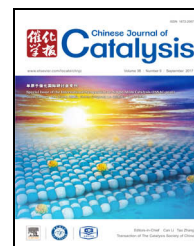


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Metal-mediated catalysis in the gas phase: A review



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ABSTRACT

This review summarizes a variety of experimentally identified gas-phase catalytic cycles, all of which are mediated by atomic metal ions, bare metal clusters, metal oxide clusters or metal complexes. Emphasis is placed on the latest advances in the unique catalytic reactivity of cluster-confined single noble metal atoms. The cycles discussed in this paper cover a wide range of inorganic and organic molecules. The use of state-of-the-art mass spectrometric instrumentation in conjunction with quantum chemistry calculations is also reported, as these techniques have determined the mechanistic details of the elementary steps of such catalytic cycles. The important role of gas-phase data in guiding the rational design of better-performing catalysts in related condensed phase reactions is also examined. In particular, this review focuses on the following three topics: (1) the catalytic oxidation of carbon monoxide, (2) the catalytic functionalization of methane, and (3) catalytic decarboxylation.

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1. Introduction

Metal-based catalysts are employed in numerous industrial [1,2] and biological processes [3–5], and are indispensable in lowering the energy barriers to chemical reactions that are thermodynamically favorable but kinetically slow under ambient conditions. The future development of catalysts with desirable properties under mild conditions will require fundamental insights into the elementary steps of catalytic processes at the molecular level. However, a comprehensive understanding of the mechanistic details of these elementary steps is still far off, as a result of the enormous complexity of so-called “real-life” catalytic environments. Under actual conditions, aggregation, solvent effects, counterions and surface defects all obscure the nature of the catalytic active sites and of intermediate species. Thus, the design of better-performing catalysts with

tailored properties remains a challenge.

Advanced mass spectrometry instrumentation combined with state-of-the-art theoretical calculations provides a powerful means of probing the energetics and kinetics of complex gas-phase chemical processes [6–22]. Gas-phase experiments can be performed under isolated, controlled and reproducible conditions and, in this unperturbed environment, the difficult-to-control or poorly defined parameters in real-life catalytic usage can be excluded. Many such gas-phase studies have examined the key steps in industrially and biologically important catalytic cycles, focusing on electronic structures, vital intermediates and the oxidation states of metal centers. Several excellent reviews have summarized gas-phase catalytic cycles [7,23], cooperative effects in clusters [24] and important elementary reactions, such as CO oxidation [15], CO₂ transformation [25], CH₄ functionalization [26] and decarboxylation

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reactions [27,28]. The focus of the present article is a review of the latest advances in gas-phase catalytic reactions, with an emphasis on cluster-confined single-atom catalysts. These materials serve as an ideal model to explore the nature of actual single-atom catalysts that allow the most efficient use of noble metals and show great potential for high activity and good product selectivity [29,30]. This review may assist in providing a clear understanding of structure-property relationships in various catalytic processes. This paper also presents an unambiguous identification of both the catalytic active sites and the reaction mechanisms that govern various catalytic reactions and may facilitate the further development of efficient catalysts. The following three topics are discussed in detail: (1) the catalytic oxidation of carbon monoxide, (2) the catalytic functionalization of methane, and (3) catalytic decarboxylation. The reactions discussed herein span a wide range of inorganic and organic molecules, including CO, CH₄, H₂, C₂H₂, C₂H₄, C₆H₆, CH₃OH, HCOOH and CH₃COOH. The experimentally-identified gas-phase catalytic reactions mediated by metal species and involving atomic metal ions, bare metal clusters, metal oxide clusters or metal complexes are summarized in Table 1.

2. Catalytic oxidation of carbon monoxide

The oxidation of CO to CO₂ is not only an important process for the removal of CO from the atmosphere but also is a typical heterogeneous process [86]. Metals or metal oxides play significant roles in this oxidation, both as catalysts and catalytic support materials [86,87]. However, despite extensive experimental and theoretical studies of bare or supported metal catalysts, the catalytically-active oxygen species [88–90], the oxidation states of the metals [29,91–93], the importance of the perimeter interface [94–96] and other factors are still debated. In this regard, gas-phase clusters serve as ideal models for studying the mechanistic details of the catalytic oxidation of CO in the condensed phase. Some important gas-phase studies of the elementary steps and catalytic cycles of CO oxidation have been reviewed [15], and there have also been several recent reports [16,97]. In this section, the latest advances in our understanding of the catalytic cycles during CO oxidation are presented, with an emphasis on the unique catalytic reactivity of single noble atoms confined by atomic clusters.

2.1. Catalytic oxidation of CO by N₂O

The catalytic conversion of CO by N₂O is of great importance, both environmentally and economically, because it removes harmful gases generated during fossil fuel combustion [98–100]. Although exothermic, the reaction between CO and N₂O will not proceed spontaneously either at ambient or elevated temperatures. Thus, metal-based heterogeneous catalysts are indispensable in lowering the energy barrier and promoting the reaction.

Since the groundbreaking work of Kappes et al. [31] in 1981 regarding the catalytic oxidation of CO by N₂O (N₂O + CO → CO₂ + N₂) with a single Fe⁺ ion as a catalyst, the catalytic conversion of CO by N₂O mediated by atomic metal cations has been exten-

sively studied [32,33,36,37] (Table 1). Such catalysis has also been reviewed [7]. In total, 59 atomic metal cations have been systematically examined to obtain a comprehensive understanding of their catalytic reactivity, including the fourth-row ions from K⁺ to Se⁺, fifth-row ions from Rb⁺ to Te⁺ (excluding Tc⁺), sixth-row ions from Cs⁺ to Bi⁺, and the lanthanide ions (excluding Pm⁺) [36,101,102]. The oxidation of CO by N₂O involves the transfer of an O atom from N₂O to CO, and thus the metal cation (M⁺) must exhibit an O atom affinity (OA) intermediate between the OA values of N₂ (1.74 eV) and CO (5.51 eV) in order to have the thermodynamic potential to catalyze the reaction. Therefore, the catalysis requires OA (N₂: 1.74 eV) < OA (M⁺) < OA (CO: 5.51 eV), sometimes referred to as the “thermodynamic window of opportunity” [36]. Among the 59 cations studied to date, 26 cations fall within this window, although only 10 exhibit catalytic activity (Ca⁺, Fe⁺, Ge⁺, Sr⁺, Ba⁺, Os⁺, Ir⁺, Pt⁺, Eu⁺, and Yb⁺) [36], as shown in Fig. 1). The remaining 16 (Cr⁺, Mn⁺, Co⁺, Ni⁺, Cu⁺, Se⁺, Mo⁺, Rn⁺, Rh⁺, Sn⁺, Te⁺, Re⁺, Pb⁺, Bi⁺, Tm⁺, and Lu⁺) do not sufficiently increase the oxidation rate at room temperature, either during the formation of the metal oxide, MO⁺, or during the subsequent reduction of this oxide by CO. The catalytic oxidation of CO by N₂O is not thermodynamically controlled but has an intrinsic reaction barrier that can reduce the efficiency of exothermic O atom transfer catalysis [102]. In addition to N₂O, several metal cations (Fe⁺, Os⁺, and Ir⁺) can also catalyze the oxidation of CO by NO and NO₂ (Table 1).

In recent years, there has been increasing interest in the catalysis of CO oxidation by N₂O using poly-atomic cluster ions [35,38–41,103], metal oxide clusters [40], and bimetallic oxide cluster ions [42,45] (Table 1). There has been an emphasis on the importance of the single electron localized atomic oxygen radical (O[•]) during the elementary steps comprising CO oxidation, such as when employing clusters including Zr_nO_{2n}⁺ (*n* = 1–4) [40], Ti₂O₄⁺ [41], AlVO₄⁺ [42,104], VO₃⁺ [44], and YAlO₃⁺ [45]. As an example, Fig. 2 shows the catalytic cycle mediated by the AlVO₄⁺/AlVO₃⁺ couple [42]. In this mechanism, the carbon atom in CO approaches and then abstracts the central radical oxygen in AlVO₄⁺ to generate CO₂ and AlVO₃⁺. The high reactivity of atomic oxygen radicals toward CO [16,105,106] and many other inorganic and organic molecules has been previously demonstrated [13,26]. Following the CO oxidation, the reductive cluster AlVO₃⁺ can be transformed back to AlVO₄⁺ using N₂O as the oxidizing agent to complete the catalytic cycle. An interesting aspect of this process is that the highly reactive O[•] is bonded to the main-group Al atom rather than the transition-metal V atom [104]. This is in sharp contrast to the traditional understanding of the V₂O₅/Al₂O₃ catalyst, in which the V₂O₅ component is almost always considered to be the active phase that induces the catalytic reactions. Therefore, the support materials in these widely-used vanadium oxide catalysts, which are normally considered to be inactive, may in fact participate directly in chemical reactions [107–109].

The above studies indicate that a single atomic metal ion can be sufficiently active so as to promote the oxidation of CO by N₂O because of the relatively low OA of N₂. However, this is not the case for the catalytic oxidation of CO by molecular O₂, as

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