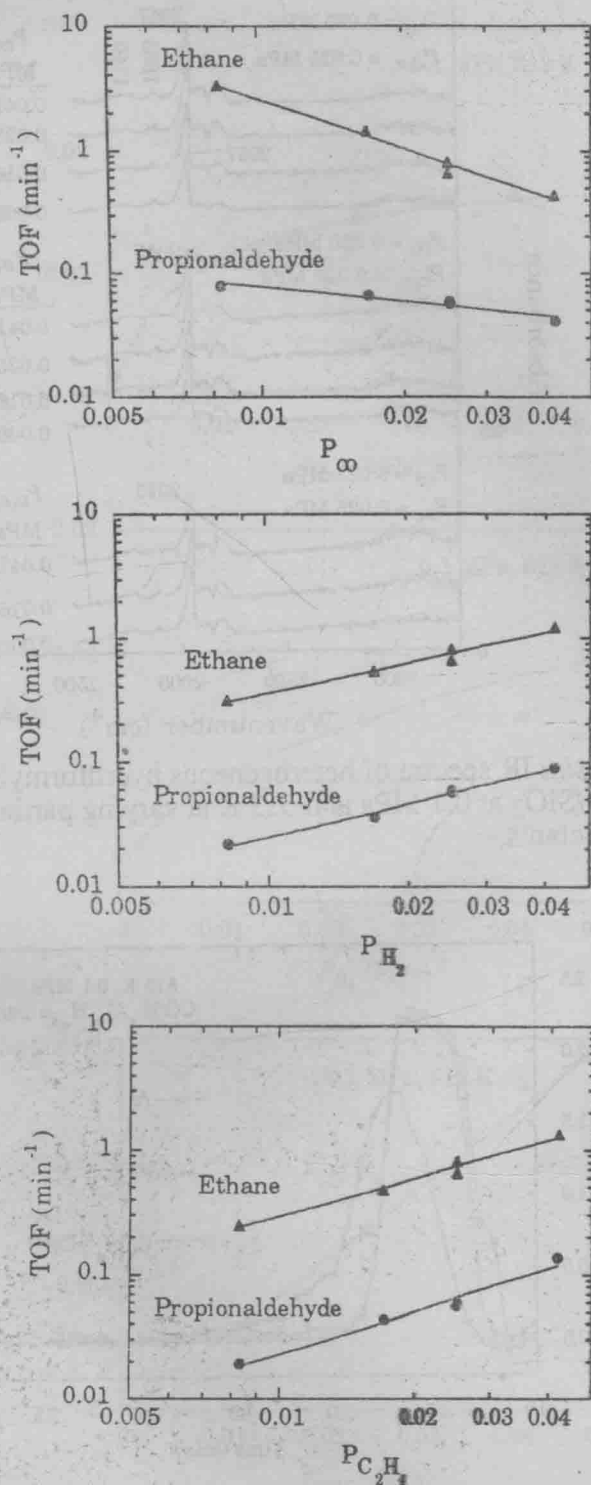


FIGURE 1. Dependence of rate of ethane and propionaldehyde formation on the partial pressures of reactants at 513 K and a total pressure of 0.1 MPa.

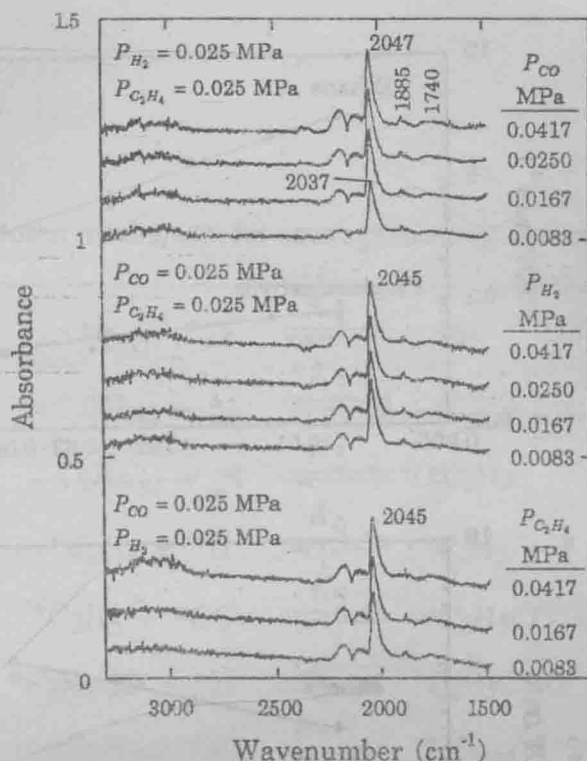


FIGURE 2. *In situ* IR spectra of heterogeneous hydroformylation on 4 wt% Rh/SiO₂ at 0.1 MPa and 513 K at varying partial pressures of reactants.

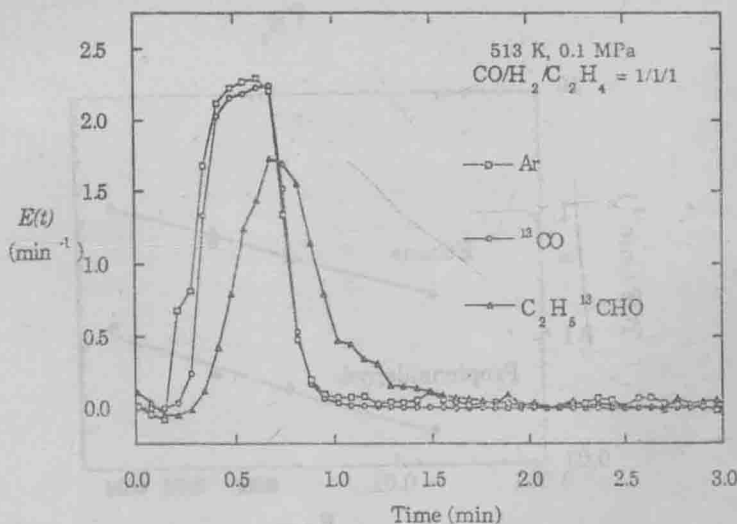


FIGURE 3. The transient response of Ar, ¹³CO, and C₂H₅¹³CHO to a pulse of ¹³CO in the ¹²CO feed during ethylene hydroformylation on 4 wt% Rh/SiO₂ at 513 K and 0.1 MPa.

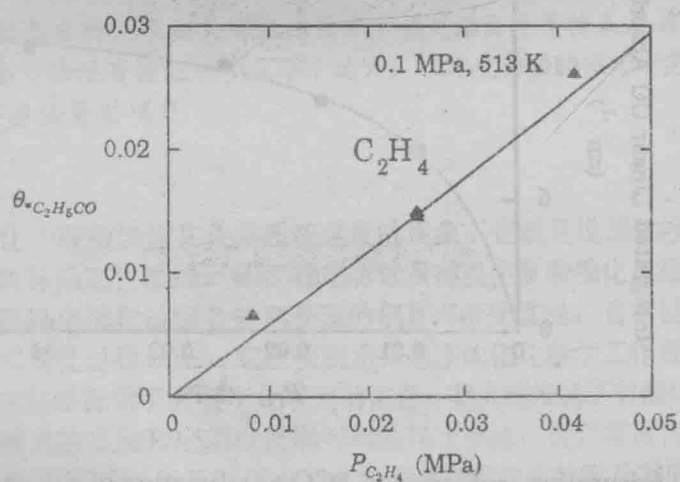
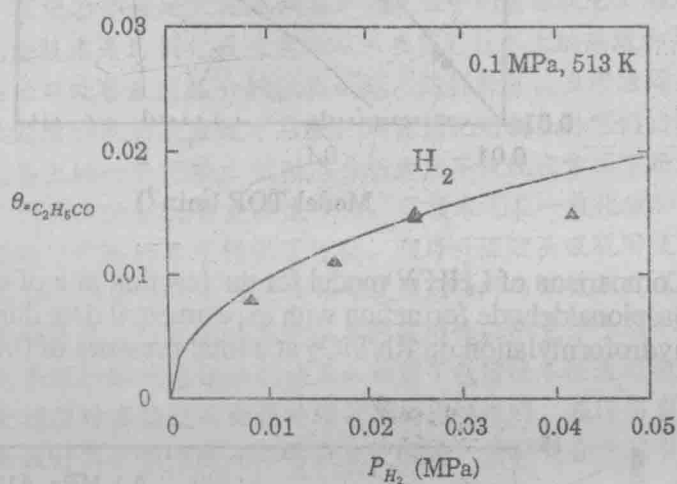
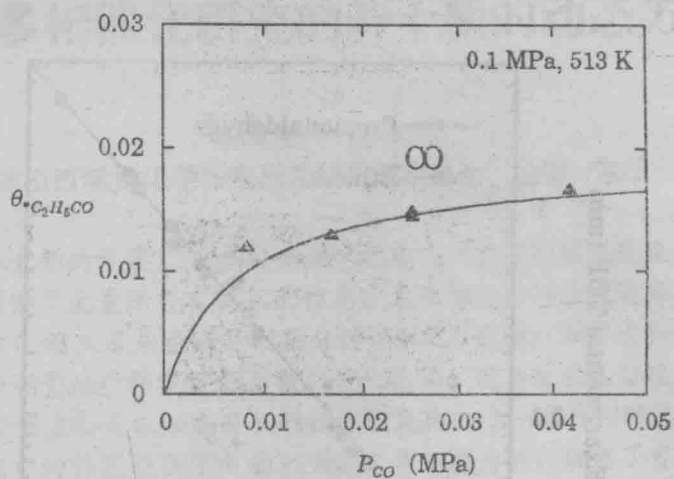


FIGURE 4. Adsorption isotherms of $*C_2H_5CO$ as a function of partial pressures of reactants.

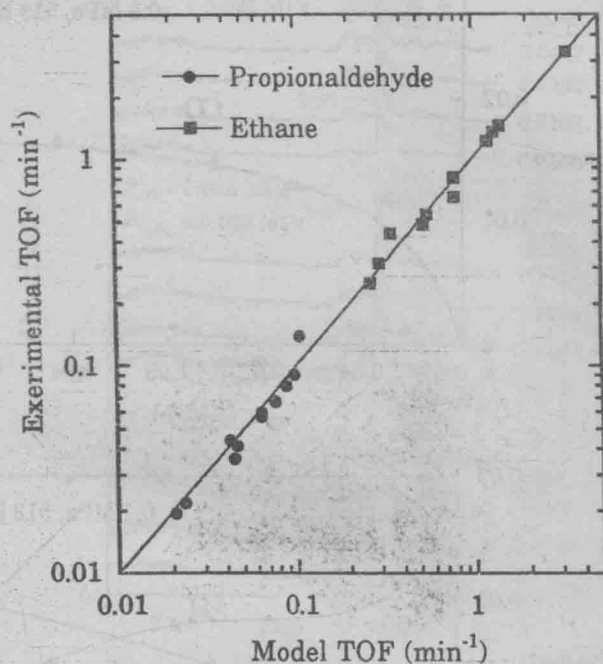


FIGURE 5. Comparison of LHHW model for the reaction rate of ethylene and propionaldehyde formation with experimental data during hydroformylation on Rh/SiO₂ at a total pressure of 0.1 MPa and 513 K.

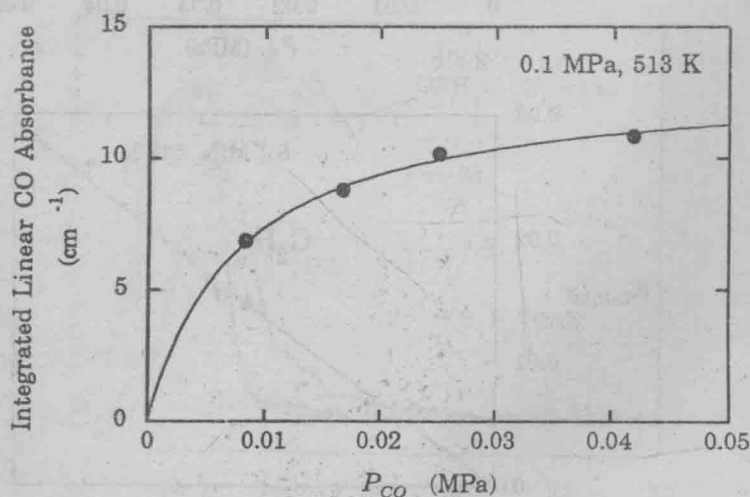


FIGURE 6. Adsorption isotherms of *CO as a function of the partial pressure of CO.

用于多相催化研究的若干新的动态方法*

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摘要 经过二三十年的发展, 动态分析技术已成为研究多相催化反应的新的有力工具并已成为多相催化研究提供了大量十分有意义的信息。本文总结介绍在我们实验室新近发展的五个新的动态分析技术: 迎头反应色谱、时间分辨催化反应色谱, 加压迎头反应色谱, 程序升温迎头吸脱附技术和测量分子筛中扩散系数的迎头色谱。迎头反应色谱技术是先前的动态—稳态法的延伸, 该方法主要是在动态分析理论上的发展, 这一发展为研究可逆和不可逆吸附物种在多相催化反应中的作用提供了可能, 并以乙炔加氢为例, 测量了可逆和不可逆吸附乙炔加氢为例, 测量了可逆和不可逆吸附乙炔在加氢反应中的贡献及它们的反应动力学参数。时间分辨催化反应色谱技术是对催化反应色谱技术在实验技术上的改进和简化, 使之更实用并能用于获得反应器出口处各反应组分的流出曲线, 这样有可能应用除矩分析方法外的其它数据处理方法来计算吸附和表面反应速率系数, 研究催化剂制备对它们的影响。加压迎头反应色谱技术是实验装备上的一个突破, 使动态分析方法不仅能在常压下而且能在加压下研究催化反应, 使其应用范围大为扩大并更具生命力, 该技术已在一氧化碳加氢反应上取得很有意义的结果并为研究压力作用的本质提供了可能。程序升温迎头吸脱附技术也是实验技术上的改进, 使之能在实际反应条件研究可逆和不可逆吸附物种与催化剂反应性能间的关系, 并以负载铂催化剂上烃类重整反应为例证实该技术的实用性。测量分子筛中扩散系数的迎头色谱技术克服了重量天平法和脉冲色谱法的缺点而保留了色谱技术快速简单方便的优点, 通过应用严格模型和简化模型对实验迎头曲线处理计算的比较证明, 在适当实验条件下可应用简化模型来处理实验曲线计算扩散系数而不导致太大误差, 为研究分子筛中的扩散提供新的快速简便方法。

新发展的五个动态分析技术都具有快速简单方便灵活价廉等特点, 易于为一般实验室采用。虽然这些新动态方法还有待进一步完善的地方, 但毕竟为多相催化研究提供了新的工具。

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一、前言

顾名思义, 催化一般指加速某化学反应速度的现象。也就是说催化涉及反应速率问题, 它本质上应该说是具有动态性质的。因而稳态方法只能提供复杂催化过程的最基本的信息, 相反动态方法有可能提供催化过程各速率步骤的信息而渐受重视。自本世纪六七十年代提出用动态方法研究多相催化过程以来, 它已受到愈来愈多的催化科学工作者的重视, 而有了飞速的发展。并为催化科学提供了大量十分有用的信息, 极大地推进了对催化过程本质的了解。为进一步促进动态技术的发展和运用以及同行间的相互交流, 世界范围内已举行了多次国际动态学术会议。国内也在1989年召开了全国多相催化中的动态技术及其应用的学术会议。

从技术和仪器设备角度看, 有以各种现代表面分析工具为手段的动态原位技术和以色谱为工具的动态技术。前者能提供许多宝贵的表面吸附态及其反应性和催化剂表面组成结构及与吸附分子相互作用方面的许多信息, 其缺点是仪器设备一般价格昂贵, 实验费用较高, 且一般离催化实际过程较远。而后者, 虽不能提供催化剂表面结构组成及与吸附分子相互作用