Dissociative Adsorption and Hydrogenolysis of Ethane over Clean and Ni-Covered Pt(111)

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The hydrogenolysis of ethane has been investigated on clean and Ni-covered Pt(111) at reactant partial pressures between 0.5 and 4 Torr of ethane and between 80 and 270 Torr of hydrogen and for surface temperatures from 550 to 640 K. On clean Pt(111) the hydrogenolysis reaction proceeds with an activation energy of 36.6 kcal/mol and reaction orders in C2H4 and H2 pressures of 1 and ~1.8, respectively. The rate of ethane hydrogenolysis increases when Ni is added to the surface. The catalytic activity of a Pt(111) surface with the equivalent of a monolayer of Ni is higher than that observed on Pt(111) but lower than those reported for Ni(100) and Ni(111). An analysis of the increase in the rate of hydrogenolysis with Ni coverage suggests an ensemble requirement of two or three nickel atoms for this reaction. The dependence of the rate of ethane hydrogenolysis with respect to the partial pressures of the reactants was analyzed according to a kinetic model that involves a rate-limiting, irreversible C-C bond cleavage step. The results indicate that the hydrocarbon fragments preceding C-C bond breaking are C2H6 or C2H5 (perhaps ethylidyne) on clean Pt(111) and C2H4 on Pt(111) surfaces with Ni coverages of 1 and 1.3 monolayers (ML). Postreaction surface analysis by Auger electron spectroscopy showed the presence of a submonolayer carbonaceous residue, the amount of which increased with reaction temperature and Ni coverage. The kinetics of the ethane decomposition reaction on Pt(111) and Ni/Pt(111) surfaces was measured under the high incident flux conditions of 0.01–0.001 Torr of ethane. The apparent activation energies for dissociation of ethane vary between 9 and 12 kcal/mol. The catalytic activities of both constituents of the mixed-metal system.

I. Introduction

The surface chemistry of bimetallic systems has been the subject of many investigations over the past several years. In part, the motivation of these studies is the fact that mixed-metal systems are superior over their single-metal counterparts in terms of catalytic activity and/or selectivity. Many fundamental studies have focused on trying to understand the roles of "ensemble" and "ligand" effects in bimetallic catalysts. Ensemble effects are defined in terms of the number of surface atoms needed for a catalytic process to occur. Ligand effects refer to those modifications in catalytic activity or selectivity that are the result of electronic interactions between the components of the bimetallic system. Work on ultrathin metal films supported on well-defined metal surfaces (Cu on Ru(0001))11 Cu, Ni, Pd, and Pt on W(110) and W(100)34-58 Fe, Ni, and Cu on Mo(110);13 and Fe and Cu on Re(0001))15-18 has shown that a metal atom in a matrix of a dissimilar metal can be significantly perturbed and that this perturbation can dramatically alter the chemical and electronic properties of both constituents of the mixed-metal system.

In this paper we present results for the dissociative chemisorption and hydrogenolysis of ethane (C2H4 + H2 \rightarrow 2CH4) over Ni supported on Pt(111). This work is a continuation of a series of studies performed in our laboratory, in which the chemical and catalytic properties of different bimetallic systems have been examined by use of the modern techniques of surface science and high pressure reaction kinetics. The system under study here is particularly interesting because it involves the addition of an active metal for hydrogenolysis (Ni) to a relatively inactive surface (Pt(111)). This fact facilitates the evaluation of ensemble and ligand effects for hydrocarbon hydrogenolysis on bimetallic catalysts.

Important background for the present study is experiments performed on well-defined surfaces. Zaaera and Somorjai investigated the hydrogenolysis of ethane on Pt(111) (Pd1110 = 100 Torr, PCH4 = 10 Torr, T = 570–630 K), obtaining an activation energy of 34 kcal/mol and observing the presence of a carbonaceous residue on the surface after the reaction. Goodman studied the hydrogenolysis of ethane on Ni(100) and Ni(111) (Pd1110 = 100, total pressure of 100 Torr, T = 440–600 K) and observed a structure-sensitive reaction with activation energies of 24 (Ni(100)) and 46 kcal/mol (Ni(111)). Finally, Sault and Goodman22 studied the dissociative chemisorption of ethane on Ni(100) (PFCH4 = 0.1 Torr, T = 350–500 K), determining an activation energy of 9.5 kcal/mol and dissociative sticking
probabilities in the range between 10^{-8} and 10^{-6} (per collision with the surface.)

The present paper is organized as follows: the next section summarizes the experimental procedures. The third section presents the results obtained for the hydrogenolysis and dissociative chemisorption of ethane on clean and Ni-covered Pt(111). The fourth section contains a discussion of these results, and in their light, we analyze different chemical phenomena that can be observed in bimetallic systems.

II. Experimental Section

The experiments were performed in an apparatus described previously. This device consists of a high-pressure reaction chamber attached to an ultra-high-vacuum chamber with facilities for Auger electron spectroscopy (AES) and thermal desorption mass spectroscopy (TDS). Both regions of the apparatus are capable of achieving base pressures of 1 \times 10^{-10} Torr. The reaction chamber can be isolated from the surface analysis chamber and pressurized to <3 atm. The Pt(111) crystal was mounted on a retraction bellows which allows translation of the sample to various positions in either chamber.

The ethane (99.99%) and hydrogen (99.999%) employed in these experiments were of research purity from Matheson. The ethane was purified further by degassing at 80 K, followed by triple distillation from a liquid pentane/solid pentane bath. Gas chromatography with flame ionization detection was used for product analysis. Temperatures were monitored with a W-5%-Re/W-26%-Re thermocouple spot-welded to the back edge of the sample. For gas pressures in the range of those used in this study, the gas and surface temperatures are essentially equivalent.

Nickel was vapor-deposited onto the clean Pt(111) surface by heating a 0.25-mm W filament wrapped with a 0.25-mm Ni wire housed in a collimating shroud. The Ni doser was outgassed thoroughly prior to Ni deposition. Nickel was deposited only onto the front face of the Pt(111) crystal, usually at a sample temperature of \sim 350 K. After dosing Ni, the surface was annealed to 650 K to desorb any accumulated CO.

The Pt(111) crystal (0.9-cm diameter and 0.1-cm thick) was cleaned of carbon by oxidation (2 Torr of O$_2$, 650 K, 2 min in the reaction chamber) and annealing (1300 K, 15 s) cycles. Nickel was removed from the Pt(111) surface by annealing briefly to \sim 1800 K. Surface cleanliness was verified by AES.

In this work, absolute coverages and specific rates are reported with respect to the number of Pt(111) surface atoms (1.505 \times 10^{15} atoms cm$^{-2}$). One adatom per Pt(111) surface atom corresponds to \theta = 1.0. The Ni coverages were determined by measuring the Ni(848)/Pt(237) Auger peak-to-peak ratio. This ratio was calibrated to absolute coverage by measuring the variation of the Ni(848) and Pt(237) Auger signals as a function of Ni deposition time.

The Ni(848)/Pt(237) Auger ratio observed for a monolayer of Ni on Pt(111) was in good agreement with that obtained previously with our instrument for a monolayer of Ni on Mo(110) taking into account the difference in Auger sensitivity factors for Pt and Mo. The amount of carbon on the surface after the experiments was measured by using the C/(272)/Pt(237) Auger peak-to-peak ratio, which was scaled to absolute coverage following the method proposed by Biberian and Somorjai. The carbon coverages obtained by using this type of scaling agree well with those that can be estimated by employing a previous calibration for carbon on Ni/(111) corrected for the difference in Auger sensitivities between nickel and platinum. For experiments on Ni-covered surfaces, the effects of the nickel on the Pt(237) Auger signal were taken into consideration in the calculation of the carbon coverages.

III. Results

III.1. Ethane Hydrogenolysis on Clean and Ni-Covered Pt(111). The kinetic of ethane hydrogenolysis on clean and Ni-covered Pt(111) was studied at various pressures of hydrogen (80, 100, 180, and 270 Torr) and ethane (0.5, 1, 2, and 4 Torr) and at temperatures in the range between 550 and 640 K. In the apparatus used in our studies, Ni could be deposited only onto the front face of the sample. The amount of product formed on this face was determined by subtracting the amount of CH$_4$ formed on the backside of the crystal (estimated by using the results of experiments on clean Pt(111)) from the total amount of CH$_4$ in the reactor. The specific rates, expressed as "turnover" frequencies (CH$_4$ molecules/(Pt surface atoms s)), were obtained by dividing the amount of CH$_4$ produced on the front face of the crystal during a given period of time (600-3000 s) by the atom density of the Pt(111) substrate (1.505 \times 10^{15} atoms cm$^{-2}$) and the corresponding surface area. For experiments on Ni-covered surfaces we assume that each Ni adatom blocks a Pt surface atom. The data reported in this section correspond to steady-state reaction rates, as verified by measuring the amount of CH$_4$ produced after various times of reaction. In all the cases examined, no induction period was detected. Characterization of the catalyst surface by Auger spectroscopy indicated almost the same Ni(848)/Pt(237) ratio before and after the reactions (differences <10%).

Specific rates of hydrogenolysis of ethane as a function of Ni coverage on Pt(111) are shown in Figure 1. The rate of ethane hydrogenolysis increases monotonically as Ni is added to the Pt(111) surface, until a maximum is reached at \theta_{Ni} = 1.3 ML. The catalytic activity of a Pt(111) surface with the equivalent of a monolayer of Ni atoms is 30 times higher than that seen for clean Pt(111). For Ni coverages in the range between 1.2 and 3.0 ML, the catalytic activity of the Ni/Pt(111) surface is lower than that reported for Ni(100) under similar experimental conditions (\sim 0.15 CH$_4$ molecule/(Ni surface atom s)) and close to that observed for Ni(111) (\sim 0.05 CH$_4$ molecule/(Ni surface atom s)).

In Figure 2, the steady-state rates of CH$_4$ production on five different Ni/Pt(111) surfaces are plotted in Arrhenius form. For clean Pt(111), Arrhenius behavior is observed over the entire temperature range studied (550-640 K) as the hydrogenolysis rate varies by almost 2 orders of magnitude. An activation energy of 36.6 \pm 3 kcal/mol was determined for ethane hydrogenolysis on clean Pt(111). For Ni-covered surfaces, Arrhenius behavior is only observed for \theta_{Ni} = 2.5 ML (apparent $E_a = 32 \pm 2$ kcal/mol). In all the other cases, there is a break in the slope of the reaction.

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rate versus 1/T curve at temperatures between 600 and 610 K. For θNi = 0.4, 1.0, and 1.3 ML, two regions can be separated in the Arrhenius plot: one region at low temperature (550-600 K), in which the apparent activation energies of the Ni/Pt(111) surfaces fall in the range between 33 and 35 kcal/mol, very close to the value of ~37 kcal/mol observed for clean Pt(111), and, a region at high temperature (600-625 K) characterized by an increase in the apparent activation energy from ~7 kcal/mol at θNi = 0.4 ML to ~23 kcal/mol at θNi = 1.5 ML. The departure from Arrhenius behavior is probably related to modifications in the morphology of the surface sites that are active for ethane hydrogenolysis (see below). In Figure 2 we can see that the catalytic activity of a Pt(111) surface with 1.3 ML of Ni is always larger than that for a Ni/Pt(111) surface with θNi = 2.5 ML. This fact is consistent with the results of Figure 1.

The response of the rate of ethane hydrogenolysis to changes in the partial pressures of the reactants is displayed in Figures 3 and 4 for various Ni/Pt(111) surfaces. In these experiments, the partial pressure of one reactant was varied, while the partial pressure of the other and the temperature were held constant. Independent of the Ni coverage, the rate of hydrogenolysis was approximately first order in ethane pressure. In contrast, the order with respect to hydrogen pressure varied as follows: θNi = 0, n = -1.8 ± 0.3; θNi = 0.4 ML, n = -2.1 ± 0.3; θNi = 1 ML, n = -2.4 ± 0.3; and θNi = 1.3 ML, n = -2.5 ± 0.3. The hydrogenolysis reaction was always negative order in hydrogen partial pressure.

and the dependence increased with Ni coverage. The last fact correlates with an increase in the catalytic activity of the Ni/Pt(111) surfaces (see Figure 1).

Figure 4. Ethane hydrogenolysis rates as a function of hydrogen partial pressure and Ni coverage (in monolayers).

Figure 5. Carbon coverages (in monolayers) present on the surface following ethane hydrogenolysis (H2/C2H6 = 100, P T = 101 Torr) at different temperatures and Ni coverages.

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Figure 2. Arrhenius plots of the rates of ethane hydrogenolysis versus Ni coverage (in monolayers) on Pt(111), at a total pressure of 101 Torr (H2/C2H6 = 100).

Figure 3. Ethane hydrogenolysis rates as a function of ethane partial pressure and Ni coverage (in monolayers).

Figure 6 shows the carbon buildup curves for exposure of the clean Pt(111) surface to 0.01 Torr of ethane in the high-pressure chamber at various gas temperatures. After exposure, the sample was transferred back into the ultra-high-vacuum analysis chamber and the surface carbon concentration was determined by measuring the C(272)/Pt(237) AES peak-to-peak ratio (see section.
Adsorption and Hydrogenolysis of Ethane on Ni/Pt(111) II. The results of Figure 6 indicate that the rate of ethane dissociation decreases with carbon coverage (or time) and increases with temperature. Similar behavior has been observed for the dissociative chemisorption of several small alkanes on nickel surfaces.\(^2\) The dissociative adsorption of ethane on clean Pt(111) surfaces was calculated from the slopes of the uptake curves of Figure 6 at \(t_0 = 0\) and are presented in Arrhenius form in Figure 7. They fall in the range \(10^{-7}-10^{-4}\) for temperatures between 515 and 635 K. The apparent activation energy is \(8.9 \pm 0.8\) kcal/mol. Experiments such as those shown in Figure 6 were carried out at 550 K, using ethane partial pressures of 0.004, 0.006, 0.008, and 0.02 Torr. At \(t_0 = 0\), the rate of dissociation was roughly first order (\(n = 0.9 \pm 0.2\)) with respect to ethane pressure. That is, the buildup of carbon was proportional to the collision frequency with temperature. Similar behavior has been observed for the surface.**\(^1\)**

Figure 7. Dissociative sticking probabilities for ethane on clean Pt(111) and on Ni/Pt(111) surfaces. The values reported in this figure were determined at the limit of zero carbon coverage.

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Figure 7. Dissociative sticking probabilities for ethane on clean Pt(111) and on Ni/Pt(111) surfaces. The values reported in this figure were determined at the limit of zero carbon coverage.

The dissociative adsorption of ethane on Ni/Pt(111) surfaces was studied at Ni coverages of 0.4, 0.7, and 1 ML and gas temperatures between 515 and 615 K. Figures 8 and 9 show typical carbon buildup curves for Ni/Pt(111) surfaces. The trends in these figures are identical with those observed in Figure 6 for ethane decomposition on Pt(111): the rate of dissociation increases with temperature and decreases with carbon coverage. The presence of Ni adatoms on the Pt(111) surface leads to an enhancement of the rate of ethane dissociation. The calculated sticking probabilities for ethane on Ni/Pt(111) surfaces are presented in Figure 7. The values for a Pt(111) surface covered with a monolayer of Ni are \(\sim 20\) times larger than those seen on clean Pt(111). The dissociative sticking probability reported for ethane on Ni(100) at \(\sim 500\) K \((\sim 6 \times 10^{-7})\) is smaller than those observed here on the Ni/Pt(111) systems. In Figure 7, the apparent activation energies for dissociation of ethane on Ni/Pt(111) surfaces vary in the range between 9 and 12 kcal/mol.

Figure 8. Kinetics of ethane decomposition on a Pt(111) surface covered with 0.4 ML of Ni. \(T = 515-615\) K, \(P_{\text{C}_{2}\text{H}_{6}} = 0.001\) Torr, \(P_{\text{argon}} = 0.999\) Torr.

Figure 9. Kinetics of ethane dissociation on a platinum(111) surface covered with 1 ML of nickel atoms. \(T = 515-615\) K, \(P_{\text{C}_{2}\text{H}_{6}} = 0.001\) Torr, \(P_{\text{argon}} = 0.999\) Torr.
of experiments for Pt adsorbed on the (111) face of Ni indicate that
the Pt adatoms have a very high mobility on the surface and
and migrate into the bulk of the substrate at temperatures above
500 K. For the Pt/Ni(111) system, work-function measurements
and photoemission of adsorbed xenon show the presence of
disordered Pt and surface alloys upon deposition of \( \approx 2/3 \) ML of
Pt on the Ni(111) substrate at temperatures \( < 180 \) K. Annealing
at temperatures above 575 \( K \) induces diffusion of Pt into the bulk
and alloy formation. On the basis of this evidence, we expect
a very large miscibility for Ni on Pt(111) at temperatures \( > 500 \) K,
with formation of surface alloys of variable composition de-
pending on the amount of deposited Ni and on the temperature
of the system.

The results of section 3.2 indicate that the Ni/Pt(111) systems
have a higher ability to dissociate ethane and to hydrogenate
hydrocarbon fragments than the Pt(111) surface. This increase
in chemical reactivity can be explained if one notes that nickel
surfaces show larger values for the sticking coefficient of ethane
and for the heat of adsorption of \( H_2 \) than the Pt(111) surface.

A comparison of deuterium exchange rates with hydrogenolysis rates for ethane on platinum and nickel surfaces indicates that
C-H bond scission is rapid relative to C-C bond scission, sug-

Figure 10. Kinetics of hydrogenation of carbonaceous layers deposited
on the Pt(111) surface by dissociation of ethane at 553 (top part) and
635 K (bottom part). The hydrocarbon fragments were removed from
the surface by titration with 100 Torr of \( H_2 \) at different temperatures.

Figure 11. Effect of Ni coverage on the hydrogenation of hydrocarbon
fragments on Ni/Pt(111) surfaces. The carbonaceous layers \( \theta_Ni \sim 0.4 \)
were deposited on the surfaces by decomposition of ethane at 595 K. The
titration was carried out with 100 Torr of \( H_2 \) at 595 K.

IV. Discussion

Experimental evidence shows that nickel and platinum can form a
series of solid solutions. The formation of Ni\(_3\)Pt and NiPt
alloys is well documented. Studies using AES, X-ray photo-
electron spectroscopy, low-energy electron diffraction, ion scat-
tering spectroscopy, and CO chemisorption have shown that the
topmost layer of Pt\(_{10}\)Ni\(_{50}\)(111), Pt\(_{50}\)Ni\(_{50}\)(111), and Pt\(_{25}\)Ni\(_{75}\)(111)
single-crystal alloys is very rich in platinum, with the atomic
concentrations of this metal varying as follows: 35% for Pt\(_{10}\)Ni\(_{50}\),
90% for Pt\(_{50}\)Ni\(_{50}\), and 95% for Pt\(_{25}\)Ni\(_{75}\). In contrast, results
apparent activation energy for ethane hydrogenolysis on Ni-covered Pt(111) to modifications in the morphology of the surface sites that are active for C-C bond breaking.

Comparing the rates for hydrogenolysis of ethane on Ni(100) (see Figure 1 in ref 21) and Pt(111) (Figure 2), one can see that the Ni(100) surface is ~150 times more active than the Pt(111) surface. However, the rates for ethane dissociation (always larger than those of hydrogenolysis) are only ~5 times higher on Ni(100) than on Pt(111) (Figure 7). Similar comparisons between Ni(100) and the Ni/Pt(111) surfaces show that ethane hydrogenolysis is faster on Ni(100) (see section III.1), while ethane dissociation is more rapid on the Ni/Pt(111) systems (see section III.2). All this experimental evidence is consistent with a rate-determining step for hydrogenolysis being the rupture of the C-C bond and not C-H bond breaking. A comparison of deuterium-exchange rates with hydrogenolysis rates for ethane on Pt(111) suggests that C-C bond scission dominates the kinetics of hydrogenolysis on this surface.

The dependence of the rate of ethane hydrogenolysis with respect to the partial pressures of the reactants shown in Figures 3 and 4 can be analyzed by using a mechanistic scheme proposed previously by Engstrom et al. The major assumptions of this kinetic model are the following: (1) pseudoequilibrium is maintained between the gas-phase reactants and a partially dehydrogenated hydrocarbon fragment (the carbon skeleton of which remains intact) and the adsorbed hydrogen atoms

\[
C_2H_6(g) \rightleftharpoons C_2H_4(a) + 2\alpha H(a)
\]

(1)

\[
H_2(g) = 2\alpha H(a)
\]

(2)

where \( \alpha = (6 - x)/2 \); (2) the rate-limiting step involves an irreversible carbon–carbon bond cleavage in the partially dehydrogenated hydrocarbon fragment

\[
C_2H_4(a) \rightarrow CH_2(a) + CH_2(a)
\]

(3)

where \( x = n + r \); and (3) hydrogenation of the resulting fragments, CH_2(a) and CH_2(a), is rapid with respect to the initial C-C bond breaking. The analysis of the mechanistic scheme of (1)–(3) gives the following expression for the total rate of ethane hydrogenolysis:

\[
R_{\text{hydr}} = K'P_{\text{ethane}}/(K''P_{\text{ethane}} + P_{\text{H}_2}^{\alpha+1/2})
\]

(4)

where \( K' \) and \( K'' \) are a combination of the rate coefficients of reactions 1–3. For the experimental conditions used in this work (\( P_{\text{H}_2} >> P_{\text{ethane}} \)), (4) can be simplified to

\[
R_{\text{hydr}} \propto K'P_{\text{ethane}}/P_{\text{H}_2}^{\alpha+1/2}
\]

(5)

The data displayed in Figure 3 indicate that the hydrogenolysis reaction is first-order in ethane pressure, in good agreement with the expectations of our kinetic model. The results of Figure 4 were fit to the functional form given by (5) for the hydrogen pressure, yielding that the hydrocarbon fragments preceding C-C bond cleavage are C_2H_4 or C_2H_2 on clean Pt(111) (\( \alpha = 1.3 \)) and C_2H_2 on Pt(111) surfaces with Ni coverages of 1 (\( \alpha = 1.9 \)) and 1.3 (\( \alpha = 2.0 \)) ML. Thus, the extent of dehydrogenation of the ethane molecule on the surfaces increases with Ni coverage. This trend is probably a consequence of the following: (1) the binding energy of hydrogen on Ni atoms (~63 kcal/mol on Ni(111) and Ni(100)) is larger than that on Pt atoms (~57 kcal/mol on Pt(111)) and (2) the deposition of Ni atoms increases the roughness of the surface, producing highly uncoordinated atoms that can dehydrogenate ethane to a higher extent than the surface atoms of Pt(111). The last speculation is consistent with the results of Figure 7 that show an enhancement in the ability to break C-H bonds of the Pt(111) surface with Ni coverage.

In previous studies, it has been proposed that ethylidyne (≡C-CH_2) is the precursor to C-C bond cleavage in the hydrogenolysis of ethane on Pt(111). This agrees well with the predictions of our kinetic model. For surfaces covered with Ni the model predicts precursors that have fewer hydrogen atoms than those found in ethylidyne. To the best of our knowledge, the ethylidyne group has not been detected as a stable adspecies on different Ni single-crystal surfaces: Ni(111), Ni(100), Ni(110), and Ni(111)×(110). Recently, ethylidyne has been observed on alumina-supported nickel as a product of the decomposition of ethylene. In that case the extra stability of the adsorbed ethylidyne species has been attributed to the effects of adsorbed hydrogen (which may allow a hydrogenation pathway to ethylidyne) and/or to interactions with adsorbed hydrocarbon fragments (which may block the decomposition of ethylidyne).

The results of Figure 1 indicate that very small amounts of Ni can produce a large increase in the rate of ethane hydrogenolysis on Pt(111). The large miscibility between Pt and Ni at the temperatures at which the hydrogenolysis experiments were carried out should lead to Ni atoms being randomly dispersed on the surface of the Ni/Pt(111) systems. Thus the data in Figure 1 are consistent with a relatively small ensemble of Ni atoms being required for ethane hydrogenolysis. The values in this figure were renormalized to a per Ni atom basis and fitted to an expression of the type

\[
R_{\text{hydr}} = K_1 n_{\text{H}_2}^\alpha (n = \text{number of atoms in the ensemble})
\]

(6)

giving an ensemble size of two or three Ni atoms for ethane hydrogenolysis. Previous studies of the hydrogenolysis of ethane over silica-supported Ni–Cu alloys suggest that an ensemble of at least 12 adjacent Ni atoms is required for this catalytic reaction. The origin of the discrepancy between our present results and those reported for supported Cu/Ni is not clear to us. The ensemble requirement calculated in this work for ethane hydrogenolysis is consistent with experimental evidence that shows that ensembles consisting of three rhenium centers, obtained as a product of the decomposition of H_2Re_3(CO)_12 on MgO, are able to catalyze the hydrogenolysis of cyclopropane to give propane, along with ethane and methane.

V. Conclusions

1. The rate of ethane hydrogenolysis on a Pt(111) surface covered with a monolayer of Ni is higher than that observed on Pt(111) but lower than those reported for Ni(100) and Ni(111) surfaces.

2. The addition of Ni to a Pt(111) surface promotes the ability of this surface to break C-H and C-C bonds. The magnitude of the hydrogenolysis rate enhancement is consistent with an ensemble requirement for ethane hydrogenolysis of two or three nickel atoms.

3. Ni/Pt (111) surfaces are able to hydrogenate hydrocarbon fragments faster than Pt(111). This property of Ni, combined with its exceptional C-C bond-breaking ability, is a key factor leading to the enhanced hydrogenolysis catalytic activity of nickel compared to platinum.

4. The rate of ethane dissociation on Ni/Pt(111) surfaces is considerably larger than those observed on Ni(100) and Pt(111). This enhancement may be due either to an electronic modification of Ni by Pt or to the lower degree of coordination of the Ni adatoms on Pt.

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