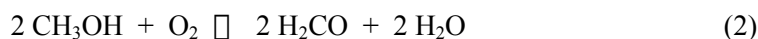
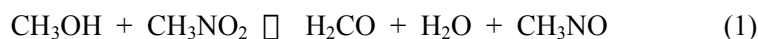


Gas phase catalysis - Investigating the site of reaction in mixed-metal oxide anions

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Gas phase experiments employing multistage mass spectrometry can be exploited to provide insights into the elementary steps of condensed phase catalytic processes. For example, the gas phase reactivity of metal-oxo ions can provide insights into heterogeneous reactions occurring at metal-oxide surfaces. The dimolybdate dianion $[\text{Mo}_2\text{O}_7]^{2-}$ (Figure 1a) can be transferred to the gas phase via electrospray ionization. The protonated dimolybdate anion $[\text{Mo}_2\text{O}_6(\text{OH})]^-$ catalyses the gas phase oxidation of methanol to formaldehyde (Figure 2, Equation 1). This gas phase catalysis may provide insights into the industrially important oxidation of methanol to formaldehyde catalysed by solid-state molybdenum-oxide based catalysts (Equation 2).



The role of the binuclear dimolybdate centre in this gas phase catalysis can be assessed by examination of the relative reactivities of the related mononuclear $[\text{MO}_3(\text{OH})]^-$ and binuclear $[\text{M}_2\text{O}_6(\text{OH})]^-$ ions ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). The related heterobinuclear 'mixed-metal' species, $[\text{MM}'\text{O}_7]^{2-}$ ($\text{M}, \text{M}' = \text{Cr}, \text{Mo}, \text{W}; \text{M} \neq \text{M}'$) are also available for comparison. Since these species are comprised of two different metal centers, the possibility of different sites of reaction often complicates an interpretation of their reactivity. For example, are reactions involving $[\text{CrMoO}_7]^{2-}$ occurring at a Cr-O group or an Mo-O group?

Experiments involving selective ^{18}O labeling of the oxo-groups of a *single* metal center in these mixed metal species will be described (Figure 1b). These experiments often provide insights into the site of reaction, thus allowing a proper comparison of reactivity with the related homobinuclear species.

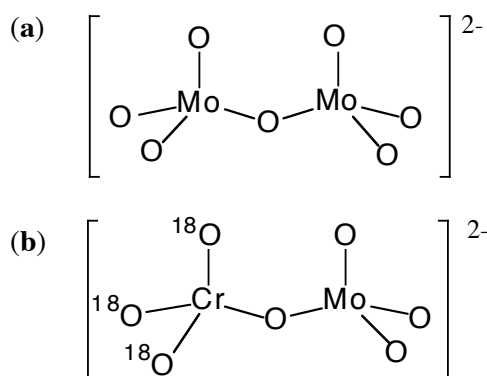


Figure 1

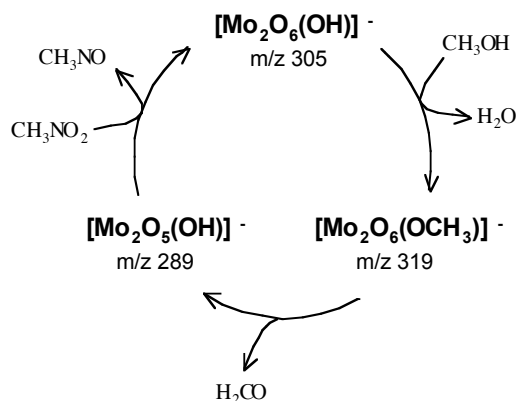


Figure 2