

Ethylene on Clusters and Transition Metal Surfaces

Arthur Pismenny

Literature Seminar

March 20, 1997

For many years people have known that rates of catalytic reactions vary substantially as the surface structure of the catalyst changes.¹ However, more recent data show that the mechanism of the reaction also varies substantially with surface structure.² Ethylene decomposition on transition metals is one of the most heavily studied examples.³ The decomposition of ethylene on metal surfaces is quite different than on small metal clusters. The reaction pathway varies much more substantially with crystal face than with metal. This shows that the geometry of the surface can control the reaction pathway. Therefore, there is the opportunity for catalyst optimization.

On a supported metal catalyst, various reaction pathways can be observed depending on pretreatment procedures or reaction conditions. Yet, the reaction follows only one pathway of them on a well-defined surface of the metal under ultrahigh vacuum (UHV) conditions.

The reactions of ethylene on transition metal surfaces have been studied for more than 30 years. The earliest studies included Arthur's and Hansen's⁴ field ion microscopy (FIM) studies of ethylene adsorption on Ir, Ertl's⁵ low energy electron diffraction (LEED) studies of ethylene adsorption on Cu(111), (100), and (110), and Morgan and Somorjai's⁶ LEED studies of ethylene adsorption on Pt(111) and (100)(5x1).

In general, ethylene decomposition on transition metals follows the pathway shown in figure 1.⁷ At low temperatures the ethylene adsorbs molecularly. Upon heating, the ethylene sequentially loses hydrogens to form a series of molecular species. Eventually, at high enough temperatures the ethylene completely dissociates to yield carbon and hydrogen.

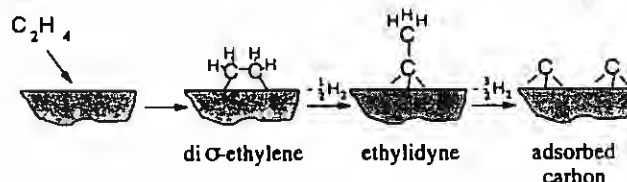


Figure 1. The mechanism of ethylene decomposition on Pt(111) proposed by Kesmodel et al.⁷ and confirmed by Ibach and Lehwald⁸ and Anson et al.⁹

Different intermediates are seen on different surface structures. The available evidence suggests that the reaction pathway is different on different surface structures even though the reactants and the products are the same. Figure 2 summarizes the data for ethylene adsorption at 100K.

Closed Packed Faces						Stepped Surfaces						Kinked Surfaces					
Cr	Mn	Fe	Co	Ni	Cu	Cr	Mn	Fe	Co	Ni	Cu	Cr	Mn	Co	Ni	Cu	
Mo	Tc	Ru	Rh	Pd	Ag	Mo	Tc	Ru	Rh	Pd	Ag	Mo	Tc	Ru	Rh	Pd	Ag
W	Re	Os	Ir	Pt	Au	W	Re	Os	Ir	Pt	Au	W	Re	Os	Ir	Pt	Au

Key					
Ir	Di-σ Ethylene	Au	π-bound ethylene	Mixture	Tc No Data

Figure 2. The molecular state of ethylene on the closed packed, stepped and kinked faces of the transition metals.²

The interaction between ethylene and transition metal surfaces has been generally understood by referring to analogous ligand-transition metal coordination.¹⁰

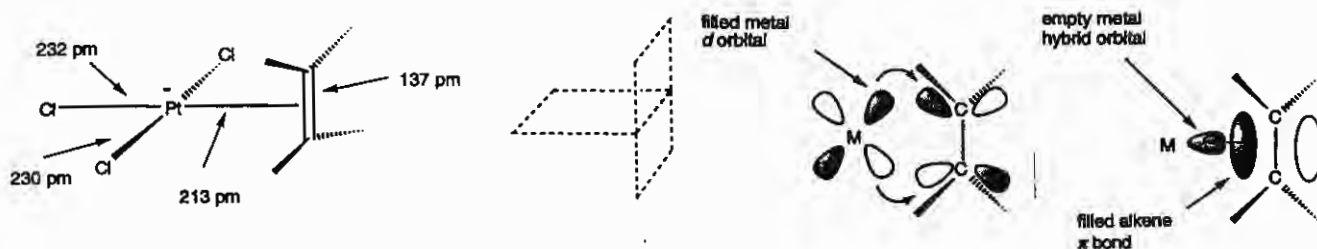


Figure 3. A schematic representation of the structure of Zeise's salt.¹¹

In terms of the DCD model, the di- σ complex can be considered as an extreme of the π -bonded complex in which the back-bonding is carried far enough so that the hybridization of the carbon atoms changes to sp^3 . In the organometallic cluster model, this change results in a metallacyclopropane, such as $Fe(CO)_4(C_2H_4)$, in which the two carbon atoms bond to one carbon atom.¹²

In the DCD model, the electron density of the metal is considered a critical factor that changes the relative importance of the σ bonding and π -back bonding between ethylene and the metal atom. Ittel and Ibers¹³ found that the C=C bond length in the ethylene complexes correlates with the first ionization potential of their central atoms; the lower the ionization potential, the longer the bond.¹³ However, the π -bonded ethylene species observed so far on transition metal surfaces do not correlate with the ionization potential.¹⁴ News¹⁵ suggested that the interstitial charge density would correlate with the bonding of ethylene. Figure 4 shows a plot of the bulk interstitial electron density for a number of metals as calculated by Moruzzi et al¹⁶ and DeBoer¹⁷ as a function of the position of the element in the periodic table.

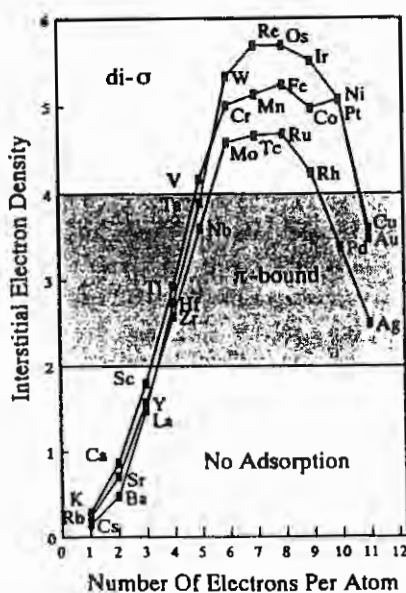


Figure 4. The interstitial electron density of the metals in the d-block of the periodic table.

References

1. Dobereiner, M., *Annales de Chimie* **1823**, *24*, 93-117.
2. (a) Yagasaki, B. and Masel, R. I., "Variation in the Mechanism of Catalytic Reactions with Crystal Face," *J. Catalysis* **1994**, *11*, 165-222. (b) Bao S., Hofmann, Ph., Schindler, K-M., Fritzsche, V., Bradshaw, A. V., Woodruff, D. P., Casado, C., and Asensio, M. C., *J. Phys. Condens. Matter* **1994**, *6*, L93-L105.
3. (a) Bent, B. E., and Somorjai, G. A., *Adv. Colloid and Interface Sci.* **1989**, *29*, 223-245. (b) Sheppard, N. and De La Cruz, C., "Vibrational Spectra of Hydrocarbons Adsorbed on Metals," *Adv. in Catalysis* **1996**, *41*, 1-111. (c) Frederick, B. G., Nyberg, G. L., and Richardson, N. V., *J. Electron Spectrosc. Relat. Phenom.* **1995**, *73*, 149-170. (d) Cooper, E., and Raval, R., *Surf. Sci.* **1995**, *94*, 331-333. (d) Bell, A. T., and Hair, M. L., "Vibrational Spectroscopy of Adsorbed Species," Plenum, New York, **1987**.
4. (a) Arthur, J. R. and Hansen, R. S., *J. Chem. Phys.* **1962**, *36*, 2062. (b) Hughes, M., Bourget, L., and Greenler, R. G., *J. Catal.* **1993**, *139*, 691-700. (c) Trunschke, A., and Knozinger, H., *Catal. Lett.* **1993**, *17*, 295-313.
5. (a) Ertl, G., *Surf. Sci.* **1967**, *7*, 309-317. (b) Fritzsche, V., and Woodruff, D. P., *Phys. Rev.* **1992**, B46-B52.
6. Morgan, A. E. and Somorjai, G. A., *Surf. Sci.* **1968**, *12*, 405-423.
7. (a) Kesmodel, L. L., Dubois, L. H., and Somorjai, G. A., *Chem. Phys. Lett.* **1978**, *56*, 267-303. (b) Klug, C. A., Slitcher, C. P., and Siñfelt, J. H., *Israel Chem* **1992**, *32*, 185-194.
8. (a) Ibach, H. and Lehwald, S., *J. Vac. Sci. Technol.* **1978**, *15*, 407-421. (b) Ibach, H., *J. Electron Spectrosc. Relat. Phenom.* **1993**, *64/65*, 819-834.
9. (a) Anson, C. E. and Bandy, B. J., *J. Elec. Spec. Relat. Phenom.* **1983**, *29*, 315-327. (b) De La Cruz, C. and Sheppard, N., *Spectrochim. Acta.* **1994**, *271*, 50A.
10. Albert, M. R., and Yates, J. T., "The Surface Scientist's Guide to Organometallic Chemistry," American Chemistry Society, Washington, DC, **1987**.
11. Winter, M. J., "d-Block Chemistry," Oxford, **1994**, 12-15.
12. (a) Collman, J. P., Hegedus, L. S., Norton, J. R., and Finke, R. G., "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley, CA, **1987**. (b) Chatt, J., and Duncanson, L. A., *J. Chem. Soc.* **1953**, *1953*, 2939. (c) Dewar, J. S., *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. (d) Gellman, A. J. and Dai, Q., *J. Am. Chem. Soc.* **1993**, *115*, 714-729.
13. Ittel, S. D., and Ibers, J. A., *Adv. Organomet. Chem.* **1976**, *14*, 33-49.
14. "CRC Handbook of Chemistry and Physics," 69th Ed., CRC Press, Boca Raton, FL, **1988**.

15. (a) News, D. M., *Phys. Rev.* **1969**, *178*, 1123-1189. (b) Hatzikos, G. H., Masel, R. I., in "Catalysis 1987," Ed. J. W. Ward, Elsevier, Amsterdam, 1988, 883-884. (c) Hatzikos, G. H., Ph.D. Thesis, University of Illinois, Urbana, 1987.
16. Morruzi, V. L., and Tanaki, J. F., "Calculated Electronic Properties of Metals," Pergamon Press, 1978.
17. DeBoer, F. R., and Boom, R., "Cohesion in Metals," North Holland, NY, 1988.