CORRELATIONS BETWEEN STRUCTURE AND REACTIVITY OF METAL SURFACES

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ABSTRACT

Single crystal nickel and iridium have been used as model catalysts to investigate the hydrogenolysis and reactive sticking reactions of small alkanes. It has been found that the Ni(100) surface is much more reactive than the Ni(111) surface toward ethane hydrogenolysis and methane reactive sticking, and that the reconstructed Ir(110)-(1x2) surface has much higher selectivity than the Ir(111) surface for ethane production from the hydrogenolysis of n-butane. These results demonstrate the correlation between structure and reactivity of metal surfaces, and the relevance between surface science studies on single crystal model catalytic surfaces and the corresponding measurements on supported metal catalysts.

1. INTRODUCTION

An important question in catalysis is the relationship between the structure and composition of a catalytic surface and the reactivity and selectivity demonstrated by that surface. The use of oriented single crystals has been shown to be particularly informative regarding the unambiguous assessment of the effects of surface composition and geometry and provides a way leading to a microscopic understanding of the catalytic properties of various catalysts [1-4]. Although there are examples of "structure-insensitive" reaction in which the reaction proceeds at the same rate and gives the same product distribution over different facets of a metal catalyst, as shown in Fig. 1 for CO oxidation reaction on several transition metal catalysts [5, 6], many reactions have been found to be "structure-sensitive". Their reactivity and selectivity depend considerably on the surface geometry or the metallic particle size of the catalyst.

In this paper, we review some of the results of our studies on the hydrogenolysis of small alkanes over nickel [7] and iridium [8, 9], and alkane reactive sticking over nickel [10-12]. These studies were all performed on single crystal surfaces at elevated pressures. The results demonstrate the correlation between structure and reactivity of metal surfaces, and the relevance between surface science investigations on single crystal model catalytic surfaces and corresponding studies on supported metal catalysts.
Fig. 1 Arrhenius plot for CO oxidation reaction on several transition metal single crystal surfaces and supported catalysts at a total reactant pressure \( P \) of 24 Torr and \( \text{CO}/\text{O}_2=2 \) [5, 6]. The data demonstrate the "structure-insensitivity" of this reaction.

2. EXPERIMENTAL

The experiments were performed in a stainless-steel, dual-chambered apparatus which has been described in detail elsewhere [2, 13]. The chambers are linked via a gate valve and each can be evacuated to \(<10^{-10}\) Torr. Crystals were mounted on a retraction bellows and translated vertically between the analysis chamber and the reaction chamber. The analysis chamber is equipped with a cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES) and a quadrupole mass analyzer for thermal desorption spectroscopy (TDS). The reaction chamber, which has a volume of \( \sim 600\text{cm}^3 \) and can be pressurized to several atmospheres, was operated as a batch microreactor.

The crystal temperature was monitored by either a chromel/alumel thermocouple (for nickel) or a W-5\%Re/W-26\%Re thermocouple (for iridium) spot-welded to the back of the crystal. The temperature of the sample was maintained during reaction by a RHK temperature programmer to \( \pm 1\text{K} \).

The single crystal preparation and cleaning, reactant handling and purification, and the experimental procedures are given in detail in ref. 7-12.

In the alkane hydrogenolysis experiments, reaction products were analyzed by gas chromatography. Absolute reaction rates were calculated from the reactor volume, duration of reaction, the
measured surface area and the known atomic density of each crystal surface.

In the alkane reactive sticking experiments, after reaction, the Auger ratio \( C(272\text{eV})/\text{Ni}(848\text{eV}) \) was measured and assumed to be proportional to the concentration of carbon atoms present on the nickel surface \([14-15]\). This ratio was then compared to the saturation C/Ni ratio, for which the exact carbon coverage is known \([16]\). This enabled the calculation of initial reaction rates expressed as alkane decomposition events per site, per second.

3. RESULTS AND DISCUSSION

3.1 Hydrogenolysis of Small Alkanes on Nickel and Iridium Single Crystal Surfaces

3.1.1 Hydrogenolysis of Ethane on Nickel

The reactivity for ethane hydrogenolysis to methane on nickel has been shown to depend critically on the particular geometry of the surface. Fig. 2 shows the specific reaction rate \( [(\text{product molecules}) \cdot (\text{substrate surface atom})^{-1} \cdot (\text{second})^{-1}] \) or turnover frequency (TOF) for methane formation from ethane over Ni\((100)\) and Ni\((111)\) surfaces plotted in Arrhenius form \([7]\). It can be seen that the more open \((100)\) surface is far more active than the close-packed \((111)\) surface. For the Ni\((100)\) surface, the data give an activation energy of 24 kcal/mole, which is remarkably close to the 25 kcal/mole obtained for the methanation reaction over the same surface \([13]\). Furthermore, the specific rates observed for both methanation and ethane hydrogenolysis on this surface are virtually identical for the same partial pressure of hydrogen. These observations strongly suggest that these two reactions over the Ni\((100)\) surface are following the same reaction pathway and are limited by the same reaction step. As previously shown for the methanation reaction \([16]\), ethane hydrogenolysis on this surface must involve a surface carbon formation step followed by its reduction by hydrogen. In contrast, the kinetic data shown in Fig. 2 for the Ni\((111)\) surface give an activation energy of 46 kcal/mole, implying that a different reaction mechanism is operative.

There could be several possibilities as to the origin of the inhibited activity of the Ni\((111)\) surface relative to the Ni\((100)\) surface toward ethane hydrogenolysis. One possibility is the differences in the electronic structure between these two surfaces. If back-bonding from the metal to the unfilled \(\sigma^*\) levels of ethane is an important first step toward carbon–carbon bond scission in
Fig. 2  Arrhenius plot for ethane hydrogenolysis reaction on Ni(100) and Ni(111) surfaces at a total reactant pressure $P_T$ of 100 Torr and $H_2/C_2H_6=100$ [7]. Also shown is the result on supported nickel catalysts at $P_T$ of 175 Torr and $H_2/C_2H_6=6.6$ [20].

ethane, then the (100) surface may be more active than the (111) surface since the appropriate nickel orbitals for such back-bonding are more available in the case of the (100) surface [17]. The second possibility is the differences in the spacing between high coordination bonding sites on these two surfaces. For the (100) surface the spacing between the four-fold hollow sites is approximately 2.5Å. The bond length of a carbon-carbon intermediate is expected to be from 1.3 to 1.5Å. Obviously for the Ni(100) surface, the carbon-carbon bond cannot remain intact and, at the same time, the carbon atoms bond in the preferred high coordination site [18]. However, for the Ni(111) surface, the 1.4Å spacing between the high coordination sites is ideally suited to maintaining the carbon-carbon bond intact while bonding each carbon to a three-fold hollow site. It follows then that ethane adsorbs on the (100) surface and dissociates to form a surface carbide or hydrogenated carbonaceous species. This species, in turn, hydrogenates to methane. For the (111) surface, however, we anticipate a stable adsorbed carbon-carbon species to form at relatively high surface concentrations. The rate limiting step for product formation then would be the carbon-carbon bond scission step. The surface should be virtually free of the single carbon species, which is an essential intermediate for methanation.

The (111) surfaces are encountered more prevalently in FCC
materials as the particle size is increased via successively higher annealing temperatures [19]. The results of this study then are consistent with rate measurements on supported nickel catalysts [20, 21], which show hydrogenolysis activity to be a strong function of particle size, the larger particles exhibiting the lower rates, as also shown in Fig. 2.

3.1.2. Hydrogenolysis of n-Butane and Propane on Iridium

The selectivity for ethane production from the hydrogenolysis of n-butane over iridium single crystals has been demonstrated to scale with the concentration of low-coordination-number metal surface atoms [8, 9]. Fig. 3 shows the results on Ir(110)-(1x2) and Ir(111) surfaces as well as the schematic representation of these iridium surfaces. The Ir(110)-(1x2) surface, which has a stable "missing-row" structure [22], has been found to produce ethane very selectively. This contrasts with the results for the close-packed Ir(111) surface, where only the statistical scission of C-C bonds has been observed. Although there is still some controversy regarding the surface structure of Ir(110) under reaction conditions, its selectivity for ethane production is clearly superior to Ir(111).

Fig. 3 Diagram showing the correlation between selectivity and structure for n-butane hydrogenolysis on iridium. (a) Schematic representation of the Ir(110)-(1x2) and Ir(111) surfaces. The z axis is perpendicular to the plane of the metal surface. Cₙ designates the coordination numbers of the metal surface atoms. (b) Selectivity for C₄H₈ production (mol % total products) for n-butane hydrogenolysis on iridium single crystals [8, 9] and supported iridium catalysts [23] at 475K. The effective particle size for the single crystal surfaces is based on the specified geometrical shapes. ▲, Ir/Al₂O₃; ■, Ir/SiO₂.
The results of this study correlate qualitatively with the observations made previously for selective hydrogenolysis of n-butane to ethane on supported iridium catalysts as a function of iridium particle size [23], which is also shown in Fig. 3. It can be seen that the results for Ir(110)-(1x2) model very well the small-particle limit whereas the results for Ir(111) relate more closely to the data for the corresponding large particles (>10nm). By assuming particle shapes the general behavior of declining selectivity with larger particle size can be accurately modelled, as illustrated in Fig. 3.

The stoichiometry of the surface intermediate leading to high ethane selectivity, based on kinetics and surface carbon coverages subsequent to reaction, is suggested to be a metalloccyclopentane [8, 9]. The Ir(110) surface undergoes a reconstruction, described as the Ir(110)-(1x2) or "missing-row" structure, resulting in rows of the highly coordinatively unsaturated "C_7" sites, as schematically shown in Fig. 3. These sterically unhindered C_7 sites can form a metalloccyclopentane species (e.g., a 1,4-diadsorbed hydrocarbon species) which has been proposed as an intermediate in the central scission of butane to ethane. Based on analogous chemistry reported in the organometallic literature [24, 25], the mechanism responsible for the hydrogenolysis of n-butane on the Ir(110)-(1x2) surface is postulated to be the reversible cleavage of the central C-C bond in this metalloccyclopentane intermediate. On the other hand, butane hydrogenolysis on the Ir(111) surface appears to operate via a different mechanism. First, dissociative chemisorption of butane and hydrogen occurs followed by irreversible cleavage of the terminal carbon-carbon bond of the adsorbed hydrocarbon. Further C-C bond cleavage prior to product desorption leads to the methane and ethane observed as initial products.

For both iridium surfaces, the extent to which hydrogenolysis proceeds increases with increasing reaction temperature. This is in keeping with the general trend for increased cracking at higher temperatures for alkane reactions. The term "roll-over" has been used to describe the fall in overall activity at the high temperatures which leads to a decrease in the selectivity for the production of ethane (shown in Fig. 4) in the hydrogenolysis of propane over these two iridium surfaces. Decreasing the partial pressure of H_2 at the temperature of onset of roll-over induces the same selectivity change as observed for an increase in reaction temperature. The origin of this effect is believed to be as follows. As the reaction temperature is raised beyond a critical temperature,
defined primarily by the hydrogen partial pressure, the hydrogen surface coverage falls below a saturation or critical coverage. The lower hydrogen coverage then reduces the efficiency of the hydrogenation of surface hydrocarbon fragments. It is shown in Fig. 4 that the roll-over onset occurs at a higher temperature on the Ir(110)-(1x2) than that on the Ir(111) surface. From previous studies, it is known that hydrogen desorbs at a higher temperature (390K at the saturation of the high temperature desorption state) from Ir(110)-(1x2) than from Ir(111) surface (255K at 250L of hydrogen) [26]. Therefore, the higher temperature of onset of roll-over on the more open Ir(110)-(1x2) surface correlates with the higher binding energy of hydrogen adatoms on this surface. This suggests that the source of the reactive hydrogen is the metal surface rather than, for example, an "active" carbonaceous overlayer.

3.2 Alkane Reactive Sticking on Nickel Single Crystal Surfaces

The reactive sticking of alkanes on nickel single crystal surfaces is strongly dependent on the surface structure. For example, methane reactivity, shown in Fig. 5 as the time-dependent carbon buildup from 1.00 Torr of methane in contact with the various low index nickel single crystal surfaces at 450K, is seen to increase in the order Ni(111)<Ni(100)<Ni(110) [10]. Initial reaction rates for the Ni(110) and Ni(100) surfaces are very similar, and are ~7 to
Fig. 5 Methane decomposition kinetics on low index nickel single crystal surfaces at 450K and methane pressure $P_{\text{methane}}$ of 1.00 Torr [10].

10 times greater than the initial rate for Ni(111) surfaces at 450K. However, both the Ni(100) and Ni(111) surfaces exhibit a strong coverage dependence in the methane decomposition rate, as evidenced by the deviation from linearity in the plots for these surfaces shown in Fig. 5. This behavior is in contrast with that of the Ni(110) surface, which does not exhibit the same downward curvature, possibly indicating islanding or less of a carbon coverage dependence for the methane reactivity on this surface.

Methane dissociative adsorption on sulfur-modified Ni(100) surface indicates that sulfur atoms poison this reaction by a simple site blocking mechanism [11]. The initial methane decomposition rate decreases linearly with sulfur coverage and drops to zero at a sulfur coverage of ~0.3ML. The results are consistent with a mechanism for the activated dissociative adsorption of methane on Ni(100) involving a direct process. However, dissociation of ethane, propane, and n-butane on Ni(100) is believed to proceed primarily via a trapped molecular precursor [12].

These studies on the alkane reactive sticking on nickel single crystal surfaces were carried out under the high incident flux conditions. The elevated pressures are required to produce measurable products, not because of the greater availability of higher velocity molecules, but rather because of the severe
competition which is inevitably present between desorption from the precursor or adsorbed state and dissociation. Since activation energies to desorption for many reactants of interests (particularly hydrocarbons) are usually smaller than the activation energies to reaction, desorption dominates and reaction probabilities are quite small, often too small to measure at UHV conditions. For these reactants, the greater number of collisions at higher pressures simply serves to overcome this limitation.

Since the alkane dissociation rates obtained in these "thermal bath" experiments are initial rates measured in the limit of zero carbon coverage, they represent a theoretical upper limit to the rates of steam reforming of these alkanes on unpromoted nickel catalysts. Based on the kinetic experiments on sulfur-passivated nickel catalysts for carbon-free steam reforming of methane, Rostrup-Nielsen found that the kinetic data can be explained in terms of simple physical blockage by chemisorbed sulfur and that an ensemble of three nickel atoms is involved in the reforming reaction [27]. These are in complete agreement with the results obtained in the "thermal bath" experiment [11] and provide another excellent example in which surface science studies on single crystal model catalytic surfaces correlate extremely well with the corresponding measurements on supported metal catalysts.

4. CONCLUSIONS

Single crystal metal surfaces allow us to study in a systematic fashion the role of surface structure on catalytic activity and selectivity. We have shown that the reactivity for ethane hydrogenolysis to methane and alkane reactive sticking on nickel, as well as the selectivity for ethane production from the hydrogenolysis of n-butane over iridium are markedly affected by surface structure. For ethane hydrogenolysis reaction, the Ni(100) surface is much more active than the Ni(111) surface, possibly due to the different electronic structure and spacing between high coordination bonding sites on the two surfaces. For methane reactive sticking on nickel, the reactivity increases in the order Ni(111)<Ni(100)<Ni(110). For n-butane hydrogenolysis on iridium, the reconstructed Ir(110)-(1x2) surface, which has a high concentration of C, low-coordination-number sites, shows a marked propensity for central bond scission. On the other hand, the Ir(111) surface exhibits non-selective hydrogenolysis, yielding a statistical distribution of the products. The selective hydrogenolysis on Ir(110)-(1x2) may involve adsorption
of the n-butane as a metallocyclopentane and subsequent cleavage at the central carbon–carbon bond. All the results summarized here from studies on single crystal metal surfaces correlate very well with measurements on supported metal catalysts.

ACKNOWLEDGEMENTS

We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

REFERENCES