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Gabor A. Somorjai and José Carrazza

Presented at the E. V. Murphree Award Symposium
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April 1985

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ABSTRACT

The rate and product distribution of chemical reactions catalyzed by metals can depend on the particle size of supported catalysts. This can be explained by the interaction between chemisorbed species and surface sites of different configuration in the metal associated with atoms in terrace, steps and kinks. Single-crystal catalysts are excellent models for studying these interactions. In this review, the contribution of single-crystal studies to the understanding of structure sensitivity in catalytic reaction is discussed. Reactions are classified in three types. Structure sensitive reactions, structure insensitive reactions and reactions that show both behaviors, depending on the experimental conditions. Several examples are discussed in each of the three categories.

INTRODUCTION

In the late sixties and early seventies several hydrocarbon reactions over platinum catalysts were studied as a function of the catalyst particle size. It was found that reactions like alkane hydrogenolysis (1) and isomerization (2) were strongly dependent on the particle size, while reactions like cyclopropane ring opening (3) and olefin hydrogenation (4) were independent of the particle size. In a review article in 1969 (5), Boudart classified the first type of reaction as structure sensitive and the second one as structure insensitive. During this period, thermal desorption studies using single crystal surfaces revealed increasingly the structure sensitivity of the surface chemical bond (6). Since the relative concentrations of terraces, steps and kinks change with catalyst particle size, it was reasonable to suggest that variations of adsorbate bond strengths due to changes in local atomic structure are responsible for the modification of reaction rates. It was not clear, however, how the bonding of chemisorbed molecules adsorbed at low pressures relates to the bonding of reaction intermediates that are present on the catalytically active surfaces under steady state reaction conditions at high pressures. In order to address this problem, a high pressure-low pressure apparatus, shown in Figure 1, was developed in our laboratory (7). With this system, surface structure and surface composition of single crystals could be determined under UHV conditions before and after determining reaction rates and product distribution at high pressure; all this, without exposing the crystal to ambient atmosphere. In this manner, many reactions have been studied using

different single-crystal surfaces. In the case of hydrocarbon reactions, the structure sensitivity and kinetic parameters over single-crystal catalysts are in excellent agreement with previous work done on high-surface-area supported metal catalysts (8-10).

In this paper, we shall review the contribution of single-crystal studies to the understanding of structure sensitivity. The discussion is divided into three sections. First we will review structure insensitive reactions, then reactions whose dependence of the rate on the surface structure of the catalyst varies with reaction conditions and finally structure sensitive reactions.

STRUCTURE INSENSITIVE REACTIONS

There are several examples of catalyzed chemical reactions where the independence of the particle size over supported catalysts correlate very well with the independence on the surface plane in single-crystal catalysts. In those cases there is also excellent agreement between kinetic parameters and product distribution. Table 1 lists reaction rates obtained for the ring opening of cyclopropane over several catalysts (11). The turnover rates obtained over single-crystal catalysts are identical, within the error of surface area and temperature measurements, with those obtained on supported catalysts. Similar agreement was obtained for the hydrogenation of cyclohexene (15) (Figure 2), the hydrogenation of carbon monoxide over rhodium to produce methane (17) (Table 2), and the hydrogenation of ethylene (22) over a wide variety of platinum catalysts (Table 3).

The explanation of the structure insensitivity of a catalytic reaction is not easy. After all, the determination of surface structures by low energy electron diffraction (LEED) and electron vibration spectroscopies (29-30) has shown that the bonding of most atom and molecules to surfaces exhibits strong structure sensitivity. However, a closer scrutiny of the variation of the chemisorption bond with coverage and a detailed surface study of ethylene hydrogenation provides reasonable models for the mechanisms of structure insensitive reactions.

The interaction between adsorbed molecules and the substrate surface can be affected by coverage. Figure 3 shows the variation of the heat of adsorption of carbon monoxide over Pd(111) surface with coverage as determined by Conrad et al. (31). At high coverages, the average heat of adsorption per molecule drops precipitously from 35 to 10 Kcal/mol due to repulsive interactions among the adsorbed carbon monoxide molecules. These weakly bound molecules are the predominant species on the palladium surface at high pressures. If they are the ones that participate in the catalytic reactions, changes in the structure of the surface have minor effects in the reaction rates, since the adsorbate-substrate interaction is weakened by the repulsive adsorbate-adsorbate interactions. Similar variations of the heat of adsorption with coverage are found for other chemisorbed molecular systems (32). This model may be the reason for the structure insensitivity of many catalytic reactions.

The hydrogenation and dehydrogenation of olefins are good examples of reactions that do not show structure sensitivity at high pressures (above 1 atm) on both supported (16) and single-crystal catalysts (33-34). The

formation of carbonaceous deposits during this reaction is almost instantaneous at high pressures. Their presence can mask the catalyst surface structure of the catalyst, making the reaction structure insensitive. In the case of the hydrogenation of ethylene, it has been proposed (22) that the reaction occurs on top of an ethylidene layer, a carbonaceous deposit strongly adsorbed on the metal surface (Figure 4). The metal only plays a secondary role, i.e., to provide atomic hydrogen for the process. The model of the reaction mechanism is shown in Figure 5. The densely packed ethylidene does not allow the adsorption of the ethylene gas molecules directly over the metal surface. Hydrogen, however, can readily adsorb in the space between the ethylidene species and atomize as indicated by the rapid H_2/D_2 exchange that can be detected (35). The reaction occurs by hydrogen transfer through the ethylidene to the weakly adsorbed ethylene in the second layer and ethane desorbs after the sequential hydrogenation is complete.

Other mechanisms can be proposed for this facile reaction. At elevated temperatures, there is a finite rate of ethylidene rehydrogenation that exposes some fraction of the metal sites which can now participate directly in the hydrogenation reaction. There is evidence from electrochemical (36) and low temperature studies (37) that preadsorbed hydrogen can rapidly react with ethylene, preventing the ethylidene formation. It has been found, however, using several techniques that at the temperature at which hydrogenation reactions are usually carried out (300 K), the ethylidene molecules are tenaciously held on the Pt(111) and Rh(111) crystal surfaces and that their rehydrogenation ratio or even the deuteration of the methyl group is

about a millionfold slower than ethylene hydrogenation rates at atmospheric pressures (see Figure 6) (38-40). Therefore, the hydrogenation process must occur on top of this carbonaceous layer. This explains the observed structure insensitivity.

In summary, the structure insensitivity observed on several reactions may be due to the presence of adsorbed species on the surface that either weaken the reactant-catalyst surface interaction or are inactive in the reaction, masking in both cases the surface structure of the catalyst.

REACTIONS WHOSE STRUCTURE SENSITIVITY IS DEPENDENT ON REACTION CONDITIONS

The H_2/D_2 exchange over Pt surfaces is a structure sensitive reaction at low pressures ($\sim 10^{-7}$ torr), as shown by molecular beam surface scattering studies performed in our laboratory (41-43). The technique is shown schematically in Figure 7. A mixed H_2 and D_2 molecular beam impinges on a crystal surface at a specific angle. Dissociation of H_2 on the surface occurs upon impact and the desorbing HD, H_2 and D_2 molecules are detected by a rotatable mass spectrometer. Since in the temperature range studied, the dissociation of H_2/D_2 on the surface is the rate limiting step in the formation of HD, the probability of dissociative adsorption of the hydrogen molecule on the surface can be obtained from the amount of HD formed. The results on several platinum surfaces are shown in Figure 8. Over the stepped Pt(332) (curve A), the HD formation increases when the angle of incidence exposes the edges of the steps. The structure of the Pt(110) surface can be thought of as a set of densely packed steps having the same geometry as those on the Pt(332)

surface. On the Pt(110) surface (curve B) the maximum in the probability of HD formation occurs when the inner atoms of the troughs (the atoms at the bottom of the steps) are fully exposed to the incident beam. Also notice that on the Pt(111) surface, which only has sites of the same geometric configuration as those on the six-atom terraces in Pt(332) surface, the probability for HD formation is almost four times lower than in the case of the Pt(110) and Pt(332) surfaces on which the step atoms are exposed. In summary, these results show that the sites at the bottom of the step are much more active for dissociation of H_2 than the exposed terrace sites. Thus, at these low coverages, the H_2/D_2 exchange is structure sensitive. When the reaction is carried out at high pressures (~ 1 atm), although the probability for H_2 dissociation is site dependent, the flux of molecules hitting the surface is so high that the hydrogen dissociative chemisorption reaches equilibrium. The H_2/D_2 exchange becomes, thus, structure insensitive under these conditions (44).

The oxidation of carbon monoxide by oxygen, catalyzed by several transition metals, is either structure sensitive or structure insensitive, depending on the reaction conditions. McCarthy et al. (45) found that, on supported platinum, at a high carbon monoxide partial pressure ($p_{CO}/p_{total} > 0.01$) the reaction is structure insensitive. If the partial pressure of carbon monoxide is low, ($p_{CO}/p_{total} < 0.004$) the rate of carbon monoxide oxidation per platinum surface atom increases monotonically with the particle size of the catalyst; i.e. the reaction is structure sensitive.

The possible steps involved in this reaction are summarized as follows:

Engel and Ertl (46) summarized the evidence suggesting that the reaction occurs via a Langmuir-Hinshelwood mechanism (equation 3a). They also include evidence proving that the Eley-Rideal mechanism (equation 3b) is not possible for this reaction. A reaction of molecular oxygen with adsorbed carbon monoxide (equation 3c) can also be ruled out, since the dissociative chemisorption of oxygen is necessary for the reaction to take place.

When the pressure of molecular oxygen is high enough, the dissociative adsorption of oxygen on the surface is at equilibrium. The rate determining step for the reaction is then given by equation (3a). The fact that the reaction rate increases with the particle size indicates that oxygen atoms adsorbed on terraces or flat surfaces should react with carbon monoxide faster than oxygen atoms adsorbed on steps and kinks. This explanation for the structure sensitivity observed for this reaction has been confirmed by Gland et al. (47), using a kinked Pt(321) single-crystal surface.

At high partial pressure of carbon monoxide, the surface is almost saturated by this gas. The dissociation of oxygen on the surface becomes the rate determining step, since it is inhibited by the presence of adsorbed carbon monoxide. Under these conditions, Ertl and Koch (48) have shown that the reaction is structure insensitive, using different single-crystal palladium surfaces.

In summary, a reaction can be structure sensitive under some experimental conditions and structure insensitive under others if the rate determining step changes due to variations in the amounts and/or type of species on the surface.

STRUCTURE SENSITIVE REACTIONS

Among the catalytic reactions that have been studied to date, the synthesis of ammonia exhibits the greatest structure sensitivity. The synthesis of ammonia from nitrogen and hydrogen gas at high pressure (~20 atm) has been studied in our laboratory, using various single-crystal faces of iron and rhenium (49-52). The results in Figures 9a and 9b show a difference in activity of several orders of magnitude among the different faces for both metals studied. In the case of iron, this marked structure sensitivity follows the same trend as the nitrogen dissociative chemisorption sticking coefficient at low pressure (53). This suggests that the dissociation of nitrogen on iron is the rate determining step for the reaction. This conclusion is supported by kinetic studies on industrial catalysts (52). Furthermore, Brill and Kurzidim (55), made the suggestion based on indirect evidence, that the

Fe(111) microplanes on the industrial catalysts were the only ones active in ammonia synthesis.

For both iron and rhenium, the roughness and openness of the surface can be related to the catalytic activity for ammonia synthesis. In the case of iron, for example, Fe(110), the closest packed surface structure, has the lowest activity; Fe(100), a more open surface, has a 25 times the activity of the Fe(110) surface, while the Fe(111) surface, the most open surface structure studied, has the highest activity (see Figure 9a). A similar situation is found in the case of rhenium (see Figure 9b). Furthermore, Figure 10 shows that when the closest packed surface of rhenium is sputtered, the activity for ammonia synthesis increases by a factor of 25 (56). A similar increase after sputtering has been reported for the Fe(110) surface, the closest packed surface of iron (49).

As mentioned in the introduction, hydrocarbon reactions catalyzed by metal surfaces include excellent examples of both structure sensitive and insensitive reactions. Table 4 summarizes several studies on hydrocarbon reactions over platinum single-crystal and supported catalysts at high pressures (~1 atm). The agreement on structure sensitivity between the supported and single crystal catalysts is excellent for all the reactions considered. Single crystals are clearly good models for the industrial catalysts in this type of reaction.

In Table 4, reactions have been divided in two groups. The first group includes reactions that involve only formation and/or breaking of carbon-hydrogen bonds. The second group includes reactions that involve

formation and/or breaking of carbon-carbon bonds.

Hydrogenation and dehydrogenation of olefins are excellent examples of reactions that only involve formation and/or breaking of carbon-hydrogen bonds. As mentioned earlier (see Structure Insensitive Reactions) these type of reactions do not show any structure sensitivity. It was proposed that a carbonaceous layer covers most of the surface during reaction conditions, masking the surface structure of the metal. The reaction can still occur on top of these layers, since they are able to transfer hydrogen from the metal surface to the reacting species.

Table 4 shows that almost all the reactions involving formation and/or breaking of a carbon-carbon bonds show structure sensitivity. In particular, for reactions where there is an increase in activity on the supported catalyst with a decrease in catalyst particle size, there is also a strong increase in activity when single crystal faces that contain kinks and steps are used. This parallel behavior is reasonable, since the concentration of kinks and edges on the surface of the supported catalyst particles is expected to increase as the particle size decreases. The structure sensitivity exhibited by platinum catalyst for hydrocarbon reactions is, then, due to the higher efficiency of kinks and steps for the breaking and/or formation of carbon-carbon bonds. Studies at low pressure ($\sim 10^{-7}$ torr) (66) indicate that kinks are the most active sites on the surface. The reason for the deactivation of catalysts for reactions that involve carbon-carbon bonds is the build-up of a disordered carbonaceous deposit. Dissociative hydrogen chemisorption

seems to inhibit this irreversible deactivation (68). As mentioned earlier, kinks and steps have a higher sticking coefficient for hydrogen dissociative chemisorption than terrace sites. Therefore, it is reasonable that these sites will have a different rate of deactivation that depends on the hydrogen pressure.

An interesting result shown in Table 4 is that the isomerization of alkanes presents structure sensitivity or insensitivity depending on the number of carbon atoms in the molecule. Isomerization alkanes smaller than neopentane show structure sensitivity for on both single-crystal (35,57) and supported catalysts (58); while the isomerization of alkanes larger than n-hexane does not show any structure sensitivity (35,57,59-61). These results are explained by the presence of two possible mechanisms for the isomerization reaction (see figure 11). One mechanism involves an intramolecular shift of the carbon-carbon bond (bond shift mechanism); while the other involves the formation of a cyclic intermediate (a five or six member ring) that further decomposes into several possible isomers (cyclic mechanism). Evidence in support of these two mechanisms, and evaluation of their relative importance has been given by Gault and coworkers (67,68) using ^{13}C -labelled molecules.

Alkanes that have less than five carbon atoms cannot form a cyclic intermediate. Therefore, isomerization can only occur via a bond-shift mechanism. Table 4 shows that the reaction is structure sensitive, since kinks and steps are more effective in breaking the carbon-carbon bonds. The situation is slightly more complicated in the case of hydrocarbons with carbon chains of six or more atoms. In this case both the bond

shift and the cyclic mechanisms are feasible. While the bond shift mechanism is favored by the presence of kinks and steps, the cyclic mechanism is favored by the presence of terraces or flat surfaces that are large enough to accommodate this cyclic intermediate (35,69). If both mechanisms are possible, then we expect minimal structure sensitivity, as in the case of large alkanes, but if only one is feasible, then the reaction is structure sensitive as in the case of light alkanes.

At present, alloy catalysts are used more frequently in the chemical and petroleum technologies than single-metal catalysts, due to their superior properties. These properties include a higher product selectivity and a greater resistance to poisoning. Despite these characteristics, the surface structure sensitivity of these alloys has rarely been investigated. Such a study, for the conversion of n-hexane in the presence of hydrogen over Au-Pt(100) and Au-Pt(111) alloy systems has been performed in our laboratory (70,72). This reaction was chosen because it is a good model for all the important reactions in catalytic reforming; i.e. isomerization, cyclization, aromatization and hydrogenolysis. The results obtained are shown in Figure 12. While the conversion drops linearly with coverage during the addition of inactive gold to the active Pt(100) surface, as expected, assuming additivity of rates at platinum and gold sites, the conversion is increased markedly by the addition of gold to the Pt(111) surface. Notice that the Pt(111)-Au alloy system, at certain compositions, is even more active than the clean Pt(111) surface. The initial turnover frequencies for the four possible reactions are plotted as a function of fractional gold coverage on the

surface in Figure 13. This shows that the enhanced activity of the Au-Pt(111) alloy is due to the twofold increase in the isomerization reaction and an exponential decay in the hydrogenolysis and aromatization reaction rates. The large increase in isomerization reaction rate can only be explained by assuming that alloying creates new sites. Because the new site was observed on the (111) surface and not the (100) surface, it must be a threefold site, since on-top and twofold sites are available on both surfaces. Also the isomerization rate on the (111) alloy surfaces decreased rapidly at surface atom fractions of gold greater than 0.75, indicating that at least one platinum atom must be present at the threefold site.

From the previous discussion on structure sensitive reactions, it is clear that by adjusting the conditions used to prepare the catalyst it is possible to obtain a desired selectivity toward a certain reaction. For example, using a catalyst for hydrocarbon reactions of appropriate particle size or an alloy of appropriate composition, one can reduce the extent of the hydrogenolysis, a highly undesirable reaction and favor isomerization, the desired reaction in the reforming process, which is of great economical interest in the petrochemical industry. Procedures that favor the synthesis of catalyst particles having a desired crystal face can increase reaction rates by two or three orders of magnitude as it is shown for the synthesis of ammonia over rhenium and iron.

SUMMARY

Using different single crystal surfaces as model catalysts, the

structure sensitivity of several reactions has been explained. The higher activity of a particular surface site toward a certain reaction is the reason for the structure sensitivity of many reactions. Adsorbed species, however, can mask the surface structure of the catalyst and be responsible for the structure insensitivity observed in some cases. Also, the structure sensitivity of a reaction can depend on reaction conditions if the rate determining step changes due to variations in the amount and/or type of species on the surface.

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Table 1^c

Comparison of Initial Specific Rate Data for the
Cyclopropane Hydrogenolysis on Platinum Catalysts

Data Source	Type of Catalyst	Calcd spec reaction rate @ Pcp°=135 Torr and T=75°C		Comments
		moles C ₂ H ₆ min-cm ² Pt	molecules C ₃ H ₄ min. Pt site	
Kahn et al. (11)	Pt(s)-[6(111)x(100)]	1.95×10^{-6}	812 ^a	E*=12.2 Kcal/mole
Hegedus (12,13)	0.04 Wt% Pt on η -Al ₂ O ₃	7.7×10^{-7} based on 100% Pt dispersion	410 ^b	
Boudart et al (3)	0.3% and 2.0% Pt on η -Al ₂ O ₃	8.9×10^{-7}	480	$\eta_{cp}=0.2$, E*=8.5 Kcal/mole
and Dougharty (14)	0.3% and 0.6% Pt on γ -Al ₂ O ₃	2.5×10^{-6}	1340	$\eta_{cp}=0.6$, E*=8.5 Kcal/mole

a Value based upon 87% (111) orientation and 13% polycrystalline orientation.

b Based upon av Pt site density of 1.12×10^{13} atoms/cm². This value would be nearly equal to average of above values if dispersion was approximately 50%.

c Taken from reference (11).

Table 2^a

Turnover Numbers for Methane Production over Several
Rhodium Catalysts

	CH ₄ TN (molecule/site/sec)	E _a (Kcal/mole)	Ref.
Rh foil, 1-6 atm. clean	0.1	24 ± 2	(18,19)
Rh/Al ₂ O ₃ , 1 atm.	0.034	24 ± 2	(20)
Rh/SiO ₂ , 7 atm.	0.030	24 ± 2	(21)
Dried Rh ₂ O ₃ 5H ₂ O, 6 atm.	0.001	26 ± 2	(17)

a Taken from reference (17).

Table 3^c

Comparison of Ethylene Hydrogenation Kinetic Parameters
for Different Platinum Catalysts

Catalyst	Log Rate ^a	a ^b	b ^b	E _a (Kcal/mole)	Ref.
Platinized foil	1.9	-0.8	1.3	10	23
Platinum evaporate film	2.7	0	1.0	10.7	24
1% Pt/Al ₂ O ₃	—	-0.5	1.2	9.9	25
Platinum wire	0.6	0.5	1.2	10	26
3% Pt/SiO ₂	1.0	—	—	10.5	27
0.05% Pt/SiO ₂	1.0	0	—	9.1	28
Pt(111)	1.4	-0.6	1.3	10.8	22

a Rate in molec/Pt atom.sec, corrected for the following conditions:
T=323 K, P_{C₂H₄}=20 torr, P_{H₂}=100 torr.

b Orders in ethylene (a) and hydrogen (b) partial pressures.

c Taken from reference (22).

Table 4

Dependence of Several Hydrocarbon Reactions on the Surface
Structure of Supported and Single-Crystal Pt Catalysts

Structure Sensitivity

	Single Crystal Catalyst	Supported Catalyst
C-H bond formation and/or breaking		
Hydrogenation of olefins + H ₂ →	very little effect (33)	structure insensitive (16)
Dehydrogenation of cyclohexane → + 3H ₂	very little effect (34)	structure insensitive (16)
C-C bond formation and/or breaking		
Isomerization of light alkanes (≤C ₄) →	strongly structure sensitive rate enhanced by presence of (100) sites. Favored by the presence of kinks and steps (35,57)	structure sensitive activity increases with decrease in particle size (58)
Isomerization of large alkanes (≥C ₆) → or	structure insensitive (35,57)	structure insensitive (59-61)
Hydrogenolysis + H ₂ → +	strongly enhanced by the presence of kinks smaller effect in the presence of steps (62)	Extremely structure sensitive - fivefold activity decrease with increase in particle size (15-60 Å) (1)
Dehydrocyclization of n-heptane to toluene → + 4H ₂	favored by presence of steps in (100) orientation - in the presence of kinks, formation of benzene (not toluene) is favored (63)	structure sensitive activity increases with decrease in particle size in particle size (64,65)

Figure Captions

- Figure 1 Schematic representation of the experimental apparatus to carry out catalytic reaction-rate studies on single crystal surfaces of low surface area at low and high pressure in the range of 10^{-7} to 10^4 torr.
- Figure 2 Arrhenius plot for cyclohexene hydrogenation over Pt(223) [15] and Pt/SiO₂ [16].
- Figure 3 Isosteric heat of adsorption for CO on Pd(111) crystal face as a function of coverage.
- Figure 4 Atomic surface structure for ethylidene adsorbed over Pt(111)
- Figure 5 Comparison of hydrogenation and exchange rates over Pt and Rh(111) single-crystal surfaces at near room temperature.
- Figure 6 Schematic representation of the mechanism for ethylene hydrogenation over Pt and Rh(111) single-crystal surfaces.
- Figure 7 Scheme of the molecular beam-surface scattering experiment.
- Figure 8 Production of HD as function of angle of incidence, σ , of the molecular beam, normalized to the incident D₂/H₂ intensity. Curve (a) Pt (332) with step edges perpendicular to the incident beam. Curve (b) Pt(110) and curve (c) Pt(111). Representation of the surfaces are given beside each curve.
- Figure 9 Structure sensitivity in the ammonia synthesis over (a) Fe and (b) Re single crystal faces. Representation of the surfaces are given above each bar.
- Figure 10 Total amount of ammonia produced as a function of time for Re(0001) surface after argon sputtering and temperature annealing.
- Figure 11 Bond shift and cyclic mechanisms for isomerization of hydrocarbons.
- Figure 12 Total conversion after two-hour reaction for the Au-Pt(111) and Au-Pt(100) alloy surfaces as a function of surface atom fraction of gold.
- Figure 13 A plot of the initial turnover frequencies per surface atom (platinum and gold) versus the surface atom fraction of gold.

Figure 1

XBL 756-3160

XBL 857-3125

Figure 2

XBL 7911-12823

Figure 3

Pt (III) + ethynidyne

XBL794-6167

Figure 4

PROPOSED MECHANISM FOR ETHYLENE HYDROGENATION

IBL 846-2494

Figure 5

Comparison of Hydrogenation Rates
over Pt(III) and Rh(III) Single-Crystal Surfaces

XBL 846-2487

Figure 6

Figure 7

(b)

XBL 812-8100

Figure 8

Fe single-crystal catalyst

XBL 857-3122

Figure 9a

Re single-crystal catalyst

Figure 9b

XBL 845-1897

Figure 10

BOND SHIFT: CYCLIC:

XBL 857-3123

Figure 11

$\text{W} + \text{H}_2$ 570K
 $\text{H}_2/\text{HC} = 10$ $P_{\text{TOT}} = 220 \text{ TORR}$

XBL 854-2031

Figure 12

$\text{W} + \text{H}_2$ 570K
 $\text{H}_2/\text{HC} = 10$ $P_{\text{TOT}} = 220 \text{ TORR}$

XBL 854-2028

Figure 13

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