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n-butane hydrogenolysis on planar and faceted Pt / W(111) surfaces

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The relationship between surface structure and reactivity is investigated by means of n-butane hydrogenolysis, a known structure sensitive reaction, for planar and faceted Pt/W(111) surfaces. The W(111) surface reconstructs to form pyramidal facets with [211] orientation upon vapor deposition of Pt (> 1.3 ML) and annealing above 750 K. The hydrogenolysis kinetics over the planar and the faceted surface are found to be quite different. The planar surface has a higher selectivity towards ethane formation and a higher reaction rate. The apparent activation energies are found to be 33 ± 4 kJ/mol for the planar surface and 76 ± 6 kJ/mol for a surface covered with ~ 20 nm facets. There appears to be a correlation between the concentration of fourfold coordination (C_4) sites on the surface and the amount of ethane produced. The C_4 concentration is altered by changing the facet size (annealing temperature). The results indicate the presence of a different intermediate on the C_4 sites as evidenced by the differences in the apparent activation energy, the reaction rate and the overall selectivity.

Keywords: n-butane hydrogenolysis; W(111); Pt; bimetallic

1. Introduction

Understanding the role of surface structure in chemical reactions is an important first step in delineating the fundamental aspects of a catalyst. The hydrogenolysis of n-butane is one reaction which has shown to be sensitive to surface structure. This is evidenced by the reaction products in which cleavage of the n-butane molecule will result in either the formation of methane and propane or in two ethane molecules depending on the surface and material used [1–8]. This structure sensitivity has been found on a wide variety of materials ranging from supported metal particles to single crystal catalysts.

The relationship between particle size and selectivity, reaction rate and activa-

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tion energy has been investigated for supported Pt [1,2], Ir [3], Rh [4] and Ni [5,6] catalysts. It is found on these catalysts that, as the particle size increases, the relative amount of ethane produced decreases. This is attributed to the presence of a different intermediate species on the low coordination number surface sites which are higher in concentration for smaller particle sizes. In addition, it is generally found that the overall reaction rate decreases and the apparent activation energy increases as the particle size is increased.

On well defined single crystal catalysts of Ir [7,8] and Rh [4] striking differences are found for the *n*-butane hydrogenolysis reaction which are attributed to the difference in surface structure. Engstrom et al. [7,8] investigated the hydrogenolysis reaction on the closed packed Ir(111) and the more open reconstructed Ir(110)-(1 × 2) surfaces. The selectivity for ethane production is higher on the (110)-(1 × 2) surface. It was interpreted that on this surface the presence of low coordination number sites allows for a mononuclear metallacycle pentane intermediate that is sterically forbidden on the (111) surface. In addition, the overall reaction rate is higher and the apparent activation energy is lower on the (110)-(1 × 2) surface. This is in agreement with the reaction occurring along different pathways on the two surfaces.

In the investigation of *n*-butane hydrogenolysis on Rh(111), (100) and (110) surfaces [4] the results are found to be quite different. The highest ethane selectivity is found on the closed packed (111) surface as opposed to the more open (100) or (110) surfaces. The results for the (111) surface resemble those for the larger supported Rh particles. The reason for the differences in the Ir and Rh surfaces is not understood.

Recently, in this laboratory an interesting surface has been investigated for determining the contribution of low coordination number atoms in the *n*-butane hydrogenolysis reaction [9–14]. The deposition of certain transition metals (i.e. Pt, Pd, Ir, Rh and Au [9]) on W(111) above a critical coverage, followed by annealing, results in the (111) surface reconstructing to form pyramidal facets with {211} orientation (see fig. 1a). In particular, the interaction of PT with the W(111) surface has been studied in great detail by means of scanning tunneling microscopy (STM), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) [10–13]. On the W(111) surface the deposition of >1.3 monolayer (ML) of Pt and annealing above 750 K results in the surface reconstructing to form facets. The facet size increases as the annealing temperature is raised with the STM results indicating average facet sizes of ~15, ~30 and ~80 nm for annealing temperatures of 880, 1200 and 1400 K, respectively. For annealing temperatures of 750–1100 K the surface is completely faceted while annealing to higher temperatures results in planar regions in addition to facets [10].

In this paper we investigate the role of surface structure in the *n*-butane hydrogenolysis reaction on a planar Pt/W(111) surface and faceted Pt/W surfaces. These results are discussed in terms of the reaction rates, apparent activation energies and selectivities for the different surfaces.

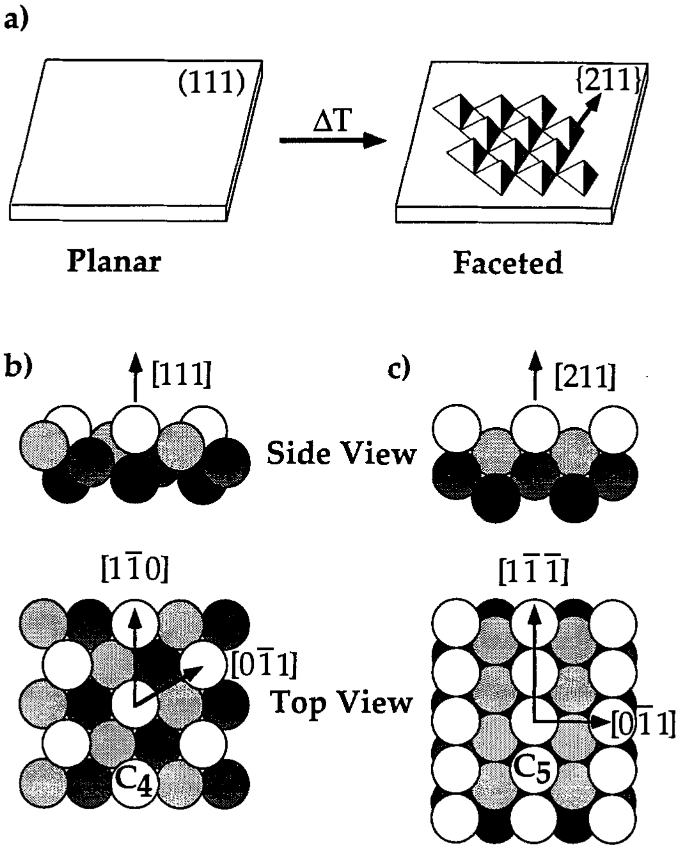

Fig. 1. (a) Schematic of the surface before and after surface reconstruction. (b) Structure of the W(111) surface. (c) Structure of the W(211) surface which is representative of the facet surface after reconstruction.

2. Experimental

The experiments have been carried out in a combined ultrahigh vacuum (UHV)–high pressure reactor system that has been described previously [14,15]. The UHV system is equipped with LEED, AES and TPD capabilities and has a working pressure of $\leqslant 5 \times 10^{-10}$ Torr.

The W(111) crystal is mounted to the manipulator by W support leads which are spotwelded to the back of the crystal and can be resistively heated to ~ 1600 K. Heating to 2300 K is achieved by an electron beam assembly. The sample temperature is monitored by means of a W–5% Re/W–26% Re thermocouple spotwelded to the sample edge. Repetitive cycles of annealing in 5×10^{-8} Torr O_2 to 2100 K followed by flashing to 2300 K are used to clean the surface [16]. Sample cleanliness and long-range order are checked by AES and LEED.

The Pt is vapor deposited from a housing which encloses a W filament wrapped with high purity Pt wire. The Pt source is thoroughly outgassed before deposition. All Pt coverages [10] are reported with respect to the number of atoms in one physical monolayer of Pt on W(111) (1.7×10^{15} atoms/cm^2) [17]; this is the coverage necessary to cover completely all exposed W atoms on the atomically rough (111) surface (fig. 1b).

The *n*-butane (Matheson research grade, 99.9% purity) is further purified by distilling from a liquid nitrogen/*n*-pentane bath. Hydrogen (Matheson research grade, 99.9995% purity) is used without further purification. The products are detected by means of gas chromatography using an Alltech column with VZ-7 packing which allows for the resolution of CH_4, C_2H_6, C_3H_8, i-C_4H_{10} and C_4H_{10}. The concentrations are calibrated using a commercial standard for C_1–C_6 *n*-paraffins (Scotty II). Turnover frequencies (TOF) are calculated using surface atom densities of 5.7×10^{14} atoms/cm^2 for the planar Pt/W(111) surface and 8.6×10^{14} atoms/cm^2 for the facet covered surfaces. The surface atom density for the completely faceted surface is 6% greater in value than that of a planar (211) surface due to the increase in surface area upon faceting [10].

3. Results and discussion

3.1. PLANAR Pt/W(111)

The W(111) surface is atomically rough and the topmost layer of the ideal surface consists of atoms that have fourfold coordination (C_4 sites) (see fig. 1b). The surface atoms have an interatomic spacing of 4.47 Å which is much larger than the atomic diameter of W (2.74 Å). Upon deposition, Pt is found to adopt the lattice parameters of the substrate resulting in pseudomorphic growth [11,12] of the ultrathin films. In our investigation we have concentrated on a W(111) surface that is covered with 1.3–1.4 ML of Pt. Prior to reaction, the surface has been annealed for one minute at 600 K, well below the temperature at which faceting is observed to occur ($\sim$ 750 K) [11,12]. We refer to this as the planar surface.

The data for the *n*-butane hydrogenolysis reaction on the planar Pt/W(111) surface are presented in Arrhenius fashion in fig. 2a. The results are obtained for a hydrogen/*n*-butane ratio of 100/1 and a total pressure of $\sim$ 100 Torr. The primary products observed are methane, ethane and propane. The concentration of the isomerization product (isobutane) is less than 3% of the total products and is not discussed. In general, it is found that the rate of ethane production is highest followed by methane and propane. The apparent activation energy is calculated to be 33 ± 4 kJ/mol under these conditions. At higher temperatures the rate of methane production deviates from Arrhenius behavior. The reason is unknown, but a similar observation is reported for the Ir(110)-(1×2) surface [7,8]. These results are quite different from those on the closed packed Pt(111) surface, in which

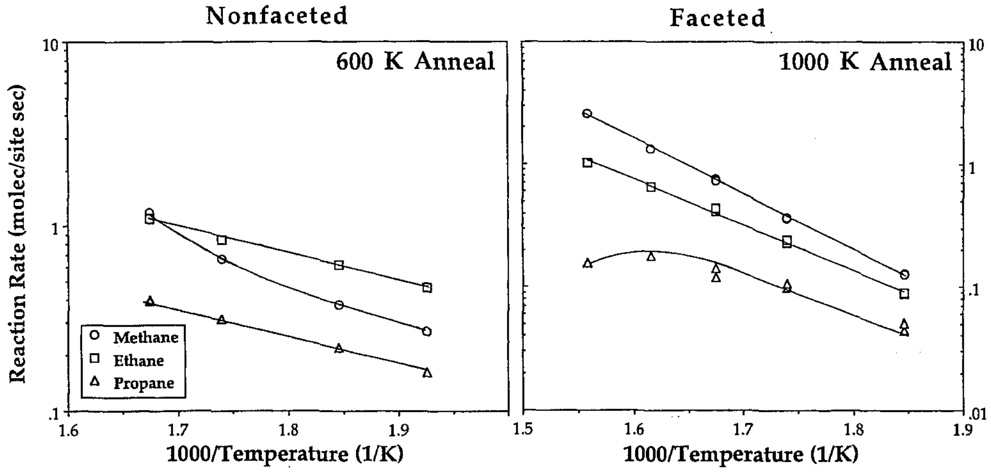

Fig. 2. (a) Kinetic data for the planar Pt/W(111) surface annealed to 600 K. (b) Data for a faceted Pt/W(111) surface, the surface is annealed to 1000 K which induces the formation of facets with {211} orientation, approximately 20 nm in size. All data are taken for a hydrogen to *n*-butane ratio of 100/1 and a total pressure of ~100 Torr.

methane is the primary product and an apparent activation energy of 115 kJ/mol is found [18]. The dissimilarity is believed to be a convolution of the difference in surface structure and a synergistic effect between the Pt and W.

Analysis of the Pt/W(111) surface after reaction by AES gives a carbon coverage of 0.30 ± 0.05 ML. The carbon coverage does not change as a function of reaction temperature. LEED indicates a (1 × 1) post analysis structure.

3.2. FACETED Pt/W(111)

Annealing Pt coverages of greater than 1.3 ML to temperatures above 750 K results in the W(111) surface reconstructing to form pyramidal facets with {211} orientation (see fig. 1a). The LEED data indicate that the surface exhibits no coherent scattering from planar (111) regions for $T \leqslant 1100$ K and STM supports this [10–12]. The ideal (211) surface is depicted in fig. 1c with the surface atoms having fivefold coordination (C_5 sites). The distance between rows in the $[0\bar{1}1]$ direction is 4.74 Å, the same as the interatomic spacing in W(111). The spacing along the $[1\bar{1}\bar{1}]$ direction is 2.74 Å, the atomic size of W atoms. The ideal faceted surface also contains edge atoms, which have fourfold coordination (C_4), at the intersection of the {211} facet planes. The concentration of C_4 sites decreases as the facet size increases while the C_5 concentration increases. Although it is not intuitively obvious the total number of top layer surface atoms remains constant regardless of the facet size.

The kinetic results have been obtained for Pt/W(111) surfaces (1.3–1.4 ML Pt) that are annealed to 800 and 1000 K for 1 min, which corresponds to facet sizes of

~10 and ~20 nm, respectively. The results are presented in fig. 2b in Arrhenius fashion for the 1000 K annealed surface. For the faceted surface, methane, ethane and propane are the primary reaction products. In contrast to the planar surface there is a higher selectivity for methane on the faceted surface, followed by ethane and propane. Also, the apparent activation energy is found to be 76 ± 6 kJ/mol, much larger than that found for the planar Pt/W(111) surface but closer to that of Pt(111). There is some rollover observed for the propane at higher temperatures, which may be due to hydrogenolysis of the propane product.

Post reaction analysis for the faceted samples indicates that the LEED pattern is still that of a {211} faceted surface and that the surface structure does not change during the reaction. The LEED spots become somewhat broadened as would be expected for a surface covered with a carbonaceous species. A carbon coverage of 0.40 ± 0.04 ML is found for the 1000 K annealed sample which is independent of reaction temperature.

To determine if the amount of ethane produced is related to the concentration of low coordination sites as suggested by Engstrom et al., it is necessary to determine if there is a correlation between the C_4 sites and rate of ethane production. In fig. 3 the calculated concentration of C_4 edge sites is plotted as a function of facet size for a completely faceted surface (no planar (111) regions). The concentration of C_4 sites for a facet size of zero corresponds to the planar W(111) surface. It is important to note that the C_4 sites existing on the faceted surface are from the edges of the facets. Plotted along with the C_4 concentration is the ethane TOF frequency for the planar and faceted surfaces. Fig. 3 suggests that the rate of ethane production scales with the concentration of C_4 sites, although we cannot eliminate the possibility that ethane is produced also on the planar (211) C_5 sites. In fig. 3 the

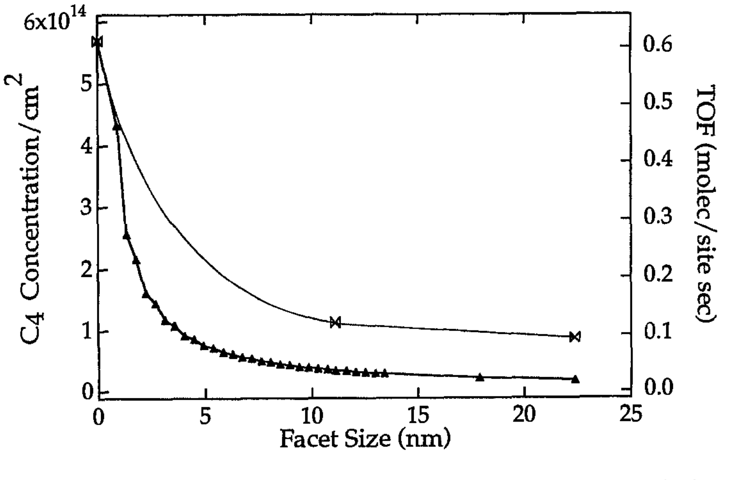

Fig. 3. C_4 site concentration and rate of ethane production (turnover frequency) plotted as a function of facet size. The planar Pt/W(111) surface is shown for a facet size of zero. The thin line through the ethane production data is intended as a guide to the eye.

Table 1
A comparison of the ensemble size and ethane selectivity for several surfaces

Substrate	Ensemble size (Å^2)	Ethane selectivity (%)
Ir(110)-(1 × 2) [7,8]	20.77	90
Ir(111) [7,8]	6.36	50
Pt/W(111) (this work)	17.31	50
faceted Pt/W(111) (this work)	12.26	35
Pt(111) [18]	6.64	25
Rh(111) [4]	6.27	50
Rh(100) [4]	7.24	35
Rh(110) [4]	10.23	35

contribution from the planar (211) regions has not been subtracted. If this is done the ethane production for the faceted surfaces could lie closer to the C_4 concentration line. To our knowledge the hydrogenolysis kinetics on the Pt/W(211) system have not been studied; this work is currently underway in our laboratory. The role of higher coordination sites is believed to be unimportant because of the steric hindrance of an intermediate containing multiple carbon atoms on these sites, and is not discussed.

The differences in the kinetics between the planar and faceted surfaces (i.e.. reaction rates, apparent activation energies and selectivity) suggests the presence of a different intermediate on the low coordination sites. In table 1 the unit cell size (ensemble size) for different Ir, Pt, Rh and Pt/W surfaces is listed along with the selectivity for ethane production. On Pt, Ir and Pt/W the more open the surface is, the higher the ethane selectivity. This would suggest that the intermediate responsible for ethane production is larger in size, such as a metallacycle pentane [7,8], than for methane and propane production. The surfaces with smaller ensemble sizes show a much reduced ethane selectivity. This trend is not found for the Rh surfaces [4], indicating the need for further investigation.

4. Conclusions

There are large differences found for the kinetics of *n*-butane hydrogenolysis on the planar Pt/W(111) surface as compared to the faceted surfaces. The planar surface is found to be much more effective in ethane production and has a much lower apparent activation energy than the faceted surface. A relationship is found between the number of C_4 sites on the surface and the amount of ethane produced. In comparing several surfaces excluding Rh it is found that the surfaces with larger interatomic distances have higher ethane selectivity.

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