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Annual Report
Selective Bond Scission During
Oxygenate Decomposition on Metals

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The object of our project is to examine selective bond scission during the reactions of oxygenates on single crystal surfaces. We have continued our studies of selective bond scission in methanol, done some work on selective bond scission during methanol oxidation on platinum, and examined selective bond scission during ethanol decomposition on platinum.

A Selective C-O Bond Scission During Methanol Decomposition on Platinum

In our last year's efforts we examined methanol decomposition on Pt(110), and found that the (1x1) reconstruction of that surface was particularly active for C-O bond scission. On (1x1)Pt(110) methanol decomposes to yield mainly water, methane hydrogen and hydrocarbons while on (2x1)Pt(110) and Pt(111) the methanol decomposes to yield CO and hydrogen. During the last year we have begun to examine what is special about the (1x1)Pt(110) surface which leads to the unusual reactivity.

Calculations of the structure and electronic properties of the (1x1)Pt(110) surface have indicated that this surface has several unique properties.

- 1) **Geometry:** The geometry of the (1x1)Pt(110) surface is rather unique, in that in this particular reconstruction, the geometry is such that if one puts a methanol in what should be its' most favorable position the C-O bond stretches. This bond extension could yield unique properties.
- 2) **Electronic Structure:** Another different aspect of the (1x1)Pt(110) surface is that it has an unusual electronic structure. If one could magically cut a (1x1)Pt(110) surface, and magically do it in a way that none of the surface atoms relax one would find that the surface contains two types of atoms C_7 atoms at the top of the ridges, and C_{11} atoms at the bottom of the steps. When one actually prepares the surface, the surface atoms relax. The electron density on the C_7 atom goes to $C_{8.7}$, while the electron density on the C_{11} atom goes to $C_{11.9}$. That can have important implications because the surface becomes so electron rich, that while it can still form strong bonds to carbon and oxygen, the surface does not form strong bonds to hydrogen. The effect is that the dehydrogenation pathway observed during methanol decomposition on Pt(111) and (2x1)Pt(110) should be strongly attenuated on (1x1)Pt(110). That may also partially explain the unusual reactivity of (1x1)Pt(110).

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- 3) The third unusual feature of (1x1)Pt(110) is that the surface atoms are unusually mobile on this surface. (1x1)Pt(110) is a metastable surface. The surface atoms are held in shallow wells. As a result the surface atoms are easy to displace. Recently, Somorjai has suggested reactivity in terms of the mobility of the surface atoms.

At this point it is not clear which of these three factors accounts for the unusual reactivity of (1x1)Pt(100); and it is probably going to be some combination of factors. However, in the next year we will try to find out. The approach will largely be experimental; we will examine methanol decomposition on hex-Pt(511) and hydrogen saturated Pd(110) to try to isolate the three effects described above. We will then measure rates of C-O bond scission. The correlation between rates and properties should tell us about the relative influence of the three factors on the rate of C-O bond scission in methanol.

B Selective Carbon-Carbon Bond Scission During Ethanol Decomposition on Platinum

We have also started to examine ethanol decomposition on platinum to see if we could find any unexpected chemistry there. So far we have examined ethanol decomposition on (2x1)Pt(110) by TPD and we are just finishing up the EELS. The results so far show that the (2x1)Pt(110) surface is able to selectively break the carbon-carbon bond in ethanol at low temperatures. When we adsorb ethanol, methanol desorbs from the surface at about 180 K. When we coadsorb methanol and hydrogen we produce methane at 160 K and methane at 200 K. Other reaction products include acetaldehyde, formaldehyde, carbon monoxide, and methyl ethyl ether. These results show that the (2x1)Pt(110) surface is able to selectively break the carbon-carbon bond in ethanol at low temperatures. This is the first time such chemistry has been observed.

C Selective Oxidation of Methanol to Formaldehyde

The other thing we examined is selective oxidation of methanol to formaldehyde, on (2x1)Pt(110) to try to take advantage of some of the unique properties of the (2x1)Pt(110) surface described in Part A. The experiments included coadsorbing oxygen, methanol, and hydrogen and using TPD to look for interesting reaction products.

The results show that under some conditions the methanol is selectively oxidized to formaldehyde at about 200 K. Some of the formaldehyde desorbs and some of the formaldehyde reacts to form andlymeric species. The polymer decomposes at about 500 K to yield CO, H, and formaldehyde. Overall reaction selectivity to gaseous formaldehyde lower than we had hoped (only 10%). However, this is the first time that significant formaldehyde was detected during methanol decomposition on any platinum surface.

We also, by chance, did some work on a calcium and silicon contaminated Pt(110) sample. There, the selectivity to formaldehyde was much higher (80%), for reasons that we do not really understand. During the next year we propose to try to sort out the effects of these contaminants on the chemistry.

D Summary

In summary then, during the last year we examined reactions of methanol and ethanol on Pt(110) and discovered some unique chemistry. We also did some calculations to try to understand how the surface is unique. Details should be published shortly.

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