

# Similarities between Reactions of Methanol with $\text{Mo}_x\text{O}_y^+$ in the Gas Phase and over Real Catalysts

Elena F. Fialko, Andrey V. Kikhtenko, Vladimir B. Goncharov,\* and Kirill I. Zamaraev

Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva 5, 630090 Novosibirsk, Russia

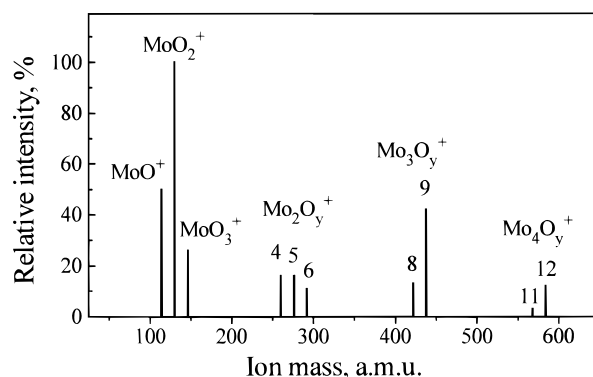
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ICR studies of the interactions between methanol and the family of  $\text{Mo}_x\text{O}_y^+$  ions ( $x = 1-3$ ,  $y = 1-9$ ) in the gas phase are reported. Molybdenum oxide ions participate in four types of reactions with the  $\text{CH}_3\text{OH}$  molecule that show rather profound similarities with the reactions of methanol over heterogeneous and homogeneous catalysts containing molybdenum–oxygen sites. Molybdenum oxide ions with three metal atoms represent coupling of two and three hydrocarbon fragments of  $\text{CH}_3\text{OH}$  to form longer hydrocarbon chains. The formation of acidic proton of  $\text{Mo}_x\text{O}_y\text{H}^+$  ( $x = 1-3$ ,  $y = 2-9$ ) was found in interactions with  $\text{CH}_3\text{OH}_2^+$  and its solvates  $\text{CH}_3\text{OH}_2^+(\text{CH}_3\text{OH})_n$  with  $n = 1, 2$ . Acidic protons are able to provide coupling of hydrocarbon fragments of alcohol molecules to produce finally alkenes and alkanes.

So far understanding of the mechanisms of heterogeneous and homogeneous catalysis has come almost solely from characterization of catalysts and reactions provided by them on gas–solid or liquid–solid interfaces and in solutions, respectively. In the meantime, studies with the ion-cyclotron resonance (ICR) technique have been shown to provide valuable information about interactions in the gas phase at low pressure of various molecules with ions of metals that are present in real catalysts. However, until now these studies were concentrated mainly on the problems of organometallic<sup>1,2</sup> rather than catalytic chemistry. Here we report our ICR studies of the interactions between methanol and the family of  $\text{Mo}_x\text{O}_y^+$  ions ( $x = 1-3$ ,  $y = 1-9$ ) that show rather profound similarities between reactions of methanol with these ions in the gas phase under ICR conditions and the reactions of methanol over heterogeneous and homogeneous catalysts containing molybdenum–oxygen sites. This fact suggests that ICR studies can be a useful tool to characterize in the gas phase, i.e. under most “pure” conditions, elementary reactions that are important for real catalysis.

All experiments were performed using a standard Bruker-Spectrospin CMS-47 Fourier transform ICR spectrometer.<sup>3</sup> The spectrometer includes a vertical type superconducting magnet (4.7 T) and a cubic (33 mm) trapping ICR cell. For vaporization of 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. The vacuum system was evacuated by means of an ionic pump with the capacity 160 L/s. Typical partial pressure of the reagents was  $10^{-8}$ – $10^{-7}$  mbar.  $\text{MoO}_3$  sample containing 97% of  $^{98}\text{Mo}$  isotope (v/o “Izotop”) was used to simplify the analysis of ICR spectra.  $\text{Mo}_x\text{O}_y^+$  ions can be trapped in an ICR cell from 0.1 to 10 s that allowed observation of both primary and secondary reactions. A double-resonance technique was used to study mechanisms of the gas-phase reactions. In this technique suppression of the daughter ions is sought by ejection of the supposed parent.<sup>4</sup>

Relative amounts of various  $\text{Mo}_x\text{O}_y^+$  ions generated in our experiments are shown in Figure 1. As is seen, the following



**Figure 1.** Positive ion spectrum of molybdenum trioxide ( $^{98}\text{MoO}_3$ ) produced using a combination of a Knudsen cell with an ICR spectrometer. There are four major groups of ions with one, two, three, and four molybdenum atoms. The concentration of ions with close stoichiometric ( $\text{MoO}_3$ ) oxygen-to-molybdenum ratio is significant.

four groups of ions are observed: monometallic ions  $\text{MoO}^+$ ,  $\text{MoO}_2^+$ , and  $\text{MoO}_3^+$ , bimetallic ions  $\text{Mo}_2\text{O}_4^+$ ,  $\text{Mo}_2\text{O}_5^+$ , and  $\text{Mo}_2\text{O}_6^+$ , trimetallic ions  $\text{Mo}_3\text{O}_8^+$  and  $\text{Mo}_3\text{O}_9^+$ , and a smaller amounts of tetrametallic ions  $\text{Mo}_4\text{O}_{11}^+$  and  $\text{Mo}_4\text{O}_{12}^+$ .

Products formed upon reaction of  $\text{Mo}_x\text{O}_y^+$  with methanol are shown in Table 1. As seen from this table, monometallic oxygenated molybdenum ions participate in four types of reactions with  $\text{CH}_3\text{OH}$  molecule, namely:

- (1) Oxidative dehydrogenation to form formaldehyde from  $\text{CH}_3\text{OH}$  reagent and  $\text{MoO}_{y-1}(\text{H}_2\text{O})^+$  ions from  $\text{MoO}_y^+$  reagents.
- (2) Abstraction of OH radical to form  $\text{MoO}_y\text{CH}_3^+$  ions.
- (3) Dehydration to form  $\text{MoO}_y\text{CH}_2^+$  ions, i.e. carbene species  $\text{CH}_2$ , coordinated to the  $\text{MoO}_y^+$  ions.
- (4) Abstraction of O atom to form  $\text{MoO}_y\text{CH}_4^+$  ions, i.e. methane coordination (perhaps, dissociatively) to  $\text{MoO}_y^+$  ions.

It is interesting that process 1 is similar to the oxidative dehydrogenation of  $\text{CH}_3\text{OH}$  into  $\text{CH}_2\text{O}$  by  $\text{O}_2$  over molybdenum oxide-containing heterogeneous catalysts.<sup>5</sup> Note also, that reactions 1, 2, and 4 proceed on two  $\text{MoO}_y^+$  species with  $y = 2$  and 3, while reaction 3 demands the presence of two oxygen ligands in the coordination sphere of the  $\text{Mo}^+$  atom.

Ions of the  $\text{Mo}_2\text{O}_y^+$  family exhibit the same reactions with  $\text{CH}_3\text{OH}$  as do  $\text{MoO}_y^+$  ones. However, the selectivity patterns for these two families of ions are different. For binuclear

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TABLE 1: Reactions of  $\text{Mo}_x\text{O}_y^+$  Ions with  $\text{CH}_3\text{OH}$  in the Gas Phase Observed with ICR

reaction	reaction number	neutral loss	relative abundance, %		
			y = 1	y = 2	y = 3
$\text{MoO}_y^+ + \text{CH}_3\text{OH} \rightarrow \text{MoO}_{y-1}(\text{H}_2\text{O})^+$	(1)	$\text{CH}_2\text{O}$	100	16	14
$\rightarrow \text{MoO}_y\text{CH}_3^+$	(2)	$\text{OH}$		32	54
$\rightarrow \text{MoO}_y\text{CH}_2^+$	(3)	$\text{H}_2\text{O}$		15	
$\rightarrow \text{MoO}_y\text{CH}_4^+$	(4)	$\text{O}$		37	32
$\text{Mo}_2\text{O}_y^+ + \text{CH}_3\text{OH} \rightarrow \text{Mo}_2\text{O}_{y-1}(\text{H}_2\text{O})^+$	(1a)	$\text{CH}_2\text{O}$	y = 4 28	y = 5 25	y = 6 6
$\rightarrow \text{Mo}_2\text{O}_y\text{CH}_3^+$	(2a)	$\text{OH}$	34	17	61
$\rightarrow \text{Mo}_2\text{O}_y\text{CH}_2^+$	(3a)	$\text{H}_2\text{O}$	38	17	33
$\rightarrow \text{Mo}_2\text{O}_y\text{CH}_4^+$	(4a)	$\text{O}$		41	
$\text{Mo}_3\text{O}_y^+ + \text{CH}_3\text{OH} \rightarrow \text{Mo}_3\text{O}_{y-1}(\text{H}_2\text{O})^+$	(1b)	$\text{CH}_2\text{O}$		y = 8 15	y = 9 21
$\rightarrow \text{Mo}_3\text{O}_y\text{CH}_3^+$	(2b)	$\text{OH}$		19	50
$\rightarrow \text{Mo}_3\text{O}_y\text{CH}_2^+$	(3b)	$\text{H}_2\text{O}$		18	
$\rightarrow \text{Mo}_3\text{O}_y\text{CH}_4^+$	(4b)	$\text{O}$		48	
$\text{Mo}_3\text{O}_y^+ + 2\text{CH}_3\text{OH} \rightarrow \text{Mo}_3\text{O}_9(\text{C}_2\text{H}_5)^+$	(5)	$\text{H}_2\text{O}, \text{OH}$			15
$\rightarrow \text{Mo}_3\text{O}_9(\text{C}_2\text{H}_6)^+$	(6)	$2\text{OH}$			4
$\text{Mo}_3\text{O}_y^+ + 3\text{CH}_3\text{OH} \rightarrow \text{Mo}_3\text{O}_9(\text{C}_3\text{H}_7)^+$	(7)	$2\text{H}_2\text{O}, \text{OH}$			8
$\rightarrow \text{Mo}_3\text{O}_9(\text{C}_3\text{H}_8)^+$	(8)	$3\text{OH}$			2
$\text{Mo}_x\text{O}_{3x}^+ + \text{CH}_3\text{OH}_2^+ \rightarrow \text{Mo}_x\text{O}_{3x}\text{H}^+$	(9)	$\text{CH}_3\text{OH}$	x = 1–4		

$\text{Mo}_2\text{O}_y^+$  reactions 1a, 2a, and 3a proceed at all values of  $y = 4, 5$ , and 6. Reaction 4a proceeds selectively only with  $\text{Mo}_2\text{O}_5^+$  species.

A very interesting reaction pattern is exhibited by trinuclear  $\text{Mo}_3\text{O}_9^+$  ions. First, they do not exhibit reactions of 3 and 4 types. Second,  $\text{Mo}_3\text{O}_9^+$  ion reacts with more than one  $\text{CH}_3\text{OH}$  molecule to yield  $\text{Mo}_3\text{O}_9(\text{C}_2\text{H}_5)^+$  ion (reaction 5),  $\text{Mo}_3\text{O}_9(\text{C}_2\text{H}_6)^+$  ion (reaction 6),  $\text{Mo}_3\text{O}_9(\text{C}_3\text{H}_7)^+$  ion (reaction 7) and  $\text{Mo}_3\text{O}_9(\text{C}_3\text{H}_8)^+$  ion (reaction 8).

Reactions 5–8 represent coupling of two and three hydrocarbon fragments of  $\text{CH}_3\text{OH}$  to form longer hydrocarbon chains. Note that such coupling is well-known for  $\text{CH}_3\text{OH}$  over acidic molybdenum oxide-based homogeneous and heterogeneous catalysis,<sup>6</sup> such as heteropolyacids  $\text{H}_{8-x}[\text{XMo}_{12}\text{O}_{40}]$ , where X stands for Si, P, or some other element and  $x$  is its oxidation state.<sup>7</sup> It is not excluded that for big enough  $\text{Mo}_3\text{O}_9^+$  ions, upon formation of hydrogen-containing species, such as, e.g.,  $\text{Mo}_3\text{O}_9\text{H}^+$ , the positive charge can be transferred to the hydrogen atom, which makes it a proton. In solutions and on solid surfaces acidic protons are indeed known to be able to provide coupling of hydrocarbon fragments of alcohol molecules to produce finally alkenes and alkanes.<sup>8</sup>

Further evidence for the formation of acidic protons upon interaction of  $\text{Mo}_3\text{O}_9^+$  with  $\text{CH}_3\text{OH}$  comes from observing with ICR in the presence of  $\text{Mo}_3\text{O}_9^+$  ion the protonized methanol species  $\text{CH}_3\text{OH}_2^+$  and its solvates  $\text{CH}_3\text{OH}_2^+ \cdot (\text{CH}_3\text{OH})_n$  with  $n = 1, 2$ . Once formed,  $\text{CH}_3\text{OH}_2^+$  reacts with various  $\text{Mo}_x\text{O}_{3x}$  neutral molecules that are present in the reaction mixture to form  $\text{CH}_3\text{OH}$  and  $\text{Mo}_x\text{O}_{3x}\text{H}^+$  (where  $x = 1-4$ ) (reaction 9).

Thus, via such processes as, perhaps, reaction of type 9, methanol can prepare in the gas phase from  $\text{Mo}_x\text{O}_y^+$  ions the

acidic forms of multinuclear oxide ions, provided that  $x$  and  $y$  are big enough (no less than 3 and 9, respectively).

Note that such phenomenon, when a catalytically active form of a metal–ligand site is prepared from some precursor in a solution or on a solid surface upon interaction with the reaction mixture, is again well-known for both homogeneous and heterogeneous catalysis.

Reactions 1–9 observed with ICR in the gas-phase are stoichiometric transformations, rather than catalytic ones. Nevertheless, they seem to adequately reproduce some steps of main-stream and side reactions over molybdenum oxide-containing catalysts.

Therefore, we believe that in the future the ICR studies of gas phase reactions between organic molecules and multinuclear metal-oxide ions may occur useful for better understanding of the mechanisms of catalysis on solid surfaces and in solutions. Thus, more comparative studies of the reactions of  $\text{M}_x\text{O}_y^+$  ions (with big enough  $x$  and  $y$ ) with various molecules in the gas phase and real catalytic transformations of the same molecules over similar sites in solutions and on solid surfaces are expedient.

## References and Notes

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