0.22, which is responsible for the very low C-H bond scission barrier. Finally, we consider the overlap of carbon s and p orbitals with metal s and p orbitals. At bonding distances (M 4s|C 2p) is somewhat smaller for vanadium and (M 4s|C 2s) is somewhat greater for vanadium. These small differences are barely distinguishable on the graphical scale of Figure 5 and are not significant. The metal p orbitals are far removed in energy from carbon levels and should play an even smaller role determining surface reactivity than the metal s orbitals. For these reasons the difference in reactivity between vanadium, iron, and nickel might be expected to be attributed to d orbital size alone. The extended Hückel method[9] was used in all calculations. The parameters are listed in Table 1.

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Molecular Orbital Studies on the Catalytic Properties of MoO_3 toward Propylene Oxidation

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MoO_3 can catalytically convert propylene into acrolein through the selective oxidation and may be used as a model to understand the catalytic properties of α-bismuth molybdates.[1] To probe the electronic implications of propylene adsorption on MoO_3, atom superposition and electron delocalization-molecular orbital (ASED-MO) calculations are carried out on both naked MoO_3 and the whole surface/adsorbate system.

In the ASED-MO theory[3] the electronic charge density of a molecule is partitioned into free atom parts and an electron delocalization bond formation component. As the atoms come together to form a molecule, the electrostatic forces on the nuclei are integrated to yield a repulsive energy due to rigid-atom densities and an attractive energy due to electron delocalization. The sum is the exact molecular binding energy. The atom superposition energy is easily calculated and the electron delocalization energy, though not directly calculable, is well approximated by one-electron molecular orbital energy obtained by using a hamiltonian which shares some features with the extended Hückel hamiltonian. Theory parameters used in the calculations for Mo and O come from an earlier study[4] of the electronic properties of crystalline MoO_3 by Anderson. For C, the respective 2s and 2p orbital exponents and ionization potentials are 1.658au, 18eV, and 1.618 au, 9.26eV; or H, the 1s parameters are 1.2au and 11.6eV.

In molybdite, MoO_3, the d^0 Mo^{VI} cations are surrounded by six oxygen anions in a distorted octahedral arrangement with varying Mo-O bond lengths from 1.84 to 2.34 Å[5]. Calculations on a MoO_6^{6-} cluster model from the crystal produce the energy level structure in Fig. 1. The MoO bonding

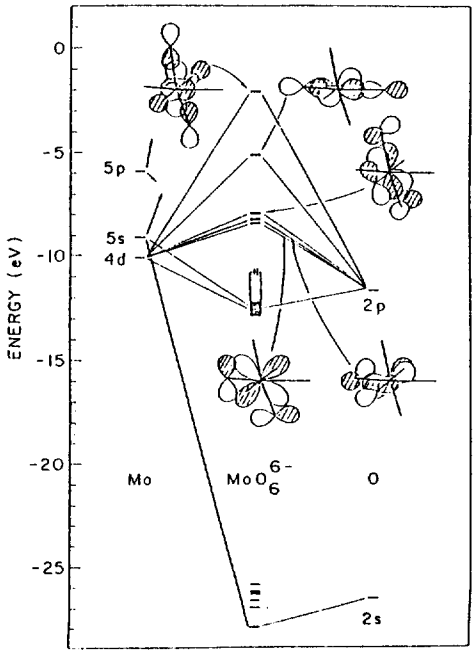

Figure 1. Correlation diagram and molecular orbitals for a MoO_6^{6-} model of MoO_3

levels are oxygen in character. The O 2p band is filled and the Mo 4d band is empty because molybdenum is present as Mo^{VI}. The empty lower slightly split "t" and more widely split upper "e" levels are a result of distortion in the lattice away from perfect octahedral symmetry. Quantum mec-

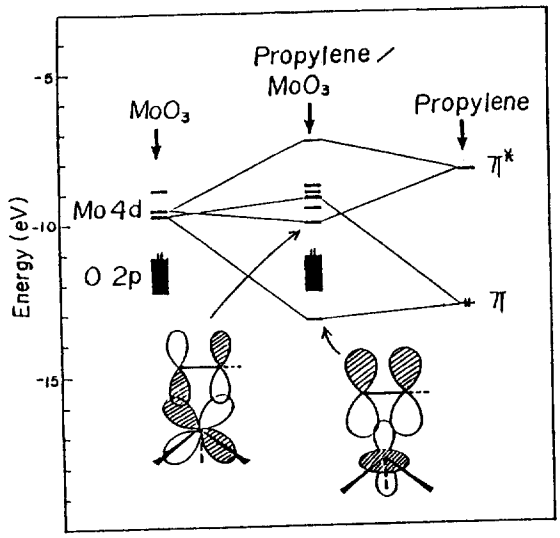

Figure 2. Schematic interaction diagram between the propylene adsorbate and the open surface Mo^{VI} cation of MoO_3.

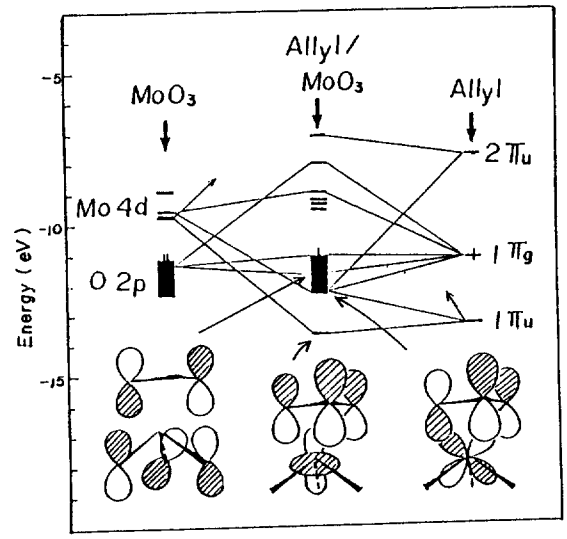

Figure 3. Correlation diagram between the allyl adsorbate and the open surface of MoO_3.

hanical perturbation argument of Salem[6] and Hoffmann[7] help explain why the upper t and e empty levels have large contributions from molybdenum in their corresponding molecular orbitals and why they are antibonding between molybdenum and the corresponding oxygen anions. Similarly, some of the lower levels are stabilized and their corresponding molecular orbitals have large oxygen contributions and are bonding between molybdenum and oxygen. However, it is not necessary to appeal to perturbation theory since Figure 1 is the result of a molecular orbital calculation for the cluster. For this cluster the calculated O 2p to Mo 4d band gap is 2.6 eV compared to an experimental determination of about 3 eV.[8]

The MoO_3 cluster model chosen for the propylene adsorption study has the coordinately unsaturated Mo^{VI} site as a π acceptor. Using this model, we find propylene π-coordinates with a stability of 0.8eV with the olefinic bond 2.1 Å away from the metal center. The C=C bond stretches 0.02Å from the calculated gas-phase value, the C-C bond shrinks 0.01Å and angles within the propylene molecule have little changed upon adsorption. The major bonding interaction is a stabilization of the olefinic π orbital due to donation to an empty d_{z^2} orbital on Mo^{VI} as shown in Figure 2. There is no significant Mo 4d back bonding into the propylene π^* orbital because the d band is empty.

Using the same surface model, we find the allyl radical binds more strongly with an adsorption energy of 1.2eV than propylene to Mo^{VI}. The Mo ion lies beneath a line connecting the terminal carbon atoms and the metal-allyl distance is 2.0Å. Bonding through two C atoms to Mo, the coordinated C=C bond stretches 0.04Å due to the interaction, becoming more single-bond like. The other C=C bond shrinks 0.02Å, becoming more double-bond like. The bonding is readily understood in terms of molecular orbital theory. As indicated in Figure 3, the bonding of the allyl radical to the surface is predominantly a result of stabilizations involving the π orbitals of allyl and Mo d orbitals. When the allyl coordinates, the Mo dπ character is amended some through hybridization but the main stabilizing overlap of the π-allyl complex is due to d π and $1\pi_g$ on the end C. The metal rehybridization allows further stabilization by mixing in $2\pi_u$ as required by the energy denominator in second order perturbation theory, lengthening the left hand C=C bond and shortening the right hand one. An allyl $1\pi_u$ donating into a molybdenum d_{z^2} orbital makes a slight contribution to stabilization. Finally, the bonding of the allyl to an O atom itself coordinated to an Mo atom is a substantial π overlap between $1\pi_g$ and O2p orbitals, as may be seen in Figure 3. This indicates the beginning of C-O bond formation. A study of oxygen insertion into the adsorbed allylic species during acrolein formation over π-bismuth molybdates is under way.[9]

On bismuth molybdates propylene adsorbs with a chemisorption bond of relatively modest strength to a surface Mo atom possessing an available coordination site. This is because there are no low-lying empty levels in Bi^{III} for π-donation bonding. The Bi 6s orbital nearest in energy to π orbitals in both propylene and allyl species are completely filled and have considerable O2p mixing, so that a closed-shell antibonding behavior to the adsorption bond between π and Bi 6s orbitals is expected to be responsible for the weak binding to Bi.[III]

We have found that the strong bonding of an allyl intermediate to a Mo^{VI} after α-hydrogen abstraction does not allow dimerization but sets the stage for oxygen insertion. The allyl intermediate might be readily oxidized by means of the oxygen percolating through the lattice and coordinating weakly to a metal center with possibly some charge gain and superoxide activity.

This molecular orbital study has provided precursory information for the α-bismuth molybdate selective oxidation reaction which yields acrolein from propylene. Now that we have decided on a tractable model and have an understanding of the fundamental orbital interactions and electronic structure, we expect to make good progress in mechanistic studies of the catalytic process with the $Bi_2Mo_3O_{12}$ system.

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Hydroalumination of Alkynes with $LiAlH_4$ in the Presence of Cp_2TiCl_2

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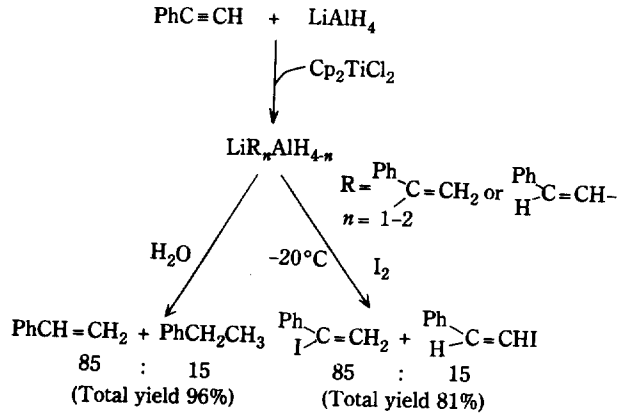
The lithium alkenylhydroaluminates, which are produced by the catalytic hydroalumination of alkynes with the Cp_2TiCl_2-$LiAlH_4$ reagent system, give corresponding iodoalkenes on iodination and alkenes on hydrolysis.

The titanium complex, which is product by the reaction of Cp_2TiCl_2 with $LiAlH_4$, efficiently promotes the catalytic hydroalumination and isomerization of alkenes.[1,2] $NaBH_4$ is also utilized as a reagent for the hydroboration of alkenes and alkynes in the presence of catalytic amounts of Cp_2TiCl_2.[3] Investigations have also proved that organoaluminium compounds act as unique nucleophiles and can be employed as useful reagents in organic synthesis.[4] It was reported that the alcohols through the hydroalumination of alkenes by use of the $TiCl_4$-$LiAlH_4$[5] or Cp_2TiCl_2–$LiAlH_4$[6] are prepared. In this communication, it is briefly discussed that the catalytic hydroalumination of alkynes in the presence of Cp_2TiCl_2, and the efficiency of the reaction was evaluated by converting the resulting alkenylaluminates to the corresponding iodoalkenes on iodination and alkenes on hydrolysis.

The hydroalumination of alkynes was carried out by a similar manner as described previously,[3] using Cp_2TiCl_2 (1.0 mmol), $LiAlH_4$ (20.0 mmol), and phenylethyne (20.0 mmol) in THF (30 ml). The resulting mixture was stirred for 5 h at 25°C under argon. The reaction mixture was added to I_2 (40.0 mmol) in THF (30ml) under argon at -20°C. The mixture was stirred for 1 h at room femperature, and then extracted with diethyl ether. The etheral extract was washed with a 10% $NaHSO_3$ solution, and dried (Na_2SO_4). Evaporation of the etheral extract gave the residue. The GLC analysis of the residue indicated that the reaction mixture contained α-iodostyrene, β-iodostyrene, and phenylethane. Also, the hydroalumination of diphenylethyne was carried out by the method described above. The mixture was treated with H_2O, and extracted with diethyl ether. The organic layer was dried (Na_2SO_4), the solvent was removed by means of a rotary evaporator. The products were obtained by column chro-



Scheme

Table 1. Hydroalumination of Diphenylethyne[a]

Molar ratio			Time	Yield of Products (%)[b]			Recovered
PhC≡CPh	$LiAlH_4$	Cp_2TiCl_2	(h)	H H / C=C / Ph Ph	H Ph / C=C / Ph H	$PhCH_2CH_2Ph$	of PhC≡CPh (%)
20	20	0	5	0	5	0	91
20	20	0	28	14	38	0	45
20[c]	20	0	28	26	54	0	trace
20	20	1	5	54	34	8	trace
20[d]	20	20	24	24	19	36	0

[a]The reaction was carried out at 25°C. [b]The yield was determined by GLC and based on diphenylethyne used. [c]The experiment was refluxed at 65°C. [c,d]Small amounts of unidentified products were detected.