

Isotopic Transient Kinetic Analysis of Ethane Hydrogenolysis on Ru/SiO₂

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Steady-state isotopic transient kinetics analysis has been applied to determine attributes of the active intermediates and the surface kinetics of ethane hydrogenolysis, known to be a very structure-sensitive reaction, on Ru/SiO₂. The abundances, coverages, and lifetimes of surface intermediates of the reaction were measured under reaction conditions and their dependence upon temperature was determined. The results show that intrinsic activities and abundances of surface di-carbon and mono-carbon species change in different ways with temperature. The surface coverage of di-carbon species is much lower than that of mono-carbon species, while the reactivity of the mono-carbon species is greater than that of the di-carbon species. The surface coverage of di-carbon species was not found to change with temperature under the conditions studied, while that of mono-carbon species increased with increasing temperature. The results suggest that the breakage of the C–C bond is the slowest step for ethane hydrogenolysis. The activation energies of the surface reactions of di- and mono-carbon species were found to be 36 ± 3 and 9 ± 3 kcal/mole, respectively. The exchange reaction of ethane with deuterium was also investigated in order to understand better the reaction mechanism. © 1995 Academic Press, Inc.

INTRODUCTION

Ethane hydrogenolysis is commonly used as a model reaction to study carbon–carbon bond rupture. This reaction has been found to be very structure sensitive (1–3). The activity of a metal catalyst for ethane hydrogenolysis depends markedly on the spatial coordination of surface metal atoms (1) and appears to require site ensembles of ca. 12 metal atoms (3). Thus, the size and morphology of supported metal crystallites greatly affect the determined turnover frequency (TOF) due to the variation caused by these parameters in the distribution of surface crystal planes exposed.

The reaction mechanism upon which most researchers in this field generally agree involves chemisorption of both ethane and hydrogen on the surface dissociatively,

dehydrogenation of the adsorbed di-carbon species, breakage of the di-carbon intermediates into mono-carbon species, and, finally, hydrogenation of the mono-carbon intermediates to form methane. While the rate-determining step is still being debated, many researchers (4–6) consider the rupture of the carbon–carbon bond to be the slowest step.

The kinds of active intermediates formed during reaction are directly related to the reaction mechanism and the nature of a metal catalyst. Somorjai and co-workers (7, 8) used LEED and TDS to study D₂–ethane exchange and ethane hydrogenolysis on Pt(111) and suggested that ethylidyne may be the major catalytically active intermediate that leads to highly deuterated ethane and methane. Further dehydrogenation of that species was suggested to create C₂H and C₂ which do not hydrogenate to produce methane because they poison active sites (7).

The exchange reaction between deuterium and ethane could provide information pertinent to our understanding of ethane hydrogenolysis. Zaera and Somorjai (8) have proposed that exchange and hydrogenolysis share the same active intermediates initially. The degree of deuteration of the ethane during the exchange reaction depends upon the chemical nature of the metal, partial pressure of deuterium and ethane, and reaction temperature.

Steady-state isotopic transient kinetic analysis (SSITKA), developed in large part by Happel (9) and Bileon (10), is one of the most powerful techniques for the investigation of surface reactions. Compared with other *in situ* techniques, it provides more definitive information about the concentration of active intermediates and their activities.

The aim of this research was to study the effect of temperature on abundances, intrinsic activities, and lifetimes of surface reaction intermediates during ethane hydrogenolysis on Ru/SiO₂ and to elucidate the surface kinetics of reaction. This research employed steady-state isotopic transient kinetic analysis for determining the above-mentioned surface reaction parameters. Deuterium–ethane exchange was also utilized in order to correct

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the SSITKA results for potentially reversible reaction steps during ethane hydrogenolysis.

EXPERIMENTAL

The Ru/SiO₂ catalyst was prepared using the incipient wetness impregnation method. Ru(NO)NO₃, dissolved in distilled water, was impregnated into Cab-O-Sil HS5 fumed silica. The catalyst precursor was dried at 90°C overnight. It was then heated in flowing hydrogen at the rate of 1°C/min to 400°C and then reduced at this temperature for 8 h. After reduction, the catalyst was washed with boiling distilled water and filtered at least five times to minimize any chloride present. The catalyst was dried again at 90°C overnight. The catalyst contained 3% ruthenium (by weight). Elemental analysis was done by Galbraith Lab, Inc. Hydrogen chemisorption, following *in situ* re-reduction, was used to measure dispersion of the supported metal catalysts, as described elsewhere (12).

The isotopic transients were measured using the system shown in Fig. 1. Two gas streams having the same gas compositions and flow rate but different isotopic concentrations were able to be switched from one to the other under the same back pressure. The system had on-line gas chromatography (GC) and mass spectroscopy (MS). A Varian 3700 GC with an FID detector and a 6-ft 60–80 mesh Porapak Q column was used. A Leybold–Inficon

Auditor-2 MS equipped with a high speed data acquisition system was interfaced to a 386-PC. The lengths of all tubing lines were minimized so that the residence time in transit was less than 6 s. A sampling assembly was installed so that the amount of gas leaking into the MS could be controlled precisely by differential pumping.

Rate measurements of ethane hydrogenolysis were made using 30 to 50 mg of the catalyst loaded at a time in a microreactor. The catalyst was re-reduced in a flow of hydrogen at a rate of 50 cc/min at 400°C for 6 h. After reduction, the catalyst bed temperature was lowered to the desired initial reaction temperature in hydrogen. Once the initial reaction temperature had been reached, the feed was switched to the reactant mixture ($P_{C_2H_6} = 0.6$ kPa, $P_{H_2} = 24.0$ kPa, $P_T = 202.6$ kPa with the balance being He, total flow rate = 50 cc/min), and samples of the products were taken and analyzed after 5 min of reaction. Labeled ethane, ¹³C₂H₆ (Isotech), was used to study the carbon reaction pathway. Switches between the two reactant streams having different isotopically labeled ethane were able to be made without perturbing the steady operation of the reaction. A trace of argon was present in the normal ethane stream in order to permit determination of gas phase hold-up. The isotopic switch was done immediately after 5 min of reaction. In order to maintain the initial state of the catalyst for reaction at the next temperature, the gas stream was switched to pure H₂ after a total of 8 min of reaction, and the catalyst was re-reduced at 400°C for 2 h before the next measurement. The measurement at each temperature was repeated three times. Finally, activity was remeasured at the first reaction temperature studied to make sure that there had been no deactivation during the collection of the temperature-dependent data. Steady-state reaction and isotopic transient kinetic data were collected at four different reaction temperatures: 150, 160, 170, and 180°C. Specific activities were calculated in terms of the rate of disappearance of ethane per gram of catalyst. The exchange reaction of ethane with deuterium during ethane hydrogenolysis was carried out by switching between H₂ and D₂. The ratio of H₂/D₂-to-ethane was 40 : 1. The composition of deuterated ethane was analyzed using linear interpolation based on measured fragmentation of both C₂H₆ and C₂D₆.

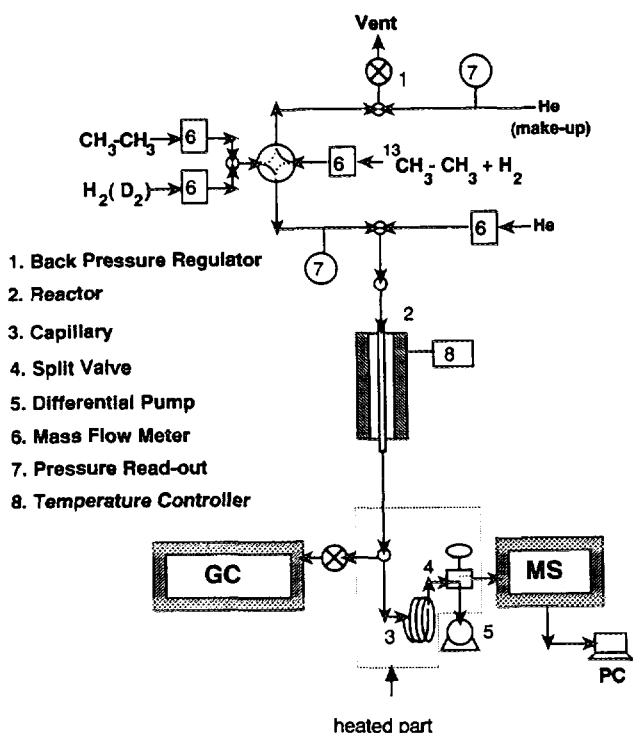


FIG. 1. Schematic of SSITKA system.

RESULTS AND DISCUSSION

Loading and Dispersion of Ru

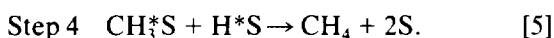
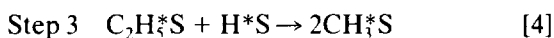
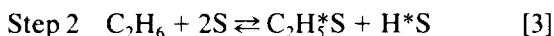
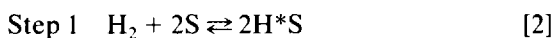
Atomic absorption results confirmed that the Ru loading was 3 wt%. Irreversible H₂ chemisorption at room temperature was used to determine the % dispersion of Ru to be 36.3%. The average Ru particle size was calculated to be 2.4 nm.

Overall Kinetic Parameters of the Reaction

The power law rate expression for ethane hydrogenolysis can be expressed as

$$R = k_0 e^{-E/RT} P_E^n P_H^m, \quad [1]$$

where E , n , and m can be measured experimentally. Table 1 shows values of the parameters from the literature as well as from this work. The general reaction mechanism, with which most researchers agree, can be expressed by



Although the above proposed mechanism may be somewhat simplistic, it includes the major hypothesized surface reactions. The rate-determining step proposed for a number of metal catalysts is summarized in Table 2. Thus, step 3 would appear to be the slowest step or rate-determining step for ethane hydrogenolysis on many metal catalysts. Dissociative adsorption of ethane, step 2 as shown in the above mechanism, according to Zaera and Somojai (8), is much slower than any further dehydrogenation steps. In other words, step 2 can be used to represent the overall adsorption and dehydrogenation of ethane in the proposed mechanism. However, the kinetic data that we report is consistent with that reported by others (Table 1).

Deuterium Exchange with Ethane

Since ethane hydrogenolysis shares a number of similar steps with hydrogen exchange of ethane, a study of the exchange between deuterium and ethane could help to

delineate aspects of active surface intermediates during ethane hydrogenolysis. The ethane and deuterium exchange reaction cannot occur in the gas phase at the temperatures used here (25–180°C). It can only occur on an active surface. Table 3 shows the results summarized from the experiment. Even at the lowest temperature of interest (150°C), the % exchange was already 100% while the conversion by hydrogenolysis was very low. A blank test using just the SiO₂ support showed that the exchange reaction could not happen in the absence of Ru.

Figure 2 shows the distribution of deuterated ethane over this Ru/SiO₂ catalyst at 150°C with D₂/C₂H₆ = 40/1. No C₂H₆ remained after exchange under these conditions. Ru has been found previously to give C₂D₆ as the most abundant product of the exchange reaction (16), as also found here. Another very interesting feature of the exchange reaction which is worth mentioning is that the rate expression for this reaction is positive-order in ethane and negative-order in deuterium (8, 16), which may imply that hydrogenolysis and hydrogen exchange share similar surface steps and intermediates. As for the exact mechanism of the exchange reaction, there is still a lot of debate about the distribution of deuterated ethane (17, 18). However, most researchers agree that the reaction proceeds by adsorption, dehydrogenation, deuteration or rehydrogenation, and desorption of the exchanged ethane.

The general features of the exchange reaction established by other investigators can be summarized as:

- The exchange of ethane with deuterium occurs much more readily than the cracking of ethane. On Pt(111), the activation energy is 19 kcal/mole for the exchange reaction versus 34 kcal/mole for hydrogenolysis (8). The activity for exchange is three orders of magnitude faster than hydrogenolysis over the temperature range studied.
- Dissociative adsorption of ethane to form an adsorbed C₂H₅^{*} species is the first step and is slower than further dehydrogenation and deuteration of adsorbed species to produce the desorption product (8, 16–18).

TABLE 1

Summary of Reaction Parameters of Ethane Hydrogenolysis

Authors	Catalyst	Reaction orders ^a		Temperature ^b (°C)	E (kcal/mole)	Temperature range (°C)
		n	m			
Smale and King (6)	4% Ru/SiO ₂	0.91	-1.37	235	34.0	200–290
Sinfelt (14)	1% Ru/SiO ₂	0.80	-1.30	188	32.0	177–210
Egawa and Iwasawa (15)	Ru(1,1,10)	0.55	-0.75	215	22.0	202–249
This work ^c	3% Ru/SiO ₂	0.84	-1.11	170	33.0	160–180

^a Rate = $kP_E^n P_H^m$.

^b Temperature for reaction order measurement.

^c $P_{\text{C}_2\text{H}_6} = 0.3\text{--}1.1$ kPa, $P_{\text{H}_2} = 10.6\text{--}26.6$ kPa, $P_{\text{T}} = 202.6$ kPa (balance He), total flow rate = 100 cc/min.

TABLE 2

Summary of Rate-Determining Step for Ethane Hydrogenolysis

Authors	Rate-determining step	Catalyst
Shang and Kenney (4)	Breakage of C-C bond	Ru/Si ₂ O ₃
Rodriguez and Goodman (13)	Breakage of C-C bond	Ni-Pt(111)
Zaera and Somorjai (8)	Breakage of C-C bond	Pt(111)
Smale and King (6)	Breakage of C-C bond	Ru/SiO ₂
Sinfelt (14)	Breakage of C-C bond	Ru/SiO ₂

• The exchange reaction over Ru, Rh, and Ir always gives C₂D₆ as the most abundant product (16).

• Highly deuterated ethane being the most abundant product from the exchange reaction suggests that the initially formed C₂H₅ ethyl moiety can be converted to multiply metal-bonded carbon species which may be directly related to the active intermediates present during ethane hydrogenolysis (20).

Therefore, a significant common component of the exchange and hydrogenolysis reactions may be that they occur via C₂H_x active surface intermediates. The differences between these two overall reactions appears to be that deuteration of C₂H_x is quite easy and fast for the exchange reaction, but that hydrogenolysis cleavage of the carbon-carbon bond in C₂H_x, which requires more energy, is slower. Under the conditions studied, it was found that every ethane atom interacted with the catalyst since the % exchange was 100%; however, the conversion of methane was significantly lower. Therefore, under the conditions studied, all ethane in the reactant stream interacted with the catalyst since deuteration cannot take place at these conditions without being catalyzed.

Isotopic Transient Kinetics during Ethane Hydrogenolysis

Blank tests showed that in the absence of the catalyst, the reactant, ethane, following an isotopic switch, estab-

TABLE 3
Ethane-Deuterium Exchange

Catalyst	Catalyst charge (mg)	Temperature (°C)	Exchange ^a (%)	Hydrogenolysis ^b (%)
Ru/SiO ₂	31.0	25	0	0
Ru/SiO ₂	31.0	150	100	1.6
Ru/SiO ₂	31.0	180	100	22.8
Cab-O-Sil HS-5	56.0	180	0	0

^a Conversion calculated based on the amount of C₂H₆ converted into deuterated ethane; % exchange is defined as $((1 - P_{C_2H_6}(\text{out})) / P_{C_2H_6}(\text{in})) * 100\%$; D₂/C₂H₆ = 40/1.

^b Conversion of ethane to methane.

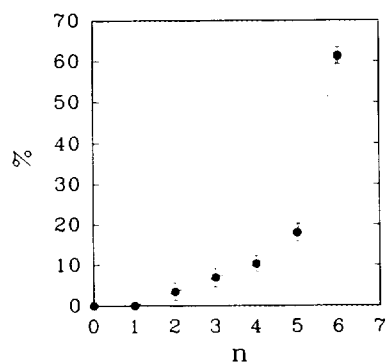


FIG. 2. Distribution of deuterated ethane as a product of the D₂-C₂H₆ exchange reaction at 150°C (n = number of deuterium atoms in effluent ethane).

lished the same isotopic transient as the inert gas (trace), argon, showing that there was no additional holdup of ethane in the absence of the catalyst.

The catalyst bed length was able to be varied by varying the weight of catalyst used. If significant readsorption of either reactants or products occurs, then surface residence time should increase with increasing weight of catalyst used. Table 4 shows that there was little effect of catalyst loading on residence time for catalyst weights ≤ 75 mg. However, since there were significant changes in residence time for both ethane and methane as the catalyst, loading was increased above 100 mg. This apparent inconsistency was due to the fact that, at low L/D ratios of the bed (catalyst weights <75 mg), channeling was able to occur. The results indicate, thus, that reversible adsorption of ethane occurred under the conditions used in this study.

Figure 3 shows a typical steady-state isotopic transient observed during ethane hydrogenolysis. Average surface residence time for the carbon in methane or ethane is given by the area between the CH₄ or C₂H₆ and the Ar transients. The different surface residence times measured at various temperatures are summarized in Table 5. From Table 5, it would appear at first view that the residence times of surface intermediates for both meth-

TABLE 4

The Residence Time of Reactant and Product during Product during Ethane Hydrogenolysis on Ru/SiO₂ at 170°C

Weight of catalyst (mg)	τ_{CH_4} (s)	$\tau_{C_2H_6}$ (s)
30.6	1.63	1.06
61.6	1.75	0.99
75.1	1.81	1.01
150.1	2.04	1.54

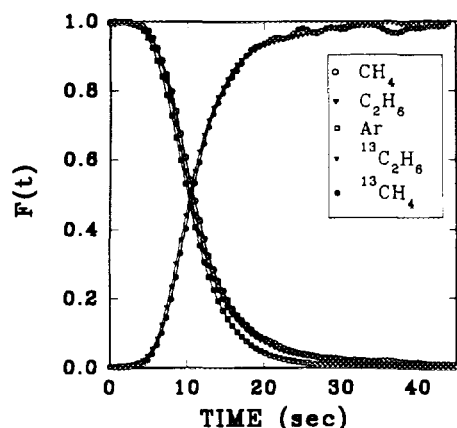


FIG. 3. Steady-state transients during ethane hydrogenolysis on Ru/SiO₂ at 180°C.

ane and ethane did not vary significantly with temperature.

To date, SSITKA has been used mainly for CO hydrogenation which is essentially an irreversible reaction. The question of how to deal with reversible reactions has not been widely addressed, although it was discussed in an early paper by Biloen *et al.* (11). However, it is of critical importance for correctly analyzing SSITKA data.

Potential Models on which to Base Isotopic Kinetic Analysis

Based on the discussion given by Biloen *et al.* (11), five potential cases can be considered to exist for the relationship of pools of surface intermediates to each other, to the reactant, and to the product during ethane hydrogenolysis. They are presented below in detail and shown schematically in Fig. 4. We will consider a reaction $A + \dots \rightleftharpoons B$ where a switch is made from lA (isotopically labeled A) to ^{ul}A (unlabeled A). Obviously, the designation of labeled vs unlabeled is arbitrary. Here labeled will refer to the isotope being switched off. The discussion will involve the following terms for a given species i leaving the reactor:

TABLE 5

Parameters from SSITKA during Ethane Hydrogenolysis

Temperature (°C)	$\tau_{CH_4}^a$ (s)	$\tau_{C_2H_6}^a$ (s)	$R_{C_2H_6}$ (nmole/g/s)	TOF_H^b ($10^{-3} s^{-1}$)
150	1.90 ± 0.13	1.20 ± 0.06	53 ± 4	0.5
160	1.71 ± 0.14	1.15 ± 0.02	138 ± 9	1.3
170	1.60 ± 0.05	1.06 ± 0.04	442 ± 17	4.1
180	1.50 ± 0.10	1.06 ± 0.01	759 ± 30	7.0

^a Surface residence time after subtracting gas phase holdup.

^b Based on irreversible H₂ chemisorption.

- i effluent species A or B
- j pool 1 or 2
- l isotopically labeled, such as for $^{12}C_2H_6$
- ul unlabeled, the opposite label as l , such as for $^{13}C_2H_6$
- ss steady-state
- ms metal surface atoms (normally from irreversible H₂ chemisorption in the case of Ru)
- $F_m^i(t)$ the fraction of labeled species, i , measured in the effluent, $i = A, B$. (This is given by the isotopic transients measured.)
- $F_c^i(t)$ the isotopic transient of labeled effluent i after correction for gas phase holdup
- $F_j(t)$ the fraction of the labeled species leaving pool j , $j = 1, 2$
- N_j surface abundance of intermediates in pool j (mole/g)
- Q_j total flow rate of (labeled + unlabeled) species through a pool j of surface intermediates (mole/g/s)
- TOF turnover frequency (s^{-1})
- R steady-state reaction rate (mole/g/s)

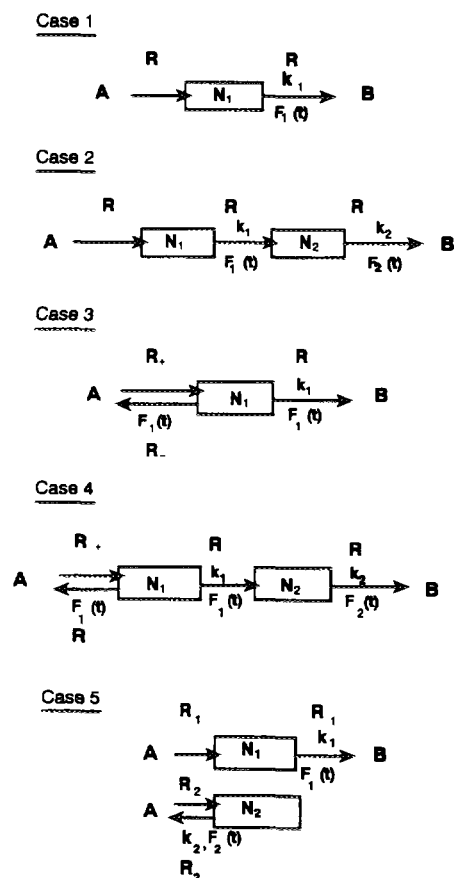


FIG. 4. Possible configurations of different pools of surface intermediates during ethane hydrogenolysis.

k_j intrinsic activity of intermediates in pool j (s^{-1})
 τ^i surface residence time of effluent species i (s)
 N_{ms} amount of metal surface atoms (mole/g)
 θ surface coverage

Case 1: One pool with unidirectional steps. This case is often what is assumed and certainly applies reasonably in the case of methanation. The abundance of surface intermediates in the each pool, $N_{1,ss} = {}^lN_1 + {}^uN_1$, is constant under steady state reaction:

$$\begin{aligned}
 dN_{1,ss}/dt &= \text{rate of adsorption} \\
 &\quad - \text{rate of consumption of intermediate} \\
 &\quad \text{in pool 1} = 0.
 \end{aligned}$$

The isotopic composition of this pool is given by

$$F_1(t) = {}^lN_1/({}^lN_1 + {}^uN_1) = {}^lN_1/N_{1,ss}$$

where $F_1(t) = F_c^B(t)$.

The time dependence of the abundance of labeled intermediates in the pool for $t \geq 0$ ($t = 0$ is the time of the isotopic switch) can be determined as follows. Since

$${}^lQ_{1,in} = 0$$

and

$${}^lQ_{1,out} = R F_c^B(t),$$

the material balance for pool 1, for $t \geq 0$, gives

$$d{}^lN_1/dt = {}^lQ_{1,in} - {}^lQ_{1,out} = -R F_c^B(t).$$

Since

$$\begin{aligned}
 d{}^lN_1/dt &= N_{1,ss} dF_1(t)/dt \quad \text{and} \quad F_1(t) = F_c^B(t), \\
 dF_c^B(t)/F_c^B(t) &= -(R/N_{1,ss}) dt.
 \end{aligned}$$

At $t = 0$ (time at which the isotopic switch occurs)

$$F^B(0) = 1.0$$

so that

$$\ln F_c^B(t) - 0 = -R/N_{1,ss} t.$$

Rearranging gives

$$F_c^B(t) = e^{-(R/N_{1,ss})t} = F_1(t).$$

If we assume that the pool is internally homogeneous,

that there is no isotopic effect so that the isotopic switch does not change the intrinsic activity of the pool, and that the reaction is *pseudo-first-order* in the surface intermediates, then

$$\text{rate of reaction} = -k_1 N_1$$

and

$$d{}^lN_1/dt = -k_1 {}^lN_1.$$

Since

$${}^lN_1 = N_{1,ss}, \quad \text{at } t = 0,$$

$${}^lN_1 = N_{1,ss} e^{-k_1 t}.$$

Thus,

$$F_1(t) = e^{-k_1 t}$$

and consequently

$$k_1 = R/N_{1,ss}.$$

Since

$$\tau^B \cong \frac{N_{1,ss}}{R} = \int_0^\infty [F_m^B(t) - F_{inert}(t)] dt = \int_0^\infty F_c^B(t) dt,$$

then

$$k_1 = \frac{1}{\tau^B}.$$

If the total number of metal surface atoms is N_{ms} ,

$$\text{TOF} = R/N_{ms}, \quad \theta_1 = N_{1,ss}/N_{ms}.$$

Therefore

$$\text{TOF} = k[\theta_1] = \frac{1}{\tau^B} [\theta_1].$$

Case 2: Two pools in series with unidirectional steps. Based on analogy to the equations developed for Case 1,

$$F_1(t) = e^{-t/\tau_1}.$$

A material balance around the second pool gives

$$\begin{aligned}
 {}^lQ_{2,in} &= R F_1(t), \quad {}^lQ_{2,out} = R F_2(t) \\
 d{}^lN_2/dt &= N_{2,ss} dF_2(t)/dt = R \{F_1(t) - F_2(t)\}
 \end{aligned}$$

with $dF_2(t)/dt = 0$ at $t = 0$

$$dF_2/dt = (R/N_{2,ss})[e^{-t/\tau_1} - F_2(t)].$$

By definition,

$$\tau_2 \equiv N_{2,ss}/R.$$

Thus,

$$dF_2(t) = \tau_2[e^{-t/\tau_1} - F_2(t)] dt.$$

Solving produces

$$F_2(t) = \frac{\tau_1}{\tau_1 - \tau_2} e^{-t/\tau_1} - \frac{\tau_2}{\tau_1 - \tau_2} e^{-t/\tau_2}$$

where

$$\tau_1 = N_{1,ss}/R, \quad \tau_2 = N_{2,ss}/R.$$

In this case, only $F_c^B(t)$ can be observed {(where $F_c^B(t) = F_2(t)$)} and $(\tau_1 + \tau_2) = \tau^B$ can be determined. In other word, τ_1 and τ_2 cannot be measured separately.

For this case, assuming a pseudo-first-order reaction,

$$\text{TOF} = k_1[\theta_1] = k_2[\theta_2],$$

where $k_1 = 1/\tau_1$ and $k_2 = 1/\tau_2$.

If $\tau_1 \gg \tau_2$, N_2 would be negligible and this case would be essentially identical to Case 1.

Case 3: Single pool with a reversible step. Biloen *et al.* (11) first gave a description of the mathematics of SSITKA for this case. Here

$$R_+ = R + R_-$$

and

$$F_c^A(t) = F_c^B(t) = F_1(t)$$

assuming all A adsorbs with no catalyst by-passing. A material balance around the pool for $t \geq 0$ gives

$${}^iQ_{1,in} = 0, \quad {}^iQ_{1,out} = (R_- + R)F_1(t)$$

and

$$d^iN_1/dt = {}^iQ_{1,in} - {}^iQ_{1,out} = -R_+F_1(t).$$

Since

$$(d^iN_1/dt)/N_{1,ss} = (-R_-/N_{1,ss})F_1(t)$$

and

$$F_1(t) = N_1/N_{1,ss},$$

we arrive at $dF_1(t)/F_1(t) = -\tau_1 dt$,

where

$$\tau_1 \equiv N_{1,ss}/R_+.$$

Thus,

$$F_1 = e^{-t/\tau_1},$$

where

$$\tau_1 = \tau^A = \tau^B.$$

$F_m^A(t)$ and $F_m^B(t)$ are observed experimentally. The transients for both the product and the desorbed reactant are identical assuming all A adsorbs; τ_1 can be determined from either $F_c^A(t)$ or $F_c^B(t)$. However, even for a pseudo-first-order rate assumption, due to the fact that the residence time τ_1 for the reactant on the surface is governed by both reaction and desorption before reaction to product, the relationship of τ_1 to k_1 is more complicated than in Case 1 (irreversible, single pool)

$$\tau_1 = N_{1,ss}/R_+ = N_{1,ss}/[R(R_- + R)/R].$$

Rearranging,

$$R = N_{1,ss}/[\tau_1(R_- + R)/R] = N_{1,ss}/[\tau_1(1 + R_-/R)].$$

Dividing both sides by N_{ms} ,

$$\text{TOF}^B = k_1\theta_1 = \theta_1/[\tau_1(1 + R_-/R)]$$

Thus,

$$k_1 = 1/\{\tau_1(1 + R_-/R)\}.$$

For the pool in which only irreversible surface reaction occurs, $R_- = 0$, $R_-/R = 0$, k_1 reduces to $1/\tau_1$, and this case becomes identical to Case 1.

For F_c^A to be identical to F_c^B , all of A must adsorb; thus, it is always better to base calculations on $F^B(t)$, since often this condition is not met in differential reactors.

Case 4: Two pools in series with the first step reversible. Again,

$$R_+ = R_- + R.$$

By analogy with Case 2, we know that

$$F_1(t) = e^{-t/\tau_1}$$

$$F_2(t) = \frac{\tau_1}{\tau_1 - \tau_2} e^{-t/\tau_1} - \frac{\tau_2}{\tau_1 - \tau_2} e^{-t/\tau_2}$$

By definition

$$\tau_1 = N_1/R_+, \quad \tau_2 = N_2/R$$

$$\text{TOF}^B = k_1\theta_1 = k_2\theta_2$$

By analogy to Case 3 for a pseudo-first-order rate assumption,

$$k_1 = 1/\{\tau_1(1 + R_-/R)\}$$

By analogy to Case 2 for a pseudo-first-order rate assumption,

$$k_2 = 1/\tau_2$$

Since both $F_c^A(t)$ and $F_c^B(t)$ can be determined separately, τ^A and τ^B can also be determined. The determination of τ_1 again requires the assumption that all A has adsorbed. If so, $\tau_1 = \tau^A$, and $\tau_1 = \tau^B - \tau_1$. Thus,

$$\tau_1 = \tau^A = \int_0^\infty [F_m^A(t) - F_{\text{inert}}(t)] dt$$

and

$$\tau_2 = \tau^B - \tau_1 = \int_0^\infty [F_m^B(t) - F_{\text{inert}}(t)] dt - \tau^A$$

Case 5: Two separate pools. By analogy to case 1

$$F_1(t) = e^{-t/\tau_1}$$

and

$$F_2(t) = e^{-t/\tau_2}$$

By definition

$$\tau_1 \equiv N_{1,ss}/R_1, \quad \tau_2 \equiv N_{2,ss}/R_2$$

Thus, for pseudo-first-order reaction to product,

$$\text{TOF}_1 = k_1\theta_1;$$

$$R_1/N_{ms} = k_1[N_{1,ss}/N_{ms}]$$

$$k_1 = R_1/N_{1,ss}$$

and

$$k_1 = 1/\tau_1 = 1/\tau^B$$

In order to analyze the SSITKA results, it is necessary to settle on one of the above cases as the best model for ethane hydrogenolysis. Thus, the experimental evidence must be examined to decide which case is best substantiated.

We know from isotopic transient kinetic measurements that some adsorption of ethane is reversible. Thus, a reversible adsorption step is involved in the reaction pathway for ethane hydrogenolysis, suggesting only Cases 3, 4, and 5 as possible models for this reaction. However, since the surface residence time of methane is always longer than that of ethane, and we know from D₂-ethane exchange that all the ethane molecules are coming in contact with the surface, methane and ethane must come from different pools. Therefore, Case 3 can be excluded here. Case 5 would consider the catalyst to be made up of two types of active sites: one capable of carrying out the irreversible adsorption of ethane followed by reaction and the other able to only reversibly adsorb ethane. If surface reactions during ethane hydrogenolysis occur as described in Case 5, there must be an amount of singly exchanged ethane (C₂H₅D) as a product during D₂-ethane exchange according to Frennet *et al.* (24, 25). However, Fig. 2 shows that only a negligible amount of C₂H₅D was produced at most. In addition, after the reactants were shut off and the catalyst was flushed first with He and then with H₂, only methane came out (see Fig. 5), providing additional evidence that Case 5 is not operable. Thus, it is suggested that Case 4 is a more suitable model for ethane hydrogenolysis where the same sites can reversibly adsorb C₂H₆ as well as carry out hydrogenolysis.

Analysis of Results Based on Case 4

In order to determine many of the desired parameters, it is necessary to accurately determine R_+ . However, even though all ethane molecules collided with the catalyst surface (based on D₂-ethane exchange), it is impossible to say whether they all adsorbed on potential ethane hydrogenolysis sites. Therefore, $R_+ \leq F_{C_2H_6}$. Consequently, the parameters calculated represent maximal or minimal values for the desired parameters. The following indicates for Case 4 a comparison of calculated values of the parameters to their actual values:

$$\tau_{1,\text{real}} = \tau^A \geq \tau_m^A, \quad \tau_{2,\text{real}} \leq \tau_{2,\text{calc}} = \tau^B - \tau_m^A$$

$$k_{1,\text{real}} \leq k_1 = 1/\{\tau_1(1 + R_-/R)\}$$

$$k_{2,\text{real}} \geq k_2 = 1/\tau_2$$

$$N_{1,\text{real}} \geq N_{1,\text{calc}}$$

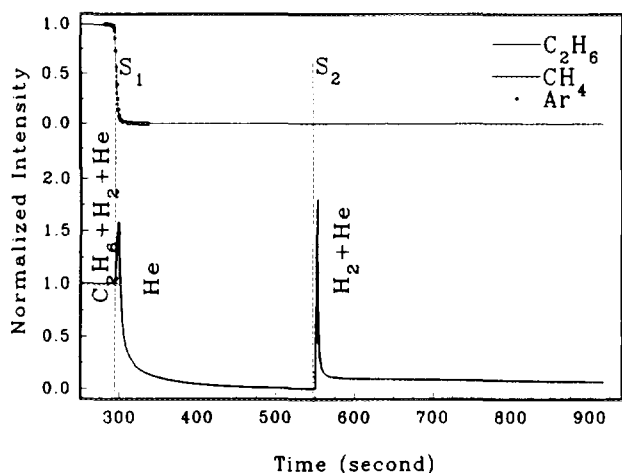


FIG. 5. Stop flow of reactant mixture followed by H_2 reaction with surface intermediates on Ru/SiO₂ at 150°C. (Period S₁: after 5 min of reaction, the mixture of C₂H₆ + H₂ was shut off and only He passed through the catalyst). (Period S₂: after 250 s flushing in He, the stream was switched to H₂ + He, the H₂ partial pressure being the same as that in the reaction mixture).

(since this represents only the adsorbed ethane which desorbs and does not include that which reacts to methane)

$$N_{2,real} \leq N_{2,calc.}$$

(since $N_{2,calc.} = N_2 +$ the part of N_1 leading to methane). While exact values cannot be determined, a sense can be gained from the estimated values as to their relative importances and how they vary with conditions.

The first pool should consist of intermediates, C₂H_x, and the second of mono-carbon species, CH_y. The values of τ_1 and τ_2 and N_1 and N_2 are able to be calculated, based on the discussion given for Case 4, and have been for different reaction temperatures (see Table 6). As shown in Table 6, the surface coverage of di-carbon intermediates accounts for around 3% of surface atoms, while the coverage of mono-carbon species is much less. The coverage in adsorbed hydrogen cannot be determined by SSITKA.

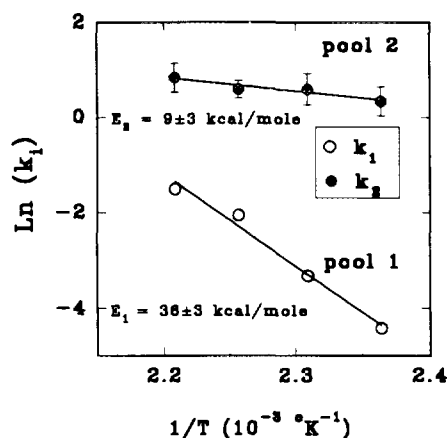


FIG. 6. The effect of temperature on intrinsic activities of the two pools of intermediates.

Since k_i and N_i can both be determined, their individual effect on overall rate of reaction as a function of temperature can be evaluated (19). Figure 6 shows the effect of temperature on intrinsic activities of the two pools. E_1 and E_2 can be calculated from the slope of $\ln k_i$ vs $1/T$ in Fig. 6. E_1 was found to be 36 ± 3 kcal/mole, approximating the overall apparent activation energy (Table 1) for ethane hydrogenolysis on supported Ru catalysts. This fits with the breakage of the C-C bond being the rate-determining step. In addition, the intrinsic activity of pool 1 was much lower than that of pool 2, also suggesting that CH_x hydrogenation and desorption cannot be the slowest step in the mechanism. Obviously, absorption of ethane is unlikely to be the rate-determining step since the rate of the D₂-C₂H₆ exchange reaction is much faster than hydrogenolysis. E_2 was found to be 9 ± 3 kcal/mole, which may represent the activation energy for the hydrogenation of the monocarbon species. This value is close to the activation energy for the hydrogenation of ethylene (8.7 kcal/mole on Ru/Al₂O₃ (21) and 8.4 kcal/mole on Ni/SiO₂ (22)). For methanation on Ni catalysts, Goodman *et al.* (23) and Yang *et al.* (19) found that the coverage of intermediates was low, although an increase in temperature increased the coverage. This is in agreement with

TABLE 6

Surface and Reaction Parameters Calculated from SSITKA during Ethane Hydrogenolysis Assuming Case 4

Temperature (°C)	τ_1 (s)	τ_2 (s)	k_1 (10 ⁻³ s ⁻¹)	k_2 (s ⁻¹)	N_i (μmole/g)		θ_i	
					$i = 1$	$i = 2$	$i = 1$	$i = 2$
150	1.20 ± 0.06	0.70 ± 0.19	12 ± 1	1.4 ± 0.5	3.9	0.03	0.036	0.0003
160	1.15 ± 0.02	0.56 ± 0.16	36 ± 4	1.8 ± 0.7	3.8	0.08	0.033	0.0007
170	1.06 ± 0.04	0.55 ± 0.09	127 ± 3	1.8 ± 0.4	3.5	0.24	0.032	0.0022
180	1.06 ± 0.01	0.44 ± 0.11	221 ± 12	2.3 ± 0.8	3.4	0.33	0.031	0.0031

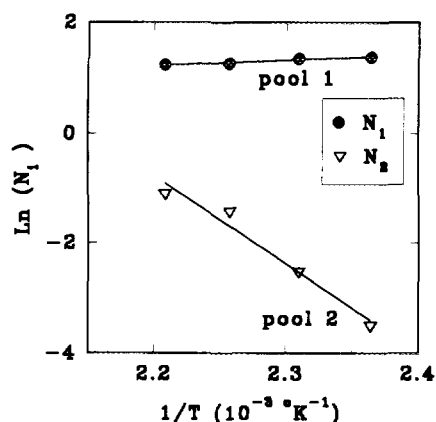


FIG. 7. The effect of temperature on the surface abundances of the two pools of reaction intermediates for ethane hydrogenolysis.

what is shown in Fig. 7. The abundance of surface intermediates for pool 2 had a tendency to increase faster with rising temperature than intrinsic activity. For the first pool, the abundance seems not to have changed greatly with temperature, suggesting that the surface was "saturated" with adsorbed ethane.

CONCLUSIONS

Evidence was found for the existence of two pools of carbon containing intermediates on the catalyst surface during ethane hydrogenolysis. The first pool was assigned to di-carbon intermediates, the second pool to mono-carbon species. Each pool was characterized by its individual intrinsic activity and abundance of intermediates. The intrinsic activity of pool 1 was lower than that of pool 2, which suggests that C-C bond breakage is a much slower step than hydrogenation. Temperature had a much bigger effect on the abundance of pool 2, where the coverage of mono-carbon intermediates increased with temperature. Temperature had very little effect on the abundance of pool 1, which suggests that the surface was "saturated" with ethane. Therefore, the rupture of the C-C bond in

di-carbon intermediates was concluded to be the slowest step, in line with conclusions from the literature based on other measurements. The activation energies of the surface reaction of di- and mono-carbon species were found to be 36 ± 3 and 9 ± 3 kcal/mole, respectively.

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