Molybdenum Oxide Cluster Ions in the Gas Phase: Reactions with Small Alcohols

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The gas-phase reactions of molybdenum oxide cluster ions $Mo_xO_y^+$ ($x = 1-3$, $y = 1-9$) with small alcohols have been investigated using Fourier transform ion cyclotron resonance mass spectrometry. The product branch ratios are reported. The reactions of $Mo_xO_y^+$ with alcohols can be envisioned as proceeding via metal insertion into C−H and C−O bonds. C−H bond insertion leads to alcohol dehydrogenation and aldehyde elimination, whereas insertion into the C−O bonds results in alcohol dehydration and formation of metal−alkyl groups. Moreover, an increase of the chain length and branching lead to C−C bond cleavage. The most intriguing process is the reaction of the $Mo_3O_9^+$ ion with more than one CH_3OH molecule yielding $Mo_3O_9(C_2H_5)^+$ and $Mo_3O_9(C_3H_7)^+$ ions. The $Mo_3O_9CH_3^+$ ion was found to be the key intermediate of the polymerization process. Molybdenum oxides are protonated in the presence of alcohols. The upper and lower limits for the Mo_xO_y proton affinities were estimated as PA(MoO) < 180 kcal/mol, PA(Mo_2O_4, Mo_2O_5, Mo_3O_8) = 188 ± 8 kcal/mol, PA(MoO_2) = 202 ± 5 kcal/mol, PA(MoO_3, Mo_2O_6, Mo_3O_9) > 207 kcal/mol.

Introduction

The supported molybdenum-containing catalysts are widely used in various fields of chemistry and oil refining.[1−3] Such large-scale processes as the hydrofining of various oil fractions, hydrogenolysis of C−S, C−N, and C−O bonds[4−8] and oil demetalation,[9] and partial oxidation of organic compounds[10−12] involve the above catalysts. Other areas that employ molybdenum oxide as a catalyst are hydrocarbon hydrogenation and dehydrogenation,[13] olefin polymerization,[14] and olefin metathesis.[15,16]

The mechanisms of oxidation reactions involving molybdenum trioxide often include an exothermic transfer of the oxide oxygen atom to an organic substrate by the oxometal groups.[17] The most important factors affecting the catalytic properties of molybdenum oxide are the structural coordination of the oxide surface and the oxidation state. For example, in methanol oxidation to formaldehyde, the coordinatively unsaturated atoms of the molybdenum surface are most likely the active catalytic centers.[18,19]

The importance of molybdenum oxides in the condensed phase has motivated several gas-phase studies. Interactions of Cr^+ and Mo^+ with small alkanes and alkenes had been studied using the ion beam technique.[20] Mo^+ was found to activate the C−H bond of hydrocarbons and to give dehydrogenation products.

The gas-phase reactions of Mo^+, MoO^+, and MoO_2^+ ions with small alkanes, alkenes, and C_6-hydrocarbons had been investigated using Fourier transform ion cyclotron resonance (FTICR) mass spectrometry.[21] Dehydrogenation was also the dominant process in these reactions. The strong Mo^+−O and MoO^+−O bonds were rarely cleaved in the reactions. While hydrocarbon oxidation was rare, the attachment of the oxygen atom to Mo^+ did affect the chemistry. The addition of ligands led to increased reaction rates. For MoO_2^+, unique reaction pathways involving the dehydration and the elimination of small hydrocarbons occurred. It suggested that MoO_2^+ was capable of inserting into the C−C bonds of organic molecules, while Mo^+ and MoO^+

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almost exclusively yielded products that resulted from C−H bond insertion. The major factor in the reactivity differences was the number of available coordination sites on molybdenum.

Reactions of gas-phase atomic transition metal ions Fe^+, Cr^+, and Mo^+ generated by multiphoton dissociation ionization with a series of aliphatic alcohols have been studied using FTICR.[22] These metal ions underwent three classes of bond insertion reactions: C−O insertion (dehydration), C−H and O−H insertion (dehydrogenation), and C−C insertion. Mo^+ was very reactive and specific in the dehydrogenation or multidehydrogenation reactions. The dehydration and C−C bond insertion reactions appeared as alternative reaction channels only when the alcohols were branched or the chain length was increased.

In our previous investigations, we have studied the formation of molybdenum oxide cluster ions $Mo_xO_y^+$ ($x = 1-5$, $y = 1-15$) and their reactions with some small molecules.[23] Large oxides with $x = 4$ and 5 were found to be unstable in the reaction conditions used. Molybdenum oxide ions react with c-C_3H_6 through C−C bond insertion, yielding dehydration products and carbon species. The reactivity of oxide ions with a different number of metal atoms was the same, whereas in reactions with ammonium, different reactivity was found. Dimer and trimer ions readily changed their oxygen ligand to NH_3, and molybdenum oxide trimers $Mo_3O_8^+$ and $Mo_3O_9^+$ dehydrogenated the NH_3 molecule, yielding a complex with nitrogen. This may be due to differences in the oxide structures.

This paper is a continuation of our work; it reports the reactivity of molybdenum oxide cluster ions $Mo_xO_y^+$ ($x = 1-3$, $y = 1-9$) with some small alcohols. A double-resonance technique was used to gain information about the reaction pathways. The results are compared with reactions occurring over solid molybdenum oxide catalysts.

Experimental Section

A Bruker CMS-47 Fourier transform ion cyclotron spectrometer has been used in all experiments. The apparatus was equipped with an Oxford Instruments vertical-type superconducting magnet maintained at 4.7 T, resolution (50%) was ca. 2×10^5. The capacity of the ion pump for the vacuum system was 160 L/s. The background pressure was 3×10^{-9} mbar. Ions were formed in the cubic (33 mm) ICR cell by electron impact (70 eV). The standard pulse sequence (quench/ionization/variable delay/RF pulse) described in the literature was used to obtain the ICR spectra. All reactions were studied at room temperature. A Bayard−Alperts ionization gauge was used to monitor the pressure. The typical partial pressure of the reagents was $10^{-8}-10^{-7}$ mbar. All chemicals used were high-purity commercial samples ("Reakhim"). Prior to use, all alcohols were treated with multiple freeze−pump−thaw cycles. Ions were monitored for periods of 0.1−5 s, which allowed observation of both the primary and subsequent secondary reactions. The branching ratios were calculated after a reaction time of 0.5 s.

An FTICR spectrum was excited by pulse sequences, which were repeated in each experiment for several dozen times to obtain a better signal-to-noise ratio. A double-resonance technique[24] was used to study the mechanisms of the gas-phase reactions. In this technique, suppression of the daughter ions is sought by ejection of the supposed parent. Some product ions were excited with the cyclotron frequency in order to increase their energy, which could result in ion dissociation.

For the vaporization of the metal oxide samples, the ICR cell was equipped with a self-made quartz effusion chamber (Knudsen cell) placed directly on the bottom trapping plate of the ICR cell. During the experiments, the samples in the Knudsen cell can be heated up to 900 K. Molybdenum oxide cations were produced by the electron impact at 70 eV of the molybdenum trioxide vapors. Since molybdenum has seven major isotopes (^{92}Mo, abundance 15.86%; ^{94}Mo, 9.12%; ^{95}Mo, 15.70%; ^{96}Mo, 16.50%; ^{97}Mo, 9.45%; ^{98}Mo, 23.75%; ^{100}Mo, 9.62%) that essentially complicate the analysis of the mass spectra, a MoO_3 sample containing 97% of the ^{98}Mo isotope (v/o Izotop) was used.

It is possible that electronically and vibrationally excited ions are produced by the electron impact. As it was shown earlier, Mo_3O_9, Mo_4O_{12}, and Mo_5O_{15} are the primary products of MoO_3 vaporization. Ionization of such large molecules should lead to the vibrational excitation rather that to electronic excitation. Quenching of the vibrational excitation should occur for $10^{-8}-10^{-6}$ s. Thus, small oxide ions such as MoO_y^+ and $Mo_2O_y^+$ are the products of the fragmentation of large oxide ions, and they should not be excited. Excited ions may have upwardly curving kinetic plots.

Results and Discussion

Reactions with Methanol. The product ion distributions for reactions of $Mo_xO_y^+$ ($x = 1-3$, $y = 1-9$) with methanol are summarized in Table 1. The four major reaction pathways of $Mo_xO_y^+$ are demonstrated in the methanol reactions: (i) formaldehyde elimination, (ii) dehydration, and (iii) formation of $Mo_xO_yCH_3^+$ and (iv) $Mo_xO_yCH_4^+$ species. Moreover, $Mo_3O_9^+$ ions undergo polymerization reactions with methanol to produce longer hydrocarbon chains.

Huang and co-workers have found that in reactions with methanol, Mo^+ yielded nearly quantitative dehydrogenation products.[22] Mo^+ was found to insert into the O−H bond and to eliminate H_2 from methanol. The loss of an H_2 molecule then leads to formation of the C═O bond. However, in our opinion, metal ion insertion into the O−H bond may not be thermodynamically favored due to the high O−H bond energy (Table 2). Insertion into the C−H bond of methanol with less bond energy could lead to the same products.

The addition of an oxygen atom to Mo^+ dramatically changes the reactivity of the metal species (Table 1). MoO^+ reacts with methanol primarily via the elimination of CH_2O rather than H_2, as Mo^+ does, eq 1. It is

$$MoO^+ + CH_3OH \rightarrow MoOH_2^+ + CH_2O \qquad (1)$$

interesting that eq 1 is similar to the oxidative dehydrogenation of CH_3OH into CH_2O by O_2 over molybdenum oxide containing heterogeneous catalysts.[25] The process of methanol oxidation over solid catalysts proceeds by the two-stage redox mechanism. The first stage is methanol oxidation followed by surface reduction. Reaction 1 could be the model of this stage. The

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Table 1. Product Ion Distribution for the Reactions of $Mo_xO_y^+$ Ions with Small Alcohols

		relative abundance, %							
alcohol	products	MoO^+	MoO_2^+	MoO_3^+	$Mo_2O_4^+$	$Mo_2O_5^+$	$Mo_2O_6^+$	$Mo_3O_8^+$	$Mo_3O_9^+$
CH_3OH	$Mo_xO_yH_2^+ + CH_2O$	100	16	14	28	25	6	15	21
	$Mo_xO_yCH_2^+ + H_2O$		15		38	17	33	18	
	$Mo_xO_yCH_3^+ + OH$		32	54	34	17	61	19	50
	$Mo_xO_yCH_4^+ + O$		37	32		41		48	
	polymerization products								29
CD_3OH	$Mo_xO_yHD^+ + CD_2O$	100	10	14	29	16	35	20	27
	$Mo_xO_yCD_2^+ + HDO$		17		29	28	27	15	
	$Mo_xO_yCD_3^+ + OH$		38	43	42	28	38	15	44
	$Mo_xO_yCD_3H^+ + O$		35	43		28		50	
	polymerization products								29
C_2H_5OH	$Mo_xO_yH_2^+ + C_2H_4O$	84	38	16	34	24	19	29	34
	$Mo_xO_yC_2H_4^+ + H_2O$	16	22	27	28	26	33	21	18
	$Mo_xO_{y-1}C_2H_2^+ + 2H_2O$		13	27	20	30	48	42	48
	$Mo_xO_yC_2H_5^+ + OH$		27	30	18	20		8	
i-C_4H_9OH	$Mo_xO_yH_2^+ + C_4H_8O$	27	17	71	22	21	38	25	31
	$Mo_xO_yCH_3^+ + C_3H_7O$		8		11	10			
	$Mo_xO_yC_2H_5^+ + C_2H_5O$		12		15	18		22	
	$Mo_xO_yC_4H_6^+ + H_2O + H_2$	31							
	$Mo_xO_yC_4H_4^+ + H_2O + 2H_2$	42							
	$Mo_xO_{y-1}C_4H_6^+ + 2H_2O$		42	17	20	9	19	16	23
	$Mo_xO_{y-1}C_4H_4^+ + 2H_2O + H_2$		21	12	32	24	28	29	28
	$Mo_xO_y\text{-}2C_4H_4^+ + 3H_2O$					18	15	8	18
t-C_4H_9OH	$Mo_xO_yH_2^+ + C_4H_8O$	23	18	15	20	12	22	18	18
	$Mo_xO_yCH_3^+ + C_3H_7O$	29	16		12	10		21	
	$Mo_xO_yC_4H_8^+ + H_2O$	11	29	27	17	12	17	10	18
	$Mo_xO_yC_4H_6^+ + H_2O + 2H_2$	37							
	$Mo_xO_{y-1}C_4H_6^+ + 2H_2O$		16	37	24	30	28	24	27
	$Mo_xO_yC_3H_6^+ + CH_3OH$		13	12	22	24	20	27	27
	$Mo_xO_{y-1}C_3H_4^+ + CH_3OH + H_2O$		8	9	5	12	13		10

Table 2. Bond Energies in Alcohol Molecules

bond	energy, kcal/mol
$CH_3{-}OH$	91.6[a]
$CH_3O{-}H$	102.4[a]
$H{-}CH_2OH$	91.7[a]
$C_2H_5{-}OH$	91.1[a]
$C_2H_5O{-}H$	101.5[a]
$CH_3CH(OH){-}H$	90.2[a]
$CH_3{-}CH_2OH$	85.1[a]
$C_2H_5CH(CH_3){-}OH$	91.3[a]
$C_2H_5CH(CH_3)O{-}H$	102.1[a]
$C_2H_5CH(OH){-}CH_3$	86.5[b]
$C_2H_5{-}CH(OH)CH_3$	77.7[a]
$(CH_3)_3C{-}OH$	92.7[a]
$(CH_3)_3CO{-}H$	103.8[a]
$CH_3{-}C(CH_3)_2OH$	81.2[b]

[a] Data from Kondratyev, V. N. *Chemical Bond Energies, Ionization Potentials and Electron Affinity*; Nauka: Moscow, 1974. [b] Data from ref 22.

second stage is surface reoxidation by air oxygen. In our system, oxidation of $MoOH_2^+$ by an oxygen molecule should also lead to the gas-phase catalytic cycle. The catalytic cycles of this type were found in the presence of Fe^+, Ti^+, Zr^+, V^+, Cr^+,[26] Mo^+, W^+,[27] and Re^+ [28] oxide ions.

No evidence is found for oxide oxygen incorporation into the hydrocarbon ligands. It should be mentioned that the $Mo^+{-}O$ bond is strong with a bond energy of >118 kcal/mol,[27] and it should not cleave in this reaction. It was shown[29] that participation of an oxygen atom in reactions depends mostly on the $M^+{-}O$ bond energy. Thus, the reactivity of FeO^+ ($D^0 = 81.4$ kcal/mol),[30] CrO^+($D^0 = 85.3$ kcal/mol),[31] and OsO^+($D^0 = 100$ kcal/mol)[32] increases in contrast to that of the "bare" metal ions. This phenomenon relates to the new exothermic reaction pathways producing such stable ligands as OH and H_2O. However, VO^+ reactivity is somewhat lower than that of V^+.[33] The bond energy of $D(V^+{-}O)$ is rather high (133 kcal/mol), and the presence of an oxygen ligand only reduces the number of coordination sites.

Reactions of MoO_2^+ with CH_3OH differ from MoO^+ reactions. MoO_2^+ eliminates both H_2O and CH_2O. There are two structural possibilities for the $MoO_2CH_2^+$ ion product: aldehyde and oxygen ligands attached to Mo^+ ($O{-}Mo^+{-}(CH_2O)$) or molybdenum carbene spices ($O_2Mo^+{=}CH_2$). Kinetic activation of this product ion produces Mo^+ (35%), MoO^+ (50%), and $MoCH_2O^+$ (15%) ions. These data indicate that the product ion contains two ligands: $O{-}Mo^+{-}CH_2O$. The product ion distribution in Table 1 indicates that the selective C−H cleavage exhibited by Mo^+ and MoO^+ is quite absent, with MoO_2^+ readily breaking the C−O bond. The oxo ligand actively participates in these reactions, as in the case of CrO_2^+ ions.[34] The major products are $MoO_2CH_3^+$ and $MoO_2CH_4^+$ ions. The formation of these products from MoO_2^+ was determined using a double-resonance technique.

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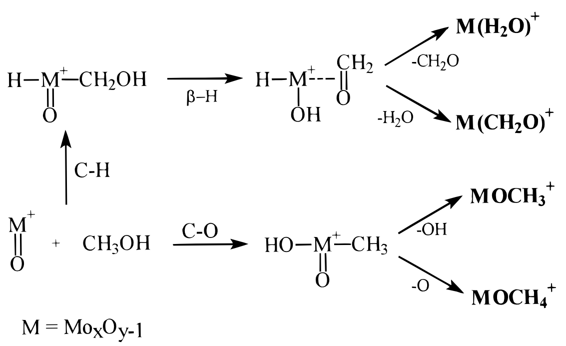
Scheme 1



The dominating reaction of MoO_3^+ with methanol is the formation of $MoO_3CH_3^+$ species. As long as Mo^+ is a five-electron system, one oxygen atom in MoO_3^+ must have a single bond with the metal ion. Moreover, the oxygen atom has a vacant valence and it can actively participate in these reactions. Thus, the addition of a CH_3 group to the oxygen atom should be very exothermic. MoO_3^+ has no vacant sites. So, reactions should occur through Mo−O group insertion into the C−H and C−O bonds followed by elimination of one ligand. The bond energy $MoO_2^+{-}O$ is about 102 kcal/mol,[27] which makes the cleavage of this bond in reactions possible.

Loss of H_2O is a major process in the reaction with $Mo_2O_4^+$. This suggests that as the number of metal atoms increases, the attachment of O and H atoms on the metal center to produce H_2O becomes more favorable.

The ions MoO_2^+, $Mo_2O_5^+$ and $Mo_3O_8^+$ have a similar structure[23] and a general stoichiometry of $Mo_xO_{3x-1}^+$. In these oxide ions, the number of oxygens attached to Mo^+ is the same, coordinative saturation is not yet achieved. This effect leads to the same product ions. There are some insignificant differences in the product distributions. Thus, for $Mo_2O_5^+$ and $Mo_3O_8^+$, insertion into C−O bonds is also the dominant process. However, the $Mo_xO_yCH_4^+$ product increases with an increase of the number of metal atoms. The loss of an oxo ligand may become more favorable due to the decrease of the $M^+{-}O$ bond energy with the increase of the oxide size.

The tendency to form $Mo_xO_yCH_3^+$ products remains for ions with a general stoichiometry of $Mo_xO_{3x}^+$. As long as MoO_3 and Mo_2O_6 have similar structures, their reactions probably occur through the same mechanism. However, the Mo_3O_9 reactivity is unique.

The reactions of $Mo_xO_y^+$ with methanol can be envisioned as proceeding via metal insertion into C−H and C−O bonds. The mechanism of $Mo_xO_y^+$ insertion into the C−H (or O−H) bond of methanol, followed by a β-hydride shift and the reductive elimination of H_2O or CH_2O molecules, is shown in Scheme 1. In the H_2O elimination process, the oxo ligand may actively participate in the reaction. Insertion into the C−O bond is followed by the formation of the $Mo_xO_y(CH_3)(OH)^+$ intermediate. Elimination of the most weekly bound ligand, OH or O, yields the products of the reaction. It should be noted that in the case of oxygen-saturated oxides $Mo_xO_{3x}^+$, molybdenum has no vacant sites and interaction with alcohol should occur via insertion of the $Mo^+{-}O$ fragment into the bonds of methanol.

In solutions, oxomolybdenum groups are generally considered to involve double bonds.[35] However, Mo^+ is a d^5 system, allowing only five covalent bonds to the metal ion in the gas-phase reactions. To explain the formation of some of the products, some steps in the $Mo_xO_y^+$ reactions must involve molybdenum-to-oxygen bonds with single-bond character. Moreover, as the number of oxygens attached to Mo^+ increases, coordinative saturation becomes more important in the reactions. This effect, undoubtedly, contributes to the differences in the product ion formation observed for $Mo_xO_y^+$.

To check the suggested mechanisms, we study the reactions of the molybdenum oxide ions with CD_3OH. The product ion distribution is presented in Table 1. The products of the $Mo_xO_y^+$ interaction with CH_3OH and CD_3OH are the same. The formation of $Mo_xO_yCD_3H^+$ uniquely confirms the proposed mechanism.

In general, molybdenum oxide ions prefer to insert into the C−O bond of methanol rather than into the C−H bond as Mo^+ does. In reactions with methanol, the increased number of oxygen atoms attached to Mo^+ causes the preferable insertion into the C−O bond. For example, a 65:35 mix of C−H and C−O bonds in the insertion products are observed for the reaction of $Mo_2O_4^+$, as opposed to a 40:60 mix for the $Mo_2O_5^+$ and $Mo_2O_6^+$ reactions. The same phenomenon was also found in reactions with CD_3OH.

A very interesting reaction pattern is exhibited by $Mo_3O_9^+$ ions. $Mo_3O_9^+$ ion reacts with more than one CH_3OH molecule to yield the $Mo_3O_9(C_2H_5)^+$ ion, eq 2, and the $Mo_3O_9(C_3H_7)^+$ ion, eq 3. The kinetic curves for

$$Mo_3O_9^+ + 2CH_3OH \rightarrow Mo_3O_9C_2H_5^+ + H_2O + OH \tag{2}$$

$$Mo_3O_9^+ + 3CH_3OH \rightarrow Mo_3O_9C_3H_7^+ + 2H_2O + OH \tag{3}$$

the methanol polymerization process by $Mo_3O_9^+$ ions are shown on Figure 1a. The addition of every CH_2 fragment occurs consecutively.

Kinetic activation of the $Mo_3O_9C_2H_5^+$ ion leads to the next major fragment ions, $Mo_3O_9C_2H_4^+$ (15%), $Mo_3O_9H^+$ (6%), $Mo_3O_9^+$ (9%), $Mo_3O_8C_2H_5^+$ (22%), $Mo_3O_8H^+$ (18%), and $Mo_3O_8^+$ (22%), and the products of the cluster fragmentation. Thus, reactions 2 and 3 represent the coupling of two and three hydrocarbon fragments of CH_3OH to form longer hydrocarbon chains. Note that such coupling is well-known for CH_3OH over acidic molybdenum oxide based homogeneous and heterogeneous catalysis, such as heteropolyacids, and also over zeolites.[36]

As mentioned above, the reactivity of molybdenum oxides depends on two factors: the molybdenum oxidation state and the structural coordination of the molybdenum atom or ion. In the case of the $Mo_3O_8^+$ and $Mo_3O_9^+$ ions, the molybdenum oxidation state does not play a significant role and the structural factor is more important. In our previous work,[23] it was found that $Mo_3O_9^+$ has a unique ring structure whereas other oxide ions are linear. The second methanol molecule could be coordinated close to the first molecule by the ring.

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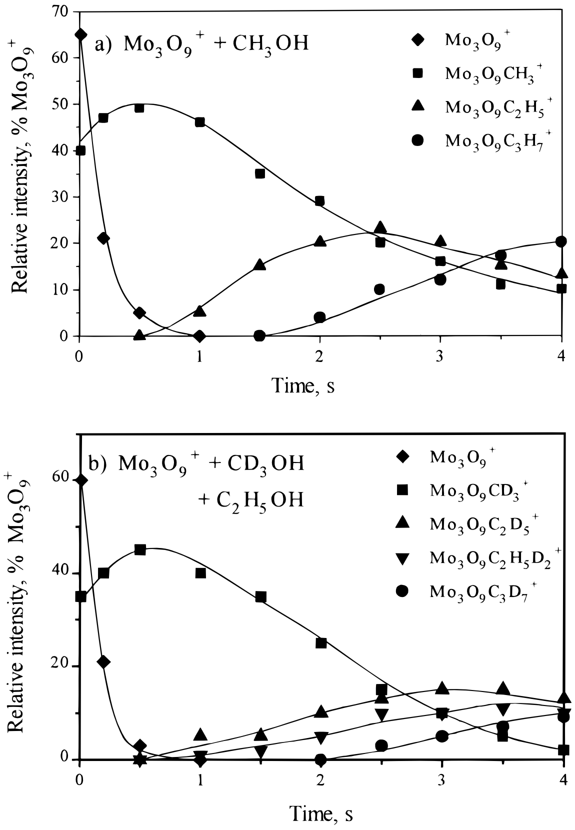
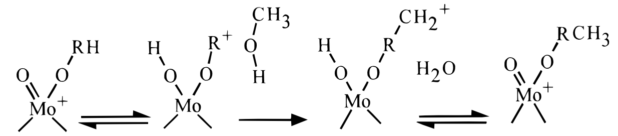


Figure 1. Kinetic curves for the polymerization reactions of (a) methanol and (b) methanol and ethanol molecules on $Mo_3O_9^+$.

Scheme 2

R = CH_2, C_2H_4



In reactions of $Mo_3O_9^+$ with CD_3OH, the polymerization products were also observed. We found the formation of the $Mo_3O_9C_2D_5^+$ and $Mo_3O_9C_3D_7^+$ ion products, moreover, some protonated products were present in the spectra: $Mo_3O_9C_2D_4H^+$ and $Mo_3O_9C_3D_6H^+$. These ions could be the products of H−D exchange reactions with CD_3OH molecules.

The mechanism of the initial C−C bond formation from methanol in the condensed phase is an unresolved question at present. Hypothetical mechanisms run the gamut from carbene to free-radical schemes.[37−41] There seems to be a majority consensus that the reactive C_1 intermediate is cationic in character, at least during some stage of its existence.[42] So, the proposed mechanism of the reaction presented in Scheme 2 includes formation of a carbocation. It is not excluded that for a big enough $Mo_3O_9CH_3^+$ ion, the positive charge can be transferred to the carbon atom followed by H transfer. In the condensed phase, formation of the carbocation may occur through proton transfer. In solutions and on solid surfaces, acidic protons are indeed known to be able to provide the coupling of hydrocarbon fragments of alcohol molecules to finally produce alkenes and alkanes.[43] It should be mentioned that although the relationship between the reactivity observed in the gas phase and that in the real catalytic system is not simple, in oure opinion, some generalizations can be made. The ion−molecular reactions observed with the ICR method in the idealized gas-phase system can be considered as models of the elementary steps of the catalytic reactions over the active sites of the oxide catalysts.

Reactions with Ethanol. As shown earlier,[22] Mo^+ is very reactive and specific in dehydrogenation and double-dehydrogenation reactions with ethanol. The $MoC_2H_4O^+$ and $MoC_2H_2O^+$ products accounted for 40% and 60% of the total ion current, respectively. Thus, Mo^+ again exhibits specific C−H insertion. Data in Table 2 indicate that in ethanol the C−H bond (90.2 kcal/mol) is stronger than the C−C bond (85.1 kcal/mol), however, the products of the C−C insertion were not observed. The preference for insertion into the C−H (or O−H) bond can be explained by the formation of more stable intermediates and products, since $D(M^+{-}OH)$ is larger than $D(M^+{-}CH_3)$.[44]

The observed ion−molecule reactions and product distributions for $Mo_xO_y^+$ with ethanol are given in Table 1. There are four major reaction pathways: (i) aldehyde elimination, (ii) single and (iii) double dehydration, and (iv) formation of the $Mo_xO_yC_2H_5^+$ product. In studies of solid MoO_3 catalysts, the same products (acetaldehyde, diethyl ether, ethylene, and water) were found to be the products of the ethanol oxidation reaction.[45] In this case, aldehyde was the dominant product (96%), however, in reactions over heteropolyacids, ethanol dehydration was the major process.[46,47]

As found in the case of methanol, MoO^+ reacts with ethanol primarily via the elimination of aldehyde yielding the $MoOH_2^+$ product. However, the product of ethanol dehydration is also observed in the spectra. Two structural possibilities exist for the $MoOC_2H_4^+$ product: an aldehyde molecule bound to Mo^+ or oxygen and ethylene ligands attached to Mo^+. Kinetic activation produces mainly MoO^+ and traces of $MoC_2H_4^+$ ions. These data indicate that the product ion contains two ligands: $O{-}Mo^+{-}C_2H_4$. The oxo ligand is not involved in the reaction due to the strong $Mo^+{-}O$ bond. However, the experiments with $C_2H_5{}^{18}OH$ may give exact information about the participation of the oxygen ligand in the reaction.

Other molybdenum oxide ions react with ethanol yielding both $Mo_xO_{y-1}(H_2O)^+$ and $Mo_xO_yC_2H_4^+$ ions. However, in our conditions, we could not determine the structure of these ions. It is well-known that Mo^+

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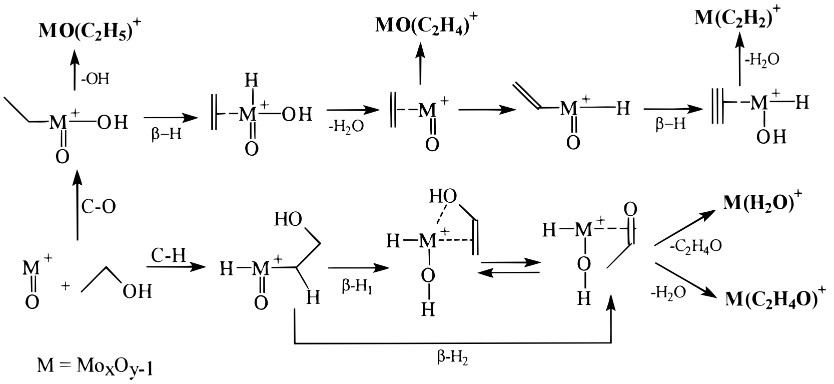
Scheme 3



specifically dehydrates small alcohols via C−H bond insertion. However, reactions of $Mo_xO_y^+$ ($x = 1-3$, $y = 2-9$) with methanol indicate that molybdenum oxides prefer to insert into the C−O bond of the alcohol, especially in the case of large ions. If this tendency is retained in the case of ethanol, the $Mo_xO_yC_2H_4^+$ ion should be the product of the C−O bond insertion and its structure should include ethylene attached to a molybdenum oxide ion. Further dehydration of this product leads to the formation of the secondary product $Mo_xO_{y-1}(C_2H_2)^+$. But it is not improbable that aldehyde dehydration may occur yielding $Mo_xO_{y-2}(C_2H_2O)^+$.

The proposed mechanism of the C−H insertion is presented in Scheme 3. The $Mo_xO_y^+$ insertion into the weakest C−H bond is followed by β-H transfer from the OH or CH_3 group to the Mo center to form a water−acetaldehyde ion complex, which may lose either aldehyde or water. Note that aldehyde elimination is observed for all molybdenum oxide ions, whereas the products of water elimination were not found.

Ethanol dehydration occurs through C−O bond insertion, formation of an ethyl−hydroxyl ion complex, and further dehydration of ethyl through consequential β-H transfers to Mo^+ and the oxo ligand. The increased size of the metal oxide facilitates the second dehydration that includes that oxide oxygen.

There are no ethanol polymerization products in the mass spectra. $Mo_3O_9^+$ reacts with ethanol by dehydration, and it does not yield the $Mo_3O_9C_2H_5^+$ product. In reactions with methanol, the primary product $Mo_3O_9CH_3^+$ was found to be the key intermediate in the polymerization reaction. As long as $Mo_3O_9C_2H_5^+$ does not form, the consequent reactions do not occur.

Experiments with a $C_2H_5OH-CD_3OH$ mixture were carried out. $Mo_3O_9CD_3^+$ was the primary product of the polymerization reaction. It was found that formation of the $Mo_3O_9C_2D_5^+$ and $Mo_3O_9C_3H_5D_2^+$ products began simultaneously (Figure 1b). Thus, $Mo_3O_9CD_3^+$ reacts either with methanol or ethanol molecules yielding the products of the secondary reactions, eqs 4 and 5. So,

$$Mo_3O_9CD_3^+ + CD_3OH \rightarrow Mo_3O_9C_2D_5^+ + HDO \quad (4)$$

$$Mo_3O_9CD_3^+ + C_2H_5OH \rightarrow Mo_3O_9C_3H_5D_2^+ + HDO \quad (5)$$

the formation of a metal−alkoxyl complex, which is not formed in reactions with ethanol, leads to the occurrence of methanol−ethanol copolymerization reactions.

Reactions with Butanols. Table 1 contains the product ion distributions for the reactions of $Mo_xO_y^+$ with butan-2-ol and 2-methylpropan-2-ol. Alcohol dehydration was found to be the major process in the $Mo_xO_y^+$ reactions. However, C−C bond cleavage also plays an important role. C−C bond insertion reactions appear as alternative reaction channels with branched alcohols.

In reactions with butanols, changing the position of the hydroxyl groups and the branching caused a decrease in the overall specificity of the Mo^+ reactions.[22] A near 80:20 mix of dehydrogenation and dehydration was observed for the reaction of Mo^+ and butanol, as opposed to a 50:50 mix for butan-2-ol and a 15:85 mix for 2-methylpropan-2-ol. The products of the C−C bond cleavage were in trace amounts.

As mentioned earlier, the strong Mo^+-O bond does not allow the oxo ligand to participate in the reactions. So, MoO^+ exhibits the same reactivity in reactions with butanols as Mo^+ does. Dehydrogenation together with dehydration were found to be the major processes in the MoO^+ reactions. However, the reactions of MoO^+ with *tert*-butyl alcohol show a branching effect whereby 30% of the products are $MoOCH_3^+$ ions, which are presumably formed by C−C bond cleavage.

There are three main reaction pathways in the interaction of other molybdenum oxide ions with butan-2-ol. First, an aldehyde elimination occurs for every oxide ion. Second, coordinately unsaturated molybdenum oxide ions (MoO_2^+, $Mo_2O_4^+$, $Mo_2O_5^+$, $Mo_3O_8^+$) are capable of inserting into the C−C bond of butanol, yielding the $Mo_xO_yCH_3^+$ and $Mo_xO_yC_2H_5^+$ ion products. Although the C−C bonds of butanol are the weakest ones, these products account for 20−30% of the total ion current. Third, oxide ions react with butan-2-ol yielding mainly dehydration and dehydrogenation products (up to three water molecules for large oxide ions). In all of these reactions, oxide oxygens are involved in the reactions. Multiple dehydrations are probably sequential; the formation of the product ions from multiple dehydration is highly exothermic. Note that under the conditions of the ICR experiment, a part of the exothermic effect of the reaction can be retained in the intermediate in the form of transitional, vibrational, or electronic excitation, e.g., the eliminated energy is not dissipated completely. This excitation can lead to an acceleration of the subsequent slow step. In contrast, on solid surfaces, energy relaxation processes are very

Table 3. Proton-Transfer Reactions

alcohol	PA, kcal/mol	MoO	MoO_2	MoO_3	Mo_2O_4	Mo_2O_5	Mo_2O_6	Mo_3O_8	Mo_3O_9
CH_3OH	180	no	yes	yes	yes	yes	yes	yes	yes
C_2H_5OH	186	no	yes	yes	slow	slow	yes	slow	yes
i-C_4H_9OH	197	no	yes	yes	no	no	yes	no	yes
t-C_4H_9OH	206	no	very slow	yes	no	no	yes	no	yes
NH_3[a]	207	no	no	yes	no	no	yes	no	yes

[a] Previous study. See ref 23.

fast so it is impossible to use the energy evolved in one reaction step to directly accelerate a subsequent slow step.[48]

There are some differences in the reactions of the molybdenum oxide ions with 2-methylpropan-2-ol. The products of an aldehyde elimination, C−C bond insertion and dehydration, are also observed in the spectra. Dehydration of 2-methylpropan-2-ol occurs to a lesser extent than in the case of butan-2-ol. Moreover, a new reaction pathway appears. All molybdenum oxide ions excepted MoO^+ eliminate methanol yielding the $Mo_xO_yC_3H_6^+$ or $Mo_xO_{y-1}C_3H_4^+$ ion products. Formation of these products could occur through an alternative CH_3 shift.

Proton Affinity. The proton affinities of Mo_xO_y were bracketed with a ladder of reference bases of known proton affinity. Reference proton affinity values were taken from the work of McMahon and Kebarle.[49] Proton affinities (PAs) were sought in the direction from the protonated alcohol to the molybdenum oxide cluster, eq 6. The occurrence of this reaction was studied using a double-resonance technique.

$$Mo_xO_y + C_nH_{2n-1}OH_2^+ \rightarrow Mo_xO_yH^+ + C_nH_{2n-1}OH \quad n = 1, 2, 4 \qquad (6)$$

The results of the various proton-transfer experiments are summarized in Table 3. Bracketing leads to PA(MoO) < 180 kcal/mol, PA(Mo_2O_4, Mo_2O_5, Mo_3O_8) = 188 ± 8 kcal/mol, PA(MoO_2) = 202 ± 5 kcal/mol), and PA(MoO_3, Mo_2O_6, Mo_3O_9) > 207 kcal/mol. The pressure of Mo_xO_y could not be determined to be reliable, precluding quantitative interpretation of the equilibrium. As long as the proton transfer is quite slow in the reactions of Mo_2O_4, Mo_2O_5, and Mo_3O_8 with $C_2H_5OH_2^+$, the PAs of these molybdenum oxides should be quite close to PA(C_2H_5OH) = 186 kcal/mol. For the same reason, PA of MoO_2 should be a little smaller than that of *t*-C_4H_9OH, PA(*t*-C_4H_9OH) = 206 kcal/mol.

Conclusion

In reactions with alcohols, the molybdenum oxide ions $Mo_xO_y^+$ ($x = 1-3$, $y = 1-9$) demonstrate three major reaction pathways: aldehyde elimination to form $Mo_xO_{y-1}(H_2O)^+$ ions, dehydration and dehydrogenation reactions, and formation of metal−alkyl species.

The addition of one oxygen ligand to Mo^+ does not significantly influence the reactivity of the metal ion. The strong Mo^+−O bond is never cleaved in the reactions. MoO^+, like Mo^+, prefers C−H bond insertion, which resulted in aldehyde elimination and alcohol dehydrogenation reactions. The increased number of oxygen atoms attached to Mo^+ causes the preferable insertion into the C−O bond, which leads to the formation of metal−alkyl groups and alcohol dehydration. The major factor affected by the differences in the reactivity of the oxide ions is the number of available coordination sites on molybdenum. An increase of the chain length and branching leads to C−C bond cleavage. C−C bond insertion reactions appear as an alternative reaction channel. In the case of 2-methylpropan-2-ol, a new reaction pathway appears: molybdenum oxide ions eliminate methanol.

The most intriguing process is the reaction of the $Mo_3O_9^+$ ion with more than one CH_3OH molecule. These reactions represent the coupling of two and three hydrocarbon fragments of CH_3OH to form longer hydrocarbon chains. Such coupling is well-known for CH_3OH over solid molybdenum oxide catalysts. The $Mo_3O_9CH_3^+$ ion was found to be the key intermediate of the polymerization process. The proposed mechanism of the C−C bond formation includes formation of a carbocation. Experiments with a C_2H_5OH−CD_3OH mixture led to an alcohol copolymerization reaction. Coordinatively saturated molybdenum oxides Mo_xO_{3x} were found to be strong bases in the gas phase. This may facilitate the coupling of alcohol molecules.

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