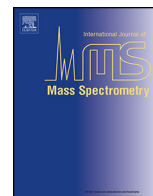




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# Mass spectrometry based studies of gas phase metal catalyzed reactions

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## ABSTRACT

Over the past three decades gas-phase catalytic cycles involving metal ions, complexes or clusters as intermediates have been discovered using either multistage mass spectrometry based experiments in trapping instruments or via flow tube methods. These studies have their foundations in: (i) the development of ion cyclotron and quadrupole ion trap mass spectrometers and the flowing afterglow technique, which date back to the 1960s; (ii) the development of ionization methods that allow the formation of gas phase metal ions, including electrospray ionization. Selected examples are reviewed that highlight the range of reaction types that are catalyzed in these processes, including: (i) oxidation of inorganic and organic substrates; (ii) decomposition of acetic acid via either water loss or decarboxylation channels (protodecarboxylation); (iii) decarboxylative C–C bond coupling reactions; and (iv) the dehydrogenation and trimerisation of ethylene to form benzene.

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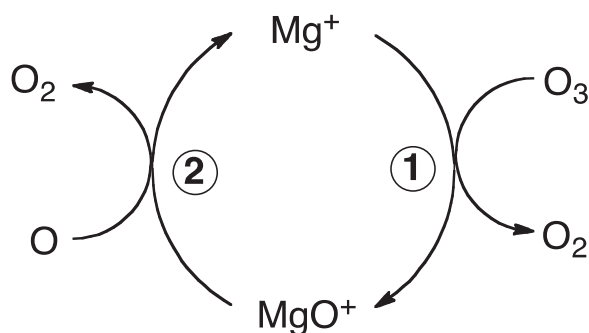
## 1. Introduction

The IUPAC definition of a catalyst is “A substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis. The catalyst is both a reactant and product of the reaction” [1]. Mass spectrometry based techniques can be used to examine gas-phase catalytic cycles that involve metal catalysts with a net charge. A range of experimental and theoretical methods have been developed over the past 50 years to provide fundamental structural, mechanistic and energetic information about intermediates and reactions associated with these catalytic cycles. These include the development of: (i) Ion Cyclotron Resonance (ICR) mass spectrometers [2]; (ii) quadrupole ion trap mass spectrometers [3]; (iii) the flowing afterglow (FA) technique [4]; (iv) ionization methods that allow the formation of gas phase metal ions [5], including electrospray ionization [6]; and (v) Density Functional Theory (DFT), which is now commonly used to probe the mechanisms of steps associated with experimentally determined gas phase catalytic cycles [7]; and the concept of two state reactivity [8].

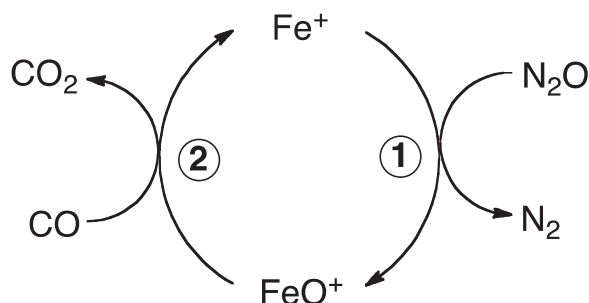
Two key classes of experimental methods have proven their worth in examining complete catalytic cycles in the gas phase: (i) trapping instruments such as Fourier-Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometers [9] and ion trap mass spectrometers [10] have proven particularly useful, since their multistage mass spectrometry ( $MS^n$ ) capabilities often allow each of the ionic intermediates in a catalytic cycle to be isolated and their reactivity explored in detail. (ii) Flow tube methods in which ions are entrained in a flowing bath gas which thermalizes the ions to the temperature of the bath gas [11]. Since different reagents can be delivered through individual ports at different distances along the flow tube, multiple ion-molecule reactions can be examined.

This article is not meant to be a comprehensive review of all gas phase metal ion chemistry of relevance to catalysis [12], which date back to early electron ionization mass spectrometry experiments on inorganic or organometallic complexes [13]. While thermochemical measurements have provided key information on bond energies associated with key metal containing intermediates associated with catalysis, these are not reviewed here [14]. I also do not review studies where mass spectrometry is used as an analytical technique to intercept possible intermediates and products of solution phase catalytic cycles [15]. Instead a 1968 report [16] and two pivotal papers from the 1980s are discussed [17,18], followed by a review of selected examples from the literature in which complete catalytic cycles have been identified using trapping instruments or

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**Scheme 1.** (1 column):  $\text{Mg}^+$  catalyzed destruction of ozone by atomic oxygen [16]. Step 1 is oxygen atom abstraction from ozone; step 2 is oxygen atom transfer.



**Scheme 2.** (1 column):  $\text{Fe}^+$  catalyzed oxidation of CO by  $\text{N}_2\text{O}$  [17]. Step 1 is oxygen atom abstraction; step 2 is oxygen atom transfer.

flow tubes. These examples have been chosen to highlight the range of catalytic reactions that have been studied.

## Two beginnings: two pivotal papers from the 1980s

The first example of a metal catalyzed reaction appears to have been Ferguson and Fehsenfeld's 1968 report on the oxygen atom decomposition of ozone (Eq. (1)) catalyzed by the magnesium cation, although they did not identify the catalytic cycle shown in Scheme 1 [16].

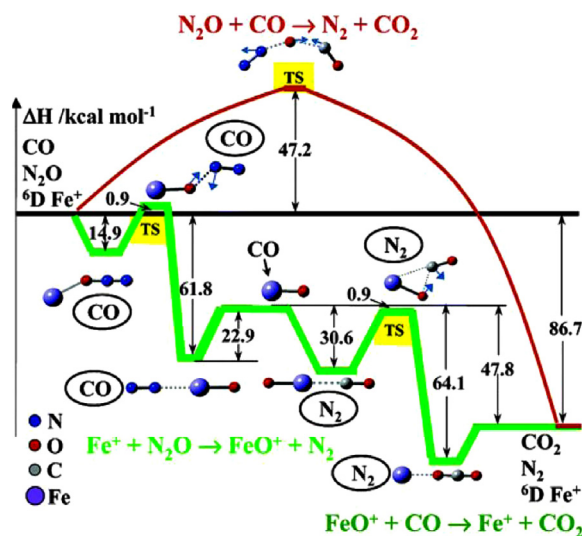


### 1.1. ICR-MS study on oxidation of CO and catalyzed by $\text{Fe}^+$

In 1981, Kappes and Staley reported the first gas-phase catalytic cycles involving ionic transition metal catalysts [17]. They used a pulsed YAG laser to produce the atomic  $\text{Fe}^+$  cation and studied its reactions in an ICR mass spectrometer. In the simplest of these cycles (Scheme 1), CO was oxidized to  $\text{CO}_2$ , with  $\text{Fe}^+$  as the catalyst and  $\text{N}_2\text{O}$  as the oxidant (Eq. (2)). In the first step,  $\text{Fe}^+$  reacted with  $\text{N}_2\text{O}$  by oxygen atom transfer to yield  $\text{FeO}^+$ , which in the second step transferred an oxygen atom to CO to yield neutral  $\text{CO}_2$ , thereby regenerating the  $\text{Fe}^+$  catalyst. Although this oxidation reaction (Eq. (2)) is exothermic ( $\Delta H^\circ = -107 \text{ kcal mol}^{-1}$ ), it does not occur at room temperature in the absence of the  $\text{Fe}^+$  catalyst (Scheme 2).



In 2005 Bohme's group revisited this catalytic cycle using a selected ion flow tube (SIFT) and DFT calculations [19a]. Their DFT calculations on the uncatalyzed and catalyzed oxidation reaction are shown in Fig. 1, which highlights that  $\text{Fe}^+$  acts as a catalyst by changing the reaction from a concerted one step reaction with a high activation energy ( $47.2 \text{ kcal mol}^{-1}$ ) to the originally proposed two step oxygen transport reaction (Scheme 1), with both steps having modest barriers.

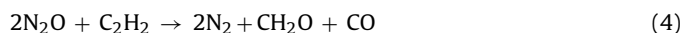


**Fig. 1.** (1 column): DFT calculated (B3LYP/SDD/6-311+G\*) energy diagram for the oxidation of CO by  $\text{N}_2\text{O}$  in the absence and presence of  $\text{Fe}^+$  ( $^6\text{D}$ ). The red profile corresponds to the neutral reaction of  $\text{N}_2\text{O}$  with CO. The green profile corresponds to the linked catalytic ion–molecule reactions of  $\text{Fe}^+$  with  $\text{N}_2\text{O}$  and of  $\text{FeO}^+$  with CO. The bold black line corresponds to the energy of the separated reactants. Spectator molecules are indicated in ovals. Transition state structures are labelled with TS; transition state vectors are sketched. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure reproduced from reference [19a].

There have been several other studies on metal catalyzed oxidation of CO using  $\text{N}_2\text{O}$  as the oxidant (Eq. (1)). Bohme's group have: (i) surveyed the reactions of 26 different atomic metal cations that lie within the thermodynamic window for O-atom transport catalysis and found only the following 10 behaved as catalysts –  $\text{Ca}^+$ ,  $\text{Fe}^+$ ,  $\text{Ge}^+$ ,  $\text{Sr}^+$ ,  $\text{Ba}^+$ ,  $\text{Os}^+$ ,  $\text{Ir}^+$ ,  $\text{Pt}^+$ ,  $\text{Eu}^+$ , and  $\text{Yb}^+$  [19a]; (ii) established that other oxides of nitrogen can be used as oxidants for the oxidation of CO [19b]; and (iii) examined the role of benzene ligands in the oxidation of CO (cf. Scheme 1) [19c]. Metal clusters can act as catalysts, as demonstrated for platinum cluster anions [19d,e] and  $[\text{Y}_2\text{O}_2]^+*$  and  $[\text{YAlO}_2]^+*$  [19f].

The other catalytic cycle that Kappes and Staley reported in their pioneering study involved the oxidation of ethyne by  $\text{N}_2\text{O}$  catalyzed by  $\text{Fe}^+$ . Two reactions occur: O atom transfer (Eq. (3)) and the production of formaldehyde and CO (Eq. (4)) via the reaction with 2 equivalents of  $\text{N}_2\text{O}$  [17]. These reactions have recently been revisited using the variable temperature SIFT method [20].



It is worth noting that  $\text{FeO}^+$  has been the subject of a large number of gas phase studies, many involving gas phase catalytic cycles, and these have been reviewed elsewhere [12a,d]. Of particular interest is C–H bond activation of typically inert substrates such as methane [21]. This work has been driven by the conceptual and electronic relationship between 'bare'  $\text{FeO}^+$  and the ferryl group at the heart of cytochrome P-450, which is involved in the hydroxylation of alkanes [22].

### 1.2. FA study on neutral–neutral reactions catalyzed by metal ions

Early in 1982, the team of Rowe, Viggiano, Fehsenfeld, Fahey and Ferguson from the NOAA Environmental Research Laboratories in Boulder noted that the rate of the gas phase reactions of  $\text{O}_3$  and  $\text{N}_2\text{O}_5$  molecules with NO (Eqs. (5) and (7)) were enhanced when the  $\text{O}_3$  and  $\text{N}_2\text{O}_5$  molecules are clustered to alkali metal cations (e.g.

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