

Figure 2. Plots of the variation of micellar parameters vs $[C_A]$, in ionic surfactant-alkane mixed micelles (data for 0.4 M SDS/hexane). Units as in Tables I-IV.

the difference in the value of k_0 , between SDS and the other micelles, reflects either the different water penetration in the two cases or the fact that pyrene solubilizes at different depths of the interface. In either case SDS provides better water protection for pyrene than the three other micelles.

Interfacial Charge Density. An important parameter in ionic micellar structures is the interfacial charge density (ions/unit of interfacial area), or its inverse A, i.e., the interfacial area per surfactant ion (angstroms squared per ion), which relates to the Coulombic energy of the interface. An estimate of A (which is usually calculated at the surface of the hydrophobic core) for pure micelles can be easily obtained by dividing the area of the sphere, which has a radius equal to the length of the all-trans conformation of the surfactant aliphatic chain, by N_s . Evidently, this approximation is legitimate at surfactant concentrations close to the cmc and at low ionic strength, when micelles have the best chance to adopt a nearly spherical shape. It is evident from the data of Tables I-IV that the value of A in each micelle remains constant, within ca. 2%, as the additive concentration increases. It is worth noticing that, in spite of its crude calculation, the value of A turns

out to be constant and independent of $[C_A]$ in all systems studied here. Recall that, on the contrary, in the case of alcohol solubilizates A increases drastically up to the point of total micellar ionization as the mole fraction of the additive increases.³¹

Another point concerning the magnitude of A in the different micelles used in this study is that the interfacial area per ion turns out to be ca. 60 $Å^2$ /ion in the amphiphiles that involve the quaternary ammonium head and ca. 50 $Å^2$ /ion in the sulfate surfactant. This evidence of a closer arrangement of ionic heads in SDS than in the other micelles agrees with the corresponding variation in the lifetime of the fluorescence of pyrene and in the ratio I_1/I_3 discussed earlier and which indicated better shielding from water when pyrene is solubilized in SDS than in the other micelles. Note, however, that in all four micelles A is quite larger than the cross section of the aliphatic chain. The interfacial area between head groups is probably filled with folded surfactant chains, water molecules, solvated counterions, or solubilized additives.

Figure 2 summarizes the results of this study concerning the effect that alkane solubilizates have on the various parameters of ionic micelles. It shows that N_s and N_A increase continuously, from their values in the pure micelle, upon addition of alkane additive. On the contrary, the rate constant of the intramicellar fluorescence quenching, k_q , decreases upon alkane addition, while the product $k_q S_{int}$ remains constant within experimental accuracy. The unquenched fluorescence decay rate constant, k_0 , is independent of $[C_A]$ (and [Q]). Another parameter shown in Figure 2 is the charge density on the micellar interface which is not altered by the solubilization of alkane additives and remains always equal to its value in the pure surfactant micelle.

Registry No. SDS, 151-21-3; CTAC, 112-02-7; TTAC, 4574-04-3; DDAPS, 14933-08-5; CPyC, 123-03-5; pyrene, 129-00-0; hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; nonane, 111-84-2; decane, 124-18-5.

(31) Lianos, P.; Zana, R. Chem. Phys. Lett. 1980, 72, 171.

Methane Photoactivation on Copper Molybdate. An Experimental and Theoretical Study

Michael D. Ward,[†] James F. Brazdil,*

Standard Oil Research & Development, Cleveland, Ohio 44128

S. P. Mehandru,[‡] and Alfred B. Anderson*

Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106 (Received: April 6, 1987)

It is shown experimentally that the activity of UV-irradiated MoO₃ for the partial oxidation of methane in the presence of O_2 at 100 °C, leading to methanol formation, is markedly enhanced when Cu^{II} is added to the catalyst. The rate of methanol formation is maximum when the concentrations of copper and molybdenum are equal. Visible light activates CuMoO₄ but not MoO_3 . We have made a molecular orbital study of the photoactivity of $CuMoO_4$ toward hydrogen abstraction from methane at O⁻ centers. The activity of CuMoO₄ in the visible region is assigned to O $2p \rightarrow Cu 3d$ excitations; the Cu 3d band levels lie below the Mo 4d band and the orbitals have a large O 2p component. Mechanisms are proposed for increasing the lifetimes of the electron-hole pairs and thereby account for the synergistic effect in CuMoO₄ which shows enhanced photoactivity compared with either CuO, which is photoinactive, or MoO₃. Empty band-gap orbitals serve to stabilize homolytic H^{\bullet} and ${}^{\bullet}CH_{3}$ adsorption on O^{2-} sites relative to MoO_{3} , and filled band-gap orbitals stabilize homolytic adsorption on Mo^{VI} sites. Heterolytic adsorption on Mo^{VI} and O^{2-} sites is stable but not on Cu^{II} and O^{2-} sites. Homolytic adsorption is unstable on Cu^{II} sites.

Introduction

The first step in the selective oxidation of methane is the abstraction of hydrogen. It has been known since the work of

Kazansky and co-workers that O⁻ radical ion sites in early transition-metal oxides, such as TiO₂, V₂O₅, MO₃, and WO₃, actively abstract H* from methane even below room temperature.¹⁻⁴ Active O⁻ centers have been prepared by chemical means,

Present address: E. I. du Pont de Nemours & Co., Experimental Station 328, Wilmington, DE 19804.
 ²On leave from K. M. College, Delhi University, Delhi 110 007, India.

⁽¹⁾ Shvets, V. A.; Vorotyntsev, V. M.; Kazansky, V. B. Kinet. Katal. 1969, 10, 356.



Figure 1. Photoreactor for methane oxidation. SCHEME I

$$M_{0}^{\underline{M}_{0}^{2}} \xrightarrow{h_{\nu}} (M_{0}^{\underline{M}_{0}^{-}})^{*}$$

$$\begin{array}{c} k_{1} & k_{et} \\ k_{2} & M_{0}^{\underline{M}_{0}^{-}} + M^{(n-1)*} \end{array}$$

by reacting $O_2^{1,2}$ and $N_2O^{2,3}$ with the partially reduced oxides, by UV charge-transfer photoexcitation,²⁻⁴ and by γ irradiation.^{2,4} Recently Lunsford and co-workers have carried out extensive studies of methane activation and subsequent oxidation products (ethane, methanol, formaldehyde, and CO₂) catalyzed by MoO₃.^{5,6} In this work the O⁻ sites were created by the N₂O route. Methane activation by Li-doped MgO possessing O- centers has also been reported.7-9

The theoretical aspects of CH bond activation by O⁻ hole centers in MoO₃ were considered recently.^{10,11} The abstraction of H by O²⁻ in the oxide surface has a high-energy barrier due to the closed-shell repulsion between the CH bond electron pair and the oxide lone pair. In the case of the O⁻ site the antibonding counterpart orbital of the closed-shell repulsion is half filled so that the CH bond order is $\frac{3}{4}$ and the OH bond order is $\frac{1}{4}$ in the transition state. As a result the energy barrier is low. This explanation should apply to the activity of O⁻ centers in other oxide surfaces which exhibit reaction with CH bonds in methane and other paraffin species and to the activity of these centers toward other single bonds, such as in C2H4 and H2,3 and NH3 and H2O12 studied by the Kazansky group, as well as α -hydrogen abstraction from propylene over irradiated TiO₂ to yield acrolein and higher oxidation products.13 Other known photoactivated reactions involving O⁻ centers include CO oxidation to CO₂ by Vycorglass-supported oxide, methane activation over Ag-exchanged zeolite Y,14 and H-atom abstraction by UO2+.15

The UV photoexcitation reactions studied by Kazansky and co-workers2-4 are associated with O 2p to metal valence d charge-transfer excitations which create active O⁻ centers. The lifetime of the electron-hole pair state is an important parameter for the activity of such O⁻ surface sites toward CH bonds in methane and other single bonds. In MoO3 this charge-transfer excited state has been found to have a lifetime of 63 μ s.¹⁶ It appears that it would be worthwhile to search for ways to lengthen

- (5) Liu, R.-S.; Iwamoto, M.; Lunsford, J. H. J. Chem. Soc., Chem. Commun. 1982, 78
- (6) Liu, H.-F.; Liu, R.-S.; Liew, K. Y.; Johnson, R. E.; Lunsford, J. H. J. Am. Chem. Soc. 1984, 106, 4117. (7) Ito, T.; Lunsford, J. H. Nature (London) 1985, 314, 721.
- (8) Driscoll, D. J.; Martir, W.; Wang, J.-X.; Lunsford, J. H. J. Am. Chem. Soc. 1985, 107, 58.
- (9) Ito, T.; Wang, J.-X.; Lin, C.-H.; Lunsford, J. H. J. Am. Chem. Soc. 1985, 107, 5062.
- (10) Anderson, A. B.; Ray, N. K. J. Am. Chem. Soc. 1985, 107, 253. (11) Mehandru, S. P.; Anderson, A. B.; Brazdil, J. F.; Grasselli, R. K. J.
- Phys. Chem. 1987, 91, 2930. (12) Vorotyntsev, V. M.; Shvets, V. A.; Kazansky, V. B. Kinet. Katal.
- 1971, 12, 1249. (13) Pichat, P.; Herrmann, J.-M.; Disdier, J.; Mozzanega, M.-N. J. Phys. Chem. 1979, 83, 3122.
- (14) Ozin, G. A.; Hughes, F. J. Phys. Chem. 1982, 86, 5174.
- (15) Greatorex, D.; Hill, R. J.; Kemp, T. J.; Stone, T. J. J. Chem. Soc., Dalton Trans. 1973, 2059.
- (16) Anpo, M.; Tanahashi, I.; Kubokawa, Y. J. Phys. Chem. 1982, 86, 1.



Time (hr)

Figure 2. % CH₄ conversion vs time for illuminated MoO₃ when CH₄:O₂ = 9:1, T = 40 °C.



Figure 3. Methanol formation vs time for MoO₃/SiO₂ and MoO₃/SiO₂ modified with cupric ion when $CH_4:O_2 = 9:1$, T = 100 °C. Numerical values are the [Cu]:[Mo] ratios in these photocatalysts.

this lifetime in order to increase the rate of photoactivation of methane. Such behavior would be realized if the Mo^V could be quenched by an electron-accepting dopant cation as shown by the $k_{\rm et}$ (electron transfer) path in Scheme I. For high efficiency, $k_{\rm et}$ must be large and k_2 must be small relative to k_1 .

A successful quenching dopant cation is most likely to be easily reducible with an acceptor orbital whose energy lies within the O 2p valence-metal d conduction band gap. The Cu²⁺ cation appears to be worth considering in this respect, as was documented recently in a homogeneous catalysis study.¹⁷ This paper presents the results of an experimental study and theoretical modeling of methane CH bond photoactivation by molybdenum trioxide, MoO₃, and Cu²⁺-doped MoO₃.

Experimental Results

The photochemical experiments were performed using a suitcase-type furnace and a 1000-W Xe lamp. The reactor was designed so that it could be placed within the furnace and could be irradiated from above with the Xe lamp. This was accomplished by the use of a quartz window which formed a seal when compressed between two Viton O-rings (Figure 1). Each photoreaction was performed by irradiation of 400 mg of the supported metal oxide catalyst contained within the reactor in the presence of methane and oxygen at 100 °C ($CH_4:O_2 = 9:1$). Due to the low yields of the reactions, a recycle design was employed to facilitate analysis of the products and to remove them efficiently from the surface of the catalyst. When 400 mg of MoO₃ on silica (100 µmol of MoO₃) was heated at 40 °C in the dark in the presence of CH₄ and O₂, no products were detected and no visual change in the catalyst was apparent after 24 h. However, when the oxide was irradiated with the Xe lamp (800 W), methanol was observed within 0.5 h. Although the total methanol yield increased with time, the rate of increase slowed (Figure 2), and the MoO₃ catalyst turned light blue, indicating partial reduction. When the reactions were performed at temperatures of 100 °C or greater, the catalyst remained unchanged in appearance, suggesting facile oxidation of the reduced form by O2 at this temperature. Elevated temperatures may also serve to promote desorption of methanol from the MoO₃/SiO₂ surface.

The methane oxidation reaction most likely begins with the formation of electron-hole pairs which are produced by the band-gap radiation such that the electron-deficient surface oxygen sites abstract H[•] from methane. The subsequently formed methyl

⁽²⁾ Kazansky, V. B. Kinet. Katal. 1977, 18, 43.

⁽³⁾ Lipatkina, N. I.; Shvets, V. A.; Kazansky, V. B. Kinet. Katal. 1978, 19, 979.

⁽⁴⁾ Kaliaguine, S. L.; Shelimov, B. N.; Kazansky, V. B. J. Catal. 1978, 55, 384.

⁽¹⁷⁾ Cameron, R. E.; Borcarsly, A. B. J. Am. Chem. Soc. 1985, 107, 6116.



Figure 4. Dependence of the rate of methanol formation on the [Cu]:[Mo] ratio in MoO₃/SiO₂ photocatalysts when CH₄:O₂ = 9:1, T = 100 °C.

radical is then oxidized to methanol, possibly through a mechanism involving surface methoxy and adsorbed H₂O as discussed by Lunsford and co-workers.5,6

In an effort to prolong the lifetime of the catalytically active photoexcited state, supported copper-containing molybdenum oxide catalysts were prepared by addition of (NH₄)₆Mo₇O₂₄·4H₂O to a SiO₂ sol, followed by calcination at 550 °C for 5 h. Photocatalysts with various Cu:Mo ratios were prepared in the range 0-2.0. Pure MoO₃ was colorless but as the ratio increased from 0, the materials took on a yellow-green color of increasing intensity. X-ray analysis of these materials showed them to be mixtures of MoO₃ and CuMoO₄, which we shall denote as Cu_xMoO_{3+x} . Irradiation of these materials under conditions identical with those employed for the MoO₃/SiO₂ photocatalyst resulted in enhanced rates of methanol formation compared to the parent compound, as shown in Figure 3. The enhancement increased as the Cu:Mo ratio increased and reached a maximum when [Cu] = [Mo](Figure 4). At larger Cu concentrations the rate of methanol formation dropped precipitously (Figure 4). Additionally, CuO alone exhibited no activity for methanol formation under these conditions. It is noteworthy that carbon monoxide or carbon dioxide were not observed in any of these experiments, suggesting selectivities near 100%. The presence of formaldehyde cannot be discounted because low concentrations may not be detectable. However, since formaldehyde is not expected to be stable under these conditions, decomposition to CO and H_2 is likely.

These results clearly show that cupric ion exerts a pronounced effect on the activity of these catalysts toward methanol formation from methane. There may be two factors contributing to the enhanced activity. The photocatalysts absorb in the visible region upon addition of cupric ion and may therefore absorb more of the incident light. When a UV filter with a 390-nm cutoff was placed between the illumination source and the reactor containing CuMoO₄, a significant rate of methanol formation (initial rate = 2.8 μ mol/h) was observed, unlike what is seen with unmodified MoO_3/SiO_2 . However, this rate was not nearly as large as that observed without the filter (ca. 6.0 μ mol/h). The CuMoO₄ sample also absorbs more strongly in the region 300-390 nm. These rates, in view of the 2.0 μ mol/h rate for full spectrum excitation of MoO₃ alone, suggest the possibility that the enhancement results from a greater number of accessible excited states. The second possibility is that Cu²⁺ "quenches" the excited electron, thereby prolonging the lifetime of the active O⁻ centers, according to the scheme discussed earlier. The following molecular orbital study discusses these possibilities.

Theoretical Results

A. Theoretical Method. The atom superposition and electron delocalization molecular orbital (ASED-MO)¹⁸ approach is used

TABLE I: Atomic Parameters Used in the Calculations; The Text **Explains Their Origin**

atom	orbital	Slater exponent, au	ionizn potential, eV
Cu	4s	1.85	10.23
	4p	1.55	6.44
	3da	5.95 (0.5691)	12.90
		2.30 (0.5986)	
Mo	5s	2.256	9.10
	5p	1.956	5.92
	$4d^a$	4,542 (0.5899)	10.06
		1.901 (0.5899)	
O ^b	2s	1.946	26.48
	2p	1.927	11.62
С	2s	1.658	14.59
	2p	1.618	9.26
Н	1s	1.20	11.60

^a Double ζ with linear coefficients in parentheses. ^bThe Slater exponents for the oxygen anions on which the transition state for C-H activation was carried out or the binding of H^{*} and CH₃^{*} radicals was considered are 2.146 and 2.127 au, respectively, to get reasonable O-H and O-C bond lengths.

to predict structures, mechanisms, and electronic properties in this study. This theory has already been employed in several other studies of CH bond breaking on oxide^{10,11,19} and metal²⁰ surfaces and by metal atoms.²¹ Parameters used in our work are in Table I. The Mo and O Slater atomic valence orbital exponents and ionization potentials are from an earlier study of the electronic properties of MoO₃.²² Because of ionicity, the oxygen s and p exponents are decreased 0.3 au from the atomic values of Clementi and Raimondi²³ and Cu⁺ d exponents of Richardson et al.²⁴ and Mo⁺ d exponents of Basch et al.²⁵ are used. The metal s and p exponents are estimated as discussed in ref 22. Because of ionicity, O ionization potentials are decreased 2 eV and Mo values are increased 2 eV from the atomic values compiled by Lotz²⁶ and Moore.²⁷ For similar reasons the H and C ionization potentials are decreased from free atom values by 2 eV (see ref 19a) and the Cu values are increased by 2.5 eV from the free atom values. As may be seen in Table II, the free atom parameters produce very accurate bond descriptions for CO and OH and the oxide surface adapted parameters work very well for CuO and CuH. Other diatomic properties are predicted, but no comparison with experiment is presently possible.

B. Electronic Structure of Copper Molybdate. Copper molybdate ($CuMoO_4$) is paramagnetic and dark green in color. Its structure type is triclinic, with lattice constants of a = 9.903Å, b = 6.783 Å, c = 8.359 Å, $\alpha = 101.08^{\circ}$, $\beta = 96.88^{\circ}$, and γ = 107.05° at 298 K, and there are six formula weights in the unit cell.²⁸ Since there is an inversion center, there are three different types of copper atoms and three different types of molybdenum atoms. Two of these copper atoms occupy axially distorted octahedra of oxygen atoms, with the four short Cu-O bond distances

^{(18) (}a) Anderson, A. B. J. Chem. Phys. 1974, 60, 2477. (b) Anderson, A. B. J. Chem. Phys. 1975, 62, 1187. (c) Anderson, A. B. J. Catal. 1981, 67, 129.

^{(19) (}a) Anderson, A. B.; Ewing, D. W.; Kim, Y.; Grasselli, R. K.; Burrington, J. D.; Brazdil, J. F. J. Catal. 1985, 96, 222. (b) Mehandru, S. P.; Anderson, A. B.; Brazdil, J. F. J. Chem. Soc., Faraday Trans. 1 1987, 83, 463.

^{(20) (}a) Anderson, A. B. J. Am. Chem. Soc. 1977, 99, 696. (b) Anderson, A. B.; Kang, D. B.; Kim, Y. J. Am. Chem. Soc. 1984, 106, 6597. (c) Me- handru, S. P.; Anderson, A. B. J. Am. Chem. Soc. 1985, 107, 844. (d) Kang,
 D. B.; Anderson, A. B. J. Am. Chem. Soc. 1985, 107, 7858. (e) Kang, D. B.; Anderson, A. B. Surf. Sci. 1985, 155, 639. (f) Kang, D. B.; Anderson, A. B. Surf. Sci. 1986, 165, 22

⁽²¹⁾ Anderson, A. B.; Baldwin, S. Organometallics 1987, 6, 1621.

⁽²²⁾ Anderson, A. B.; Kim, Y.; Ewing, D. W.; Grasselli, R. K.; Tenhover, M. Surf. Sci. 1983, 134, 237

 ⁽²³⁾ Clementi, E.; Raimondi, D. L. J. Chem. Phys. 1963, 38, 2686.
 (24) Richardson, J. W.; Nieuwpoort, W. C.; Powell, R. R.; Edgell, W. F. J. Chem. Phys. 1962, 36, 1057. (25) Basch, H.; Gray, H. B. Theor. Chim. Acta 1966, 4, 367.

⁽²⁶⁾ Lotz, W. J. Opt. Soc. Am. 1970, 60, 206.
(27) Moore, C. E. Atomic Energy Levels; Natl. Bur. Std. (US) Circ. 467.
US Government Printing Office: Washington, DC, 1958.

⁽²⁸⁾ Abrahams, S. C.; Bernstein, J. L.; Jamieson, P. B. J. Chem. Phys. 1968, 48, 2619.

TABLE II: Calculated Diatomic Configurations, Bond Lengths (R_*) , Harmonic Force Constants (k_*) , and Dissociation Energies (D_*) for Some Heteronuclear Diatomics^a

molecule	valence confign	state	R _e , Å	$k_{\rm e}$, mdyn/Å	D_{e} , ^b eV
OHc	$(1\sigma)^2(2\sigma)^2(1\pi)^3$	$^{2}\pi$	0.97, 1.04 (0.97)	8.32, 5.91 (7.74)	5.56, 4.27 (4.62)
CO^{c}	$(1\sigma)^2(2\sigma)^2(1\pi)^4(3\sigma)^2$	${}^{1}\Sigma$	1.11, 1.19 (1.13)	19.78, 13.11 (18.86)	10.96, 7.78 (11.22)
CuO	$(1\sigma)^2(2\sigma)^2(1\pi)^4(1\delta)^4(3\sigma)^2(2\pi)^3$	2π	1.74 (1.72)	2.93 (3.05)	1.62 (2.83)
CuH	$(1\sigma)^2(2\sigma)^2(1\delta)^6(3\sigma)^2$	$^{1}\Sigma$	1.56 (1.46)	3.50 (2.18)	3.33 (2.85)
CuC	$(1\sigma)^2(1\pi)^4(1\delta)^4(2\sigma)^2(3\sigma)^1(2\pi)^2$	4Σ	1.83	3.96	3.07
MoO	$(1\sigma)^2(1\pi)^4(2\sigma)^2(1\delta)^2(3\sigma)^1(2\pi)^1$	5π	1.69	6.04	$4.22 (5.0)^d$
MoC	$(1\sigma)^2(1\pi)^4(2\sigma)^1(1\delta)^2(3\sigma)^1$	5Σ	1.79	7.83	6.26
MoH	$(1\sigma)^2(\delta)^2(\pi)^2(2\sigma)^1$	6Σ	1.65	3.32	$2.44 \ (2.30)^{d,e}$

^a Numbers in parentheses are the experimental values and, unless otherwise stated, are taken from Constants of Diatomic Molecules; Huber, K. P., Herzberg, G., Eds.; van Nostrand: New York, 1979. For calculating the two-body repulsion energy, H density was used for CuH and MoH, C density was used for CuC and MoC, and O density was used for the rest. ^b Calculated D_e are based on separated atom populations for OH and CO, and on M⁺ (s⁰dⁿ) and O⁻ or C⁻ or H⁻ populations for the rest. The first numbers are the results obtained by using the standard parameters and the second numbers are the results by using the surface adapted parameters. ^dD₀ values. ^eTolbert, M. A.; Beauchamp, J. L. J. Phys. Chem. 1986, 90, 5015.



Figure 5. $Cu_3Mo_3O_{21}^{18-}$ cluster model of copper molybdate used in the calculations. The arrow indicates the oxygen site used for hydrogenabstraction studies. The black circles are Mo atoms, the shaded circles are Cu atoms, and the open circles are O atoms.

in each octahedron ranging between 1.933 and 1.980 Å, and the two axial Cu-O bond lengths being 2.213 and 2.619 Å. The third copper atom occupies a distorted tetragonal pyramidal arrangement of oxygen atoms, with the four basal Cu-O distances ranging from 1.894 to 1.985 Å, and the apical Cu-O distance being 2.341 Å. The three independent molybdenum atoms are surrounded by a slightly distorted tetrahedral arrangement of oxygen atoms with Mo-O bond lengths varying between 1.701 and 1.862 Å.

The cluster model used in our calculations, $Cu_3Mo_3O_{21}$ ¹⁸⁻, is shown in Figure 5. This cluster constitutes a portion of the unit cell of copper molybdate and includes all different oxygen coordination arrangements around the metal atoms. It carries a formal charge of -18 so that copper, molybdenum, and oxygen atoms are in their respective oxidation states of +2, +6, and -2. These charges do not affect the Hamiltonian or calculated electronic structure in ASED-MO theory.

First, we shall consider the electronic structures of MoO₃ and CuO. A previous ASED-MO study²² using a $Mo_6O_{25}^{14-}$ model produced a band gap of 2.6 eV between the filled O^{2-} 2p band and the empty Mo^{vi} 4d band, which is comparable to the ~ 3.2 eV optical bulk band gap.^{29,30} The electronic structure of a cluster with only surface O^{2-} is given in Figure 6. It is noted that the distorted octahedral coordination of molybdenum splits the octahedral degeneracy. In particular, the doubly degenerate Mo 4d e-set splits into two bands because two axial Mo-O distances are substantially longer than the other four. To an extent, cupric oxide has a similar local coordination. The structure type of CuO is monoclinic, with each copper atom in an approximately square planar coordination.³¹ Using the minimal CuO_4^{6-} cluster, the calculated electronic structure, shown in Figure 7, is quite different from that of MoO_3 . This is because the O 2p levels lie above the metal d levels in CuO, rather than below them as in MoO₃. Because of this the filled O 2p band orbitals are antibonding to



Figure 6. Relationship of calculated electronic structure of copper molybdate to those of cupric oxide and molybdenum trioxide. The shaded bands represent doubly occupied orbitals.



Figure 7. Calculated electronic structure of CuO_4^{6-} model of cupric oxide.

the filled Cu 3d band orbitals. Considerable copper and oxygen character is present in each band. Due to the approximately square planar Cu coordination, the half-filled antibonding counterpart to the Cu $d_{x^2-y^2}$ + O 2s + O 2p orbital is less stable than the remaining O 2p band orbitals, as may be seen for CuO_4^{6-} in Figure 7 and for $Cu_{12}O_{29}^{34-}$ in Figure 6. In the CuO_4^{6-} cluster this orbital has, by the Mulliken partitioning, about 40% Cu character. The calculated energy ordering for all of the crystal field split orbitals is $d_{x^2-y^2} > d_{xy} > d_{xz,yz} > d_{z^2}$. This order matches with that expected for the square planar configuration of ligands around the central transition metal atom. A self-consistent-field $X\alpha$ calculation³² on CuO₄⁶⁻ has predicted the same order and an energy gap of \sim 2.3 eV compared to our value of 2.0 eV.

A UPS spectrum of CuO shows a 5-eV-wide band which was assigned to overlapping Cu 3d and O 2p levels.³³ Our calculations,

⁽²⁹⁾ Hoppmann, G.; Salje, E. Opt. Commun. 1979, 30, 199.
(30) Ivanovskii, A. L.; Zhukov, V. P.; Slepukhin, V. K.; Gubanov, V. A.;
Shveikin, G. P. J. Struct. Chem. 1980, 21, 30.

⁽³¹⁾ Wyckoff, R. W. G. Crystal Structures, 2nd ed.; Wiley: New York, 1964; Vol. 2.

 ⁽³²⁾ Tossell, J. A. Chem. Phys. 1976, 15, 303.
 (33) Benndorf, C.; Caus, H.; Egert, B.; Seidel, H.; Thieme, F. J. Electron Spectrosc. Relat. Phenom. 1980, 19, 77.



Figure 8. Orbital correlation diagram for hydrogen-atom abstraction transition state with an electron-hole pair present, as indicated by the notation for a single electron at the bottom of the Mo 4d band and another at the top of the O 2p band. The second column of levels has methane in the transition-state structure with the surface cluster removed.

using the finitely sized $Cu_{12}O_{29}^{34-}$ cluster model, give a width of 4.5 eV. The half-filled Cu $3d_{x^2-y^2}-O$ 2p band in our calculations appears to match a shoulder near the Fermi energy which is discernible in the UPS spectrum in ref 33. If appears reasonable, therefore, to conclude that our calculations give a good description of the electronic structure of cupric oxide.

The Cu₃Mo₃O₂₁¹⁸⁻ cluster model of copper molybdate produces the electronic structure shown in the middle column of Figure 6. The band structure of the occupied orbitals is nearly that of adding the bands of the constituent CuO and MoO₃ oxides. A similar relationship between α -bismuth molybdate and the oxides Bi₂O₃ and MoO₃ was predicted in an earlier ASED-MO study.^{19a} The empty band structure shows noticeable deviation from the sum of the component oxides of copper molybdate, but this does not affect our study of CH activation.

C. Methane C-H Bond Activation on Copper Molybdate. The hydrogen abstraction mechanism in the presence of O⁻ has been examined as in our studies of methane activation on MoO_3^{11} . The products of H[•] abstraction are OH⁻(ads) and CH₃•(g). The methyl radical can bind only weakly to the surface, forming a single bond to Mo^V .

Despite the presence of band-gap Cu^{2+} orbitals in the nonphotoactivated catalyst, the initial interaction of a methane CH bond and an O^{2-} lone pair is a closed-shell one. Consequently the surface is expected to be inactive at low temperatures.

The effect of UV induced O $2p \rightarrow Mo$ 4d charge-transfer excitation on the methane CH bond scission barrier can be studied by occupying the cluster orbitals so that there is an electron at the bottom of Mo 4d band and a hole at the top of the O 2p band. When this is done, we find that the H[•] abstraction transition state is reached when the CH bond is stretched by 0.15 Å from its equilibrium value and the H atom is at a distance of 1.45 Å from the surface oxygen atom. The calculated barrier is 1.3 eV. This is 0.5 eV higher than the one we calculated for the photoactivated MoO₃.¹¹ Part of this difference is due to the different carbon 2s ionization potential³⁴ and the remaining difference is due to the top of the O 2p band being higher by about 0.35 eV for copper molybdate than for MoO₃. The orbital correlation diagram for the transition state and its structure with the photoexcited copper molybdate are shown in Figure 8. It is evident that the electron-hole is transferred to the CH-O σ^* level as it rises above the O 2p band, with the result that the CH bond order is reduced from 1 to 3/4 and the OH bond order is increased from 0 to 1/4. As long as hydrogen abstraction proceeds before electron-hole pair recombination, the reaction will be photoactivated.

Given the above electronic structure prediction and the predicted activity of copper molybdate when surface O^- are formed by light-induced O 2p to Mo 4d charge-transfer excitations, it is now possible to provide an explanation for the experimental results given earlier. It seems highly probable that the activity of Cu-

(34) Mehandru, S. P.; Anderson, A. B.; Ross, P. N. J. Catal. 1986, 100, 210.

SCHEME II



SCHEME III



 MoO_4 toward methane which is induced by visible light, an activity not possessed by MoO_3 , comes from excitations to the half-filled Cu $d_{x^2-y^2}$ -O 2p antibonding counterpart band. The doubling of the activity of CuMoO₄ when the UV filter is removed is a result of additional higher energy O 2p to Mo 4d excitations. Both of these excitations produce active surface O⁻ species.

In addition to the doubling of the rate when the UV filter is removed, there is evidently a synergistic effect due to the presence of copper and molybdenum in the oxide. According to Figure 3, the rate of methanol formation over MoO₃ in the presence of UV + visible light is 2.0 μ mol/h. From this and from the rate over CuMoO₄, 6.0 μ mol/h, and the rate over CuMoO₄ due to visible light alone, 2.8 μ mol/h, it can be deduced that the presence of copper increases the rate due to UV light by 1.2 μ mol/h. Furthermore, the presence of molybdenums must be influencing the activity due to excitations to the band-gap orbitals because CuO shows no photoactivity due to these excitations. An electron-trapping mechanism can be proposed to account for at least part of the increased rate due to UV light for CuMoO4. The basic postulate which leads to the mechanism is that electron transfer between nearest neighbors is much faster than between nextnearest neighbors. The suggested scheme for trapping photoelectrons and stabilizing surface O⁻ hole centers is given in Scheme II. Here the photoelectron, promoted to Mo^{VI} to form Mo^V, drops into a Cu $d_{x^2-y^2}$ -O 2p band orbital. Though this orbital is delocalized, about half on copper and half on the set of coordinated oxygens, it is formally considered a reduction of Cu^{II} to Cu^I as shown in Scheme II. This effectively removes the electron from the O⁻ hole center. This electron-hole pair should have a long lifetime because of a comparatively small dipole transition amplitude, which is overlap dependent. The activity of CuMoO₄ due to visible light absorption suggests that the holes that are formed adjacent to copper must migrate away. A suggested mechanism for this is in Scheme III. Here a visible photon excites an electron from a bonding Cu-O orbital to an antibonding counterpart in the O 2p-Mo 4d band gap. This hole can be stabilized if it moves to occupy a surface oxygen lone-pair orbital. The energies of such orbitals lie at ~ -11 eV in Figure 6. This separates the hole from the Cu center just as in Scheme II.

D. Reactions of H[•] and [•]CH₃ with Copper Molybdate. In the abstraction mechanism discussed so far, H[•] is transferred to a surface O⁻ and [•]CH₃ has been ignored. If the methyl radical does not depart as a gas-phase molecule it will adsorb to the surface. Lunsford has seen the formation of gas-phase radicals over various oxides,³⁵ but it is not known if some or all of them resided for some time on the surface and then desorbed. Our study¹¹ of MoO₃ predicted [•]CH₃ desorption energies from O²⁻ of ~0.4 eV, suggesting the radicals would be mobile on the anion-covered basal plane surface and that they would not possess long residence times. We found that if a methyl radical were to come upon an O⁻ hole center it would be trapped with a strong bond as a surface methoxy group. Such methoxy species would be long-lived when the O⁻ are formed chemically but might be expected to decompose to O²⁻ and CH₃[•] when they are formed by photoexcitation. It was

(35) Driscoll, D. J.; Lunsford, J. H. J. Phys. Chem. 1985, 89, 4415.



Figure 9. Electronic structure and cation adsorption sites for a $Cu_3Mo_3O_{17}^{10-}$ cluster model.

also predicted in ref 11 that heterolytic adsorption at layer edges of the photoactivated surface with H[•] bonded to O⁻ to give OH⁻ and CH₃[•] bonded to Mo^V was the only stable outcome for adsorption.

In this section the of stabilities of H[•] and ${}^{\circ}CH_3$ adsorbed in various ways on copper molybdate are explored. To make some partially coordinated cation sites available, we removed four oxygen atoms from the fully coordinated cluster model of Figure 5. The resulting cluster and its energy levels are shown in Figure 9. The partially coordinated cations give rise to two empty Mo dangling bond orbitals which drop down to positions ~0.5 eV beneath the Mo 4d band in Figure 9. These antibonding orbitals become stabilized compared to bulk because of the reduced coordination of the surface cations. Orbitals in the half-filled Cu $3d_{x^2-y^2}$ -O 2p band are similarly stabilized.

Table III shows that homolytic adsortion of methane on Cu^{II} centers and heterolytic adsorption on O²⁻ and Cu^{II} centers are unstable. This is because the Cu band-gap orbitals become occupied, resulting in the electron destabilization in these cases (see Figure 10). Heterolytic adsorptions to yield OH⁻ and Mo^{VI}:CH₃ and OCH₃⁻ and MoH⁻ are both stable and homolytic adsorption on Mo^{VI} centers has comparable stability. The abstraction mechanism would yield the first product; mechanisms and energetics for rearrangement to the other two stable products have not been calculated. The homolytic adsorption on oxygen sites is less destabilized than it was on MoO₃ in our earlier study¹¹ because of the low-lying half-filled $3d_{x^2-y^2}$ -O 2p band which is below the empty Mo 4d band. This low-lying band is more easily

Ward et al.

TABLE III: Calculated Structures and Reaction Energies, ΔE , for Methane Chemisorption on the Cu₃Mo₃O₁₇¹⁰⁻ Cluster Model

mode of adsorpn	$R_{\rm H}, R_{\rm C}, {\rm \AA}$	∠HCH, deg	$R_{\rm CH}$, ^{<i>a</i>} Å	ΔE , eV
H/O ²⁻ , CH ₃ /O ²⁻	1.01, 1.51	112	1.22	0.4
$H/O^{2-}, CH_3/Mo^{VI}$	1.02, 2.12	113	1.20	-0.3
H/Mo ^{VI} , CH ₃ /O ²⁻	1.67, 1.51	112	1.22	-0.6
H/Mo ^{VI} , CH ₃ /Mo ^{VI}	1.67, 2.12	113	1.20	-0.6
H/O ²⁻ , CH ₃ /Cu ^{II}	1.01, 2.14	115	1.20	0.6
H/Cu ^{II} , CH ₃ /O ²⁻	1.65, 1.51	112	1.22	0.6
H/Cu ^{II} , CH ₃ /Cu ^{II}	1.65, 2.14	115	1.20	2.3

^a Methyl CH bond lengths are overestimated by 0.1 Å in ASED-MO calculations.

reduced by the two OH and OC σ^* orbital electrons than the Mo 4d conduction band, see Figure 10. Both heterolytic modes are predicted to be possibilities for dissociative chemisorption of methane on CuMoO₄. The electronic structure for one such case is in Figure 10. Interestingly, homolytic adsorption on Mo centers is predicted to have a stability comparable to the heterolytic modes. This was not the case on MoO₃ in the work of ref 11 where a 1.9-eV instability was encountered. The stability comes from the charge-transfer stabilization of two Cu d_{x²-y²}-O 2p band electrons as indicated in Figure 10. In contrast, on the MoO₃ surface homolytic adsorption to Mo^{VI} would lead to the formation of two holes at the top of the O 2p band, which lies lower than the band-gap orbitals, so the bond strengths to this surface are much less.

Concluding Remarks. The experimental observations contained here clearly show that MoO_3 photocatalysts containing copper are more active for heterolytic carbon-hydrogen bond activation of methane than pure MoO_3 . We have attempted to account for this enhanced photoactivity of CuMoO₄ theoretically in terms of its electronic and geometric structure.

For CuMoO₄ we predict the presence of empty and filled orbitals of a Cu d–O 2p band in the band-gap region between the O 2p and Mo 4d bands. This allows for light absorption in the visible by means of excitations to empty band-gap orbitals from the lower filled Cu d–O 2p band. The hole states thus formed appear to account for the observed increase in activity when the UV filter is removed from the light source. We have proposed a scheme for stabilizing the holes formed by visible light against recombination with the electron on Cu^I, a recombination which is probably responsible for the inactivity of CuO. The essence of the argument is that some holes will become stabilized by the alternative pathway of going to surface O^{2–} lone-pair sites rather



Figure 10. Important orbital stabilizations and electron transfers for various types of adsorption using the cluster model of Figure 9. The CH_3 energy level indicates the position of the methyl radical orbital which is half filled and the H energy level indicates the position of the hydrogen 1s energy level.

than to Cu^I sites. This leads to an electron-hole pair separation and an increase in the lifetime of the active O⁻ sites. The enhanced activity due to UV excitations of CuMoO₄ compared with MoO₃ may also be the result of increased hole lifetimes. We have proposed for this case that active O⁻ sites are produced by band-gap irradiation resulting in a $Mo^{VI}-O^2 \rightarrow Mo^V-O^-$ transition. The Mo^V is "quenched" by adjacent Cu^{II}, resulting in efficient electron-hole separation.

The Cu d-O 2p band gap orbitals also influence hydrogen atom and methyl radical adsorption stabilities. Heterolytic adsorption product stabilities on Mo^{VI} and O²⁻ sites are similar to those calculated in our past MoO₃ study, but because of the low-lying empty band-gap orbitals on copper molybdate, homolytic adsorption on O^{2-} sites is more stable. This is because the gap orbitals are more easily reduced than empty Mo 4d band orbitals. Furthermore, the filled band-gap orbitals stabilize homolytic adsorption on Mo^{VI} sites by charge transfer to the MoH bonding orbitls, making this mode stable whereas it is not stable on MoO₃. Finally, homolytic adsorption on Cu^{II} and heterolytic adsorption on Cu^{II} and O²⁻ are relatively weak.

Registry No. MoO₃, 1313-27-5; O₂, 7782-44-7; CH₄, 74-82-8; CH₃-OH, 67-56-1; Cu^{II}, 15158-11-9; CuMoO₄, 13767-34-5; H₂, 1333-74-0; CuO₄⁶⁻, 56509-86-5; Cu₁₂O₂₉³⁴⁻, 111057-65-9; Cu₃Mo₃O₂₁¹⁸⁻, 110970-91-7; Mo₃O₁₄¹⁰⁻, 111058-56-1.

Ultraviolet Photolysis in a Laser Vaporization Cluster Source: Synthesis of Novel Mixed-Metal Clusters

K. LaiHing, P. Y. Cheng, and M. A. Duncan*

Department of Chemistry, School of Chemical Sciences, University of Georgia, Athens, Georgia 30602 (Received: May 8, 1987)

A new variation of the laser vaporization/pulsed nozzle metal cluster source is described for the production of mixed-metal clusters. This source incorporates UV laser photolysis of a gas-phase metal-containing complex with the same laser used for and in the same region of solid metal vaporization. This method is generally useful for the production of mixed-metal, metal-semimetal, and metal-semiconductor clusters and may be especially useful for cluster studies in which alloys of desired components are not readily available. Data are presented for clusters of Bi/Cr and Mn/Ag produced by this method.

Introduction

The past few years have witnessed an almost explosive growth in the study of small metal clusters.¹⁻⁸ This interest has been stimulated primarily by the development of laser vaporization^{9,10} as a general technique producing clusters of metals, semiconductors, and other materials. Based on this technology, new experiments have examined the molecular electronic structure of clusters (diatomic and triatomic electronic spectra,^{4,6} ionization potentials,¹¹ electron affinities,¹² ion fragmentation¹³) as well as their chemical properties,¹⁴⁻¹⁶ revealing a rich variety of behavior.

- (6) Morse, M. D. Chem. Rev. 1986, 86, 1049.
- (7) Phillips, J. C. Chem. Rev. 1986, 86, 619.
- (a) Koutecky, J.; Fantucci, P. Chem. Rev. 1986, 86, 539.
 (b) Dietz, T. G.; Duncan, M. A.; Powers, D. E.; Smalley, R. E. J. Chem. Phys. 1981, 74, 6511
- (10) Bondybey, V. E.; English, J. H. J. Chem. Phys. 1981, 74, 6978.
- (11) (a) Rohlfing, E. A.; Cox, D. M.; Kaldor, A.; Johnson, K. H. J. Chem.
 Phys. 1984, 81, 3846. (b) Whetten, R. L.; Zakin, M. R.; Cox, D. M.; Trevor, D. J.; Kaldor, A. J. Chem. Phys. 1986, 85, 1697.

Over this same time period, the quantum theory of cluster bonding has achieved increasing sophistication and has both stimulated and complemented experimental work.8 As metal-cluster research is rapidly coming of age, practical applications of cluster technology are also being considered, such as molecular beam vapor deposition to form thin films or supported catalysts.¹⁷ For both fundamental and practical motivations, it is desirable to extend these cluster studies to more complicated materials containing mixtures of elements. For example, bimetallic systems form an important class of catalysts exhibiting activity not found with pure metals.¹⁸ The optical, electronic, and magnetic properties of materials also depend critically on well-chosen stoichiometric mixtures of elements. To meet some of these increasing demands in cluster technology, we have developed a variation of the pulsed laser vaporization technique which makes it possible to produce a variety of mixed-element clusters. This method incorporates laser photolysis of a volatile metal-containing complex, such as a metal carbonyl, within the laser vaporization source region. This technique provides a surprisingly clean and efficient source of mixed-element clusters that could not be produced easily by other methods.

A variety of heteronuclear diatomic species have been studied previously in cryogenic rare gas matrices.^{3,4} In the gas phase, alloy

Davis, S. C.; Klabunde, K. J. Chem. Rev. 1982, 82, 153.
 Gole, J. L.; Stwalley, W. C., Eds. Metal Bonding and Interactions in High Temperature Systems; ACS Symposium Series 179; American Chem-

⁽a) Society: Washington, DC, 1982.
(3) Ozin, G. A.; Mitchell, S. A. Angew. Chem., Int. Ed. Engl. 1983, 22, 674.

⁽⁴⁾ Weltner, W., Jr.; Van Zee, R. J. Annu. Rev. Phys. Chem. 1984, 35, 291.

⁽⁵⁾ Moskovits, M. Metal Clusters; Wiley: New York, 1986.

<sup>D. J.; Kaldor, A. J. Chem. Phys. 1986, 63, 1697.
(12) Zheng, L. S.; Karner, C. M.; Brucat, P. J.; Yang, S. H.; Pettiette, C. L.; Craycraft, M. J.; Smalley, R. E. J. Chem. Phys. 1986, 85, 1697.
(13) Brucat, P. J.; Zheng, L. S.; Pettiette, C. L.; Yang, S.; Smalley, R. E. J. Chem. Phys. 1986, 84, 3078.
(14) (a) Geusic, M. E.; Morse, M. D.; O'Brien, S. C.; Smalley, R. E. J. Chem. Phys. 1985, 82, 590. (b) Morese, M. D.; Geusic, M. E.; Heath, J. R.; Smalley, P. E. Chem. Phys. 1985, 82, 590.</sup> Smalley, R. E. J. Chem. Phys. 1985, 83, 2293.

^{(15) (}a) Whetten, R. L.; Cox, D. M.; Trevor, D. J.; Kaldor, A. Phys. Rev. Lett. 1985, 54, 1494. (b) Trevor, D. J.; Whetten, R. L.; Cox, D. M.; Kaldor, A. J. Am. Chem. Soc. 1985, 107, 518.

⁽¹⁶⁾ Richtsmeier, S. C.; Parks, E. K.; Liu, K.; Pobo, L. G.; Riley, S. J. J. Chem. Phys. 1985, 82, 3659.

^{(17) (}a) Yamada, I.; Tagaki, K. Thin Solid Films 1981, 80, 105. (b)
Yamada, I.; Inakawa, H.; Tagaki, K. J. Appl. Phys. 1984, 56, 2746.
(18) (a) Sinfelt, J. H.; J. Catal. 1973, 29, 308. (b) Sinfelt, J. H. Acc.
Chem. Res. 1977, 10, 15. (c) Sinfelt, J. H. Bimetallic Catalysts: Discoveries, Concepts, and Applications; Wiley: New York, 1983.