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Isotopic Transient Kinetic Analysis of Ethane Hydrogenolysis on Cu Modified Ru/SiO_2

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Since Cu is known to decorate Ru surfaces but is not active for ethane hydrogenolysis, it provides a means to study the effect of modifier decoration on this highly structure sensitive reaction. The effect of this decoration on the concentration of the active intermediates and the surface kinetics during ethane hydrogenolysis on Ru/SiO_2 has been studied using isotopic transient kinetics analysis. The abundances, coverages, and lifetimes of active surface intermediates of the reaction were measured under initial reaction conditions. Approximate intrinsic activities and abundances of surface dicarbon and monocarbon species were found to change significantly with the addition of Cu. The results show that low loadings of Cu appeared to block preferentially the sites which were the most active but much less abundant on the Ru surface, confirming the theoretical calculations of Strohl and King [(*J. Catal.* 116, 540 (1989)] which suggested a nonuniform distribution of Cu on Ru crystallites. Ensemble sizes for ethane adsorption and hydrogenolysis were found to be ca. 5 and 12, respectively, based on a correlation between the change in surface abundance of each reactive intermediate species and the fraction of Ru surface atoms exposed. Approximate intrinsic activity related to breakage of the C–C bond during ethane hydrogenolysis varied significantly for different sites, while that related to hydrogenation of monocarbon species was essentially the same for all sites.

INTRODUCTION

Promoted transition metal catalysts are very commonly used for reactions such as Fischer–Tropsch synthesis (1–7), hydrocarbon processing (8) and ammonia synthesis (9). However, how promoters decorate and modify metal catalysts is still not clear, although this is probably highly dependent on the nature of the promoter, the metal catalyst, and the presence of a support. It is obvious that a more complete understanding of these issues could have a significant impact on the design of better commercial catalysts.

Ru–Cu catalysts constitute an interesting catalytic system. Ru is a highly active catalyst for certain reactions, such as hydrogenolysis of alkanes and hydrogenation of CO, while Cu can be considered to be inactive (10). A theoretical study of Ru–Cu by Strohl and King (11) suggested that Cu blocks edges and corners of Ru crystallites initially, before occupying the basal surfaces. However, due to the assumptions that the model was based on, conclusions were not able to be made about the homogenous or heterogeneous distribution of Cu on different planes of Ru.

Ethane hydrogenolysis is a very structure sensitive reaction (12–14, 32). The activity of a metal catalyst for this reaction depends markedly on the spacial coordination of the surface metal atoms (crystallite planes exposed and coordination numbers) and appears to require site ensembles of ca. 12 atoms (13–17). Thus, the size and morphology of supported metal crystallites greatly affect the determined TOF (turnover frequency) due to the variation in these parameters caused by the distribution of surface crystal planes exposed. Partial decoration of an active metal surface by a poison or a promoter can have a pronounced effect on rate due to the blockage of even a single metal atom of a site. Martin's method, which is based on a statistical model (14), permits calculation of the site ensemble size based on the change in relative global rate for a structure sensitive reaction with the surface coverage of an added second component. Direct evidence for site ensemble requirements during ethane hydrogenolysis for ethane adsorption and methane formation was found independently for a series of poisoned Ni catalysts by using magnetic susceptibility (13–17). Hoost and Goodwin (18), analyzing results for ethane hydrogenolysis on K^+-promoted Ru/SiO_2 using an extension of Martin's method developed by them, were able to conclude that K^+ was not uniformly distributed on the Ru surface. Martin's method, however, does not permit a determination of the surface reaction parameters.

Isotopic transient kinetic analysis is an unique technique that can provide important information about surface reac-

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tions at temperature and pressure (19–27). The aim of this research was to study, using isotopic switching, the effect of Cu on surface abundances and approximate intrinsic activities of intermediates on Ru/SiO_2 during ethane hydrogenolysis and to elucidate the surface kinetics of the reaction and the heterogeneity of the active sites on the catalytic surface.

EXPERIMENTAL

The Ru/SiO_2 base catalyst was prepared using the incipient wetness impregnation method. $Ru(NO)NO_3$ (Alfa Chemical), dissolved in distilled water, was impregnated into Cab-O-Sil HS5 fumed silica (184 m^2/g) to incipient wetness, and the catalyst precursor was then dried at 90°C overnight. The catalyst was reduced in flowing hydrogen at a heating rate of 1°C/min to 400°C and then held at this temperature for 8 h. After reduction, the catalyst was washed with boiling distilled water and filtered five times to minimize any chloride ions present. The catalyst was dried again at 90°C overnight. The resulting catalyst contained 3 wt% ruthenium.

Different amounts of Cu were added to separate portions of the Ru/SiO_2 base catalyst using the incipient wetness impregnation method and an aqueous solution of Cu nitrate (Alfa Chemical). The Cu-modified catalysts were dried and then re-reduced using the same conditions as given above. The nomenclature used to identify the catalysts is Cu/RuS*xx*, where *xx* indicates the nominal Cu/Ru atomic ratio in percent, and S stands for the silica support. Five catalysts with different Cu/Ru ratios (0, 0.05, 0.1, 0.2, 0.5) were prepared. The catalyst with Cu/Ru = 0 was simply impregnated with pure distilled water. Elemental analysis was done by Galbraith Lab., Inc. Irreversible hydrogen chemisorption at 77 K, following *in situ* re-reduction, was used to determine the number of surface exposed Ru atoms on the supported metal catalysts as described elsewhere (28). The term ‘‘irreversible’’ will be used to describe that portion of hydrogen chemisorbed strongly enough such that it cannot be removed on evacuation for 10 min. While this quantity is known to be a function of a variety of variables (duration of evacuation, catalyst metal, temperature, etc.) (33), the procedures used here to determine it have been independently verified to accurately determine the number of surface exposed Ru atoms in supported Ru catalysts (28, 34), excluding of course Ru on SMSI supports following high temperature reductions.

The reaction rate and isotopic transients were measured using the reaction system described previously (21). Two gas streams having the same gas compositions and flow rates but different isotopic labeling were able to be switched from one to the other under the same back pressure. The system had on-line a gas chromatograph (GC) and a mass spectrometer (MS). A Varian 3700 GC with an FID detector and a 6-foot, 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 length of all tubing lines was minimized so that the residence time of the gases in transit through the system 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 a catalyst loaded in a microreactor. Prior to reaction, the catalyst was re-reduced in a flow of 50 cc/min of hydrogen at 400°C for 6 h. After reduction, the catalyst-bed temperature was lowered to the desired initial reaction temperature in hydrogen flow, and the feed was switched to the reactant mixture ($P_{C2H6} = 0.6$ kPa, $P_{H2} = 24.0$ 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. Switches between two reactant streams having different isotopically-labeled ethane, $^{12}C_2H_6$ and $^{13}C_2H_6$ (Isotech), 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 holdup. Isotopic switching was done immediately after 5 min of reaction. In order to maintain the initial state of the catalyst for reaction during Arrhenius measurements, the gas stream was switched to pure H_2 after a total of eight minutes of reaction, and the catalyst was re-reduced at 400°C for 2 h before the next reaction temperature. The measurement at each reaction 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. Specific activities were calculated in terms of the rate of disappearance of ethane per gram of catalyst and per hydrogen atom adsorbed irreversibly at 77 K (TOF). Isotopic-transient-kinetic data were only collected at 180°C.

Stop-flow measurements were used to accurately determine the total amount of surface-carbon species present during the reaction at 180°C. After 5 min of reaction, the reactant mixture ($C_2H_6 + H_2 + Ar$) was shut off, and only He was allowed to flow over the catalyst. Four minutes later, H_2, which had the same partial pressure as that in the reactant mixture, was added to the He in order to remove the carbonaceous intermediates remaining on the surface. The effluent gas was continuously monitored by MS.

RESULTS

H_2 Chemisorption on Ru–Cu/SiO_2 Catalysts

H_2 Chemisorption on the Ru–Cu/SiO_2 catalysts was carried out at 77 K in order to determine the number of Ru

TABLE 1

H_2 Chemisorption on Ru–Cu/SiO_2 (28)

Catalyst	Irreversible H_2 uptake (μmol/g) 298 K	77 K	θ_{Ru}[a]
Cu/RuS00	54.0	56.4	1.00
Cu/RuS05	46.7	48.2	0.85
Cu/RuS10	39.7	30.2	0.54
Cu/RuS20	43.1	19.5	0.35
Cu/RuS50	44.2	11.5	0.20

[a] Fraction of Ru surface atoms exposed. Calculated by assuming $H_{irrev}/Ru_s = 1$ at 77 K and $\theta_{Ru} = H_{irrev}(Cu/RuSxx)/H_{irrev}(Cu/RuS00)$.

surface atoms and to exclude hydrogen spillover onto the Cu which can occur at room temperature. This technique has been shown to lead to an accurate determination of surface-exposed Ru atoms (28). Irreversible H_2 chemisorption at room temperature was used to determine that the % dispersion of Ru in the base Ru/SiO_2 catalyst (Cu/RuS00) was 36%, assuming $H_{irr}/Ru_s = 1$ (34). The average Ru particle size was calculated to be 2.4 nm using the equation

$$d_{avg} = \frac{5}{S_{Ru}\,\rho_{Ru}},$$

where ρ_{Ru} is the density of Ru (12.3 g/cc), S_{Ru} is the surface area of Ru per g of Ru determined from $H_{irr} \times$ (8.17 Å^2/Ru surface atom) $\times$ (100/wt% Ru). This average Ru particle size was assumed not to change with addition of Cu since Cu was impregnated sequentially to different loadings onto the pre-reduced Ru catalyst. This has been shown to be the case for other modified Ru catalysts prepared in a similar manner (29). As can be seen in Table 1, Cu significantly blocked hydrogen chemisorption sites on the Ru particles.

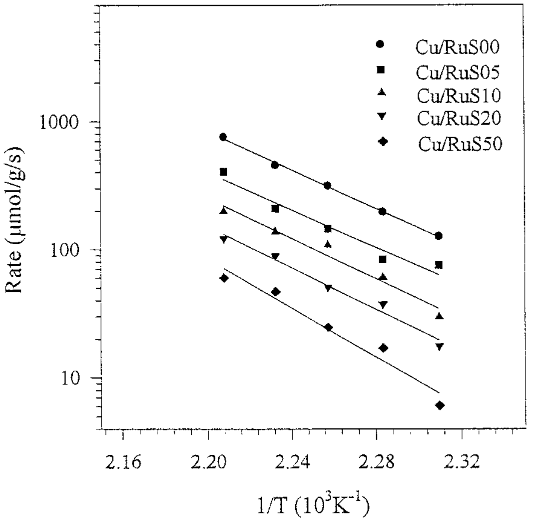

FIG. 1. Arrhenius results for different loadings of Cu.

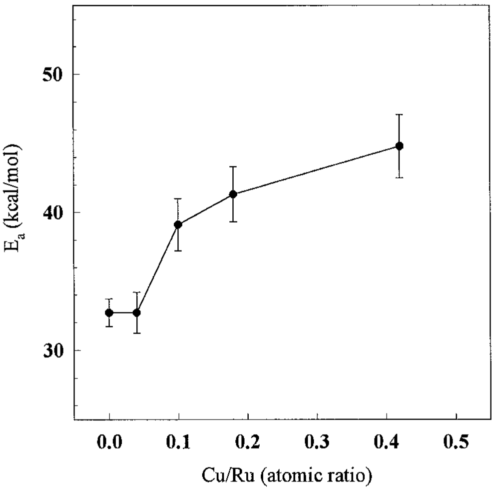

FIG. 2. Apparent activation energy of ethane hydrogenolysis as a function of Cu loading on Ru/SiO_2 (temperature range: 160–200°C).

Global Reaction Rate Measurements

Figure 1 gives the Arrhenius results for Ru/SiO_2 with different loadings of Cu. As can be seen, addition of Cu significantly reduced the overall rate of the reaction. In addition, the apparent activation energy, E_a, increased significantly from ca. 32 to 43 kcal/mol with Cu loading (Fig. 2). The apparent activation energy determined for the base catalyst (Cu/Ru = 0) is consistent with that found by Sinfelt (10). Given the values of E_a and the linearity of all the Arrhenius plots, no mass and heat transfer limitations are evident for the conditions studied. Table 2 presents the specific reaction rates and TOF's for the catalysts at 180°C.

TABLE 2

Reaction Parameters for Ethane Hydrogenolysis at 180°C

Catalyst	R_E (nmol/g/s)	TOF[a] (10^{-3} s^{-1})	τ_M[b] (s)	τ_E[b] (s)
Cu/RuS00	759 ± 28	7.0	1.50 ± 0.10	1.06 ± 0.01
Cu/RuS05	405 ± 10	4.2	1.44 ± 0.14	1.01 ± 0.07
Cu/RuS10	200 ± 16	3.3	1.64 ± 0.16	1.11 ± 0.08
Cu/RuS20	122 ± 9	3.2	1.58 ± 0.18	1.12 ± 0.10
Cu/RuS50	60 ± 6	2.6	1.66 ± 0.21	1.13 ± 0.12

[a] Based on irreversible H_2 chemisorption at 77 K.

[b] Surface residence time.

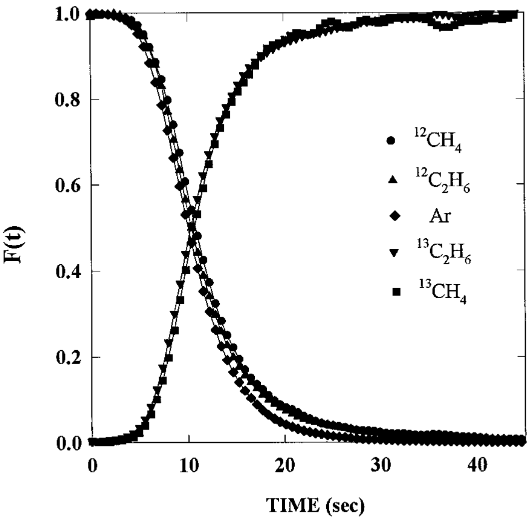

FIG. 3. Isotopic transients during ethane hydrogenolysis on Ru/SiO$_2$ at 180°C.

As can be seen, both parameters decreased significantly with Cu loading.

Isotopic Transient Kinetics during Ethane Hydrogenolysis

Isotopic transient kinetic analysis overcomes many of the deficiencies of global kinetic methods. It provides information directly related to the surface kinetics, such as a measure of approximate intrinsic activity and the abundances of surface intermediates.

Figure 3 shows typical normalized isotopic transients observed during ethane hydrogenolysis. *Average* surface residence times for the carbon in methane (τ_M) or in ethane (τ_E) are given by the areas between the CH$_4$ or the C$_2$H$_6$ and the Ar transients, respectively. The surface residence times measured for the different Cu/Ru catalysts are summarized in Table 2. Surface abundancies of intermediates, N_i, leading to methane or desorbed ethane are determined by multiplying τ_i by the corresponding flow rate of i, F_i, exiting the reactor. These latter values are exact and are not averages since their calculation is based on mass balances.

Stop-Flow Measurements during Ethane Hydrogenolysis

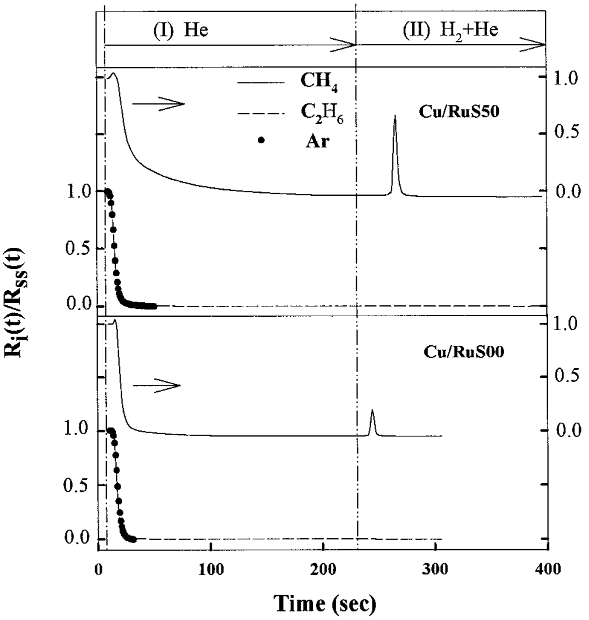

FIG. 4. Stop flow of the reactants at 180°C for Cu/RuS00 and Cu/RuS50.

Figure 4 shows the normalized results of stop-flow experiments [$H_2 + C_2H_6 \Rightarrow$ He (flush) $\Rightarrow H_2$] for Cu/RuS00 and for Cu/RuS50 at 180°C. As can be seen in Fig. 4, there was no time delay between Ar (indicating the gas phase hold-up) and C$_2$H$_6$, which suggests that no adsorbed ethane molecules left the surface following stop-flow of the reactants. The experiments included two periods: (I) the first during which both C$_2$H$_6$ and H$_2$ were stopped, (II) the second during which the H$_2$ flow was resumed to hydrogenate surface carbon. The amount of carbon removed from the surface during period (I) as CH$_4$, N_I, was calculated by multiplying the area, A_I [obtained by subtracting the area under the CH$_4$ curve from that under the Ar curve (Fig. 4) for period (I)], by the steady-state methane formation rate, R_{ss}, and a correction factor, F_I, to account for the change in flow rates (see footnote to Table 3). The amount of carbon removed from the surface during period (II) as CH$_4$, N_{II}, was calculated by multiplying the area,

TABLE 3

Parameters from Stop-Flow Experiments during Ethane Hydrogenolysis at 180°C

Catalyst	A_I (s)	A_{II} (s)	$N_I{}^a$ (μmol/g)	$N_{II}{}^b$ (μmol/g)	N_{Total} (μmol/g)
Cu/RuS00	4.2	1	3.1	0.8	3.9
Cu/RuS05	7.0	1.7	2.5	0.7	3.2
Cu/RuS10	12.3	2.1	2.2	0.4	2.6
Cu/RuS20	13.6	2.6	1.6	0.4	2.0
Cu/RuS50	24.9	3.0	1.2	0.2	1.4

[a] $N_I = R_{ss} * F_I * A_I$, where N_I is the amount of surface carbon desorbed during the first time period as methane; R_{ss} is the steady-state rate of methane formation (μmol/g/s); F_I is a correction factor because of the change in total flow, in this case, $F_I = (F_{total} - F_{H2} - F_{C2H6})/F_{total} = (50 - 6 - 0.15)/50 = 0.877$.

[b] $N_{II} = R_{ss} * F_{II} * A_{II}$, where N_{II} is surface carbon collected in the second time period; F_{II} is a correction factor, $F_{II} = (F_{total} - F_{C2H6})/F_{total} = (50 - 0.15)/50 = 0.997$.

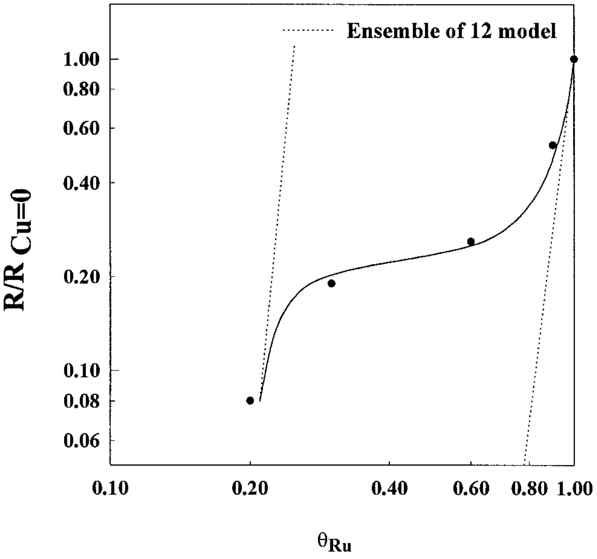

FIG. 5. The relative rate of ethane hydrogenolysis versus fraction of Ru_s exposed.

A_{II} [derived by integrating the curve for CH_4 formed during period (II) and subtracting the area under that for Ar (~0)], by the steady-state methane formation rate, R_{ss}, and a correction factor, F_{II}. N_{Total}, given in Table 3, is equal to the total amount of reactive surface carbon able to be removed during periods I and II ($N_{Total} = N_I + N_{II}$). Comparing the results for Cu/RuS00 to those for Cu/RuS50 (Fig. 4), one can see that it took a much longer time for surface carbon species to leave the Cu-covered Ru surface under the same conditions. Table 3 shows all parameters determined from the stop-flow experiments.

DISCUSSION

Heterogeneity of Cu Dispersion on Ru

Martin (14) applied statistical methodology in order to write an expression relating the rate of ethane hydrogenolysis to surface blockage of the metal catalyst:

$$R/R_{p=0} = (1 - \Theta_p)^n,$$

where p is the second component (blockage agent), Θ_p is the surface coverage of p on the catalytically active component, and n is the ensemble size (number of surface metal atoms) required by the reaction. Hoost and Goodwin (18) extended this method in order to determine whether the distribution of K^+ was homogeneous or heterogeneous on a Ru catalyst. It was shown mathematically that $\log(R/R_{p=0})$ vs $\log(1 - \Theta_p)$ follows a straight line for a structure-sensitive reaction if the blocking agent is homogeneously dispersed on the catalyst surface. Otherwise, nonhomogeneous dispersion would be indicated.

As can be seen in Figure 5, the plot of $\log(R/R_{p=0})$ vs $\log \theta_{Ru}$, where the fraction of Ru surface atoms exposed (θ_{Ru}) = $1 - \theta_{Cu}$, for ethane hydrogenolysis on this series of Ru catalysts does not exhibit a straight line. However, the tangent line as Cu decoration goes to zero ($\theta_{Ru} = 1$) exhibits a slope of ca. 12, typical of the site requirement of 12 metal atoms required for ethane hydrogenolysis. The relative rate decreased significantly for low Cu coverages (at high θ_{Ru}), leveled off from $\theta_{Ru} = 0.8 - 0.3$, and then decreased rapidly again with decreasing θ_{Ru}. Thus, based on the model developed in Ref. (18), it can be concluded that Cu was not distributed homogeneously on the Ru surface. This is in agreement with the thermodynamic calculations of Strohl and King (11) which suggest that Cu preferentially decorates Ru surface atoms having low coordination numbers.

Surface Reaction Model of Ethane Hydrogenolysis and Kinetic Parameter Calculation

Most researchers agree that, on a catalytically active surface, ethane adsorbs dissociatively, followed by C–C bond breakage and hydrogenation of CH_x species to give methane (10–11). Therefore, it was proposed (21) that the surface reaction can be considered to proceed approximately via two pools of intermediates in series. The first pool can be considered to contain the dicarbon species which are the surface intermediates before C–C bond cleavage. The second one can be considered to contain monocarbon species which are able to be hydrogenated to form methane. It was shown using isotopic transient kinetic analysis that breakage of surface dicarbon species into monocarbon species was the slowest step on a Ru surface (21).

The surface abundances of dicarbon and monocarbon species (N_1 and N_2, respectively) and the pseudo-first order rate constants of these two pools (k_1 and k_2) are able to be estimated from the isotopic transients. These two pseudo-first order rate constants can, however, possibly contain the surface concentration of hydrogen during reaction. Since hydrogen is well known to inhibit ethane hydrogenolysis (21, 30, 35, 36), hydrogen partial pressure was held constant during these measurements. Inhibition of reaction by hydrogen does not appear to be, however, strongly affected by Cu coverage (30, 31).

The *measured* surface residence time of reversibly adsorbed ethane, $\tau_{E,m}$, is only an average value for the time of surface holdup for *all ethane molecules* (some of which undoubtedly did not adsorb). The surface residence time for only that fraction of ethane which adsorbs reversibly on the active sites (τ_E) can not be determined. Hence, $\tau_{E,m} \leq \tau_E$. The relationship of the reaction model parameters to the theoretical and measured experimental parameters are shown in Table 4.

TABLE 4

Calculation of the SSITKA Parameters and Their Relationships to the Theoretical Values

Parameter	Theoretical relationship	Relationship to measurements used to estimate parameters
N_1	$N_T - N_2$	$\geq N_T - R_E * (\tau_{M,m} - \tau_{E,m})$
N_2	N_2	$\geq R_E * (\tau_{M,m} - \tau_{E,m})$
τ_1	τ_E	$\geq \tau_{E,m}$
τ_2	τ_M	$\leq \tau_{M,m} - \tau_{E,m}$
k_1	R_M/N_1	$\leq R_E/[N_T - R_E * (\tau_{M,m} - \tau_{E,m})]$
k_2	$1/(\tau_M - \tau_E)$	$\geq 1/(\tau_{M,m} - \tau_{E,m})$

Note. N_1 = the surface abundance of intermediates in pool 1 ($*C_2$), μmol/g. N_2 = the surface abundance of intermediates in pool 2 ($*C_1$), μmol/g. N_T = the surface abundance of intermediates in pool 1 and 2 ($*C_1 + *C_2$), μmol/g. $R_{E,m}$ = initial reaction rate, μmol/g/s. $\tau_{M,m}$ = measured surface residence time of carbon in effluent methane, s. τ_E = measured surface residence time of carbon in effluent ethane, s. τ_1 = the surface residence time in pool 1, s. τ_2 = the surface residence time in pool 2, s. k_1 = pseudo-first order rate constant of breakage $*C_2$ to $*C_1$, s^{-1}. k_2 = pseudo-first order rate constant of $*C_1$ hydrogenation, s^{-1}.

TABLE 5

Surface and Reaction Parameters on Ru–Cu/SiO$_2$ Calculated from Isotopic Transient Kinetics during Ethane Hydrogenolysis

			N_i (μmol/g)		$\Theta_i \times 10^{2}$[a]	
Catalyst	k_1 (s^{-1})	k_2 (s^{-1})	$i = 1$	$i = 2$	$i = 1$	$i = 2$
Cu/RuS00	0.21	2.3	3.6	0.33	3.3	0.031
Cu/RuS05	0.13	2.4	3.0	0.17	3.1	0.017
Cu/RuS10	0.08	1.9	2.5	0.11	4.1	0.018
Cu/RuS20	0.06	2.2	2.0	0.06	5.2	0.015
Cu/RuS50	0.04	2.1	1.5	0.02	6.4	0.009

[a] Θ_i is the fractional surface coverage of the available Ru surface atoms by pool i:

$$\Theta_i = N_i/H_{irrev,77\,K}.$$

The results from stop-flow of reactants provide an estimation of the total active surface carbon during the steady-state reaction ($N_T = N_I + N_{II}$, see Table 3, where N_I and N_{II} are the amounts of surface carbon reacted to methane during periods I and II, respectively). In ref. (21), N_T was obtained from SSITKA via the relationship, $N_T = R_+ * \tau_E + R * (\tau_M - \tau_E)$, which requires one to assume that the rate of ethane adsorption $R_+ = F_E$ (molar flow rate of ethane) in order to calculate N_T. However, this assumption has been found valid only for Ru/SiO$_2$, as shown by both stop-flow and D$_2$-ethane exchange experiments (21). In this study, N_T has been directly measured from the stop-flow experiments. Since the surface abundance of monocarbon species can be calculated based on the developed model ($N_2 = \tau_2 * R$, where τ_2 is the residence time for intermediates in the pool 2 and R is the rate for the reaction) (21), the surface abundance of dicarbon species can be easily obtained from a carbon balance, $N_1 = N_T - N_2$. Thus, if pseudo-first order surface reactions are assumed ($R = k_1 * N_1 = k_2 * N_2$), the pseudo-first order rate constants, k_1 and k_2, can be obtained for reactions of the dicarbon and monocarbon intermediates, respectively (see Table 4) (21). Table 5 presents the results calculated based on the above discussion.

The Effect of Cu on the Surface Kinetic Parameters

As Fig. 5 shows, ethane hydrogenolysis on Ru/SiO$_2$ demands ca. 12 adjacent surface atoms. However, the method for estimating ensemble size is based on the change in the relative global reaction rate with the coverage of the active metal by adatoms such as Cu. The global rate, of course, can be affected both by a change in site activity as well as by one in surface coverage in intermediates. Decorating adspecies such as Cu potentially might have different effects on these two parameters. Isotopic transient kinetic analysis permits one to decouple the reaction rate into the approximate intrinsic activity (pseudo-first order rate constant) and the surface abundance of the intermediates under practical reaction conditions (19–27). Figures 6 and 7 show the relative changes of surface abundances of dicarbon and monocarbon species with exposed Ru surface atoms. The reader should remember that pool 1 contains N_1 carbon atoms in the form of C_2^* (dicarbon) species and that pool 2 contains N_2 carbon atoms in the form of C_1^* (monocarbon) species. Figures 6 and 7 do not show single straight lines, which also suggests that the Ru surface was not uniformly blocked by Cu. Careful drawing of tangent lines at the beginning and the end of the curves gave ap-

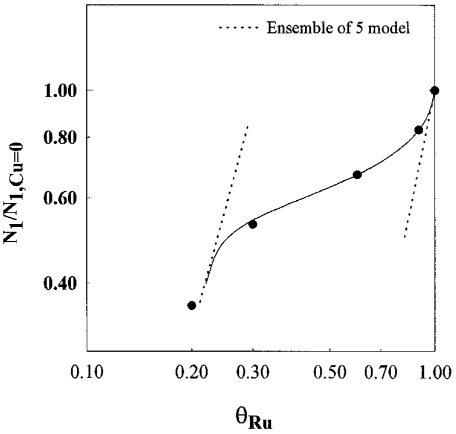

FIG. 6. The effect of Cu coverage on the surface abundance of the dicarbon species.

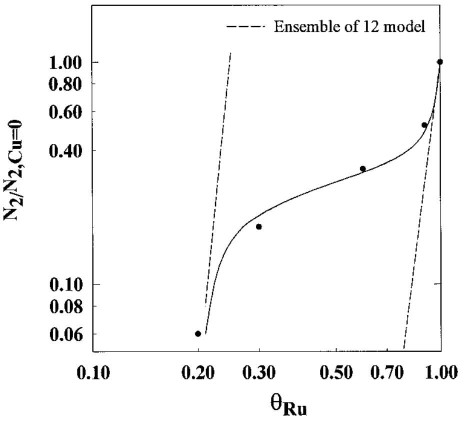

FIG. 7. The effect of Cu coverage on the surface abundance of the monocarbon species.

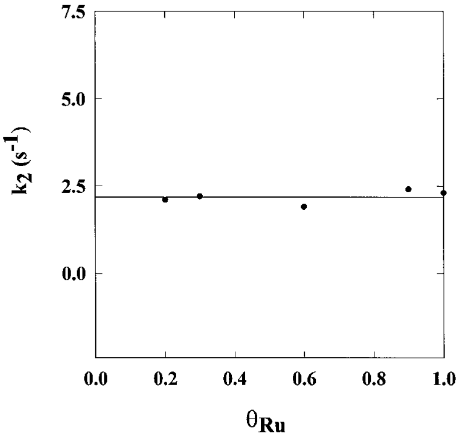

FIG. 8. The effect of Cu coverage on hydrogenation of the monocarbon intermediates.

proximate estimations of the ensemble sizes required for C_2^* and C_1^* intermediates of 5 and 12 (these numbers are only approximate due to the limited number of experimental points), respectively, similar to the findings of Dalmon *et al.* (17). These authors found that two kinds of adsorbed ethane species on a pure Ni catalyst were detectable: the first one at room temperature occupied 6 Ni atoms per ethane and was responsible for a partial dehydrogenation of the ethane molecule without C–C bond rupture, and the second species which was able to form methane was observed above 72°C and required 12 surface Ni atoms per ethane. The calculated amounts of di- and monocarbon species show that the abundance of monocarbon species (with surface coverages between 9×10^{-5} and 3.1×10^{-4}) was always less than that of dicarbon species (with surface coverages between 3.3×10^{-2} and 6.4×10^{-2}) on all the Ru–Cu catalysts. This suggests that the C–C bond cleavage is the slowest step on the surface for all catalysts. This finding agrees in large part with previous conclusions (12–14).

As mentioned earlier, the pseudo-first order rate constant determined may contain a dependence on the surface concentration of hydrogen. This dependence may be expressed as

$$k_i = k_i' N_{\mathrm{H}}$$

where k_i' is the "true" intrinsic site activity, and N_{H} is the surface abundance of hydrogen. Thus, any variation in k_i with Cu coverage could be due to an effect on hydrogen coverage rather than an effect on site activity. Figures 8 and 9 are not *Martin-type* plots since site activities should not follow a statistical variation with coverage. Figure 8 presents k_2, the pseudo-first order rate constant for hydrogenation of surface monocarbon species, CH_x. As can be seen, k_2 ($= k_2' N_{\mathrm{H}}$) did not change with Cu coverage of the Ru surface. Since rate of hydrogenation should be highly dependent on the coverage of hydrogen, the fact that k_2 did not change suggests that hydrogen abundance did not change greatly with Cu loading under the conditions studied. This is substantiated by the fact that the apparent reaction order of hydrogen has not been found to change significantly with Cu coverage for temperatures <235°C (30–31).

Figure 9 shows, on the other hand, that k_1, the pseudo-first order rate constant for breakage of the C–C bond on the surface, decreased monotonically with Cu loading. C–C bond breakage is assisted by surface hydrogen, although probably much less dependent upon surface abundance of hydrogen than hydrogenation of the monocarbon species. Therefore, based on the lack of variation in k_2 and in apparent H_2 reaction order with Cu coverage, the variation in k_1 with Cu coverage is suggested to be due to a change in the average intrinsic activity of the available reaction

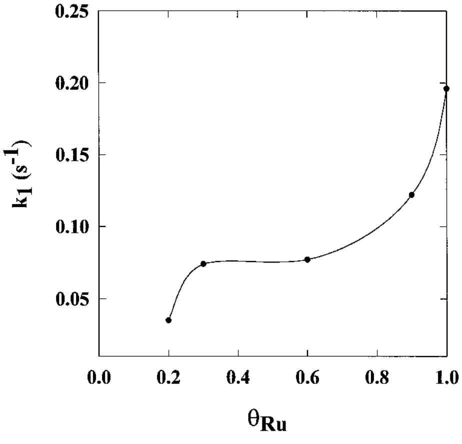

FIG. 9. The effect of Cu coverage on the C–C bond cleavage.

sites. The results suggest a heterogeneous distribution of active Ru sites with Cu preferentially decorating the more active sites. This conclusion about the nonhomogeneous decoration is consistent with the results of Kim *et al.* (37) based on photoemission studies of Xe physisorbed on Ru–Cu surfaces. The heterogeneity of the Ru surface would be due to different coordination numbers of the Ru surface atoms on the corners, edges, and various planes of the metal crystallites. Preferential decoration of certain low coordination Ru surface atoms by Cu, as suggested by the model of Strohl and King (11) is concluded to lead to the variation in the average value of k_1 measured. This may also explain the increase in the apparent activation energy with Cu loading as shown in Fig. 2. The results confirm that hydrogenation is not structure sensitive while C–C bond breakage is.

CONCLUSIONS

Ru–Cu catalysts offered an ideal system for studying decoration of a metal catalyst by a modifier since Cu was not active for ethane hydrogenolysis and did not alloy with Ru. Thus, issues such as distribution of the modifier and influence on reaction were able to be explored without direct promotion of the reaction. The nature of the decrease in the specific activity/TOF (turnover frequency) for ethane hydrogenolysis with addition of Cu indicated a non-homogeneous distribution of the Cu and the presence of a kinetically heterogeneous Ru surface. The variation in measured surface abundance of intermediates with Cu coverage also suggested that there were primarily at least two kinds of kinetically active sites for ethane hydrogenolysis on the Ru surface. The approximate intrinsic activity for hydrogenation of the monocarbon species did not change with Cu loading, suggesting that hydrogen coverage did not vary significantly with Cu loading under the conditions studied. However, the approximate intrinsic activity for C–C bond breakage decreased significantly with addition of Cu, confirming that there was a distribution of active sites for C–C bond breakage on the Ru surface and that the Cu was not homogeneously distributed. Ethane adsorption (potentially leading to C–C bond breakage) required ca. 5 surface metal atoms, while ethane hydrogenolysis required ca. 12.

Based on the results, it was confirmed that the Ru surface was kinetically heterogeneous for ethane hydrogenolysis. It was concluded that Cu preferentially blocks the more active sites on the surface before covering the less active ones, consistent with the theoretical calculations of King and co-workers (11, 30).

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