# Synergistic effect in the dehydrogenation of cyclohexene on C/W(111) surfaces modified by submonolayer coverage Pt

Ning Liu and Jingguang G. Chen *
*Center for Catalytic Science and Technology (CCST), Department of Materials Science and Engineering,*
*University of Delaware, Newark, DE 19716, USA*
E-mail: jgchen@udel.edu

Received 8 June 2001; accepted 7 August 2001

The dehydrogenation and decomposition of cyclohexene on the Pt-modified C/W(111) surfaces have been studied by temperature-programmed desorption (TPD), Auger electron spectroscopy (AES) and high-resolution electron energy loss spectroscopy (HREELS). The objective of the current study is to investigate how the surface reactivity of tungsten carbide is modified by the presence of submonolayer Pt. Similar to that observed on Pt(111), Pt(100) and C/W(111) surfaces, the characteristic reaction pathway on Pt/C/W(111) is the selective dehydrogenation of cyclohexene to benzene. At a Pt coverage of 0.52 monolayer, the selectivity to the gas-phase benzene product is 86 ± 7%, which is slightly higher than that on Pt(111) (75%) and on C/W(111) (67 ± 7%). More importantly, the desorption of benzene on Pt/C/W(111) is a reaction-limited process that occurs at 290 K, which is much lower than the benzene desorption temperature of ∼400 K from Pt(111).

**KEY WORDS:** cyclohexene; benzene; W(111); C/W(111); Pt; Pt/C/W(111)

## 1. Introduction

It is well known that carbides of early transition metals (groups IV–VI) often have catalytic advantages over their parent metals in activity, selectivity and resistance to poisoning [1,2]. Their catalytic activities are often similar to those of the more expensive Pt-group (Pt, Pd, Ir, Rh, Ru) metals, especially in reactions involving C–H bond transformation, such as dehydrogenation and hydrogenation reactions [1,2]. In previous studies, our group has demonstrated that the carbide-modified V(110), Mo(110) and W(111) surfaces possess Pt-like properties in the transformation reactions of hydrocarbon molecules [3–11].

The introduction of low concentrations of Pt-group metals onto a carbide support offers the possibility to reduce the loading of Pt-group metals by taking advantage of the Pt-like properties of the carbide support [12]. In the current paper, we compare the reactivities of Pt-modified C/W(111) with those of unmodified C/W(111) and of bulk Pt. Our primary interest in studying the reactivity of Pt-modified C/W(111) surfaces is to determine whether there is a synergistic effect by depositing submonolayer coverages of Pt onto the tungsten carbide surface.

The selective dehydrogenation of cyclohexene to produce benzene is a characteristic reaction on Pt-group metal surfaces. The reaction of cyclohexene on Pt(111) has been studied by several research groups using a variety of surface analytical techniques [13–17]. For example, previous results on Pt(111) revealed that cyclohexene underwent selective dehydrogenation to form benzene, with the selectivity to gas-phase benzene being approximately 75% [8,15]. In our previous study, we found that the selectivity to benzene formation was ∼0% on clean W(111) and ∼67% on C/W(111) [10]. In the current study, the decomposition and dehydrogenation of cyclohexene were used as probe reactions to directly compare the surface reactivities of Pt-modified C/W(111) to those of C/W(111), Pt(111) and Pt(100).

## 2. Experimental

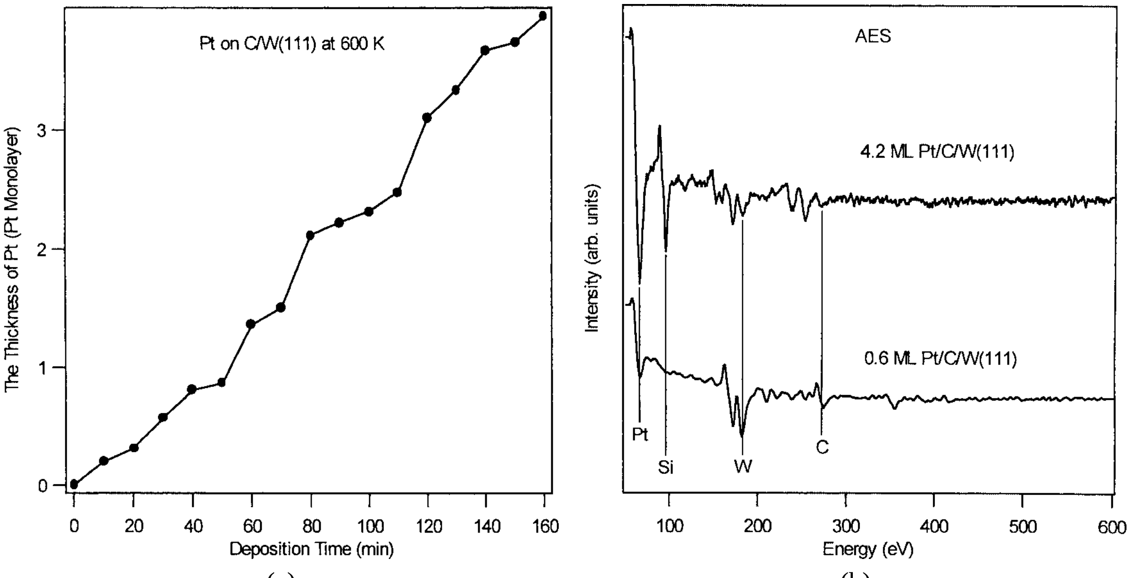
The experiments were carried out in a multi-level UHV chamber, which was equipped with Auger electron spectroscopy (AES), temperature-programmed desorption (TPD), low-energy electron diffraction (LEED) and high-resolution electron energy loss spectroscopy (HREELS). A detailed description of this UHV system and the preparation procedures for the C/W(111) surface has been published elsewhere [10]. The TPD data were collected using a Teknivent data acquisition system, which enabled us to collect up to 12 masses simultaneously. A linear heating rate of 3 $\mathrm{K\,s^{-1}}$ was used for all experiments. The beam energy in the HREELS measurements was approximately 6 eV with a typical resolution between 47 and 55 $\mathrm{cm^{-1}}$.

Cyclohexene (99%) was purchased from Aldrich Chemical Company and was purified by successive freeze–pump–thaw cycles. Oxygen (99.997%) was obtained from Matheson and was used without further purification. The purity of the chemicals was verified *in situ* by mass spectrometry. All chemicals were introduced into the vacuum chamber *via* leak valves and the gas pressures were measured by uncorrected ion gauges.

---

* To whom correspondence should be addressed.

1011-372X/01/1100-0035$19.50/0



(a) (b)

Figure 1. (a) The thickness of Pt *vs.* deposition time; (b) AES spectra of 0.6 and 4.2 ML Pt/C/W(111).

Pt wire (0.127 mm in diameter, 99.9% purity) was purchased from Alfa Aesar. The Pt metal source was constructed by tightly wrapping Pt wire onto a W wire (0.5 mm in diameter) that served as a heating filament. This filament was connected to a vacuum feedthrough and housed in a stainless-steel shroud with an aperture of 15 mm diameter. To deposit Pt onto the C/W(111) surface, the Pt/W filament was resistively heated to the Pt evaporation temperature, with the metal source positioned at 10 mm away from the crystal surface. The crystal temperature was held at 600 K during Pt deposition to prevent the adsorption of CO and $H_2$ from the residue gases in the UHV chamber. A typical deposition rate was about 1 monolayer (ML) Pt per 50 min, as shown in figure 1(a). The coverage of Pt, $D$ (in the unit of Pt monolayer), was estimated by

$$D = \frac{\lambda \ln(I_0/I)}{d}, \tag{1}$$

where $\lambda$ (Å) is 4.82 Å, the attenuation length of the W Auger electrons with an energy of 182 eV [21]; $I_0$ is the original intensity of the W (182 eV) AES transition from C/W(111); $I$ is the intensity of the W (182 eV) transition from Pt-modified C/W(111), and $d$ is 2.76 Å, the diameter of a Pt atom. It is important to point out that equation (1) is valid only for layer-by-layer growth. This equation is used in the current study to obtain an estimated coverage of Pt. In figure 1(b), the AES spectra of 0.6 ML Pt/C/W(111) and a multilayer Pt/C/W(111) are shown. In the top spectrum of the 0.6 ML Pt/C/W(111) surface, there was no detectable amount of Si impurity. At multilayer Pt coverages, however, the observation of the Auger transition at 91 eV indicated the presence Si impurity [20], which was the only impurity on the surface. The source of Si was most likely from the heating of the evaporation source assembly during deposition. Despite our efforts in designing Pt sources with different evaporation source configurations and in purchasing Pt wires from different vendors, we were unable to obtain a Pt multilayer that was completely free of Si. We therefore limited our investigation of the Pt-modified C/W(111) surfaces to Pt coverages less than 0.6 ML.

The preparation of the C/W(111) surfaces was obtained by reacting the W(111) surface with cyclohexene, as described in detail previously [10]. The C/W(111) surface is characterized by a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern. Upon the deposition of submonolayer Pt the surface retains the $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern. We did not observe the $(2\times1)$-reconstructed LEED pattern that was reported upon the deposition of near-monolayer coverage Pt on the clean W(111) surface [21–23].

## 3. Results and interpretation

### 3.1. TPD results

Figure 2 shows the TPD spectra of cyclohexene (82 amu), benzene (78 amu) and hydrogen (2 amu) following the dehydrogenation of 2.2 L cyclohexene on C/W(111) and two Pt-modified C/W(111) surfaces, with an estimated Pt coverage of 0.35 and 0.52 ML, respectively. From our previous studies, an exposure of 2.2 L corresponds to a surface coverage of 0.088 cyclohexene per W atom [10]. Cyclohexene, benzene and hydrogen are the only gas-phase products and carbon is the only residual surface species on Pt/C/W(111) after TPD measurements. At present we are unable to differentiate whether carbon is in the atomic, graphitic or cluster form based on the AES measurements. For comparison, figure 2(a) also shows a TPD spectrum obtained after exposing 10 L cyclohexene to the C/W(111) surface, which corresponds to the onset of multilayer cyclohexene desorption. The peak areas of cyclohexene, after 2.2 L exposures of cyclohexene to C/W(111) and two Pt-modified C/W(111) surfaces, are approximately less than 3% of the peak area of the 10 L TPD spectrum. This observation suggests that

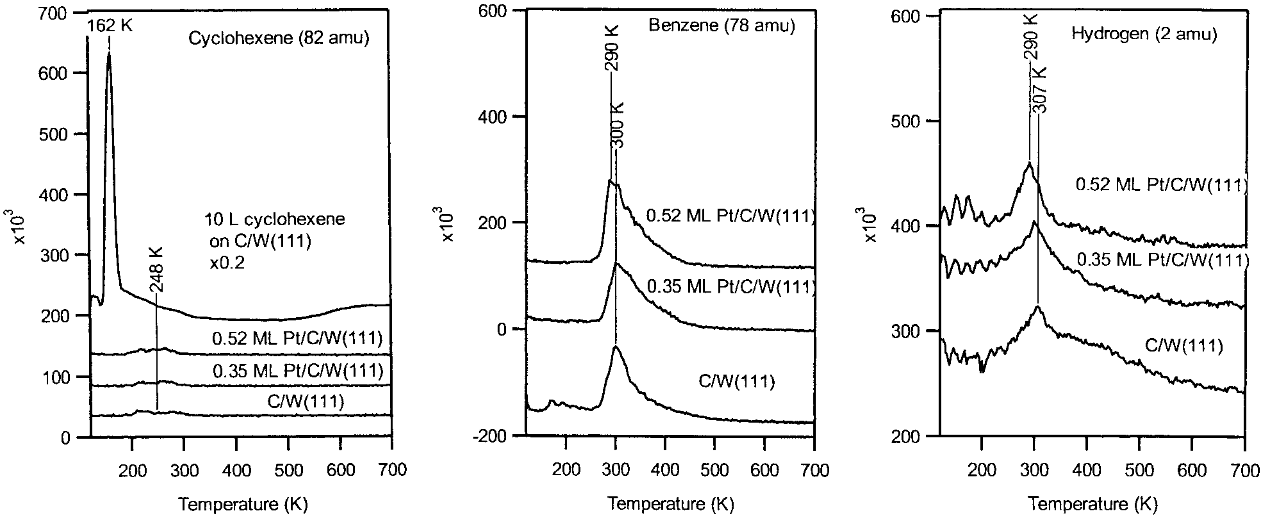


Figure 2. TPD spectra of cyclohexene (82 amu), benzene (78 amu) and hydrogen (2 amu) after exposing C/W(111), 0.35 ML Pt/C/W(111) and 0.52 ML Pt/C/W(111) to 2.2 L c-$C_6H_{10}$ at 90 K.

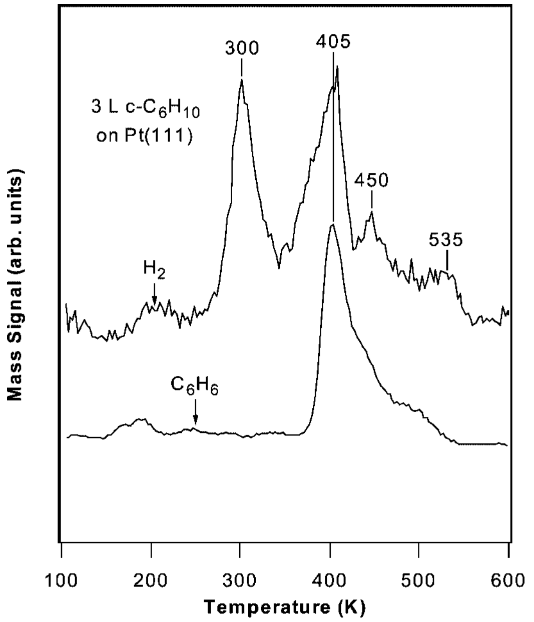


Figure 3. TPD spectra of benzene (78 amu) and hydrogen (2 amu) after exposing Pt(111) to 3 L $C_6H_{10}$ at 90 K.

the amount of molecularly desorbed cyclohexene is nearly negligible after the exposure of 2.2 L cyclohexene, and that almost all chemisorbed cyclohexene undergoes dissociation. On these three surfaces, the desorption features of the benzene product in figure 2(b) are observed respectively around 300, 300 and 290 K, indicating that dehydrogenation is one of the reaction pathways of cyclohexene molecules on all three surfaces. Figure 2(c) compares the production of hydrogen from the reaction of 2.2 L cyclohexene on the three surfaces. Relatively broad hydrogen desorption features are observed at 307, 307 and 290 K on the three surfaces, respectively.

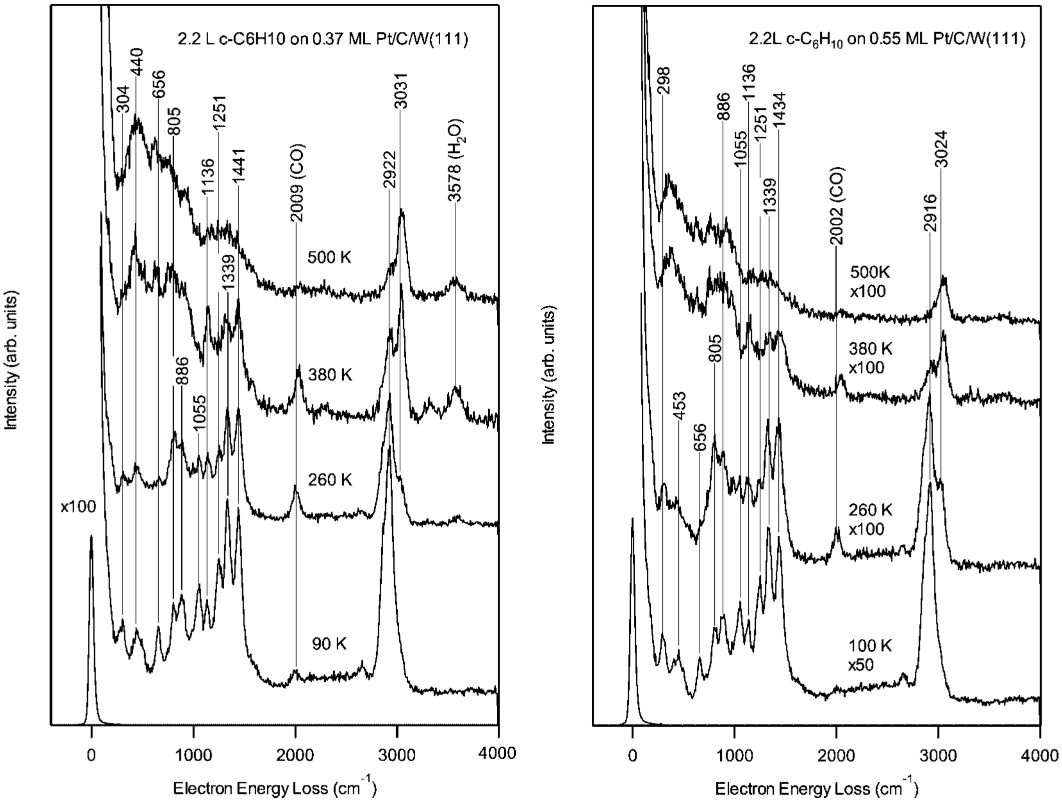
For comparison, figure 3 shows TPD spectra of benzene (78 amu) and hydrogen (2 amu) after exposing Pt(111) to 3 L cyclohexene at 90 K. As well documented in [13–17] and also described in our previous study, on Pt(111) cyclohexene undergoes both dehydrogenation and complete decomposition, and the desorption of the benzene product is a desorption-limited process. There are several hydrogen features at approximately 300, 405, 450 and 535 K; the origin of these peaks has been discussed in detail by Rodriguez and Campbell [14]. The most important observation in figure 3 is that the desorption temperature of benzene from Pt(111) is at 405 K, which is about 100 K higher than that observed on C/W(111) and Pt-modified C/W(111) surfaces.

### 3.2. *Product yields of benzene on Pt-modified C/W(111)*

On the C/W(111) and Pt/C/W(111) surfaces, benzene and hydrogen are the only gas-phase products (figure 2) because of the negligible amount of gas-phase cyclohexene, and atomic carbon is the only surface species after the TPD measurements. Therefore, the reactions of cyclohexene on these three surfaces can be described by two pathways (equations (2) and (3)). The symbols $a$ and $b$ represent the amounts of c-$C_6H_{10}$ (cyclohexene molecule per W atom) involved in each of the reaction pathways on the unmodified C/W(111) surface. The symbols $c$ and $d$ represent the amounts of c-$C_6H_{10}$ involved in each of the reaction pathways on the 0.35 ML Pt/C/W(111) surface, and the symbols $e$ and $f$ represent the amounts of c-$C_6H_{10}$ involved in each of the reaction pathways on the 0.52 ML Pt/C/W(111) surface:

$$\begin{array}{ccccc} \text{c-}C_6H_{10} & \rightarrow & C_6H_6(g) & + & 2H_2(g) \\ a & & a & & 2a \\ c & & c & & 2c \\ e & & e & & 2e \end{array} \tag{2}$$

$$\begin{array}{ccccc} \text{c-}C_6H_{10} & \rightarrow & 6C(a) & + & 5H_2(g) \\ b & & 6b & & 5b \\ d & & 6d & & 5d \\ f & & 6f & & 5f \end{array} \tag{3}$$



(a) (b)

Figure 4. (a) HREEL spectra monitoring thermal properties of 2.2 L c-$C_6H_{10}$ adsorbed on 0.37 ML Pt/C/W(111); (b) HREEL spectra monitoring thermal properties of 2.2 L c-$C_6H_{10}$ adsorbed on 0.55 ML Pt/C/W(111).

Based on our previous study [10], the values of $a$ and $b$ were determined to be ~0.059 and ~0.029 cyclohexene molecule per W atom, respectively. Therefore, the TPD area of benzene from 2.2 L cyclohexene on C/W(111) should correspond to the desorption of ~0.059 benzene molecule per W atom. By comparing the TPD areas of benzene from the 0.35 and 0.52 ML Pt/C/W(111) surfaces to that from C/W(111), we obtained the peak area ratio of ~1.06 and ~1.29, respectively. This in turn leads to the following relationships:

$$\frac{c}{a} = 1.06, \tag{4}$$

$$\frac{e}{a} = 1.29. \tag{5}$$

Furthermore, by comparing the $H_2$ TPD areas from the 0.35 ML Pt/C/W(111) and 0.52 ML Pt/C/W(111) surfaces to that from C/W(111), we obtained the peak area ratio of ~0.86 and ~0.82, respectively:

$$\frac{5d + 2c}{5b + 2a} = 0.86, \tag{6}$$

$$\frac{5f + 2e}{5b + 2a} = 0.82. \tag{7}$$

By solving equations (4)–(7), we determine that the values of $c$, $e$, $d$ and $f$ are ~0.063 [0.059 × 1.06], ~0.076 [0.059 × 1.29], ~0.020 and 0.013 cyclohexene molecule per W atom, respectively. On 0.35 ML Pt/C/W(111) the values correspond to a selectivity of ~76% cyclohexene dehydrogenating to form benzene, with the other ~24% cyclohexene undergoing complete decomposition. On 0.52 ML Pt/C/W(111) the values correspond to a selectivity of 86 ± 7% cyclohexene dehydrogenating to form benzene, with the other 14 ± 7% cyclohexene undergoing complete decomposition. The selectivity of benzene on both Pt/C/W(111) surfaces is higher than that observed on unmodified C/W(111) (67 ± 7%) [10]. The error bars were obtained based on three separate TPD/AES measurements on the C/W(111) and 0.52 ML Pt/C/W(111) surfaces.

### 3.3. HREELS results

HREELS measurements have been performed to determine the nature of surface intermediates of cyclohexene on the Pt-modified C/W(111) surfaces. Detailed HREELS studies of cyclohexene on unmodified C/W(111) are reported previously [10]. Figure 4 shows the HREELS results following the thermal behavior of cyclohexene on 0.37 ML Pt-modified C/W(111) (figure 4(a)) and 0.55 ML Pt-modified C/W(111) (figure 4(b)). To monitor the reaction mechanism of cyclohexene on these surfaces, each of the surfaces is flashed to the indicated temperatures and cooled back to 90 K for HREELS measurements. The vibrational assignments are summarized in table 1 for chemisorbed cyclohexene. The different temperatures, 90, 260, 380 and 500 K, were chosen primarily based on the TPD results.

Table 1
Vibrational assignments for cyclohexene on C/W(111), 0.37 and 0.55 ML Pt/C/W(111) at 90 K.

| Mode description | Liquid [19] | c-$C_6H_{10}$ on C/W(111) | c-$C_6H_{10}$ on 0.37 ML Pt/C/W(111) | c-$C_6H_{10}$ on 0.55 ML Pt/C/W(111) |
|---|---|---|---|---|
| Ring deformation | 175 | | | |
| Ring deformation | 280 | | 304 | 298 |
| Ring deformation | 393 | | | |
| Ring deformation | 452 | 460 | 440 | 453 |
| $\nu$(metal–C) | | | | |
| $\nu$(metal–O) | | | | |
| Skeletal distortion | 640, 670 | 656 | 656 | 656 |
| $\delta$(C=C) (out-of-plane) | 720 | 737 | | |
| $\nu$(C–C) | 810 | 819 | 805 | 805 |
| $\nu$(C–C) | 905, 917 | 913 | 886 | 886 |
| $\nu$(C–C) + $\rho(CH_2)$ | 1038 | 1062 | 1055 | 1055 |
| $\omega CH_2$(rock) | 1138 | 1143 | 1136 | 1136 |
| $\omega CH_2$(twist) | 1241, 1264 | 1265 | 1251 | 1251 |
| $\omega CH_2$(wag) | 1321–1350 | 1333 | 1339 | 1339 |
| $\delta(CH_2)$(scissors) | 1438–1456 | 1448 | 1441 | 1434 |
| $\nu$(C=C) | 1653 | | | |
| $\nu$(–C–H) | 2840–2993 | 2922 | 2922 | 2916 |
| $\nu$(=C–H) | 3026, 3065 | | | |

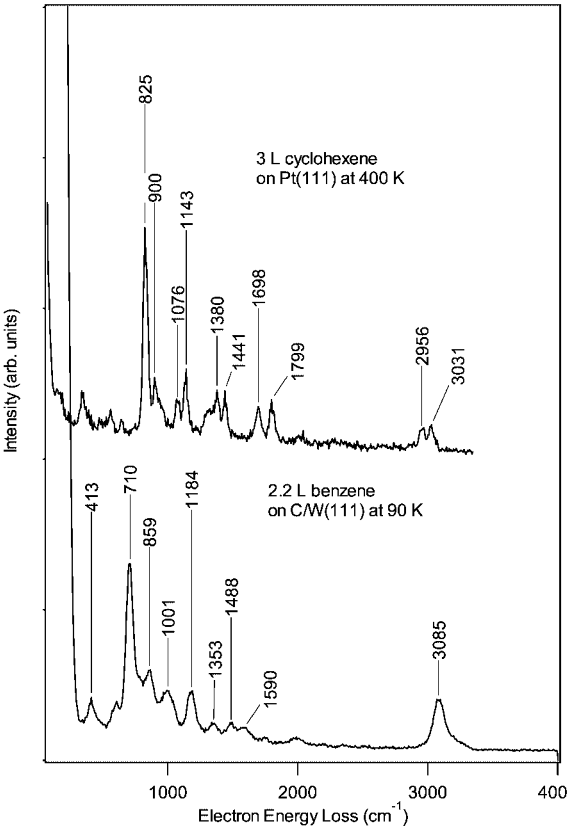


Figure 5. HREEL spectra of 2.2 L $C_6H_6$ on C/W(111) at 90 K and 3 L c-$C_6H_{10}$ on Pt(111) after heating to 400 K.

As compared in figure 4 and table 1, at 90 K there is a strong similarity in the vibrational frequencies on Pt-modified C/W(111) to those observed on C/W(111). Similar to that described earlier for cyclohexene on C/W(111) [10], the absence of the $\nu$(C=C) and $\delta$(C=C) modes suggests that cyclohexene is strongly bonded to the Pt/C/W(111) surfaces, most likely in the di-$\sigma$ configuration. The subsequent thermal decomposition of the di-$\sigma$ bonded cyclohexene on Pt/C/W(111) is essentially the same as that observed on C/W(111) [10]. The most noticeable changes occur between 260 and 380 K. The onset of the $\nu$(C–H) modes at 3024–3031 cm$^{-1}$ indicates the formation of highly dehydrogenated $C_xH_y$ intermediates, which eventually undergo complete decomposition [10]. It is important to point out that the intensity of this $\nu$(C–H) peak is less intense on the 0.55 ML Pt/C/W(111) than on the 0.37 ML Pt/C/W(111) surfaces. This observation is consistent with the TPD observation that the selectivity to complete decomposition is lower on the ~0.5 ML Pt/C/W(111) surfaces.

The most important observation in figure 4 is the absence of the intense $\gamma$(C–H) feature of benzene between 260 and 380 K. For comparison, figure 5 shows the HREEL spectra of benzene on the surfaces of C/W(111) and Pt(111). The bottom HREEL spectrum in figure 5 was recorded after exposing 2.2 L benzene on C/W(111) at 90 K. As described in our previous paper [10], the molecularly adsorbed benzene on the C/W(111) surface is characterized by an intense $\gamma$(C–H) mode at 710 cm$^{-1}$ (out-of-plane C–H deformation). The top HREEL spectrum in figure 5 was recorded after heating the $C_6H_{10}$/Pt(111) surface to 400 K. As described in previous studies [10,13–15], the dominant surface intermediate at this temperature is chemisorbed benzene, which is characterized by a sharp and intense $\gamma$(C–H) mode of benzene at 825 cm$^{-1}$.

The comparison between figures 4 and 5 clearly indicates that benzene is not produced as a surface intermediate on the Pt-modified C/W(111) surfaces. Therefore, the desorption of gas-phase benzene, as detected in the TPD measurements, is a reaction-limited process. This conclusion is similar to that observed in the production of benzene from the unmodified C/W(111) surfaces [10]. However, this is different from that observed in the reaction of cyclohexene over bulk Pt surfaces, such as Pt(111) and Pt(100). For example, the conversion of cyclohexene to chemisorbed benzene starts to occur at 300 K on Pt(111) [10,15], and the desorption of benzene is a desorption-limited process that occurs at ∼400 K. Similarly, in the HREELS studies of cyclohexene on Pt(100) by Lamont *et al.* [24], the formation of the benzene surface intermediate, as indicated by the intense $\gamma$(C–H) mode of benzene at 810 $\text{cm}^{-1}$, is observed at 200 K. The benzene intermediate is stable on the surface at temperatures up to 400 K.

Overall, the Pt-modified C/W(111) surfaces, with submonolayer coverages of Pt, show important similarities to Pt(111) and Pt(100) in that they are all efficient in the conversion of cyclohexene to benzene. However, the difference is that the desorption of benzene is desorption-limited on bulk Pt surfaces while reaction-limited on Pt/C/W(111). The latter desorption mechanism is the same as that on the unmodified C/W(111). The desorption of benzene at lower temperatures would prevent the subsequent thermal decomposition of the benzene intermediate, which is most likely the origin for the higher benzene selectivity from Pt/C/W(111) than from bulk Pt surfaces. Furthermore, the presence of submonolayer coverages of Pt on C/W(111) facilitates the selective conversion of cyclohexene to benzene, which results in an enhanced benzene selectivity over unmodified C/W(111) surfaces. These comparisons clearly demonstrate the synergistic effect of Pt-modified C/W(111) in the selective dehydrogenation of cyclohexene to benzene.

## 4. Conclusion

On Pt-modified C/W(111) surfaces, cyclohexene molecules primarily dehydrogenate to form benzene. For example, on the 0.52 ML Pt/C/W(111) surface, 86 ± 7% cyclohexene undergoes dehydrogenation, while 14 ± 7% cyclohexene completely decomposes to produce atomic carbon and hydrogen. Overall, the selectivity to gas-phase benzene on Pt/C/W(111) is higher than that from unmodified C/W(111) (67 ± 7%), and even slightly higher than that from Pt(111) (∼75%). Furthermore, the desorption of benzene from Pt/C/W(111) is a reaction-limited process, and the desorption temperature is about 100 K lower than that observed on Pt(111). These observations clearly demonstrate a synergistic effect of Pt/C/W(111) surfaces in the selective dehydrogenation of cyclohexene. The results presented here also point out the potential catalytic synergy of using transition metal carbides to support low concentrations of Pt catalysts.

## Acknowledgement

The authors acknowledge the financial support from the Department of Energy, Basic Energy Sciences (DOE/BES Grant No. DE-FG02-00ER15104).

## References

[1] S.T. Oyama, *The Chemistry of Transition Metal Carbides and Nitrides* (Blackie Academic and Professional, Glasgow, 1996).
[2] J.G. Chen, Chem. Rev. 96 (1996) 1477, and references therein.
[3] J.G. Chen, M.D. Weisel, Z.M. Liu and J.M. White, J. Am. Chem. Soc. 115 (1993) 8875.
[4] B. Fruhberger and J.G. Chen, J. Am. Chem. Soc. 118 (1996) 11599.
[5] B. Fruhberger and J.G. Chen, Surf. Sci. 342 (1995) 38.
[6] J. Eng Jr., B.E. Bent, B. Fruhberger and J.G. Chen, J. Phys. Chem. B 101 (1997) 4404.
[7] J. Eng Jr. and J.G. Chen, Surf. Sci. 414 (1998) 374.
[8] J.G. Chen and B. Fruhberger, Surf. Sci. 367 (1996) L102.
[9] J. Eng Jr., B.E. Bent, B. Fruhberger and J.G. Chen, Langmuir 14 (1998) 1301.
[10] N. Liu, S.A. Rykov, H.H. Hwu, M.T. Buelow and J.G. Chen, J. Phys. Chem. B 105 (2001) 3894.
[11] N. Liu, S.A. Rykov and J.G. Chen, Surf. Sci. 487 (2001) 107.
[12] S. Hantzer, M.S. Touvelle and J.G. Chen, US Patent 5 811 624.
[13] D.P. Land, W. Erley and H. Ibach, Surf. Sci. 289 (1993) 237.
[14] J.A. Rodriguez and C.T. Campbell, J. Catal. 115 (1989) 500.
[15] F.C. Henn, A.L. Diaz, M.E. Bussell, M.B. Hugenschmidt, M.E. Domagala and C.T. Campbell, J. Phys. Chem. 96 (1992) 5965, and references therein.
[16] S.M. Davis and G.A. Somorjai, Surf. Sci. 91 (1980) 73.
[17] S.M. Davis and G.A. Somorjai, in: *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, eds. D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1984) p. 4.
[18] NIST Electron Inelastic-Mean-Free-Path-Database, NIST Standard Reference Database 71.
[19] N. Neto, C. Dilauro, E. Castellucci and S. Califano, Spectrochim. Acta 23A (1967) 1763.
[20] K.D. Childs, B.A. Carlson, L.A. LaVanier, J.F. Moulder, D.F. Paul, W.F. Stickle and D.G. Watson, *Handbook of Auger Electron Spectroscopy*, 3 Ed. (Physical Electronics, 1995).
[21] C.Z. Dong, S.M. Shivaprasad, K.-J. Song and T.E. Madey, J. Chem. Phys. 99 (1993) 9172.
[22] T.E. Madey, K.-J. Song, C.-Z Dong and R.A. Demmin, Surf. Sci. 247 (1991) 175.
[23] K. Pelhos, J.B. Hannon, G.L. Kellogg and T.E. Madey, Surf. Sci. 432 (1999) 115.
[24] C.L.A. Lamont, M. Borbach, R. Martin, P. Gardner, T.S. Jones, H. Conrad and A.M. Bradshaw, Surf. Sci. 374 (1997) 215.